Supporting Information

CoH-Catalyzed Radical Hydroalkylation of Alkenes with 1,3-Dicarbonyls

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I. General Information

All reactions were carried out under an argon atmosphere with dry solvents using anhydrous conditions unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reaction solvents were distilled over sodium or CaH₂ and stored under nitrogen atmosphere. All reactions were monitored by thin layer chromatography (TLC) using Macherey - Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300 - 400 mesh ASTM, purchased from Taizhou, China). Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. ¹H, ²H, ¹³C and ¹⁹F NMR spectra were recorded at 25 °C on a Varian 500 or on a Bruker 600 MHz spectrometer. ¹H NMR chemical shifts were referenced to CDCl₃ signal (7.26 ppm). ¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃). The following abbreviations (or combinations) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet, h = heptlet. High-resolution mass spectra HRMS (ESI-TOF) were recorded on Brucker microtof. Enantiomeric excesses (ee) were determined by Agilent 1260 Series HPLC. Co(salen) catalyst [Co]-1∼[Co]-5,¹ Co(III)-OAc,² 1b-1i,³ 1v-1x,⁴ 2k-2n,⁵ 2o-2p,⁶ and 2q⁷ were prepared according to the previously reported literatures.
II. Optimization of Reaction Conditions

Table S1. The screening of silanes and catalysts for aliphatic alkene.ª

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Silane (x equiv)</th>
<th>Yieldb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co]-1</td>
<td>TMDSO (2.0)</td>
<td>81%</td>
</tr>
<tr>
<td>2</td>
<td>[Co]-2</td>
<td>TMDSO (2.0)</td>
<td>50%</td>
</tr>
<tr>
<td>3</td>
<td>[Co]-3</td>
<td>TMDSO (2.0)</td>
<td>52%</td>
</tr>
<tr>
<td>4</td>
<td>[Co]-4</td>
<td>TMDSO (2.0)</td>
<td>29%</td>
</tr>
<tr>
<td>5</td>
<td>[Co]-3</td>
<td>PhSiH₃ (2.0)</td>
<td>37%</td>
</tr>
<tr>
<td>6</td>
<td>[Co]-3</td>
<td>PhMe₂SiH (2.0)</td>
<td>34%</td>
</tr>
<tr>
<td>7</td>
<td>[Co]-1</td>
<td>TMDSO (4.0)</td>
<td>99%</td>
</tr>
</tbody>
</table>

ªReaction conditions: 1a (0.1 mmol), 2a (1.5 equiv), [Co] catalyst (3 mol%), silane (x equiv), 3a (2.0 equiv), toluene (0.1 M), rt, 3 h. bYield determined by ¹H NMR spectroscopy using CH₂Br₂ as an internal standard.
Table S2. The screening of oxidants for aliphatic alkene.\(^a\)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant (x equiv)</th>
<th>Yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a (1.2)</td>
<td>33%</td>
</tr>
<tr>
<td>2</td>
<td>PhIO (1.2)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>3</td>
<td>3b (1.2)</td>
<td>30%</td>
</tr>
<tr>
<td>4</td>
<td>NFSI (1.2)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>5</td>
<td>Selectfluor (1.2)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>6</td>
<td>'BuOOH (1.2)</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>7</td>
<td>3a (2.0)</td>
<td>52%</td>
</tr>
<tr>
<td>8</td>
<td>3a (0.5)</td>
<td>21%</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 1a (0.1 mmol), 2a (1.5 equiv), [Co]-3 (3 mol%), TMDSO (2.0 equiv), oxidant (x equiv), toluene (0.1 M), rt, 3 h. \(^b\)Yield determined by \(^1\)H NMR spectroscopy using CH\(_2\)Br\(_2\) as an internal standard. NFSI = N-Fluorobenzenesulfonimide; Selectfluor = 1-Chloromethyl-4-fluoro-1,4-diaziobicyclo[2.2.2]octane-bis(tetrafluoroborate).
**Table S3.** The screening of solvents for aliphatic alkenes.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>33%</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>9%</td>
</tr>
<tr>
<td>3</td>
<td>DCM</td>
<td>14%</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>26%</td>
</tr>
<tr>
<td>5</td>
<td>CF$_3$Ph</td>
<td>34%</td>
</tr>
<tr>
<td>6</td>
<td>THF/MeCN (5:1)</td>
<td>13%</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: $\textbf{1a}$ (0.1 mmol), $\textbf{2a}$ (1.5 equiv), $\textbf{[Co]-3}$ (3 mol%), TMDSO (2.0 equiv), $\textbf{3a}$ (1.2 equiv), solvent (0.1 M), rt, 3 h.  
$^b$Yield determined by $^1$H NMR spectroscopy using CH$_2$Br$_2$ as an internal standard. TMDSO = 1,1,3,3-tetramethyldisiloxane.
Table S4. Optimization of reaction conditions for activated alkenes.$^a$

![Chemical structure](attachment:chemical_structure.png)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co]-2</td>
<td>3a</td>
<td>99%</td>
</tr>
<tr>
<td>2</td>
<td>[Co]-3</td>
<td>3a</td>
<td>56%</td>
</tr>
<tr>
<td>3</td>
<td>[Co]-4</td>
<td>3a</td>
<td>66%</td>
</tr>
<tr>
<td>4</td>
<td>[Co]-2</td>
<td>'BuOOH</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>[Co]-2</td>
<td>'BuOO'Bu</td>
<td>0%</td>
</tr>
<tr>
<td>6</td>
<td>[Co]-2</td>
<td>PhI(OAc)$_2$</td>
<td>0%</td>
</tr>
<tr>
<td>7</td>
<td>[Co]-2</td>
<td>K$_2$S$_2$O$_8$</td>
<td>0%</td>
</tr>
<tr>
<td>8</td>
<td>[Co]-2</td>
<td>selectfluor</td>
<td>0%</td>
</tr>
<tr>
<td>9</td>
<td>[Co]-2</td>
<td>NFSI</td>
<td>5%</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 5a (0.1 mmol), 2a (1.5 equiv), [Co] catalyst (3 mol%), TMDSO (2.0 equiv), oxidant (1.2 equiv), THF (0.1 M), rt, 3h. $^b$Yield determined by $^1$H NMR spectroscopy using CH$_2$Br$_2$ as an internal standard.
Table S5. Optimization of reaction conditions for acyclic 1,3-diketone.  

![Diagram showing the reaction of 5a with 2j to form 7j](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Silane</th>
<th>Solvent</th>
<th>Yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co]-1</td>
<td>TMDSO</td>
<td>MeCN</td>
<td>33%</td>
</tr>
<tr>
<td>2</td>
<td>[Co]-2</td>
<td>TMDSO</td>
<td>MeCN</td>
<td>55%</td>
</tr>
<tr>
<td>3</td>
<td>[Co]-3</td>
<td>TMDSO</td>
<td>MeCN</td>
<td>36%</td>
</tr>
<tr>
<td>4</td>
<td>[Co]-4</td>
<td>TMDSO</td>
<td>MeCN</td>
<td>26%</td>
</tr>
<tr>
<td>5</td>
<td>[Co]-3</td>
<td>PhSiH(_3)</td>
<td>MeCN</td>
<td>15%</td>
</tr>
<tr>
<td>6</td>
<td>[Co]-3</td>
<td>Et(_3)SiH</td>
<td>MeCN</td>
<td>39%</td>
</tr>
<tr>
<td>7</td>
<td>[Co]-2</td>
<td>TMDSO</td>
<td>DCM</td>
<td>23%</td>
</tr>
<tr>
<td>8</td>
<td>[Co]-2</td>
<td>TMDSO</td>
<td>THF</td>
<td>8%</td>
</tr>
<tr>
<td>9(^c)</td>
<td>[Co]-2</td>
<td>TMDSO</td>
<td>MeCN</td>
<td>66%</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: 5a (0.1 mmol), 2j (1.5 equiv), [Co] catalyst (3 mol%), silane (2.0 equiv), 3a (1.2 equiv), solvent (0.1 M), rt. \(^b\)Yield determined by \(^1\)H NMR spectroscopy using CH\(_2\)Br\(_2\) as an internal standard. \(^c\)3a (2.0 equiv).
Table S6. Optimization of reaction conditions for malonates.\textsuperscript{a}

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\text{Bu} & \quad \text{Bu}
\end{align*}
\]

\[\text{[Co]-2}\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\text{Bu} & \quad \text{Bu}
\end{align*}
\]

\[3a\]

\[
\begin{align*}
\text{Me} & \quad \text{OMe} \\
\text{OTMS} & \quad \text{COOMe}
\end{align*}
\]

\[2q'\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation from above conditions</th>
<th>5a\textsuperscript{d}</th>
<th>13\textsuperscript{d}</th>
<th>Yield\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{b}</td>
<td>using NaH as additive</td>
<td>86%</td>
<td>33%</td>
<td>nr.</td>
</tr>
<tr>
<td>2\textsuperscript{c}</td>
<td>using LDA as additive</td>
<td>100%</td>
<td>52%</td>
<td>nr.</td>
</tr>
<tr>
<td>3\textsuperscript{c}</td>
<td>using LHMDS as additive</td>
<td>98%</td>
<td>46%</td>
<td>nr.</td>
</tr>
<tr>
<td>4</td>
<td>using 2q' instead of 2q</td>
<td>94%</td>
<td>31%</td>
<td>nr.</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 5a (0.1 mmol), 2q (2.0 equiv), [Co]-2 (3 mol%), TMDSO (2.0 equiv), 3a (2.0 equiv), MeCN (0.1 M), 50 °C, 18 h. \textit{Note:} the metal enolates derived from malonates were pre-synthesized in a separate dry Schlenk tube.\textsuperscript{b}The malonate 2q was preactivation with NaH (1.1 equiv) in THF at 0 °C under N\textsubscript{2} for 0.5 h. The malonate 2q was preactivation with additive (1.1 equiv) in THF at -78 °C under N\textsubscript{2} for 0.5 h. \textsuperscript{c}Yield determined by 1H NMR spectroscopy using CH\textsubscript{2}Br\textsubscript{2} as an internal standard. LDA = Lithium diisopropylamide; LHMDS = Lithium bis(trimethylsilyl)amide.

