An Efficient Method for retro-Claisen-type C-C Bond Cleavage of Diketones with Tropylium Catalyst

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Supporting Information

Table of Contents

General Methods ................................................................................................................................................2
General Procedure for Optimization Studies .................................................................................................3
General Procedures for the Tropylium-Promoted retro-Claisen Reactions .................................................5
Characterization Data of Products ................................................................................................................7
Enamine Formation with 1,3-Cyclohexanediones as Reaction Substrates ..................................................17
General Procedure for the retro-Claisen Reactions in Continuous Flow ..................................................20
Dehydrative Thiolation of 1,3-Diketones with Thiols ..................................................................................22
Mechanistic NMR Studies ..........................................................................................................................26
NMR Spectra .................................................................................................................................................29
**General Methods**

Reactions, unless otherwise stated, were conducted under a positive pressure of argon in oven-dried glassware. Water for the hydration reactions was deionized water. Commercially available solvents and reagents were used as purchased unless otherwise noted. Analytical thin layer chromatography was performed using aluminium plates precoated with silica gel 60 F$_{254}$ (0.2 mm). Flash chromatography employed 230-400 mesh silica gel. Solvents used for chromatography are quoted as volume/volume ratios.

NMR spectroscopy was performed at 298 K using an Avance III HD 400 (400.1 MHz, $^1$H; 100.6 MHz, $^{13}$C, 376.5 MHz, $^{19}$F) or an Avance III 300 (300 MHz, $^1$H; 75 MHz, $^{13}$C; 282.5 MHz, $^{19}$F). Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform, 5.27 ppm for dichloromethane) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). $^{13}$C NMR spectra were recorded at 298 K with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ 77.2 ppm for the central peak of deuterated chloroform).

Infrared spectra were obtained on a Thermo Nicolet Avatar 370 FT-IR spectrometer and are reported in wavenumbers (cm$^{-1}$). HRMS were performed at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre at the University of New South Wales on an Orbitrap LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) ion trap mass spectrometer.

Flow reactions were conducted on a Vapourtec R-Series flow reactor.
Table S1. Optimization of tropylium-promoted hydrolysis reaction of substrate 2a[^a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>mol% cat.</th>
<th>solvent</th>
<th>T (°C)</th>
<th>time[^b]</th>
<th>Yield[^c]</th>
</tr>
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<tbody>
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<td>18%</td>
</tr>
<tr>
<td>2</td>
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<td>24</td>
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</tr>
<tr>
<td>3</td>
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<td>24</td>
<td>96%</td>
</tr>
<tr>
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<td>16</td>
<td><strong>99%</strong></td>
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<td>16</td>
<td>62%</td>
</tr>
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<tr>
<td>9[^d]</td>
<td>10</td>
<td>water as solvent</td>
<td>100</td>
<td>16</td>
<td>80%</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>MeCN</td>
<td>reflux</td>
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<td>45%</td>
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<tr>
<td>11</td>
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</tr>
<tr>
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<td>reflux</td>
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</tr>
<tr>
<td>14</td>
<td><strong>10</strong></td>
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<td>rt</td>
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</tr>
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<td>21%</td>
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<td>rt</td>
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</tr>
<tr>
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<td>toluene</td>
<td>rt</td>
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</tr>
<tr>
<td>18</td>
<td>10</td>
<td>DCE</td>
<td>rt</td>
<td>48</td>
<td>64%</td>
</tr>
<tr>
<td>19[^e]</td>
<td>10% HBF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>no solvent</td>
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<td>24</td>
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</tr>
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<td>22[^e]</td>
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<td>TFE</td>
<td>rt</td>
<td>48</td>
<td>76%</td>
</tr>
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</table>

[a] Conditions: diketone 2a (1 mmol), water (3a, 2 mmol) and cat. 1 (0.1 mmol) in the indicated solvent (0.6 mL) under N<sub>2</sub> atmosphere. [b] Reaction time (hour) until no further or total consumption of substrate 2a. [c] Yield of the isolated product. [d] 0.5 mL water was used. [e] 10 mol% of a Brønsted acid catalyst was used instead of tropylium catalyst 1.

A mixture of 2-acetylcyclopentanone (2a, 1 mmol), water (3a, 2 mmol) and a corresponding amount tropylium tetrafluoroborate catalyst 1 was charged into a 4 mL reaction vial and the reaction mixture was topped up with 0.6 mL of the indicated solvent. The reaction was stirred.
at the indicated temperature for the indicated reaction time. The reaction was monitored by TLC or $^1$H NMR. The reaction mixture was subsequently concentrated under reduced pressure. The product was isolated by column chromatography (silica-gel, ethyl acetate: hexane = 1:9) to obtain 6-oxoheptanoic acid $4a$ as a yellowish solid.
General Procedures for the Tropylium-Promoted retro-Claisen Reactions

Procedure A

\[ \begin{align*}
\text{R}^1\text{O} & \quad \text{R}^2\text{O} \quad \text{R}^3 \\
\text{2} & + \quad \text{R-XH} \\
\text{cat. BF}_4^- (1, 10\, \text{mol%}) & \\
\text{neat, 100 °C, 16 h} & \\
\rightarrow & \\
\text{R}^1\text{X} & \quad \text{R} \quad \text{O} \\
\text{4} & + \quad \text{H} \quad \text{O} \\
\text{R}^2\text{R}^3 & \\
\text{5} &
\end{align*} \]

A mixture of 1,3-diketone 2 (1 mmol, 1 equiv), nucleophile 3 (water, alcohol, amine or thiol, 2 mmol, 2 equiv) and tropylium tetrafluoroborate catalyst 1 (0.1 mmol, 10 mol%) was charged into a 4 mL reaction vial and the reaction mixture was stirred at 100 °C for 16 h under solvent free and closed-vessel conditions. The reaction was monitored by TLC or $^1$H NMR. The reaction mixture was subsequently concentrated under reduced pressure. The product was isolated by column chromatography (silica-gel, ethyl acetate: hexane = 1:9) to obtain product 4.