For the dimerization by-product 13 of malonates, we speculated that it may be resulted from the exchange between enol metal intermediate with cobalt(III) species in the reaction mixture to produce the enol cobalt(III) complex, which then isomerized into carbon-Co(III), and then split to produce carbon free radicals.
Table S7. Some inferior results during the scope of compounds.

a. Alkenes

<table>
<thead>
<tr>
<th>Alkenes (0.1 mmol), 2a (1.5 equiv), [Co]-2 (3 mol%), TMDSO (2.0 equiv), 3a (2.0 equiv), toluene (0.1 M), rt. bUsing 1.2 equivalent of 3a in THF.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structures" /></td>
</tr>
</tbody>
</table>

b. 1,3-Dicarbonyls

<table>
<thead>
<tr>
<th>Alkenes (0.1 mmol), 1,3-dicarbonyls (2.0 equiv), [Co]-2 (3 mol%), TMDSO (2.0 equiv), 3a (2.0 equiv), MeCN (0.1 M), rt. bUsing mixed solvent (MeCN: 1,3-dicarbonyls = 5:1) (0.1 M). cUsing 50 ºC instead of rt.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image6" alt="Chemical Structures" /></td>
</tr>
</tbody>
</table>

| Reaction conditions: 5a (0.1 mmol), Meldrum's acid (1.5 equiv), [Co]-2 (3 mol%), TMDSO (2.0 equiv), TMFP-BF₄ (2.0 equiv), MeCN (0.1 M), rt, 24 h. bTHF instead of MeCN. c50 ºC instead of rt. | ![Chemical Structures](image7) |
|--------------------------------------------------|
| ![Chemical Structures](image8) |
| ![Chemical Structures](image9) |
| ![Chemical Structures](image10) |

<table>
<thead>
<tr>
<th>Reaction conditions: 1a (0.1 mmol), Meldrum's acid (1.5 equiv), [Co]-1 (3 mol%), TMDSO (4.0 equiv), TMFP-BF₄ (2.0 equiv), toluene (0.1 M) at room temperature for 24 h.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image11" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image12" alt="Chemical Structures" /></td>
</tr>
<tr>
<td><img src="image13" alt="Chemical Structures" /></td>
</tr>
</tbody>
</table>

8
III. General Procedures of CoH-catalyzed Reaction

**Method A**: To a dry Schlenk tube containing a magnetic stir bar were added [Co]-1 (0.006 mmol, 3 mol%), TMFP-BF$_4$ (0.40 mmol, 2.0 equiv), and dry toluene (2 mL) in sequence. After the reaction mixture was stirred for 5 min at room temperature, olefin (0.20 mmol, 1.0 equiv) and 1,3-diketone (0.30 mmol, 1.5 equiv) were added. Subsequently, TMDSO (0.80 mmol, 4.0 equiv) was added dropwise to the reaction. After stirring at room temperature for 3 hours, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H$_2$O, extracted with DCM (3×10ml), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

**Method B**: To a dry Schlenk tube containing a magnetic stir bar were added [Co]-2 (0.006 mmol, 3 mol%), TMFP-BF$_4$ (0.24 mmol, 1.2 equiv), and dry THF (2 mL) in sequence. After the reaction mixture was stirred for 5 min at room temperature, olefin (0.20 mmol, 1.0 equiv) and 1,3-diketone (0.30 mmol, 1.5 equiv) were added. Subsequently, TMDSO (0.40 mmol, 2.0 equiv) was added dropwise to the reaction mixture. After stirring at room temperature for 3 hours, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H$_2$O, extracted with DCM (3×10ml), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

**Method C**: To a dry Schlenk tube containing a magnetic stir bar were added [Co]-2 (0.006 mmol, 3 mol%), TMFP-BF$_4$ (0.40 mmol, 2.0 equiv), and dry MeCN (2 mL) in sequence. After the reaction mixture was stirred for 5 min at room temperature, olefin (0.20 mmol, 1.0 equiv) and 1,3-diketone (0.30 mmol, 1.5 equiv) were added. Subsequently, TMDSO (0.40 mmol, 2.0 equiv) was added dropwise to the reaction mixture. After stirring at room temperature for 3 hours, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H$_2$O, extracted with DCM (3×10ml), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.
Method D: To a dry Schlenk tube containing a magnetic stir bar were added [Co]-2 (0.006 mmol, 3 mol%), TMFP-BF4 (0.40 mmol, 2.0 equiv), and dry MeCN (2 mL) in sequence. After the reaction mixture was stirred for 5 min at room temperature, olefin (0.20 mmol, 1.0 equiv) and TMS-enol ethers (0.40 mmol, 2.0 equiv) were added. Subsequently, TMDSO (0.40 mmol, 2.0 equiv) was added dropwise to the reaction mixture. After stirring at 50 °C for 18 hours, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with H2O, extracted with DCM (3×10 ml), and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.
IV. Analytical Data of Products

3-Hydroxy-2-(4-phenylbutan-2-yl)cyclohex-2-en-1-one (4a):

Following Method A, 4a was obtained as colorless oil (48.4 mg, 99% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. $^1$H NMR (600 MHz, CDCl₃) $\delta$ 7.28 (t, $J = 7.2$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.16 (d, $J = 7.2$ Hz, 2H), 5.31 (s, 1H), 4.32 – 4.25 (m, 1H), 2.76 – 2.61 (m, 2H), 2.41 – 2.32 (m, 4H), 2.07 – 2.00 (m, 1H), 2.00 – 1.94 (m, 2H), 1.86 (m, 1H), 1.91 – 1.82 (d, $J = 6.0$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl₃) $\delta$ 199.8, 177.0, 141.1, 128.5, 128.3, 126.1, 103.0, 73.8, 37.6, 36.7, 31.7, 29.5, 21.2, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₆H₂₀NaO₂ ([M + Na]$^+$), 267.1262, found, 267.1263.

3-Hydroxy-2-(4-((p-tolyl)butan-2-yl)cyclohex-2-en-1-one (4b):

Following Method A, 4b was obtained as colorless oil (30.0 mg, 58% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. $^1$H NMR (600 MHz, CDCl₃) $\delta$ 7.09 (d, $J = 7.8$ Hz, 2H), 7.03 (d, $J = 7.8$ Hz, 2H), 5.29 (s, 1H), 4.26 (h, $J = 6.0$ Hz, 1H), 2.70 – 2.56 (m, 2H), 2.39 – 2.33 (m, 4H), 2.31 (s, 3H), 2.03 – 1.93 (m, 3H), 1.86 – 1.79 (m, 1H), 1.27 (d, $J = 6.0$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl₃) $\delta$ 199.9, 177.0, 138.0, 135.6, 129.2, 128.2, 103.0, 73.8, 37.7, 36.7, 31.2, 29.5, 21.2, 21.0, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₇H₂₂NaO₂ ([M + Na]$^+$), 281.1644, found, 281.1646.

3-Hydroxy-2-(4-((m-tolyl)butan-2-yl)cyclohex-2-en-1-one (4c):

Following Method A, 4c was obtained as colorless oil (27.4 mg, 53% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. $^1$H NMR (600 MHz, CDCl₃) $\delta$
7.17 (t, \( J = 7.8 \) Hz, 1H), 7.01 (d, \( J = 7.8 \) Hz, 1H), 6.98 – 6.93 (m, 2H), 5.30 (s, 1H), 4.26 (h, \( J = 6.0 \) Hz, 1H), 2.70-2.54 (m, 2H), 2.40-2.32 (m, 4H), 2.32 (s, 3H), 2.05 – 1.95 (m, 3H), 1.88-1.80 (m, 1H), 1.28 (d, \( J = 6.0 \) Hz, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 199.8, 177.0, 141.0, 138.1, 129.2, 128.4, 126.8, 125.3, 103.1, 73.8, 37.6, 36.8, 31.6, 29.5, 21.4, 21.2, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C\(_{17}\)H\(_{22}\)NaO\(_2\) ([M + Na]\(^+\)), 281.1644, found, 281.1643.

2-(4-(4-Fluorophenyl)butan-2-yl)-3-hydroxycyclohex-2-en-1-one (4d):

Following Method A, 4d was obtained as colorless oil (33.0 mg, 63% yield), TLC: \( R_f = 0.3 \) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.12 – 7.08 (m, 2H), 7.00 – 6.94 (m, 2H), 5.30 (s, 1H), 4.27 (h, \( J = 6.0 \) Hz, 1H), 2.72 – 2.56 (m, 2H), 2.36 (dt, \( J = 10.2, 6.6 \) Hz, 4H), 2.04 – 1.93 (m, 3H), 1.87 – 1.79 (m, 1H), 1.29 (d, \( J = 6.0 \) Hz, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 199.9, 176.9, 161.4 (d, \( J = 244.6 \) Hz),136.7 (d, \( J = 3.0 \) Hz), 129.7 (d, \( J = 6.0 \) Hz), 115.3 (d, \( J = 21.1 \) Hz), 103.1, 73.7, 37.7, 36.7, 30.9, 29.5, 21.2, 19.1. \(^1\)F NMR (565 MHz, CDCl\(_3\)) \( \delta \) -117.25 – -117.32 (m, 1F). HRMS (ESI-TOF) (m/z): Calcd for C\(_{16}\)H\(_{19}\)FNaO\(_2\) ([M + Na]\(^+\)), 285.1382, found, 285.1384.

![2-(4-(4-Fluorophenyl)butan-2-yl)-3-hydroxycyclohex-2-en-1-one](image)

2-(4-(4-Chlorophenyl)butan-2-yl)-3-hydroxycyclohex-2-en-1-one (4e):

Following Method A, 4e was obtained as colorless oil (35.6 mg, 64% yield), TLC: \( R_f = 0.4 \) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.25 (d, \( J = 8.4 \) Hz, 2H), 7.08 (d, \( J = 8.4 \) Hz, 2H), 5.30 (s, 1H), 4.30 – 4.23 (m, 1H), 2.71 – 2.57 (m, 2H), 2.35 (q, \( J = 6.6 \) Hz, 4H), 2.02 – 1.94 (m, 3H), 1.87 – 1.79 (m, 1H), 1.28 (d, \( J = 6.0 \) Hz, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 199.8, 176.8, 139.6, 131.8, 129.7, 128.6, 103.1, 73.7, 37.5, 36.7, 31.1, 29.4, 21.2, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C\(_{16}\)H\(_{19}\)ClNaO\(_2\) ([M + Na]\(^+\)), 301.0989, found, 301.0989.
2-(4-(4-Bromophenyl)butan-2-yl)-3-hydroxycyclohex-2-en-1-one (4f):

Following Method A, 4f was obtained as colorless oil (38.8 mg, 60% yield), TLC:
Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV].

\[ \text{H NMR (600 MHz, CDCl}_3 \text{)} \delta 7.40 (d, J = 8.4 \text{ Hz, 2H}), 7.03 (d, J = 8.4 \text{ Hz, 2H}), 5.30 (s, 1H), 4.26 (h, J = 6.0 \text{ Hz, 1H}), 2.71 – 2.55 (m, 2H), 2.40 – 2.30 (m, 4H), 2.02 – 1.94 (m, 3H), 1.87 – 1.79 (m, 1H), 1.28 (d, J = 6.0 \text{ Hz, 3H}). \text{C NMR (150 MHz, CDCl}_3 \text{)} \delta 199.8, 176.8, 140.1, 131.6, 130.1, 119.8, 103.1, 73.7, 37.4, 36.7, 31.2, 29.4, 21.2, 19.1. \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{16}\text{H}_{19}\text{BrNaO}_2 ([M + Na]^+), 345.0582, found, 345.0583.}

3-Hydroxy-2-(4-(4-(trifluoromethyl)phenyl)butan-2-yl)cyclohex-2-en-1-one (4g):

Following Method A, 4g was obtained as colorless oil (38.0 mg, 61% yield), TLC:
Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV].

\[ \text{H NMR (600 MHz, CDCl}_3 \text{)} \delta 7.54 (d, J = 7.8 \text{ Hz, 2H}), 7.27 (d, J = 7.8 \text{ Hz, 2H}), 5.31 (s, 1H), 4.29 (h, J = 6.0 \text{ Hz, 1H}), 2.82 – 2.66 (m, 2H), 2.42 – 2.28 (m, 4H), 2.07 – 2.00 (m, 1H), 2.00 – 1.94 (m, 2H), 1.93 – 1.84 (m, 1H), 1.30 (d, J = 6.0 \text{ Hz, 3H}). \text{C NMR (150 MHz, CDCl}_3 \text{)} \delta 199.8, 176.8, 145.4, 128.7, 128.5 (d, J = 31.7 Hz), 125.4 (q, J = 3.6 Hz), 124.3 (d, J = 271.8 Hz), 103.1, 73.7, 37.3, 36.7, 31.6, 29.4, 21.2, 19.1. \text{F NMR (565 MHz, CDCl}_3 \text{)} \delta = -62.36. \text{HRMS (ESI-TOF) (m/z): Calcd for C}_{17}\text{H}_{19}\text{F}_3\text{NaO}_2 ([M + Na]^+), 335.1350, found, 335.1352.}

2-(4-[(1,1'-Biphenyl)-4-yl]butan-2-yl)-3-hydroxycyclohex-2-en-1-one (4h):
Following Method A, 4h was obtained as colorless oil (31.4 mg, 49% yield), TLC: 
Rr = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.57 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 5.33 (s, 1H), 4.32 (h, J = 6.0 Hz, 1H), 2.79 – 2.63 (m, 2H), 2.36 (dt, J = 11.4, 6.6 Hz, 4H), 2.10 – 2.02 (m, 1H), 1.98 (p, J = 6.6 Hz, 2H), 1.93 – 1.85 (m, 1H), 1.31 (d, J = 6.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 200.0, 177.0, 140.9, 140.3, 139.1, 128.8, 128.8, 128.8, 127.3, 127.1, 127.0, 103.1, 73.9, 37.6, 36.8, 31.4, 29.5, 21.3, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C22H24NaO2 ([M + Na]+ ), 343.1659, found, 343.1657.