Procedure B

\[ \begin{align*}
\text{R}^1\text{O} & \quad \text{R}^2\text{O} \quad \text{R}^3 \\
\text{2} & + \quad \text{R-XH} \\
\text{cat. BF}_4^- (1, 10\, \text{mol%}) & \\
\text{TFE, rt, 24 h} & \\
\rightarrow & \\
\text{R}^1\text{X} & \quad \text{R} \quad \text{O} \\
\text{4} & + \quad \text{H} \quad \text{O} \\
\text{R}^2\text{R}^3 & \\
\text{5} &
\end{align*} \]

A mixture of 1,3-diketone 2 (1 mmol, 1 equiv), nucleophile 3 (water, alcohol, amine or thiol, 2 mmol, 2 equiv) and tropylium tetrafluoroborate catalyst 1 (0.1 mmol, 10 mol%) was charged into a 4 mL reaction vial containing 2,2,2-trifluoroethanol (0.6 mL) and the reaction mixture was stirred at room temperature for 24 h. The reaction was monitored by TLC or $^1$H NMR. The reaction mixture was subsequently concentrated under reduced pressure. The product was isolated by column chromatography (silica-gel, ethyl acetate: hexane = 1:9) to obtain product 4.

Procedure C

\[ \begin{align*}
\text{R}^1\text{O} & \quad \text{R}^2\text{O} \quad \text{R}^3 \\
\text{2} & + \quad \text{R-XH} \\
\text{cat. BF}_4^- (1, 10\, \text{mol%}) & \\
\text{TFE, 100 °C, 12 h} & \\
\rightarrow & \\
\text{R}^1\text{X} & \quad \text{R} \quad \text{O} \\
\text{4} & + \quad \text{H} \quad \text{O} \\
\text{R}^2\text{R}^3 & \\
\text{5} &
\end{align*} \]
A mixture of 1,3-diketone 2 (1 mmol, 1 equiv), nucleophile 3 (water, alcohol, amine or thiol, 2 mmol, 2 equiv) and tropylium tetrafluoroborate catalyst 1 (0.1 mmol, 10 mol%) was charged into a 4 mL reaction vial containing 2,2,2-trifluoroethanol (0.6 mL) and the reaction mixture was stirred at 100 °C for 12 h under closed-vessel conditions. The reaction was monitored by TLC or $^1$H NMR. The reaction mixture was subsequently concentrated under reduced pressure. The product was isolated by column chromatography (silica-gel, ethyl acetate: hexane = 1:9) to obtain product 4.
Characterization Data of Products

6-Oxoheptanoic acid\(^1\) (compound number 4a): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and water to give the title compound as a yellowish solid (100 mg, 99% yield).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CO}_2H
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.46 (t, \(J = 6.7\) Hz, 2H), 2.36 (t, \(J = 7.0\) Hz, 2H), 2.14 (s, 3H), 1.66-1.59 (m, 4H), ppm;

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 208.8, 179.6, 43.3, 33.9, 30.0, 24.2, 23.2 ppm.

Methyl 6-oxo-heptanoate\(^2\) (compound number 4b): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and methanol to give the title compound as a yellowish liquid (130 mg, 97% yield).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{O}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.65 (s, 3H), 2.44 (t, \(J = 6.8\) Hz, 2H), 2.31 (t, \(J = 7.1\) Hz, 2H), 2.12 (s, 3H), 1.62-1.57 (m, 4H) ppm;

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 208.8, 174.0, 51.7, 43.4, 33.9, 30.0, 24.5, 23.3 ppm.

Ethyl 6-oxo-heptanoate\(^3\) (compound number 4c): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and ethanol to give the title compound as a yellow oil (160 mg, 94% yield).

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{O}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.13 (q, \(J = 7.1\) Hz, 2H), 2.43 (t, \(J = 6.9\) Hz, 2H), 2.29 (t, \(J = 7.1\) Hz, 2H), 2.12 (s, 3H), 1.62-1.54 (m, 4H), 1.23 (t, \(J = 7.1\) Hz, 3H) ppm;

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.0, 173.6, 60.5, 43.4, 34.1, 29.9, 24.5, 23.3, 14.3 ppm.


**n-Propyl 6-oxoheptanoate** (compound number 4d): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and n-propanol to give the title compound as a pale-yellow oil (156 mg, 84% yield).

\[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.01 (t, \(J = 6.7\) Hz, 2H), 2.44 (t, \(J = 6.7, 6.9\) Hz, 2H), 2.31 (t, \(J = 7.2, 6.9\) Hz, 2H), 2.13 (s, 3H), 1.67-1.58 (m, 6H), 0.92 (t, \(J = 7.5\) Hz, 3H) ppm;

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 209.1, 173.2, 66.2, 43.4, 34.2, 30.0, 24.5, 23.3, 22.0, 10.1 ppm.

**Allyl 6-oxoheptanoate** (compound number 4e): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and allyl alcohol to give the title compound as a yellowish liquid (180 mg, 97% yield).

\[\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.94-5.85 (m, 1H), 5.32-5.20 (m, 2H), 4.56 (dt, \(J = 1.4, 1.3\) Hz, 2H), 2.44 (t, \(J = 6.7\) Hz, 2H), 2.33 (t, \(J = 7.0\) Hz, 2H) 2.12 (s, 3H), 1.63-1.57 (m, 4H) ppm;

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 208.9, 173.2, 132.3, 118.4, 65.2, 43.4, 34.0, 29.9, 24.5, 23.3, ppm.

**Prop-2-ynyl 6-oxoheptanoate** (compound number 4f): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and propargyl alcohol to give the title compound as a yellowish oil (135 mg, 74% yield).

\[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\]

---

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.67 (d, $J = 2.5$ Hz, 2H), 2.45 (t, $J = 7.0$ Hz, 2H), 2.37 (t, $J = 7.0$ Hz, 2H), 2.13 (s, 3H), 1.68-1.56 (m, 4H) ppm (C$_{\text{alkyne}}$-H signal not observed);
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.6, 172.7, 77.8, 74.9, 52.0, 43.3, 33.9, 30.0, 24.4, 23.2 ppm.

Isopropyl 6-oxoheptanoate$^1$ (compound number 4g): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and isopropanol to give the title compound as a yellowish oil (131 mg, 70% yield).

![Isopropyl 6-oxoheptanoate](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.97-4.88 (m, 1H), 2.39 (t, $J = 6.4$, 6.6 Hz, 2H), 2.21 (p, $J = 4.2$, 2.7, 2.9, 3.7 Hz, 2H), 2.08 (s, 3H), 1.54 (p, $J = 3.5$ Hz, 4H), 1.16 (d, $J = 6.3$ Hz, 6H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.7, 173.1, 67.6, 43.4, 34.5, 29.9, 24.5, 23.3, 21.9 ppm.

$n$-Butyl 6-oxoheptanoate$^1$ (compound number 4h): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and $n$-butyl alcohol to give the title compound as a yellowish liquid (185 mg, 92% yield).

![n-Butyl 6-oxoheptanoate](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.05 (t, $J = 6.6$ Hz, 2H), 2.43 (t, $J = 6.9$ Hz, 2H), 2.45 (t, $J = 6.9$ Hz, 2H), 2.12 (s, 3H), 1.62-1.55 (m, 6H), 1.40-1.31 (m, 2H), 0.91 (t, $J = 7.8$ Hz, 3H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.9, 173.7, 64.4, 43.4, 34.2, 30.8, 29.9, 24.5, 23.3, 19.2, 13.8 ppm.

Cyclohexyl 6-oxoheptanoate (compound number 4i): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and cyclohexanol to give the title compound as a yellowish oil (152 mg, 67% yield).

![Cyclohexyl 6-oxoheptanoate](image)
\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}) \(\delta\) 4.77-4.70 (m, 1H), 2.44 (t, \(J = 6.7\) Hz, 2H), 2.28 (t, \(J = 7\) Hz, 2H), 2.12 (s, 3H), 1.83 (q, \(J = 5.8\) Hz, 2H), 4.13 (q, \(J = 5.8\) Hz, 2H), 1.60 (p, \(J = 3.5\) Hz, 4H), 1.43-1.22 (m, 6H) ppm;

\textbf{13C NMR (100 MHz, CDCl}\textsubscript{3}) \(\delta\) 208.7, 172.9, 72.4, 43.4, 34.6, 31.8, 30.1, 25.5, 24.7, 23.9, 23.3 ppm;

\textbf{IR (KBr)} 2933, 2858, 1715, 1450, 1358 cm\(^{-1}\);

\textbf{HRMS (ESI+)} m/z: [M+Na]\(^+\) Calcd. for C\textsubscript{13}H\textsubscript{22}O\textsubscript{3}Na 249.1461; Found 249.1461.

\textbf{Benzyl 6-oxoheptanoate} (compound number \textit{4j}): Prepared using the general procedure A from (2-acetylcyclopentanone \textit{2a}) and benzyl alcohol to give the title compound as a yellow oil (131 mg, 70% yield).

\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}) \(\delta\) 7.38-7.30 (m, 5H), 5.11 (s, 2H), 2.43 (t, \(J = 7.0\) Hz, 2H), 2.37 (t, \(J = 7.0\) Hz, 2H), 2.12 (s, 3H), 1.68-1.57 (m, 4H) ppm;

\textbf{13C NMR (100 MHz, CDCl}\textsubscript{3}) \(\delta\) 208.6, 173.4, 136.1, 128.7 (two coincident resonances), 128.4, 66.4, 43.4, 34.1, 30.0, 24.5, 23.3 ppm;

\textbf{IR (KBr)} 2947, 1731, 1713, 1603, 1529, 1453 cm\(^{-1}\);

\textbf{HRMS (ESI+)} m/z: [M+Na]\(^+\) Calcd. for C\textsubscript{14}H\textsubscript{18}O\textsubscript{3}+Na 257.1148; Found 257.1147.

\textbf{6-Oxo-heptanoic acid phenethyl ester}\textsuperscript{5} (compound number \textit{4k}): Prepared using the general procedure A from (2-acetylcyclopentanone \textit{2a}) and 2-phenylethanol to give the title compound as a colorless oil (176 mg, 71% yield).

\textbf{1H NMR (400 MHz, CDCl}\textsubscript{3}) \(\delta\) 7.32-7.20 (m, 5H), 4.28 (t, \(J = 7.0\) Hz, 2H), 2.93 (t, \(J = 7.0\) Hz, 2H), 2.41 (t, \(J = 6.7\) Hz, 2H), 2.29 (t, \(J = 6.7\) Hz, 2H), 2.12 (s, 3H), 1.61-1.54 (m, 4H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 208.7, 173.5, 137.9, 129.0, 128.6, 126.7, 64.5, 43.4, 35.2, 34.1, 30.0, 24.5, 23.3 ppm.

$N$-butyl-6-oxoheptanamide (compound number 4l): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and $n$-butyl amine to give the title compound as a white solid (165 mg, 83% yield).

\[
\begin{align*}
\text{O} & \text{H} \\
\text{N} & \text{C-C-C} \\
\text{H} & \text{O}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.57 (s, 1H), 3.25 (q, $J = 7.0$ Hz, 2H), 2.46 (t, $J = 6.7$ Hz, 2H), 2.16 (t, $J = 6.7$ Hz, 2H), 2.13 (s, 3H), 1.61 (p, $J = 3.6$ Hz, 4H), 1.48 (p, $J = 7.0$ Hz, 2H), 1.39-1.29 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 209.1, 172.6, 43.4, 39.4, 36.6, 31.9, 30.1, 25.2, 23.3, 20.2, 13.9 ppm;

IR (KBr) 3292, 3084, 2930, 2867, 1710, 1639, 1544, 1437 cm$^{-1}$;

HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{11}$H$_{21}$NO$_2$Na 222.1465; Found 222.1465.

1-(Pyrrolidin-1-yl) heptane-1,6-dione (compound number 4m): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and pyrrolidine to give the title compound as a yellowish oil (170 mg, 86% yield).

\[
\begin{align*}
\text{O} & \text{H} \\
\text{N} & \text{C-C-C} \\
\text{H} & \text{O}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 3.43 (s, 4H), 2.46 (t, $J = 6.6$ Hz, 2H), 2.28 (t, $J = 6.6$ Hz, 2H), 2.13 (s, 3H), 1.93 (d, $J = 26.0$ Hz, 4H), 1.66-1.59 (m, 4H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 209.1, 171.4, 46.7, 45.8, 43.7, 34.6, 30.0, 26.2, 24.5, 23.7, 22.6 ppm;

IR (KBr) 2947, 2872, 1708, 1619, 1436 cm$^{-1}$;

HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{11}$H$_{19}$NO$_2$Na 220.1308; Found 220.1309.
1-(Piperidin-1-yl) heptane-1,6-dione (compound number 4n): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and piperidine to give the title compound as a yellow oil (179 mg, 85% yield).