3-Hydroxy-2-(4-(naphthalen-2-yl)butan-2-yl)cyclohex-2-en-1-one (4i):

Following Method A, 4i was obtained as colorless oil (34.2 mg, 58% yield), TLC: Rr = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.78 (dt, J = 18.0, 8.4 Hz, 3H), 7.58 (s, 1H), 7.47 – 7.40 (m, 2H), 7.29 (dd, J = 8.4, 1.8 Hz, 1H), 5.32 (s, 1H), 4.32 (h, J = 6.0 Hz, 1H), 2.92 – 2.74 (m, 2H), 2.40 – 2.25 (m, 4H), 2.15 – 2.06 (m, 1H), 2.00 – 1.89 (m, 3H), 1.31 (d, J = 6.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.8, 176.9, 138.6, 133.6, 132.1, 128.1, 127.6, 127.4, 127.1, 126.4, 126.1, 125.3, 103.1, 73.9, 37.5, 36.7, 32.0, 29.5, 21.2, 19.2. HRMS (ESI-TOF) (m/z): Calcd for C20H22NaO2 ([M + Na]+ ), 317.1527, found, 317.1529.

2-(1-(3,4-Dimethoxyphenyl)propan-2-yl)-3-hydroxycyclohex-2-en-1-one (4j):

Following Method A, 4j was obtained as colorless oil (39.0 mg, 67% yield), TLC: Rr = 0.3 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (500 MHz, CDCl3) δ 6.80 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.69 (s, 1H), 5.38 (s, 1H), 4.46 (h, J = 6.0 Hz, 1H), 3.87 (d, J = 3.5 Hz, 7H), 2.95 (dd, J = 14.0, 6.0 Hz, 1H), 2.75 (dd, J = 14.0, 6.0 Hz, 1H), 2.41 – 2.29 (m, 4H), 2.01 – 1.90 (m, 2H), 1.27 (d, J = 6.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.9, 176.8, 148.8, 147.8, 129.7, 121.4, 112.6, 111.2, 103.1, 75.3, 55.9, 41.6, 36.7, 29.5, 21.2, 18.8. HRMS (ESI-TOF) (m/z): Calcd for C17H22NaO3 ([M + Na]+ ), 313.1300, found, 313.1302.
2-(4-Bromobutan-2-yl)-3-hydroxycyclohex-2-en-1-one (4k):

Following Method A, 4k was obtained as colorless oil (14.8 mg, 30% yield), TLC: 
R_f = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (500 MHz, CDCl₃) δ 5.40 (s, 1H), 4.54-4.46 (m, 1H), 3.43 (t, J = 6.5 Hz, 2H), 2.44 – 2.30 (m, 4H), 2.29 – 2.20 (m, 1H), 2.11 – 2.02 (m, 1H), 1.98 (p, J = 6.5 Hz, 2H), 1.30 (d, J = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.7, 176.5, 103.4, 72.3, 38.9, 36.7, 29.3, 28.7, 21.2, 18.7. HRMS (ESI-TOF) (m/z): Calcd for C₁₀H₁₅BrNaO₂ ([M + Na]^+ ), 269.0245, found, 269.0235.

2-(6-Bromohexan-2-yl)-3-hydroxycyclohex-2-en-1-one (4l):

Following Method A, 4l was obtained as colorless oil (41.2 mg, 75% yield), TLC: 
R_f = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (600 MHz, CDCl₃) δ 5.34 (s, 1H), 4.28 (h, J = 6.0 Hz, 1H), 3.41 (t, J = 6.6 Hz, 2H), 2.38 (q, J = 6.0 Hz, 2H), 2.36 – 2.32 (m, 2H), 1.98 (p, J = 6.6 Hz, 2H), 1.87 (p, J = 7.2 Hz, 2H), 1.74 – 1.66 (m, 1H), 1.62 – 1.44 (m, 3H), 1.27 (d, J = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.8, 177.0, 103.0, 74.3, 36.7, 34.9, 33.4, 32.4, 29.5, 23.9, 21.2, 19.1. HRMS (ESI-TOF) (m/z): Calcd for C₁₂H₁₉BrNaO₂ ([M + Na]^+ ), 297.0576, found, 297.0575.

5-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)hexyl acetate (4m):

Following Method A, 4m was obtained as colorless oil (34.6 mg, 68% yield), TLC: 
R_f = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (500 MHz, CDCl₃) δ 5.37 (s, 1H), 4.30 (h, J = 6.0 Hz, 1H), 4.09 (t, J = 6.5 Hz, 2H), 2.39 (dt, J = 13.5, 6.0 Hz, 4H), 2.08 (s, 3H), 2.01 (p, J = 6.5 Hz, 2H), 1.79 – 1.70 (m, 1H), 1.66 (q, J = 7.0 Hz, 2H), 1.64 – 1.57 (m, 1H), 1.53 – 1.35 (m, 2H), 1.29 (d, J = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.8, 177.0, 171.1, 103.0, 74.4, 64.2, 36.7, 35.4, 29.5,
Methyl-10-(2-hydroxy-6-oxocyclohex-1-en-1-yl)undecanoate (4n):

Following **Method A**, 4n was obtained as colorless oil (45.4 mg, 73% yield), TLC:

\[ R_f = 0.4 \] (Petroleum ether : Ethyl acetate = 2:1) [UV].

**1H NMR** (600 MHz, CDCl₃) \( \delta \)

5.34 (s, 1H), 4.25 (h, \( J = 6.0 \) Hz, 1H), 3.67 (s, 3H), 2.37 (td, \( J = 6.0 \), 3.0 Hz, 2H), 2.34 (t, \( J = 6.6 \) Hz, 2H), 2.30 (t, \( J = 7.8 \) Hz, 2H), 1.98 (p, \( J = 6.6 \) Hz, 2H), 1.72 – 1.65 (m, 1H), 1.62 (p, \( J = 7.2 \) Hz, 2H), 1.56 – 1.47 (m, 1H), 1.37 – 1.27 (m, 1H), 1.25 (d, \( J = 6.0 \) Hz, 3H).

**13C NMR** (150 MHz, CDCl₃) \( \delta \)


TBSO

2-(4-((Tert-butyldimethylsilyl)oxy)butan-2-yl)-3-hydroxycyclohex-2-en-1-one (4o):

Following **Method A**, 4o was obtained as colorless oil (25.6 mg, 43% yield), TLC:

\[ R_f = 0.5 \] (Petroleum ether : Ethyl acetate = 2:1) [UV].

**1H NMR** (500 MHz, CDCl₃) \( \delta \)

5.34 (s, 1H), 4.46 (h, \( J = 6.0 \) Hz, 1H), 3.69 – 3.61 (m, 2H), 2.40 – 2.24 (m, 4H), 2.34 (t, \( J = 6.6 \) Hz, 2H), 1.98 (p, \( J = 6.6 \) Hz, 2H), 1.72 – 1.65 (m, 1H), 1.62 (p, \( J = 7.2 \) Hz, 2H), 1.56 – 1.47 (m, 1H), 1.37 – 1.27 (m, 1H), 1.25 (d, \( J = 6.0 \) Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **13C NMR** (125 MHz, CDCl₃) \( \delta \)


2-((1S,4R)-Bicyclo[2.2.1]heptan-2-yl)-3-hydroxycyclohex-2-en-1-one (4p):

Following **Method A**, 4p was obtained as colorless oil (18.2 mg, 44% yield), TLC:

\[ R_f = 0.4 \] (Petroleum ether : Ethyl acetate = 2:1) [UV].

**1H NMR** (500 MHz, CDCl₃) \( \delta \)

5.31 (s, 1H), 4.03 (d, \( J = 7.0 \) Hz, 1H), 2.41 (d, \( J = 5.0 \) Hz, 1H), 2.37 – 2.29 (m, 5H), 1.98 (p, \( J = 6.6 \) Hz, 2H), 1.72 – 1.65 (m, 1H), 1.62 (p, \( J = 7.2 \) Hz, 2H), 1.56 – 1.47 (m, 1H), 1.37 – 1.27 (m, 1H), 1.25 (d, \( J = 6.0 \) Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **13C NMR** (125 MHz, CDCl₃) \( \delta \)

2.00 – 1.92 (m, 2H), 1.71 (ddd, J = 13.5, 7.0, 2.5 Hz, 1H), 1.57 – 1.51 (m, 2H), 1.51 – 1.44 (m, 2H), 1.19 (d, J = 10.0 Hz, 1H), 1.14 – 1.04 (m, 2H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 199.8, 176.7, 103.7, 81.3, 41.0, 39.8, 36.7, 35.3, 35.3, 29.3, 28.2, 24.1, 21.3. \text{HRMS (ESI-TOF) (m/z):}\ Calcd for C\(_{13}\)H\(_{18}\)NaO\(_2\) ([M + Na]\(^{+}\)), 229.1197, found, 229.1199.

2-Cyclopentyl-3-hydroxycyclohex-2-en-1-one (4q):

Following \text{Method A}, 4q was obtained as colorless oil (17.4 mg, 48% yield), TLC: \(R_f = 0.5\) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^{1}\text{H NMR}\) (600 MHz, CDCl\(_3\)) \(\delta\) 5.34 (s, 1H), 4.62 (tt, J = 6.0, 2.4 Hz, 1H), 2.39 – 2.31 (m, 4H), 1.97 (p, J = 6.6 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.82 – 1.77 (m, 2H), 1.76 – 1.70 (m, 2H), 1.65 – 1.56 (m, 2H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 199.8, 177.1, 103.7, 80.5, 36.7, 32.7, 29.4, 24.1, 21.3. \text{HRMS (ESI-TOF) (m/z):}\ Calcd for C\(_{11}\)H\(_{16}\)NaO\(_2\) ([M + Na]\(^{+}\)), 203.1146, found, 203.1145.

3-Hydroxy-2-(4-phenoxybutan-2-yl)cyclohex-2-en-1-one (4r):

Following \text{Method A}, 4r was obtained as colorless oil (26.4 mg, 51% yield), \(r_r = 6:1\) (C2 :C3), TLC: \(R_f = 0.3\) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^{1}\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.27 (t, J = 7.0 Hz, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 5.40 (s, 1H), 4.58 (h, J = 6.0 Hz, 1H), 4.02 (t, J = 5.5 Hz, 2H), 2.37 – 2.29 (m, 4H), 2.17 – 2.09 (m, 1H), 2.08 – 2.00 (m, 1H), 1.99 – 1.90 (m, 2H), 1.33 (d, J = 6.0 Hz, 3H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 199.8, 176.7, 158.7, 129.5, 120.9, 114.5, 103.3, 71.5, 63.8, 36.7, 35.7, 29.4, 23.7, 21.2, 19.2, 9.5. \text{HRMS (ESI-TOF) (m/z):}\ Calcd for C\(_{16}\)H\(_{20}\)NaO\(_3\) ([M + Na]\(^{+}\)), 283.1213, found, 283.1211.

3-Hydroxy-2-(undecan-2-yl)cyclohex-2-en-1-one (4s):
Following **Method A**, 4s was obtained as colorless oil (34.6 mg, 65% yield), TLC: 

\[
R_f = 0.6 \text{ (Petroleum ether : Ethyl acetate = 2:1) [UV].} 
\]

\[ \text{^{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta 5.32 (s, 1H), 4.24 (p, J = 6.0 Hz, 1H), 2.43} \]
\[ \text{– 2.26 (m, 4H), 1.96 (p, J = 6.5 Hz, 2H), 1.71} \]
\[ \text{– 1.59 (m, 1H), 1.55 – 1.45 (m, 1H), 1.31 – 1.17 (m, 17H), 0.87 (t, J = 7.0 Hz, 3H).} \]

\[ \text{^{13}C NMR (150 MHz, CDCl\textsubscript{3}) \delta 199.9, 177.1, 102.9, 74.7, 36.7, 35.8, 31.9, 29.5,} \]
\[ 29.5, 29.4, 29.3, 25.3, 22.6, 21.2, 19.1, 14.1.} \]

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C\textsubscript{17}H\textsubscript{30}NaO\textsubscript{2} ([M + Na]\textsuperscript{+}), 289.1950, found, 289.1952.} \]

![Structural diagram](image)

2-(1-Cyclohexylethyl)-3-hydroxycyclohex-2-en-1-one (4t): 

Following **Method A**, 4t was obtained as colorless oil (37.4 mg, 84% yield), TLC: 

\[
R_f = 0.6 \text{ (Petroleum ether : Ethyl acetate = 2:1) [UV].} 
\]

\[ \text{^{1}H NMR (600 MHz, CDCl\textsubscript{3}) \delta 5.34 (s, 1H), 4.06 (p, J = 6.0 Hz, 1H), 2.40} \]
\[ \text{– 2.36 (m, 2H), 2.36 – 2.33 (m, 2H), 1.97} \]
\[ \text{(p, J = 6.6 Hz, 2H), 1.82 – 1.71 (m, 3H), 171 – 1.63 (m, 2H), 1.58 – 1.50 (m, 1H),} \]
\[ 1.27 – 1.21 (m, 2H), 1.20 (d, J = 6.0 Hz, 3H), 1.15 (tt, J = 12.6, 3.0 Hz, 1H), 1.07 –} \]
\[ 0.93 (m, 2H).} \]

\[ \text{^{13}C NMR (150 MHz, CDCl\textsubscript{3}) \delta 200.0, 177.4, 102.8, 78.6, 42.5, 36.7,} \]
\[ 29.5, 28.6, 28.2, 26.4, 26.0, 25.9, 21.2, 15.9.} \]

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C\textsubscript{14}H\textsubscript{22}NaO\textsubscript{2} ([M + Na]\textsuperscript{+}), 245.1408, found, 245.1408.} \]

![Structural diagram](image)

3-Hydroxy-2-(2-methyl-4-phenylbutan-2-yl)cyclohex-2-en-1-one (4u): 

Following **Method A**, 4u was obtained as colorless oil (13.4 mg, 26% yield), TLC: 

\[
R_f = 0.4 \text{ (Petroleum ether : Ethyl acetate = 2:1) [UV].} 
\]

\[ \text{^{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta 7.29 (d, J = 7.5 Hz, 2H), 7.22 – 7.15 (m, 3H), 5.55 (s, 1H), 2.70} \]
\[ \text{– 2.63 (m, 2H), 2.32} \]
\[ \text{(q, J = 6.0 Hz, 4H), 2.08 – 2.00 (m, 2H), 1.95 (p, J = 6.5 Hz, 2H), 1.51 (s, 6H).} \]

\[ \text{^{13}C NMR (150 MHz, CDCl\textsubscript{3}) \delta 200.0, 175.3, 141.7, 128.5, 128.3, 126.0, 106.2, 82.9,} \]
\[ 43.3, 36.5, 30.5, 30.2, 26.2, 21.3.} \]

\[ \text{HRMS (ESI-TOF) (m/z): Calcd for C\textsubscript{17}H\textsubscript{22}NaO\textsubscript{2} ([M + Na]\textsuperscript{+}), 281.1402, found, 281.1400.} \]

![Structural diagram](image)
(8S,9R,13R,14R)-3-((5-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)hexyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4v):

Following Method A, 4v was obtained as colorless oil (56.6 mg, 61% yield), dr = 1:1, TLC: Rf = 0.3 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (600 MHz, CDCl₃) δ 7.19 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.64 (s, 1H), 5.34 (s, 1H), 4.28 (p, J = 6.0 Hz, 1H), 3.93 (t, J = 6.0 Hz, 2H), 2.95 – 2.83 (m, 2H), 2.50 (dd, J = 19.2, 8.4 Hz, 1H), 2.42 – 2.30 (m, 5H), 2.28 – 2.21 (m, 1H), 2.18 – 2.10 (m, 1H), 2.09 – 2.02 (m, 1H), 2.02 – 1.90 (m, 4H), 1.84 – 1.70 (m, 4H), 1.66 – 1.57 (m, 3H), 1.55 – 1.45 (m, 5H), 1.46 – 1.39 (m, 1H), 1.27 (d, J = 6.0 Hz, 3H), 0.91 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 220.9, 199.9, 177.1, 157.0, 137.8, 132.0, 126.3, 114.5, 112.1, 103.0, 74.5, 67.5, 50.4, 48.0, 44.0, 38.4, 36.7, 35.9, 35.6, 31.6, 29.7, 29.5, 29.1, 26.6, 25.9, 22.1, 21.6, 21.2, 19.1, 13.9. HRMS (ESI-TOF) (m/z): Calcd for C₃₀H₄₀NaO₄ ([M + Na]⁺), 487.2614, found, 487.2616.

5-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)hexyl-2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (4w):

Following Method A, 4w was obtained as colorless oil (42.8 mg, 46% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (600 MHz, CDCl₃) δ 8.11 (d, J = 2.4 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.42 (dd, J = 8.4, 2.4 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 5.31 (s, 1H), 5.17 (s, 2H), 4.23 (h, J = 6.0 Hz, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.63 (s, 2H), 2.37 – 2.28 (m, 4H), 1.95 (p, J = 6.6 Hz, 2H), 1.71 – 1.60 (m, 3H), 1.58 – 1.49 (m, 1H), 1.45 – 1.37 (m, 1H), 1.36 – 1.30 (m, 1H), 1.22 (d, J = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.8, 190.8, 176.9, 171.4, 160.4, 140.4, 136.3, 135.5, 132.8, 132.4, 129.4, 129.2, 127.8, 125.1, 121.0, 102.9, 74.3, 73.6, 64.6, 40.2, 36.7, 35.4, 29.6, 29.4, 28.4, 21.7, 21.1, 19.0. HRMS (ESI-TOF) (m/z): Calcd for C₂₈H₃₀NaO₆ ([M + Na]⁺), 485.1938, found, 485.1936.
5-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)hexyl-2-(4-isobutylphenyl)propanoate (4x):

Following **Method A**, 4x was obtained as colorless oil (52.8 mg, 66% yield), dr = 1:1, TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (500 MHz, CDCl3) δ 7.24 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.35 (s, 1H), 4.28 – 4.20 (m, 1H), 4.10 (t, J = 6.5 Hz, 2H), 3.72 (q, J = 7.0 Hz, 1H), 2.48 (d, J = 7.0 Hz, 2H), 2.43 – 2.33 (m, 4H), 2.01 (p, J = 6.5 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.71 – 1.58 (m, 3H), 1.57 – 1.48 (m, 2H), 1.42 – 1.30 (m, 4H), 1.25 (dd, J = 6.0, 3.0 Hz, 3H), 0.93 (d, J = 6.5 Hz, 6H). **13C NMR** (150 MHz, CDCl3) δ 199.8, 177.0, 165.1, 140.5, 137.8, 137.8, 129.3, 127.1, 103.0, 74.4, 74.4, 64.3, 64.3, 45.2, 45.0, 36.7, 35.3, 35.3, 30.2, 29.5, 28.4, 28.3, 22.4, 21.7, 21.2, 19.0, 18.5. **HRMS** (ESI-TOF) (m/z): Calcd for C25H36NaO4 ([M + Na]+), 423.2322, found, 423.2332.

3-Hydroxy-2-(1-(p-tolyl)ethyl)cyclohex-2-en-1-one (6a):

Following **Method B**, 6a was obtained as colorless oil (42.8 mg, 93% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (600 MHz, CDCl3) δ 7.18 – 7.12 (m, 4H), 5.28 (s, 1H), 5.17 (q, J = 6.6 Hz, 1H), 2.47 – 2.37 (m, 2H), 2.32 (s, 3H), 2.30 – 2.21 (m, 2H), 1.98-1.88 (m, 2H), 1.56 (d, J = 6.6 Hz, 3H). **13C NMR** (150 MHz, CDCl3) δ 199.7, 176.0, 174.8, 140.5, 137.8, 137.8, 129.3, 127.1, 103.0, 74.4, 74.4, 64.3, 64.3, 45.2, 45.0, 36.7, 35.3, 35.3, 30.2, 29.5, 28.4, 28.3, 22.4, 21.7, 21.2, 19.0, 18.5. **HRMS** (ESI-TOF) (m/z): Calcd for C15H18NaO2 ([M + Na]+), 253.1199, found, 253.1199.

3-Hydroxy-2-(1-(o-tolyl)ethyl)cyclohex-2-en-1-one (6b):

Following **Method B**, 6b was obtained as colorless oil (42.4 mg, 92% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (600 MHz, CDCl3) δ 7.28 (d, J = 7.2, 1.8 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.13 (dd, J = 7.2, 1.8 Hz, 1H), 5.37 (q, J = 6.6 Hz, 1H), 5.12 (s, 1H), 2.53 – 2.41 (m, 2H), 2.34 (s, 3H), 2.32 – 2.23 (m, 2H), 2.03 – 1.91 (m, 2H), 1.55 (d, J = 6.6 Hz, 3H). **13C NMR** (150 MHz, CDCl3) δ 199.7, 176.5, 139.4, 133.8, 130.8, 127.8, 126.7, 124.3, 104.4, 73.8, 36.7, 29.4, 22.0,

3-Hydroxy-2-(1-(m-tolyl)ethyl)cyclohex-2-en-1-one (6c):

Following **Method B**, 6c was obtained as colorless oil (43.2 mg, 94% yield), TLC: R<sub>f</sub> = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **¹H NMR** (600 MHz, CDCl₃) δ 7.23 (t, J = 7.8 Hz, 1H), 7.11 – 7.05 (m, 3H), 5.28 (s, 1H), 5.16 (q, J = 6.6 Hz, 1H), 2.51 – 2.40 (m, 2H), 2.35 (s, 3H), 2.32 – 2.23 (m, 2H), 2.01 – 1.90 (m, 2H), 1.56 (d, J = 6.6 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 199.8, 176.6, 141.3, 138.5, 128.7, 126.1, 122.4, 104.6, 77.3, 77.1, 76.8, 76.7, 36.7, 29.4, 23.7, 21.5, 21.2. **HRMS (ESI-TOF) (m/z):** Calcd for C₁₅H₁₈NaO₂ ([M + Na]⁺), 253.1199, found, 253.1194.

2-(1-(3,4-Dimethylphenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6d):

Following **Method B**, 6d was obtained as colorless oil (48.4 mg, 99% yield), TLC: R<sub>f</sub> = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **¹H NMR** (600 MHz, CDCl₃) δ 7.10 (d, J = 7.8 Hz, 1H), 7.03 (s, 1H), 7.00 (d, J = 7.8 Hz, 1H), 5.29 (s, 1H), 5.14 (q, J = 6.6 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.32 – 2.26 (m, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 2.00 – 1.90 (m, 2H), 1.56 (d, J = 6.6 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 199.8, 176.7, 138.8, 137.0, 136.5, 130.0, 126.8, 122.8, 104.5, 76.7, 36.7, 29.4, 23.7, 21.2, 19.9, 19.5. **HRMS (ESI-TOF) (m/z):** Calcd for C₁₆H₂₀NaO₂ ([M + Na]⁺), 267.1453, found, 267.1433.