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 3.51 (d, 4H), 2.45 (t, J = 6.9 Hz, 2H), 2.31 (t, J = 7.2 Hz, 2H), 2.12 (s, 3H), 1.65-1.52 (m, 10H), ppm;} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{) } \delta 208.9, 170.9, 46.7, 43.5, 33.0, 29.9, 25.6, 24.8, 24.6, 23.6 ppm;} \]

\[ \text{IR (KBr) } 2934, 2858, 1704, 1609, 1445 \text{ cm}^{-1}; \]

\[ \text{HRMS (ESI+) m/z: [M+Na]^+ Calcd. for C}_{12}\text{H}_{21}\text{NO}_2\text{Na 234.1465; Found 234.1465.} \]

\[ \text{N-benzyl-6-oxoheptanamide (compound number 4o): Prepared using the general procedure A from (2-acetylcyclopentanone 2a) and benzylamine to give the title compound as a yellow oil (178 mg, 76% yield).} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.34-7.24 (m, 5H), 5.91 (s, 1H), 4.34 (d, J = 5.8 Hz, 2H), 2.45 (t, J = 6.9 Hz, 2H), 2.21 (t, J = 6.9 Hz, 2H), 2.12 (s, 3H), 1.68-1.56 (m, 4H) ppm;} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{) } \delta 208.9, 172.6, 138.5, 128.8, 127.9, 127.5, 43.7, 43.4, 36.4, 30.0, 25.1, 23.33 ppm;} \]

\[ \text{IR (KBr) 2932, 1705, 1639, 1542, 1452, 1424 \text{ cm}^{-1};} \]

\[ \text{HRMS (ESI+) m/z: [M+Na]^+ Calcd. for C}_{14}\text{H}_{19}\text{NO}_2\text{Na 256.1308; Found 256.1306.} \]

5-Oxohexanoic acid\(^6\) (compound number 4p): Prepared using the general procedure A from (1,3-cyclohexanedione) and water to give the title compound as a colourless oil (116 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.53 (t, $J = 7.2$ Hz, 2H), 2.39 (t, $J = 7.2$ Hz, 2H), 2.15 (s, 3H), 1.90 (p, $J = 7.2$, 7.1 Hz, 2H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.1, 178.5, 42.4, 32.9, 30.1, 18.7 ppm.

**Methyl 5-oxohexanoate**$^7$ (compound number 4q): Prepared using the general procedure A from (1,3-cyclohexanedione) and methanol to give the title compound as a colourless oil (130 mg, 88% yield)

![Methyl 5-oxohexanoate](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.64 (s, 3H), 2.48 (t, $J = 7.2$ Hz, 2H), 2.32 (t, $J = 7.2$ Hz, 2H), 2.11 (s, 3H), 1.86 (p, $J = 7.2$, 7.3 Hz, 2H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.1, 173.7, 51.7, 42.5, 33.1, 30.0, 18.9 ppm.

**Ethyl 5-oxohexanoate**$^8$ (compound number 4r): Prepared using the general procedure A from (1,3-cyclohexanedione) and ethanol to give the title compound as a colourless oil (121 mg, 76% yield).

![Ethyl 5-oxohexanoate](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.12 (q, $J = 7.2$, 7.0 Hz, 2H), 2.49 (t, $J = 7.2$ Hz, 2H), 2.31 (t, $J = 7.2$ Hz, 2H), 2.13 (s, 3H), 1.88 (p, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.2, 173.3, 60.5, 42.6, 33.4, 30.1, 19.0, 14.4 ppm.

**5-Oxohexanoic acid**$^9$ (compound number 4s): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and water to give the title compound as a white solid (108 mg, 75% yield).

![5-Oxohexanoic acid](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.50 (t, $J = 7.2$ Hz, 2H), 2.45-2.37 (m, 4H), 1.91 (p, $J = 7.2$, Hz, 2H), 1.05 (t, $J = 7.3$ Hz, 3H) ppm;

---

Methyl 5-oxoheptanoate\textsuperscript{10} (compound number 4t): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and methanol to give the title compound as a colourless oil (123 mg, 78\% yield).

\begin{center}
\includegraphics[width=0.5\textwidth]{methyl_5-oxoheptanoate}
\end{center}

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 3.66 (s, 3H), 2.49-2.32 (m, 6H), 1.89 (p, \(J = 7.2\) Hz, 2H), 1.05 (t, \(J = 7.3\) Hz, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 210.9, 173.8, 51.7, 41.2, 36.0, 33.2, 19.1, 7.9 ppm.

Ethyl 5-oxoheptanoate\textsuperscript{11} (compound number 4u): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and ethanol to give the title compound as a colourless oil (122 mg, 72\% yield).

\begin{center}
\includegraphics[width=0.5\textwidth]{ethyl_5-oxoheptanoate}
\end{center}

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 4.13 (q, \(J = 7.1\) Hz, 2H), 2.48-2.38 (m, 4H), 2.31 (t, \(J = 7.2\) Hz, 2H), 1.88 (p, \(J = 7.1, 7.3\) Hz, 2H), 1.24 (t, \(J = 7.2, 6.9\) Hz, 3H), 1.05 (t, \(J = 7.3\) Hz, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 210.9, 173.3, 60.5, 41.2, 36.0, 33.5, 19.1, 14.3, 7.9 ppm.

1-(Pyrrolidin-1-yl) heptane-1,5-dione\textsuperscript{12} (compound number 4w): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and pyrrolidine to give the title compound as a yellowish oil (138 mg, 70\% yield).

\begin{center}
\includegraphics[width=0.5\textwidth]{1-(pyrrolidin-1-yl)heptane-1,5-dione}
\end{center}


**Ethyl benzoate**

(Compound number 4y1): Prepared according to the general procedure A from (1,3-diphenylpropane-1,3-dione) and ethanol to give the title compound as a colorless oil (80 mg, 53% yield).