2-(1-(3,4-Dimethylphenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6e):

Following **Method B**, 6e was obtained as colorless oil (45.8 mg, 84% yield), TLC: R<sub>f</sub> = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **¹H NMR** (600 MHz, CDCl₃) δ
7.37 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.32 (s, 1H), 5.21 (q, J = 6.6 Hz, 1H), 2.52-2.41 (m, 2H), 2.37 – 2.24 (m, 2H), 2.03-1.92 (m, 2H), 1.59 (d, J = 6.6 Hz, 3H), 1.33 (s, 9H). \( ^{13} \text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 199.8, 176.6, 150.9, 138.2, 125.7, 125.1, 104.5, 76.6, 34.6, 31.3, 29.4, 23.5, 21.2. \( \text{HRMS} \) (ESI-TOF) (m/z): Calcd for C\(_{18}\)H\(_{24}\)NaO\(_2\) ([M + Na]\(^+\)), 295.1548, found, 295.1549.

![3-Hydroxy-2-(1-(4-methoxyphenyl)ethyl)cyclohex-2-en-1-one (6f):](image)

3-Hydroxy-2-(1-(4-methoxyphenyl)ethyl)cyclohex-2-en-1-one (6f):

Following Method B, 6f was obtained as colorless oil (48.8 mg, 99% yield), TLC: \( R_f = 0.5 \) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \( ^{1} \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 7.21 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.30 (s, 1H), 5.17 (q, J = 6.5 Hz, 1H), 3.80 (s, 3H), 2.49 – 2.36 (m, 2H), 2.34 – 2.23 (m, 2H), 2.01 – 1.88 (m, 2H), 1.56 (d, J = 6.5 Hz, 3H). \( ^{13} \text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 199.8, 176.7, 159.3, 133.4, 126.8, 114.2, 104.5, 76.4, 55.3, 36.6, 29.4, 23.5, 21.2. \( \text{HRMS} \) (ESI-TOF) (m/z): Calcd for C\(_{15}\)H\(_{18}\)NaO\(_3\) ([M + Na]\(^+\)), 269.1147, found, 269.1148.

![3-Hydroxy-2-(1-phenylethyl)cyclohex-2-en-1-one (6g):](image)

3-Hydroxy-2-(1-phenylethyl)cyclohex-2-en-1-one (6g):

Following Method B, 6g was obtained as colorless oil (26.8 mg, 62% yield), TLC: \( R_f = 0.5 \) (Petroleum ether : Ethyl acetate = 2:1) [UV]. \( ^{1} \text{H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.34 (t, J = 7.2 Hz, 2H), 7.27 (t, J = 9.0 Hz, 3H), 5.27 (s, 1H), 5.20 (q, J = 6.6 Hz, 1H), 2.51 – 2.40 (m, 2H), 2.34 – 2.23 (m, 2H), 2.02 – 1.91 (m, 2H), 1.58 (d, J = 6.6 Hz, 3H). \( ^{13} \text{C NMR} \) (150 MHz, CDCl\(_3\)) \( \delta \) 199.7, 176.5, 141.4, 128.8, 128.0, 125.4, 104.6, 76.7, 36.7, 29.4, 23.7, 21.2. \( \text{HRMS} \) (ESI-TOF) (m/z): Calcd for C\(_{14}\)H\(_{16}\)NaO\(_2\) ([M + Na]\(^+\)), 239.1041, found, 239.1043.
2-(1-((1,1′-Biphenyl)-4-yl)ethyl)-3-hydroxycyclohex-2-en-1-one (6h):

Following Method B, 6h was obtained as colorless oil (57.8 mg, 99% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.59 (d, J = 7.8 Hz, 4H), 7.46 (t, J = 7.8 Hz, 2H), 7.39 – 7.35 (m, 3H), 5.35 (s, 1H), 5.28 (q, J = 6.6 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.39 – 2.26 (m, 2H), 2.06 – 1.93 (m, 2H), 1.65 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.7, 176.5, 141.1, 140.6, 140.3, 128.8, 127.6, 127.4, 127.1, 125.9, 104.7, 76.4, 36.7, 29.4, 21.2. HRMS (ESI-TOF) (m/z): Calcd for C20H20NaO2 ([M + Na]+), 315.1432, found, 315.1432.

![Image](image1.png)

2-(1-(4-Fluorophenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6i):

Following Method B, 6i was obtained as colorless oil (45.0 mg, 96% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.30 – 7.24 (m, 2H), 7.05 (t, J = 8.4 Hz, 2H), 5.27 (s, 1H), 5.21 (q, J = 6.6 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.36 – 2.26 (m, 2H), 2.04 – 1.91 (m, 2H), 1.58 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.6, 176.3, 162.3 (d, J = 246.9 Hz), 137.1 (d, J = 3.4 Hz), 127.1 (d, J = 8.1 Hz), 115.7 (d, J = 21.0 Hz), 104.6, 75.9, 36.6, 29.3, 23.6, 21.1. 19F NMR (565 MHz, CDCl3) δ -113.98 – -114.05 (m, 1F). HRMS (ESI-TOF) (m/z): Calcd for C14H15FNaO2 ([M + Na]+), 257.0946, found, 257.0948.

![Image](image2.png)

2-(1-(4-Chlorophenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6j):

Following Method B, 6j was obtained as colorless oil (34.0 mg, 68% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.32 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 5.23 (s, 1H), 5.17 (q, J = 6.6 Hz, 1H), 2.51 – 2.38 (m, 2H), 2.34 – 2.24 (m, 2H), 2.01 – 1.91 (m, 2H), 1.56 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.6, 176.2, 139.9, 133.8, 129.1, 126.8, 19
2-(1-(4-Bromophenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6k):

Following Method B, 6k was obtained as colorless oil (34.8 mg, 59% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.49 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 5.24 (s, 1H), 5.18 (q, J = 6.6 Hz, 1H), 2.53–2.40 (m, 2H), 2.36–2.25 (m, 2H), 2.04–1.92 (m, 2H), 1.57 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.5, 176.1, 140.4, 132.0, 127.1, 121.9, 104.7, 75.9, 36.6, 29.3, 23.5, 21.1. HRMS (ESI-TOF) (m/z): Calcd for C14H15BrNaO2 ([M + Na]+), 317.0145, found, 317.0147.

3-Hydroxy-2-(1-(4-(trifluoromethoxy)phenyl)ethyl)cyclohex-2-en-1-one (6l):

Following Method B, 6l was obtained as colorless oil (34.8 mg, 58% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.31 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 5.26–5.19 (m, 2H), 2.53–2.39 (m, 2H), 2.35–2.25 (m, 2H), 1.97 (qt, J = 7.2, 6.0 Hz, 2H), 1.57 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.6, 176.2, 148.8, 140.0, 126.8, 121.3, 120.4 (q, J = 255.0 Hz), 104.6, 75.7, 36.6, 29.3, 23.6, 21.1. 19F NMR (565 MHz, CDCl3) δ = -57.85. HRMS (ESI-TOF) (m/z): Calcd for C15H15F3NaO3 ([M + Na]+), 323.0963, found, 323.0965.

2-(1-(4-(Chloromethyl)phenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6m):
Following Method B, 6m was obtained as colorless oil (36.4 mg, 69% yield), TLC: 
R_f = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ^1H NMR (600 MHz, CDCl_3) δ
7.39 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 5.26 (s, 1H), 5.22 (q, J = 6.6 Hz, 1H),
4.59 (s, 2H), 2.53 – 2.41 (m, 2H), 2.36 – 2.25 (m, 2H), 2.04 – 1.92 (m, 2H), 1.59
(d, J = 6.6 Hz, 3H). ^13C NMR (150 MHz, CDCl_3) δ 199.6, 176.3, 141.6, 137.3, 129.1,
125.8, 104.7, 76.2, 45.8, 36.7, 29.3, 23.6, 21.1. HRMS (ESI-TOF) (m/z): Calcd for
C_{15}H_{17}ClNaO_2 ([M + Na]^+), 287.0634, found, 287.0635.

4-(1-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)ethyl)phenyl acetate (6n):
Following Method B, 6n was obtained as colorless oil (50.4 mg, 92% yield), TLC:
R_f = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ^1H NMR (600 MHz, CDCl_3) δ
7.30 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 5.29 (s, 1H), 5.22 (q, J = 6.6 Hz, 1H),
2.53 – 2.39 (m, 2H), 2.36 – 2.26 (m, 5H), 2.03 – 1.91 (m, 2H), 1.58 (d, J = 6.6 Hz, 3H). ^13C NMR (150 MHz, CDCl_3) δ 199.6, 176.3, 169.3, 150.3, 138.8, 126.6,
121.9, 104.5, 76.0, 36.6, 29.4, 23.5, 21.1. HRMS (ESI-TOF) (m/z): Calcd for
C_{16}H_{18}NaO_4 ([M + Na]^+), 297.1008, found, 297.1009.

3-Hydroxy-2-(1-(4-((trimethylsilyl)ethynyl)phenyl)ethyl)cyclohex-2-en-1-one
(6o):
Following Method B, 6o was obtained as colorless oil (65.0 mg, 40% yield), TLC:
R_f = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ^1H NMR (500 MHz, CDCl_3) δ
7.44 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.22 (s, 1H), 5.17 (q, J = 6.5 Hz, 1H),
2.51 – 2.36 (m, 2H), 2.34 – 2.20 (m, 2H), 2.04 – 1.86 (m, J = 6.5 Hz, 2H), 1.55
(d, J = 6.5 Hz, 3H), 0.24 (s, 8H). ^13C NMR (150 MHz, CDCl_3) δ 199.6, 176.3, 141.7,
132.5, 125.3, 123.0, 104.8, 104.6, 94.8, 76.2, 36.8, 29.4, 23.5, 21.2, 0.00. HRMS
(ESI-TOF) (m/z): Calcd for C_{15}H_{24}NaO_2Si ([M + Na]^+), 335.1386, found, 335.1388.
2-(1-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)ethyl)-3-hydroxycyclohex-2-en-1-one (6p):

Following Method B, 6p was obtained as colorless oil (28.8 mg, 44% yield), TLC:

\[ R_f = 0.3 \] (Petroleum ether : Ethyl acetate = 2:1) [UV].

\[^1H\text{ NMR}\] (500 MHz, CDCl\(_3\)) \( \delta \)

- 7.76 (d, \( J = 8.0 \) Hz, 2H),
- 7.24 (d, \( J = 8.0 \) Hz, 2H),
- 5.24 (s, 1H),
- 5.19 (q, \( J = 6.5 \) Hz, 1H),
- 3.75 (s, 4H),
- 2.50 – 2.35 (m, 2H),
- 2.33 – 2.20 (m, 2H),
- 2.01 – 1.87 (m, 2H),
- 1.56 (d, \( J = 6.5 \) Hz, 3H),

\[^{13}C\text{ NMR}\] (150 MHz, CDCl\(_3\)) \( \delta \)

- 199.7, 176.5, 143.7, 134.4, 124.5, 104.6, 76.7, 72.3, 36.7, 31.9, 29.7, 29.4, 23.5, 21.9, 21.2.

\[^{1}H\text{ NMR}\] (500 MHz, CDCl\(_3\)) \( \delta \)

- 7.76 (d, \( J = 8.0 \) Hz, 2H),
- 7.24 (d, \( J = 8.0 \) Hz, 2H),
- 5.24 (s, 1H),
- 5.19 (q, \( J = 6.5 \) Hz, 1H),
- 3.75 (s, 4H),
- 2.50 – 2.35 (m, 2H),
- 2.33 – 2.20 (m, 2H),
- 2.01 – 1.87 (m, 2H),
- 1.56 (d, \( J = 6.5 \) Hz, 3H),

\[^{13}C\text{ NMR}\] (150 MHz, CDCl\(_3\)) \( \delta \)

- 199.7, 176.5, 143.7, 134.4, 124.5, 104.6, 76.7, 72.3, 36.7, 31.9, 29.7, 29.4, 23.5, 21.9, 21.2.

3-Hydroxy-2-(1-(naphthalen-2-yl)ethyl)cyclohex-2-en-1-one (6q):

Following Method B, 6q was obtained as colorless oil (52.2 mg, 98% yield), TLC:

\[ R_f = 0.5 \] (Petroleum ether : Ethyl acetate = 2:1) [UV].

\[^1H\text{ NMR}\] (600 MHz, CDCl\(_3\)) \( \delta \)

- 7.84 (d, \( J = 8.4 \) Hz, 1H),
- 7.81 (dt, \( J = 7.2, 2.4 \) Hz, 2H),
- 7.72 (s, 1H),
- 7.53 – 7.44 (m, 2H),
- 7.40 (dd, \( J = 8.4, 1.8 \) Hz, 1H),
- 5.37 (q, \( J = 6.6 \) Hz, 1H),
- 5.34 (s, 1H),
- 2.54 – 2.43 (m, 2H),
- 2.34 – 2.21 (m, 2H),
- 2.03 – 1.89 (m, 2H),
- 1.66 (d, \( J = 6.6 \) Hz, 3H).

\[^{13}C\text{ NMR}\] (150 MHz, CDCl\(_3\)) \( \delta \)

- 199.7, 176.5, 138.7, 133.2, 133.1, 128.9, 128.0, 127.8, 126.4, 126.2, 124.5, 123.1, 104.7, 76.8, 36.7, 29.4, 23.7, 21.2.

HRMS (ESI-TOF) (m/z): Calcd for C\(_{19}\)H\(_{25}\)BNaO\(_4\) ([M + Na]\(^+\)), 351.1582, found, 351.1580.

2-(1-(Benzo[b]thiophen-5-yl)ethyl)-3-hydroxycyclohex-2-en-1-one (6r):

2-((Benzo[b]thiophen-5-yl)ethyl)-3-hydroxycyclohex-2-en-1-one (6r):
Following **Method B**, 6r was obtained as colorless oil (38.2 mg, 70% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (600 MHz, CDCl₃) δ 7.85 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 5.4 Hz, 1H), 7.31 (dd, J = 5.4, 0.6 Hz, 1H), 7.28 – 7.26 (m, 1H), 5.35 – 5.30 (m, 2H), 2.54 – 2.41 (m, 2H), 2.34 – 2.22 (m, 2H), 2.03 – 1.89 (m, 2H), 1.64 (d, J = 6.6 Hz, 3H). **13C NMR** (150 MHz, CDCl₃) δ 199.7, 176.5, 139.8, 139.4, 137.9, 127.4, 123.8, 123.0, 121.7, 120.5, 104.7, 76.8, 36.7, 29.4, 24.0, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C₁₆H₁₆NaO₂S ([M + Na]+), 295.0955, found, 295.0966.

**3-Hydroxy-2-(1-phenylpropyl)cyclohex-2-en-1-one (6s):**

Following **Method B**, 6s was obtained as colorless oil (31.4 mg, 68% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (500 MHz, CDCl₃) δ 7.33 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 1H), 7.23 (d, J = 7.0 Hz, 2H), 5.24 (s, 1H), 4.92 (t, J = 6.5 Hz, 1H), 2.53 – 2.39 (m, 2H), 2.33 – 2.21 (m, 2H), 2.01 – 1.90 (m, 3H), 1.87 – 1.77 (m, 1H), 0.92 (t, J = 7.5 Hz, 3H). **13C NMR** (150 MHz, CDCl₃) δ 199.7, 176.8, 140.0, 128.7, 128.0, 125.9, 104.7, 82.0, 36.6, 30.7, 29.3, 21.1, 9.9. **HRMS** (ESI-TOF) (m/z): Calcd for C₁₅H₁₈NaO₂ ([M + Na]+), 253.1308, found, 253.1306.

**2-(2,3-Dihydro-1H-inden-1-yl)-3-hydroxycyclohex-2-en-1-one (6t):**

Following **Method B**, 6t was obtained as yellow solid (31.4 mg, 99% yield, m.p. 123°C), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. **1H NMR** (500 MHz, CDCl₃) δ 7.41 (d, J = 7.5 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.25 (t, J = 7.0 Hz, 1H), 5.63 (dd, J = 7.0, 3.5 Hz, 1H), 5.59 (s, 1H), 3.12 (ddd, J = 15.5, 8.5, 6.0 Hz, 1H), 2.91 (ddd, J = 16.0, 9.0, 5.0 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.45-2.34 (m, 4H), 2.18-2.10 (m, 1H), 2.05-1.96 (m, 2H). **13C NMR** (150 MHz, CDCl₃) δ 199.8, 177.3, 144.3, 140.2, 129.4, 126.9, 125.5, 125.0, 103.8, 82.1, 36.8, 31.7, 30.2, 29.4, 21.2. **HRMS** (ESI-TOF) (m/z): Calcd for C₁₅H₁₆NaO₂ ([M + Na]+), 251.1041, found, 251.1043.
6-Hydroxy-[1,1'-bi(cyclohexane)]-2',6-dien-2-one (6u):

Following Method B, 6u was obtained as colorless oil (38.4 mg, 71% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (500 MHz, CDCl3) δ 6.00 (dt, J = 10.0, 3.5 Hz, 1H), 5.77 (dd, J = 10.0, 3.0 Hz, 1H), 5.41 (s, 1H), 4.75 – 4.62 (m, 1H), 2.40 (t, J = 6.5 Hz, 2H), 2.35 (t, J = 6.5 Hz, 2H), 2.16 – 2.00 (m, 2H), 2.01 – 1.95 (m, 2H), 1.93 – 1.80 (m, 2H), 1.80 – 1.72 (m, 1H), 1.68 – 1.58 (m, 1H). 13C NMR (150 MHz, CDCl3) δ 199.7, 176.9, 133.4, 124.5, 103.2, 71.5, 36.7, 29.6, 27.8, 24.9, 21.2, 18.7. HRMS (ESI-TOF) (m/z): Calcd for C12H16NaO2 ([M + Na]⁺), 215.0964, found, 215.0964.

(E)-3-hydroxy-2-(4-phenylbut-3-en-2-yl)cyclohex-2-en-1-one (6v):

Following Method B, 6v was obtained as colorless oil (37.2 mg, 77% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 7.37 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 16.2 Hz, 1H), 6.15 (dd, J = 16.2, 6.6 Hz, 1H), 5.44 (s, 1H), 4.89 (p, J = 6.6 Hz, 1H), 2.42 (t, J = 6.6 Hz, 2H), 2.37 – 2.29 (m, 2H), 1.98 (p, J = 6.6 Hz, 2H), 1.48 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 199.7, 176.9, 133.4, 124.5, 103.2, 71.5, 36.7, 29.6, 27.8, 24.9, 21.2, 18.7. HRMS (ESI-TOF) (m/z): Calcd for C16H18NaO2 ([M + Na]⁺), 265.1365, found, 265.1362.

3-Hydroxy-2-(2-phenylpropan-2-yl)cyclohex-2-en-1-one (6w):

Following Method B, 6w was obtained as colorless oil (39.6 mg, 86% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. 1H NMR (500 MHz, CDCl3) δ 7.33 – 7.28 (m, 2H), 7.23 (dd, J = 15.0, 8.0 Hz, 3H), 4.76 (s, 1H), 2.39 (t, J = 6.0 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.91 (p, J = 6.5 Hz, 2H), 1.72 (s, 6H). 13C NMR (150 MHz, CDCl3) δ 199.4, 174.2, 143.8, 128.8, 127.5, 124.6, 108.3, 82.7, 36.4, 30.1, 29.3, 21.2.
HRMS (ESI-TOF) (m/z): Calcd for C_{15}H_{18}NaO_2 ([M + Na]^+), 253.1308, found, 253.1306.

3-Hydroxy-2-(2-(p-tolyl)butan-2-yl)cyclohex-2-en-1-one (6x):

Following Method B, 6x was obtained as colorless oil (46.4 mg, 90% yield), TLC: R_f = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (600 MHz, CDCl₃) δ 7.17 – 7.06 (m, 4H), 4.81 (s, 1H), 2.47 – 2.35 (m, 2H), 2.31 (s, 3H), 2.25 – 2.21 (m, 2H), 2.07 – 1.99 (m, 1H), 1.97 – 1.91 (m, 2H), 1.91 – 1.83 (m, 1H), 1.72 (s, 3H), 0.83 (t, J = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.5, 174.3, 140.0, 137.0, 129.3, 125.0, 108.4, 85.2, 37.1, 36.5, 30.1, 23.0, 21.2, 21.0, 8.1. HRMS (ESI-TOF) (m/z): Calcd for C_{17}H_{22}NaO_2 ([M + Na]^+), 281.1514, found, 281.1512.

Ethyl 3-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-3-phenylpropanoate (6y):

Following Method B, 6y was obtained as colorless oil (34.6 mg, 60% yield), TLC: R_f = 0.3 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (600 MHz, CDCl₃) δ 7.37 (t, J = 7.8 Hz, 2H), 7.32 (t, J = 7.8 Hz, 3H), 5.55 (dd, J = 9.0, 4.8 Hz, 1H), 5.30 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.00 (dd, J = 16.2, 9.0 Hz, 1H), 2.74 (dd, J = 16.2, 4.8 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.38 – 2.19 (m, 2H), 2.03 – 1.86 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 199.5, 176.0, 169.6, 138.6, 129.0, 128.6, 125.8, 105.2, 76.8, 60.9, 43.1, 36.6, 29.0, 21.1, 14.2. HRMS (ESI-TOF) (m/z): Calcd for C_{17}H_{20}NaO_4 ([M + Na]^+), 311.1118, found, 311.1117.

3-Hydroxy-2-(3-morpholino-3-oxo-1-phenylpropyl)cyclohex-2-en-1-one (6z):

Following Method B, 6a was obtained as colorless oil (31.0 mg, 47% yield), TLC: R_f = 0.3 (Petroleum ether : Ethyl acetate = 2:1) [UV]. ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, J = 6.5 Hz, 2H), 7.30 (d, J = 7.0 Hz, 3H), 5.66 (dd, J = 8.0, 4.5 Hz, 1H), 5.28 (s, 1H), 3.68 – 3.56 (m, 5H), 3.49 – 3.39 (m, 2H), 3.37 – 3.29 (m, 1H), 3.04 (dd, J = 15.5, 8.0 Hz, 1H), 2.68 (dd, J = 15.5, 4.5 Hz, 1H), 2.51 – 2.36 (m, 2H), 2.33 – 2.20 (m,
2H), 2.02 – 1.87 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 199.4, 175.7, 167.6, 139.4, 129.0, 128.5, 125.7, 105.5, 77.2, 66.8, 66.5, 46.1, 42.1, 41.2, 36.6, 29.1, 21.0. HRMS (ESI-TOF) (m/z): Calcd for C$_{19}$H$_{23}$NNaO$_4$ ([M + Na]$^+$), 352.1657, found, 352.1656.

3-Hydroxy-5,5-dimethyl-2-(1-(p-tolyl)ethyl)cyclohex-2-en-1-one (7b):

Following Method B, 7b was obtained as colorless oil (51.2 mg, 99% yield), TLC: R$_f$ = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.16 (s, 4H), 5.27 (s, 1H), 5.20 (q, J = 6.6 Hz, 1H), 2.38 – 2.27 (m, 5H), 2.21 – 2.11 (m, 2H), 1.58 (d, J = 6.6 Hz, 3H), 1.09 (s, 3H), 1.03 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 199.6, 174.9, 138.4, 137.7, 129.5, 125.3, 103.5, 76.6, 50.6, 43.3, 32.5, 28.3, 28.2, 23.7, 21.1. HRMS (ESI-TOF) (m/z): Calcd for C$_{17}$H$_{22}$NaO$_2$ ([M + Na]$^+$), 257.1535, found, 257.1536.