![Ethyl benzoate structure](image)

**N-Butylbenzamide**

(Compound 4y2): Prepared according to the general procedure A from (1,3-diphenylpropane-1,3-dione) and n-butylamine to give the title compound as a white solid (79 mg, 45% yield).

![N-Butylbenzamide structure](image)

---

1H NMR (400 MHz, CDCl3) δ 8.07-8.03 (m, 2H), 7.56-7.51 (m, 1H), 7.45-7.40 (m, 2H), 4.38 (q, J = 8.0 Hz, 2H), 1.39 (t, J = 8.0 Hz, 3H) ppm;

13C NMR (100 MHz, CDCl3) δ 166.7, 132.9, 130.7, 129.6, 128.4, 61.0, 14.4 ppm.

---


*N-Benzyacetamide*\(^{15}\) (compound 4z): Prepared according to the general procedure A from acetoacetone and benzylamine to yield a white solid (80 mg, 54% yield).

\[
\text{\textbf{H NMR (400 MHz, CDCl}_3) \delta 7.45-7.25 (m, 5H), 6.52 (bs, 1H), 4.36 (d, J = 4.0 Hz, 2H), 1.96 (s, 3H) ppm;}\]

\[
\text{\textbf{C NMR (100 MHz, CDCl}_3) \delta 171.1, 136.1, 128.7 (two coincident resonances), 128.4, 66.5, 21.1 ppm.}\]

Enamine Formation with 1,3-Cyclohexanediones as Reaction Substrates

Reactions between 1,3-cyclohexanedione (substrate 2b) and 2-methyl-1,3-cyclohexanedione (substrate 2c) and amines did not lead to the C-C bond cleavage but form the enamine condensation products 4’b and 4c’ instead. This difference in reactivity between amines and alcohol substrates (see retro-Claisen products 4p-4r above) could be attributed to the relative stability of these conjugated enamine products under the reaction conditions.

\[
\begin{align*}
2b & \quad + \quad R-\text{NH}_2 \quad \text{cat.} \quad \text{BF}_4^- (1, 10 \text{ mol%}) \\
\text{neat, 100 °C, 16 h} & \quad \rightarrow \\
\text{4'b} & \quad + \quad \text{HOH}
\end{align*}
\]

3-(n-Butylamino)cyclohex-2-enone\textsuperscript{16} (compound number 4’b1): Prepared using the general procedure A from (1,3-cyclohexanedione) and n-butyl amine to give the title compound as a yellow oil (136 mg, 81% yield).

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \delta 5.12 (s, 1H), 4.43 (s, 1H), 3.09 (q, J = 7.0, 5.5 Hz, 2H), 2.31 (t, J = 6.5 Hz, 4H), 1.96 (p, J = 6.2 Hz, 2H), 1.60-1.53 (m, 2H), 1.41-1.32 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H) ppm; \\
\text{13C NMR (100 MHz, CDCl}_3) & \delta 197.4, 97.1, 42.8, 36.5, 30.7, 22.1, 20.3, 13.8 ppm.
\end{align*}
\]

3-(Pyrrolidin-1-yl)cyclohex-2-enone\textsuperscript{17} (compound number 4’b2): Prepared using the general procedure A from (1,3-cyclohexanedione) and pyrrolidine to give the title compound as a yellow oil (104 mg, 63% yield).

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) & \delta 5.08 (s, 1H), 3.45 (t, J = 5.3 Hz, 2H), 3.22 (t, J = 5.5 Hz, 2H), 2.44 (t, J = 6.2 Hz, 2H), 2.28 (t, J = 6.3 Hz, 2H), 1.99-1.95 (m, 6H) ppm;
\end{align*}
\]


\textsuperscript{17} J. Zhang, Q. Jiang, D. Yang, X. Zhao, Y. Dong, R. Liu, Chem. Sci., \textbf{2015}, 6, 4674-4680.
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.7, 90.6, 49.7, 49.4, 27.8, 25.0, 24.6, 20.6 ppm.

3-(Piperidin-1-yl)cyclohex-2-enone$^{18}$ (compound number 4’b3): Prepared using the general procedure A from (1,3-cyclohexanedione) and piperidine to give the title compound as a yellow oil (135 mg, 75% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.29 (s, 1H), 3.33 (t, $J = 5.3$ Hz, 4H), 2.40 (t, $J = 6.2$ Hz, 2H), 2.28 (t, $J = 6.0$, 6.8 Hz, 2H), 1.98 (p, $J = 6.2$, 6.4 Hz, 2H), 1.68-1.56 (m, 6H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.3, 194.7, 99.5, 47.7, 35.6, 27.2, 25.6, 24.5, 22.4 ppm.

3-(Benzy lamino)cyclohex-2-enone$^{9}$ (compound number 4’b4): Prepared using the general procedure A from (1,3-cyclohexanedione) and benzylamine to give the title compound as a yellow oil (152 mg, 73% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.17 (m, 5H), 5.91 (s, 1H), 5.05 (s, 1H), 4.14 (d, $J = 5.3$ Hz, 2H), 2.33 (t, $J = 6.2$ Hz, 2H), 2.18 (t, $J = 6.3$ Hz, 2H), 1.86 (q, $J = 6.5$, 6.2 Hz, 2H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.4, 165.2, 136.9, 128.8, 128.6, 127.7, 96.9, 47.1, 36.3, 29.5, 21.9 ppm.

---

3-(butylamino)-2-methylcyclohex-2-en-1-one (compound number 4c’1): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and n-butyl amine to give the title compound as a white solid (169 mg, 93% yield).

\[ \text{O} \begin{array}{c} \text{N} \\ \text{H} \end{array} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.42 (s, 1H), 3.26 (q, $J$ = 7.0, 6.0 Hz, 2H), 2.44 (t, $J$ = 6.2, Hz, 2H), 2.31 (t, $J$ = 6.4, 6.7 Hz, 2H), 1.93 (p, $J$ = 6.5 Hz, 2H), 1.69 (s, 3H), 1.61-153 (m, 4H), 1.44-1.35 (m, 2H), 0.96 (t, $J$ = 7.3, Hz, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.5, 161.5, 104.4, 43.1, 36.2, 32.9, 25.4, 21.4, 20.1, 13.9, 7.6 ppm;

IR (KBr) 2935, 2868, 1731, 1612, 1418 cm$^{-1}$;

HRMS (ESI$^+$) m/z: [M+Na]$^+$ Calcd. for C$_{11}$H$_{19}$NONa 204.1359; Found 204.1357.

3-(benzylamino)-2-methylcyclohex-2-en-1-one (compound number 4c’2): Prepared using the general procedure A from (2-methyl-1,3-cyclohexanedione) and benzylamine to give the title compound as a (150 mg, 70% yield).

\[ \text{O} \begin{array}{c} \text{N} \\ \text{H} \end{array} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.24 (m, 5H), 5.91 (s, 1H), 4.43 (d, $J$ = 5.7 Hz, 2H), 2.45 (t, $J$ = 7.0 Hz, 2H), 2.21(t, $J$ = 7.0 Hz, 2H), 2.12 (s, 3H), 1.68-1.56 (m, 4H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 2.8, 172.6, 138.5, 128.7, 127.9, 127.5, 43.7, 43.4, 36.4, 30.0, 25.5, 23.3 ppm;

IR (KBr) 3061, 2938, 2861, 1708, 1655, 1530, 1449, 1403 cm$^{-1}$;

HRMS (ESI$^+$) m/z: [M+H]$^+$ Calcd. for C$_{14}$H$_{18}$NO 216.1383; Found 216.1381.
General Procedure for the *retro*-Claisen Reactions in Continuous Flow

Flow reactions were conducted on a Vapourtec R-Series flow reactor.

Optimization of catalyst loading for flow chemistry: The *retro*-Claisen ethanolysis reactions of substrate 2a to form 4c with 10, 5 and 2.5 mol% tropylium tetrafluoroborate in flow indicated that 5 mol% catalyst loading is optimal for the reaction.

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>Yield of 4c</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol%</td>
<td>97%</td>
</tr>
<tr>
<td>5 mol%</td>
<td>95% (at 1 mmol scale) 93% (at 20 mmol scale)</td>
</tr>
<tr>
<td>2.5 mol%</td>
<td>88%</td>
</tr>
</tbody>
</table>

**Reaction conditions:**

A solution of diketone 2 (1.0 equiv) and tropylium tetrafluoroborate 1 (0.05 equiv, 5 mol%) in TFE (0.5 M, solution #1) and a solution of nucleophile 3 (2.0 equiv) in TFE (1 M, solution #2) were prepared as stock solutions. The flow system was fitted with a high temperature 10
mL tube reactor and a \((8 + 8 = 16)\) bar back-pressure regulator and the entire reactor was flushed with TFE. The solution of reagents was injected at flow rates corresponding to the residence time of 30 minutes (pump #1 for solution #1: 0.33 mL/min, pump #2: 0.33 mL/min). The resulting reaction mixture was collected and concentrated under reduced pressure before being worked up in similar fashion to batch reactions.
Dehydrative Thiolation of 1,3-Diketones with Thiols

1-(2-(Dodecylthio)cyclopent-1-en-1-yl)ethan-1-one (compound number 8a): Prepared using the general procedure A from (2-acetylcyclopentanone) and 1-dodecanethiol to give the title compound as a yellow oil (216 mg, 69% yield).

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3) & \delta 2.81 (t, J = 7.4 \text{ Hz, 4H}), 2.72 (t, J = 7.6, 7.2 \text{ Hz, 2H}), 2.20 (s, 3H), 1.97 (p, J = 7.5 \text{ Hz, 2H}), 1.61 (p, J = 7.2, 7.6 \text{ Hz, 2H}), 1.41-1.24 (m, 20H), 0.87 (t, J = 7.0, 6.5 \text{ Hz, 3H}) ppm; \\
\text{C NMR (100 MHz, CDCl}_3) & \delta 195.6, 157.1, 131.9, 37.4, 33.9, 32.0, 31.9, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 22.8, 22.6, 14.2 \text{ ppm}; \\
\text{IR (KBr)} & 2921, 2851, 1645, 1525, 1461, 1425 \text{ cm}^{-1}; \\
\text{HRMS (ESI+)} m/z: [M+Na]^+ \text{ Calcd. for C}_{19}H_{34}OSNa 333.2223, Found 333.2220. 
\end{align*}
\]

1-(2-(Cyclohexylthio)cyclopent-1-en-1-yl)ethan-1-one (compound number 8b): Prepared using the general procedure A from (2-acetylcyclopentanone) and cyclohexyl thiol to give the title compound as a yellowish liquid (183 mg, 82% yield).

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3) & \delta 3.08 (t, J = 3.4, 3.6, 3.9 \text{ Hz, 1H}), 2.86 (t, J = 7.6, 7.4 \text{ Hz, 2H}), 2.71 (t, J = 7.5, 7.2 \text{ Hz, 2H}), 2.22 (s, 3H), 1.96 (t, J = 7.4 \text{ Hz, 4H}), 1.80 (dt, J = 3.7 \text{ Hz, 2H}), 1.70-1.50 (t, J = 4.3 \text{ Hz, 2H}), 1.47-1.18 (s, 4H) ppm; \\
\text{C NMR (100 MHz, CDCl}_3) & \delta 195.7, 155.9, 132.3, 44.3, 37.3, 34.7, 33.8, 29.7, 26.2, 25.5, 22.7 \text{ ppm}; \\
\text{IR (KBr)} & 2925, 2849, 1698, 1642, 1522, 1429 \text{ cm}^{-1}; \\
\text{HRMS (ESI+)} m/z: [M+Na]^+ \text{ Calcd. for C}_{13}H_{20}OSNa 247.1127, Found 247.1129. 
\end{align*}
\]
1-(2-(Phenylthio)cyclopent-1-en-1-yl)ethan-1-one (compound number 8c): Prepared using the general procedure A from (2-acetylcyclopentanone) and thiophenol to give the title compound as a yellow oil (155 mg, 71% yield).