5-Hydroxy-4-(1-(p-tolyl)ethyl)-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (7c):

Following Method B, 7c was obtained as colorless oil (62.0 mg, 99% yield), dr = 1:1, TLC: R$_f$ = 0.5 (Petroleum ether : Ethyl acetate = 2:1) [UV]. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.37-7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 7.21-7.17 (m, 2H), 7.15 (s, 2H), 5.37 (s, 1H), 5.26-5.17 (m, 1H), 3.41-3.25 (m, 1H), 2.77 – 2.43 (m, 4H), 2.34 (d, J = 4.5 Hz, 3H), 1.58 (dd, J = 10.0, 6.5 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 198.8, 175.7, 175.5, 142.8, 138.3, 138.1, 137.9, 129.6, 129.5, 128.8, 127.0, 126.7, 125.4, 125.4, 104.4, 104.4, 77.2, 76.8, 43.8, 39.4, 39.2, 37.0, 36.9, 23.7, 21.2. HRMS (ESI-TOF) (m/z): Calcd for C$_{21}$H$_{22}$NaO$_2$ ([M + Na]$^+$), 329.1512, found, 329.1513.
5-Hydroxy-4-((1-(p-tolyl)ethyl)-2H-pyran-3(6H)-one (7d):

Following Method B, 7d was obtained as colorless oil (46.0 mg, 99% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.16 (s, 4H), 5.38 (s, 1H), 5.21 (q, \(J = 6.5\) Hz, 1H), 4.34 – 4.21 (m, 2H), 4.02 (d, \(J = 3.5\) Hz, 2H), 2.34 (s, 3H), 1.59 (d, \(J = 6.5\) Hz, 3H). \(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 194.9, 173.9, 138.3, 137.5, 129.6, 125.4, 101.8, 77.7, 71.4, 65.8, 23.4, 21.2. \textbf{HRMS (ESI-TOF)} (m/z): Calcd for C\(_{14}\)H\(_{16}\)NaO\(_3\) ([M + Na]\(^+\)), 255.1148, found, 255.1148.

3-Hydroxy-2-((1-(p-tolyl)ethyl)cyclopent-2-en-1-one (7e):

Following Method C, 7e was obtained as colorless oil (15.2 mg, 35% yield), TLC: Rf = 0.5 (Petroleum ether : Ethyl acetate = 5:1) [UV]. \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.21 – 7.13 (m, 4H), 5.18 (s, 1H), 5.16 (q, \(J = 6.5\) Hz, 1H), 2.69 – 2.54 (m, 2H), 2.41 – 2.35 (m, 2H), 2.34 (s, 3H), 1.63 (d, \(J = 6.5\) Hz, 3H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 206.1, 188.9, 138.2, 137.8, 129.5, 125.6, 106.4, 80.5, 33.8, 28.9, 23.3, 21.2. \textbf{HRMS (ESI-TOF)} (m/z): Calcd for C\(_{14}\)H\(_{16}\)NaO\(_2\) ([M + Na]\(^+\)), 239.0970, found, 239.0971.

4-Hydroxy-3-((1-(p-tolyl)ethyl)pentan-2-one (7f):

Following Method C, 7f was obtained as colorless oil (28.6 mg, 65% yield), keto : enol = 1:1.3, TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 2:1) [UV]. \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.17 (s, 4H), 7.09 (q, \(J = 8.0\) Hz, 4 H), 5.39 (s, 1H), 5.15 (q, \(J = 6.5\) Hz, 1H), 4.02 (d, \(J = 11.5\) Hz, 1 H), 3.56 (dq, \(J = 13.5, 7.0\) Hz, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 2.30 (s, 3 H), 2.27 (s, 3 H), 2.02 (s, 3H), 1.85 (s, 3 H), 1.54 (d, \(J = 6.5\) Hz, 3H), 1.20 (d, \(J = 7.0\) Hz, 3 H). \(^{13}\text{C NMR}\) (150 MHz, CDCl\(_3\)) \(\delta\) 203.7, 197.0, 170.6, 140.0, 138.9, 137.5, 136.6, 129.5, 129.4, 127.1, 125.2, 101.8, 77.0, 76.0, 40.1, 32.0, 29.8, 29.7, 23.9, 21.1, 21.0, 20.0. \textbf{HRMS (ESI-TOF)} (m/z): Calcd for C\(_{14}\)H\(_{18}\)NaO\(_2\) ([M + Na]\(^+\)), 241.1204, found, 241.1206.
5-Hydroxy-2,6-dimethyl-4-(1-p-tolyl)ethylhept-4-en-3-one (7g):

Following Method C, 7g was obtained as colorless oil (19.8 mg, 36% yield), TLC: 
R<sub>f</sub> = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.16 (s, 4H), 5.22 (s, 1H), 5.09 (q, <i>J</i> = 6.5 Hz, 1H), 4.02 – 3.91 (m, 1H), 2.33 (s, 4H), 1.53 (d, <i>J</i> = 6.5 Hz, 3H), 1.12 (d, <i>J</i> = 7.0 Hz, 3H), 1.09 (d, <i>J</i> = 7.0 Hz, 3H), 0.97 (d, <i>J</i> = 7.0 Hz, 3H), 0.89 (d, <i>J</i> = 7.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 203.2, 177.8, 139.2, 137.4, 129.3, 125.1, 98.5, 75.4, 42.1, 29.6, 23.7, 21.1, 19.8, 19.7, 18.8, 18.8. 

HRMS (ESI-TOF) (m/z): Calcd for C<sub>18</sub>H<sub>26</sub>NaO<sub>2</sub> ([M + Na]<sup>+</sup>), 297.1694, found, 297.1696.

1-Phenyl-2-(1-p-tolyl)ethylbutane-1,3-dione (7i):

Following Method C, 7i was obtained as colorless oil (29.2 mg, 52% yield), dr = 1:1.4, TLC: R<sub>f</sub> = 0.5 (Petroleum ether : Ethyl acetate = 10:1) [UV]. The characterization data of 7i was full agreement with the reported literature. <sup>8</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.09 (d, <i>J</i> = 10 Hz, 2H), 7.81 (d, <i>J</i> = 7.5 Hz, 2H), 7.61 (t, <i>J</i> = 7.5 Hz, 1H), 7.53 - 7.49 (m, 2H), 7.47 - 7.43 (m, 1H), 7.36 (t, <i>J</i> = 7.5 Hz, 2H), 7.17 (d, <i>J</i> = 8.0 Hz, 2H), 7.12 (d, <i>J</i> = 7.5 Hz, 2H), 7.08 (d, <i>J</i> = 8.0 Hz, 2H), 6.97 (d, <i>J</i> = 8.0 Hz, 2H), 4.88 (d, <i>J</i> = 11.5 Hz, 1H), 4.80 (d, <i>J</i> = 11.0 Hz, 1H), 3.87 - 3.78 (m, 2H), 2.32 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H), 1.92 (s, 3H), 1.28 (d, <i>J</i> = 7.0 Hz, 3H), 1.19 (d, <i>J</i> = 6.8 Hz, 3H).

1,3-Diphenyl-2-(1-p-tolyl)ethylpropane-1,3-dione (7j):

Following Method C, 7j was obtained as colorless oil (45.2 mg, 66% yield), TLC: 
R<sub>f</sub> = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ
8.06 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 5.62 (d, J = 10.0 Hz, 1H), 4.11 – 4.02 (m, 1H), 2.22 (s, 3H), 1.33 (d, J = 7.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 195.1, 194.7, 140.9, 137.2, 137.0, 136.1, 133.6, 133.0, 129.1, 128.9, 128.6, 128.5, 127.6, 65.1, 40.8, 21.0, 20.4. 


1,3-Di-p-tolyl-2-(1-(p-tolyl)ethyl)propane-1,3-dione (7k):

Following Method C, 7k was obtained as yellow solid (59.2 mg, 80% yield, m.p. 171°C), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. 1H NMR (500 MHz, CDCl3) δ 7.97 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 5.56 (d, J = 10.0 Hz, 1H), 4.10 – 4.00 (m, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.22 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 194.8, 194.2, 144.4, 143.8, 141.2, 136.0, 134.8, 134.6, 129.5, 129.1, 128.9, 128.6, 127.5, 65.0, 40.7, 21.6, 21.5, 21.0, 20.5. HRMS (ESI-TOF) (m/z): Calcd for C26H26NaO2 ([M + Na]+), 393.1720, found, 393.1722.

1,3-Di-m-tolyl-2-(1-(p-tolyl)ethyl)propane-1,3-dione (7l):

Following Method C, 7l was obtained as colorless oil (39.2 mg, 53% yield), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. 1H NMR (500 MHz, CDCl3) δ 7.84 (d, J = 7.5 Hz, 1H), 7.80 (s, 1H), 7.58 – 7.50 (m, 2H), 7.39 – 7.30 (m, 2H), 7.22 (d, J = 7.5 Hz, 1H), 7.20 – 7.12 (m, 3H), 6.99 (d, J = 7.5 Hz, 2H), 5.56 (d, J = 10.0 Hz, 1H), 4.07 – 3.98 (m, 1H), 2.36 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 1.31 (d, J = 7.0 Hz,
13C NMR (150 MHz, CDCl3) δ 195.3, 194.9, 141.1, 138.7, 138.2, 137.3, 137.1, 136.0, 134.3, 133.7, 129.2, 129.0, 128.6, 128.2, 127.6, 126.1, 125.7, 65.1, 40.7, 21.3, 21.2, 20.9, 20.2. HRMS (ESI-TOF) (m/z): Calcd for C26H26NaO2 ([M + Na]+), 393.1720, found, 393.1720.

1,3-Bis(4-methoxyphenyl)-2-(1-(p-tolyl)ethyl)propane-1,3-dione (7m):

Following Method C, 7m was obtained as yellow solid (79.6 mg, 99% yield, m.p. 165°C), TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 8.09 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 7.8 Hz, 2H), 5.46 (d, J = 10.2 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.24 (s, 3H), 1.32 (d, J = 7.2 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ 193.8, 193.2, 163.8, 163.4, 141.3, 135.9, 131.3, 131.0, 130.3, 130.1, 129.1, 127.5, 114.0, 113.6, 65.3, 55.5, 55.4, 40.6, 21.0, 20.6. HRMS (ESI-TOF) (m/z): Calcd for C26H26NaO4 ([M + Na]+), 425.1592, found, 425.1593.

1-(4-Methoxyphenyl)-3-(p-tolyl)-2-(1-(p-tolyl)ethyl)propane-1,3-dione (7n):

Following Method C, 7n was obtained as yellow solid (37.2 mg, 48% yield, m.p. 170°C), dr = 1:1, TLC: Rf = 0.4 (Petroleum ether : Ethyl acetate = 10:1) [UV]. 1H NMR (600 MHz, CDCl3) δ 8.05 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 9.0 Hz, 1H), 6.76 (d, J = 9.0 Hz, 1H), 5.48 (d, J = 10.0 Hz, 1H), 4.04 (dq, J = 10.2, 7.2 Hz, 1H), 3.81 (d, J = 43.2 Hz, 3H), 2.34 (d, J = 52.2 Hz, 3H), 2.22 (s, 3H), 1.29 (dd, J = 7.2, 1.8 Hz,
Ethyl-2-acetyl-3-(p-tolyl)butanoate (8a):

Following Method D, 8a was obtained as colorless oil (20.9 mg, 42% yield), dr = 1:1, TLC: Rf = 0.6 (Petroleum ether : Ethyl acetate = 5:1) [UV]. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.12 – 7.06 (m, 8H), 4.22 (q, $J$ = 7.2 Hz, 2H), 3.90 (q, $J$ = 7.2 Hz, 2H), 3.76 (d, $J$ = 10.8 Hz, 1H), 3.71 (d, $J$ = 10.8 Hz, 1H), 3.58 – 3.45 (m, 2H), 2.29 (m, 9H), 1.94 (s, 3H), 1.32 – 1.26 (m, 6H), 1.21 (d, $J$ = 7.2 Hz, 3H), 0.97 (t, $J$ = 7.2 Hz, 3H).