![1-(2-(Phenylthio)cyclopent-1-en-1-yl)ethan-1-one structure]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54-7.51 (m, 2H), 7.39-7.31 (m, 3H), 2.78-2.73 (m, 2H), 2.50-2.25 (tt, $J = 1.9$ Hz, 2H), 2.25 (s, 3H), 1.83 (p, $J = 7.4$ Hz, 2H) ppm; $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.9, 156.5, 135.2, 132.1, 131.7, 129.3, 129.0, 38.7, 34.2, 29.3, 22.4 ppm; IR (KBr) 2947, 2845, 1647, 1530 cm$^{-1}$; HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{13}$H$_{14}$OSNa 241.0663, Found 241.0658.

1-(2-(Benzy1thio)cyclopent-1-en-1-yl)ethan-1-one (compound number 8d): Prepared using the general procedure A from (2-acetylcyclopentanone) and benzyl mercaptan to give the title compound as a brown liquid (200 mg, 86% yield).

![1-(2-(Benzy1thio)cyclopent-1-en-1-yl)ethan-1-one structure]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.24 (m, 5H), 4.08 (s, 2H), 2.84 (tt, $J = 1.7$ Hz, 2H), 2.73 (tt, $J = 1.7$, 1.9, 1.8 Hz, 2H), 2.21 (s, 3H), 1.97 (p, $J = 7.7$, 7.4, 7.5 Hz, 2H) ppm; $^13$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.9, 156.4, 137.1, 132.0, 128.8, 128.7, 127.3, 37.5, 36.6, 33.6, 29.3, 22.5 ppm; IR (KBr) 2920, 2916, 2850, 1629, 1564, 1457, cm$^{-1}$; HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{14}$H$_{16}$OSNa 255.0820, Found 255.0813.

3-(Dodecylthio)-2-methylcyclohex-2-en-1-one (compound number 8e): Prepared using the general procedure A from (2-methylcyclohexane-1,3-dione) and 1-dodecanethiol to give the title compound as a white solid (186 mg, 60% yield).
\[ \text{O} \quad \text{S} \quad \text{10} \]

$^1$H NMR (400 MHz, CDCl$_3$) \( \delta \) 2.84 (t, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 2.61 (td, \( J = 1.6 \text{ Hz}, 2\text{H} \)), 2.39 (t, \( J = 6.1, 7.1 \text{ Hz}, 2\text{H} \)), 2.01 (p, \( J = 6.4, 6.2, 6.3 \text{ Hz}, 2\text{H} \)), 1.84 (t, \( J = 1.6 \text{ Hz}, 3\text{H} \)), 1.63 (p, \( J = 7.0, 7.5, 7.6 \text{ Hz}, 2\text{H} \)), 1.43-1.26 (m, 18H), 0.87 (t, \( J = 6.7, 7.0 \text{ Hz}, 3\text{H} \)) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) \( \delta \) 194.7, 158.3, 129.6, 36.9, 31.9, 30.8, 29.9, 30.0, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0, 28.8, 22.8, 22.7, 14.2, 11.9 ppm;

IR (KBr) 2916, 2850, 1629, 1564, 1457 cm$^{-1}$;

HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{19}$H$_{34}$OSNa 333.2223, Found 333.2221.

3-(Cyclohexylthio)-2-methylcyclohex-2-en-1-one (compound number 8f): Prepared using the general procedure A from (2-methylcyclohexane-1,3-dione) and cyclohexyl thiol to give the title compound as a yellow oil (175 mg, 78% yield).

\[ \text{O} \quad \text{S} \quad \text{18} \]

$^1$H NMR (400 MHz, CDCl$_3$) \( \delta \) 3.17-3.10 (m, 1H), 2.16 (td, \( J = 1.6, 1.5, 1.6 \text{ Hz}, 2\text{H} \)), 2.35 (t, \( J = 6.1, 7.1 \text{ Hz}, 2\text{H} \)), 1.99-1.88 (m, 4H), 1.80 (t, \( J = 1.6 \text{ Hz}, 3\text{H} \)), 1.78-1.73 (m, 2H), 1.61-1.17 (m, 6H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) \( \delta \) 195.0, 157.8, 130.3, 43.3, 37.1, 34.4, 29.3, 26.0, 25.4, 22.9, 12.1 ppm;

IR (KBr) 2927, 2851, 1712, 1686, 1566, 1446 cm$^{-1}$;

HRMS (ESI+) m/z: [M+Na]$^+$ Calcd. for C$_{13}$H$_{20}$OSNa 247.1127, Found 247.1126.

2-Methyl-3-(phenylthio)cyclohex-2-en-1-one (compound number 8g): Prepared using the general procedure A from (2-methylcyclohexane-1,3-dione) and thiophenol to give the title compound as a yellowish solid (175 mg, 80% yield).

\[ \text{O} \quad \text{S} \quad \text{2} \]

S24
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50-7.47 (m, 2H), 7.41-7.35 (m, 3H), 2.36 (t, $J = 6.2$, 7.0 Hz, 2H), 2.19-2.14 (m, 2H), 1.95 (t, $J = 1.7$ Hz, 3H), 1.90-1.70 (p, $J = 6.3$, 6.7, 6.2, 6.0 Hz, 2H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.4, 157.8, 135.5, 130.2, 129.5, 129.4, 37.2, 30.4, 22.8, 12.3 ppm;

IR (KBr) 3281, 3054, 2940, 1756, 1650, 1574, 1474, 1437 cm$^{-1}$;

HRMS (ESI+) $m/z$: [M+Na]$^+$ Calcd. for C$_{13}$H$_{14}$OSNa 241.0663, Found 241.0657.

3-(Benzylthio)-2-methylycyclohex-2-en-1-one (compound number 8h): Prepared using the general procedure A from (2-methylcyclohexane-1,3-dione) and benzyl mercaptan to give the title compound as a yellow oil (179 mg, 72% yield).

![Chemical Structure]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.27 (m, 5H), 4.10 (s, 2H), 2.60 (td, $J = 1.4$, 1.2 Hz, 2H), 2.37 (t, $J = 6.3$, 7.0 Hz, 2H), 1.98 (p, $J = 6.3$, 6.4, 6.2 Hz, 2H) 1.85 (s, 3H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.9, 157.5, 136.4, 130.0, 128.9, 128.8, 127.7, 36.9, 35.6, 29.5, 22.7, 12.0 ppm;

IR (KBr) 2939, 1640, 1569, 1493, 1424 cm$^{-1}$;

HRMS (ESI+) $m/z$: [M+Na]$^+$ Calcd. for C$_{14}$H$_{16}$OSNa 255.0820, Found 255.0816.
Mechanistic NMR Studies

$^1$H NMR studies of mixtures of substrate 2a (2-acetylcyclopentanone) and tropylium tetrafluoroborate (1) in 1:1 ratio or 10:1 ratio (equal to the typical catalyst loading of 10 mol% of 1 in retro-Claisen reactions) both showed clear evidence of the coordination of tropylium ion to 2a.

Deuterated 6-oxoheptanoic acid (compound number 4aD): Prepared using the general procedure A from (2-acetylcyclopentanone) and deuterium oxide to give the title compound as a colorless oil (128 mg, ~88% yield, accurate yield cannot be determined).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.47-2.33 (m, 2.6H), 2.13-2.09 (m, 1H), 1.67-1.60 (m, 4H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 209.1, 179.6, 43.3, 43.1, 42.9, 42.7, 42.5, 42.3, 42.2, 33.9, 33.8, 33.7, 33.6, 33.4, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 24.1, 24.0, 23.1, 23.0, 22.1 ppm

IR (KBr) 2937, 2870, 1699, 1456, 1407 cm$^{-1}$;

HRMS (ESI+) m/z: See spectrum below.

**Deuterated d$_3$-ethyl 6-oxoheptanoate** (compound number 4bD): Prepared using the general procedure A from (2-acetylcyclopentanone) and deuterated methanol to give the title compound as a colorless oil (122 mg, $\sim$74% yield, accurate yield cannot be determined).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.50-2.30 (m, 3.1H), 2.13-2.09 (m, 1.8H), 1.62-1.58 (m, 4H) ppm;

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$  208.6, 208.6, 208.5, 208.5, 173.9, 51.3, 51.0, 50.8, 50.6, 50.4, 43.3, 43.1, 42.1, 42.7, 42.5, 42.4, 33.9, 33.8, 33.7, 33.5, 33.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0 ppm

IR (KBr) 2924, 2864, 1731.7, 1664, 1510, 1444, 1426 cm$^{-1}$;

HRMS (ESI+) m/z: See spectrum below.
NMR Spectra

6-Oxoheptanoic acid (4a); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Methyl 6-oxo-heptanoato (4b); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Ethyl 6-oxo-heptanoate (4c); $^1\text{H NMR}$ (400 MHz, CDCl$_3$), $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$).
Propyl 6-oxoheptanoate (4d); \( ^1H \) NMR (400 MHz, CDCl\(_3\)), \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)).
Allyl 6-oxoheptanoate (4e); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Prop-2-ynyl 6-oxoheptanoate (4f); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Isopropyl 6-oxoheptanoate (4g); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Butyl 6-oxoheptanoate (4h); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Cyclohexyl 6-oxoheptanoate (4i); \(^1H\) NMR (400 MHz, CDCl\(_3\)), \(^{13}C\) NMR (100 MHz, CDCl\(_3\)).
Benzyl 6-oxoheptanoate (4j); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
6-Oxo-heptanoic acid phenethyl ester (4k); $^1\text{H NMR}$ (400 MHz, CDCl$_3$), $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$).
N-butyl-6-oxoheptanamide (4l); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-(Pyrrolidin-1-yl) heptane-1,6-dion (4m), $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-(Piperidin-1-yl) heptane-1,6-dione (4n); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
N-benzyl-6-oxoheptanamide (4o): \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)), \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)).
5-Oxohexanoic acid (4p); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Methyl 5-oxohexanoate (4q): $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Ethyl 5-oxohexanoate (4r); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
5-Oxohexanoic acid (4s); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Methyl 5-oxoheptanoate (4t); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Ethyl 5-oxoheptanoate (4u); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-Pyrrolidin heptane-1,5-dione (4w); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
Ethyl benzoate (4y1); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
N-Butylbenzamide (4y2); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
N-Benzylacetamide (4z); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
3-(Butylamino)cyclohex-2-enone (4′b1); \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(^{13}\)C NMR (100 MHz, CDCl\(_3\)).
2-(Pyrrolidin-1-yl) cyclohexane-1,3-dione (4'b2); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-(Piperidin-1-yl) hexane-1,5-dione (4’b3); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
N-benzyl-5-oxohexanamide (4′b4); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
3-(butylamino)-2-methyloclohex-2-en-1-one (4c’1); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).

![Chemical Structure](image)

![NMR Spectra](image)
3-(benzylamino)-2-methylocyclohex-2-en-1-one (4c’2), $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-(2-(Dodecylthio)cyclopent-1-en-1-yl)ethan-1-one (8a); \( ^1H \) NMR (400 MHz, CDCl\(_3\)), \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)).
1-(2-(Cyclohexylthio)cyclopent-1-en-1-yl)ethan-1-one (8b); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
1-(2-(Phenylthio)cyclopent-1-en-1-yl)ethan-1-one (8c); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}), \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{spectrum}
\end{figure}
1-(2-(Benzylthio)cyclopent-1-en-1-yl)ethan-1-one (8d); $^1$H NMR (400 MHz, CDCl₃), $^{13}$C NMR (100 MHz, CDCl₃).
3-(Dodecylthio)-2-methylcyclohex-2-en-1-one (8e); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
3-(Cyclohexylthio)-2-methylecyclohex-2-en-1-one (8f); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
2-Methyl-3-(phenylthio)cyclohex-2-en-1-one (8g); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
3-(Benzylthio)-2-methylcyclohex-2-en-1-one (8h); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).
6-Oxoheptanoic-5,7,7,7-d₄ acid-d (4aD); $^1$H NMR (400 MHz, CDCl₃), $^{13}$C NMR (100 MHz, CDCl₃).
Methyl-d$_3$ 6-oxoheptanoate-5,7,7,7-d$_4$ (4bD); $^1$H NMR (400 MHz, CDCl$_3$), $^{13}$C NMR (100 MHz, CDCl$_3$).