Ethyl-2-(4-methoxybenzoyl)-3-(p-tolyl)butanoate (8b):

Following Method D, 8b was obtained as colorless oil (30.6 mg, 45% yield), dr = 1:1.4, TLC: Rf = 0.6 (Petroleum ether : Ethyl acetate = 5:1) [UV]. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.10 (d, $J$ = 9.0 Hz, 2H), 7.87 (d, $J$ = 9.0 Hz, 2H), 7.20 (d, $J$ = 7.8 Hz, 2H), 7.11 (d, $J$ = 7.8 Hz, 4H), 6.98 (d, $J$ = 7.8 Hz, 2H), 6.96 (d, $J$ = 9.0 Hz, 2H), 6.85 (d, $J$ = 9.0 Hz, 2H), 4.62 (d, $J$ = 10.8 Hz, 1H), 4.56 (d, $J$ = 10.8 Hz, 1H), 4.23 – 4.10 (m, 2H), 3.88 (s, 3H), 3.85 – 3.78 (m, 7H), 2.31 (s, 3H), 2.21 (s, 3H), 1.34 (d, $J$ = 6.0 Hz, 3H), 1.24 – 1.19 (m, 6H), 0.90 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 192.3, 191.9, 169.0, 168.4, 164.0, 163.7, 141.1, 140.6, 136.2, 135.9, 131.2, 130.9, 130.1, 129.8, 129.1, 127.6, 127.2, 113.9, 113.7, 77.3, 77.0, 76.8, 61.5, 61.5, 61.1, 61.1, 55.6, 55.5, 39.8, 39.2, 21.1, 21.0, 20.8, 20.5, 14.1, 13.7. HRMS (ESI-TOF) (m/z): Calcd for C$_{21}$H$_{24}$NaO$_4$ ([M + Na]$^+$), 363.1567, found, 363.1568.
Tetramethylethane-1,1,2,2-tetracarboxylate (13):

12 was obtained as yellow oil, TLC: R_f = 0.6 (Petroleum ether : Ethyl acetate = 5:1) [UV].  \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 4.81 (s, 2H), 3.98 (s, 12H).  \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 175.7, 67.6, 55.4.  \(\text{HRMS (ESI-TOF) (m/z)}\): Calcd for C\(_{10}\)H\(_{14}\)NaO\(_8\) ([M + Na]\(^+\)), 285.0581, found, 285.0581.
V. Mechanistic Experiments

a) Radical inhibition experiment

To a dry Schlenk tube containing a magnetic stir bar were added [Co]-2 (0.003 mmol, 3 mol%), TMFP-BF₄ (0.12 mmol, 1.2 equiv), and dry THF (1 mL) in sequence. After stirred for 5 min, olefin 5a (0.10 mmol, 1.0 equiv), 1,3-diketone 2a (0.15 mmol, 1.5 equiv) and radical inhibitors Tempo (0.2 mmol, 1.5 equiv) were added. Then TMDSO (0.20 mmol, 2.0 equiv) was added dropwise. After stirring for 3 hours, the reaction mixture was extracted with DCM, and the combined organic layers were concentrated in vacuo.

In the system of Tempo, the formation of 6a was almost completely suppressed. In particular, the Tempo-trapped product 9 was detected by high-resolution mass spectrometry (HRMS) analysis, as shown signal at m/z 276.2322 in Figure S1. This result suggested that an alkyl radical intermediate is probably involved in this transformation, consistent with the speculated metalhydride HAT process.

Fig. S1  Tempo trapped alkyl radical intermediate
b) Radical clock experiment

To a dry Schlenk tube containing a magnetic stir bar were added [Co]-1 (0.003 mmol, 3 mol%), TMFP-BF₄ (0.20 mmol, 2.0 equiv), and dry toluene (1 mL). After stirred for 5 min, olefin 1z (0.10 mmol, 1.0 equiv) and 1,3-diketone 2a (0.15 mmol, 1.5 equiv) were added. Then TMDSO (0.40 mmol, 4.0 equiv) was added dropwise. After stirring for 3 hours, the reaction mixture was extracted with DCM, and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

It shows that the hydrocarbonization product 4z has not been detected, while the ring-opening/carbonization product 10 and 11 was detected in 19% and 15%, respectively. These phenomena suggest that an alkyl radical intermediate is probably involved in this transformation, in line with the speculated CoH-mediated HAT process. The formation of compound 11 probably undergo ring-opening isomerization of olefin 1z to 1, 3-diene 1aa, followed by CoH-mediated hydrofunctionalization process. To test this hypothesis, we use presynthesized 1,3-dienes 1aa to conduct the reaction under standard conditions. As we expected, the desired product 11 was obtained in 19% yield with excellent stereoselectivity.

3-Hydroxy-2-(1-phenylpent-3-en-1-yl)cyclohex-2-en-1-one (10):

^1^H NMR (500 MHz, CDCl₃) δ 7.32 (t, J = 7.5 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 5.61 – 5.43 (m, 1H), 5.37 – 5.27 (m, 1H), 5.23 (s, 1H), 4.99 (dt, J = 14.0, 6.5 Hz, 1H), 2.74 – 2.37 (m, 4H), 2.32 – 2.20 (m, 2H), 2.02 – 1.86 (m, 2H), 1.63 (dd, J = 6.5, 1.5 Hz, 1H), 1.51 (dd, J = 6.5, 1.5 Hz, 1.5H). ^1^C NMR (150 MHz, CDCl₃) δ 199.7, 176.6, 139.7, 139.7, 129.0, 128.7, 128.7, 128.1, 128.1, 127.5, 125.9,
125.9, 125.4, 124.4, 104.9, 104.8, 80.7, 80.3, 40.9, 36.7, 35.3, 29.3, 21.1, 18.0, 12.9.

**HRMS (ESI-TOF) (m/z):** Calcd for C_{17}H_{20}NaO_2 ([M + Na]^+ ), 279.1356, found, 279.1366.

**(E)-3-hydroxy-2-(1-phenylpent-1-en-3-yl)cyclohex-2-en-1-one (11):**

^1H NMR (500 MHz, CDCl_3) \(\delta\) 7.36 (d, \(J = 7.0\) Hz, 2H), 7.31 (t, \(J = 7.5\) Hz, 2H), 7.27 – 7.25 (m, 1H), 6.54 (d, \(J = 16.0\) Hz, 1H), 6.07 (dd, \(J = 16.0, 7.5\) Hz, 1H), 5.41 (s, 1H), 4.61 (q, \(J = 6.5\) Hz, 1H), 2.43 (td, \(J = 6.5, 2.0\) Hz, 2H), 2.32 (t, \(J = 6.5\) Hz, 2H), 1.98 (p, \(J = 6.5\) Hz, 3H), 1.84 (dq, \(J = 14.5, 7.0\) Hz, 1H), 1.74 (dq, \(J = 14.0, 7.0\) Hz, 1H), 0.96 (t, \(J = 7.5\) Hz, 3H). ^13C NMR (150 MHz, CDCl_3) \(\delta\) 199.9, 177.0, 135.9, 132.9, 128.6, 128.1, 127.0, 126.6, 104.1, 80.6, 36.7, 29.4, 29.4, 28.3, 21.2, 9.5.

**HRMS (ESI-TOF) (m/z):** Calcd for C_{17}H_{20}NaO_2 ([M + Na]^+ ), 279.1356, found, 279.1356.

![Fig. S3 ^1H NMR data of 10](image-url)
Fig. S4  $^{13}$C NMR data of 10

Fig. S5  $^1$H NMR data of 11
c) Deuterium experiment

**Preparation of Me₂PhSiD:** To a stirring suspension of LiAlD₄ (210 mg, 5 mmol) in dry Et₂O (12 mL) was added Me₂PhSiCl (2.55g, 15 mmol) dropwise at ambient temperature under Ar. The reaction mixture was refluxed at 40 °C for 12 h. The reaction was cooled to room temperature. Then, the reaction was quenched by adding aqueous solution of sodium hydroxide (15 mL, 10 wt%) into the crude reaction mixture, which was subsequently extracted by diethyl ether for three times. The combined organic layers were dried over Na₂SO₄, evaporated under reduced pressure, and purified by column chromatography on silica gel to give PhMe₂SiD in 82% yield (1.70g, >99% D). **¹H NMR** (500 MHz, CDCl₃) δ 7.55 – 7.53 (m, 2H), 7.37 – 7.34 (m, 3H), 4.44 – 4.42 (m, 0.00H), 0.34 (s, 6H).
Fig. S7  \(^1\text{H} \) NMR data of Me\(_2\)PhSiD

A deuterium-labeled experimental reaction of 1a using PhMe\(_2\)SiD (\(>99\%\) D) was conducted to afford \(d\)-4a in 58% yield with \(>98\%\) D at the terminal carbon site, which demonstrated that the hydrogen came from hydrosilane and the HAT process was irreversible.

To a dry Schlenk tube containing a magnetic stir bar were added [Co]-1 (0.003 mmol, 3 mol%), TMFP-BF\(_4\) (0.20 mmol, 2.0 equiv), and dry toluene (1 mL). After stirred for 5 min, olefin 1a (0.10 mmol, 1.0 equiv) and 1,3-diketone 2a (0.15 mmol, 1.5 equiv) were added. Then PhMe\(_2\)SiD (0.40 mmol, 4.0 equiv) was added dropwise. After stirring for 3 hours, the reaction mixture was extracted with DCM, and the combined organic layers were concentrated in vacuo. The resulting crude product was purified by flash column chromatography on silica gel to obtain product.

\(d\)-4a: \(^1\text{H} \) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.26 (m, 2H), 7.22 – 7.12 (m, 3H), 5.30 (s, 1H), 4.27 (p, \(J = 6.0\) Hz, 1H), 2.85 – 2.58 (m, 2H), 2.45 – 2.30 (m, 4H), 2.06 – 1.94 (m, 3H), 1.90 – 1.81 (m, 1H), 1.27 (d, \(J = 6.0\) Hz, 2H). \(^{13}\text{C} \) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 199.9, 176.9, 141.1, 128.5, 128.3, 126.1, 103.1, 77.3, 77.1, 76.9, 73.8, 37.6, 36.8, 31.7, 29.5, 29.4, 21.2, 18.8 (t, \(J = 18.9\) Hz). \(^2\text{H} \) NMR (77 MHz, ) \(\delta\) 1.29.
Fig. S8  $^1$H NMR data of d-4a

Fig. S9  $^{13}$C NMR data of d-4a
d) Stoichiometric experiments

We performed the preliminary stoichiometric experiments using easily prepared cobalt(III)-salen complexes, and a small amount of desired product 6a were obtained in the absence of oxidant. These results indicate that cobalt(III) species might be as the single electron oxidant enabling the hydrocarbonization.

e) Control experiments with TMS-2a
The compound TMS-2a was prepared from 2a using the procedure described for reference 9. To a dry Schlenk tube containing a magnetic stir bar were added [Co]-2 (0.003 mmol, 3 mol%), TMFP-BF$_4$ (0.12 mmol, 1.2 equiv), and dry THF (1 mL). After stirred for 5 min, olefin 5a (0.10 mmol, 1.0 equiv) and compound TMS-2a (0.15 mmol, 1.5 equiv) were added. Then TMDSO (0.20 mmol, 2.0 equiv) was added dropwise. After stirring for 3 hours, the reaction mixture was extracted with DCM, and the combined organic layers were concentrated in vacuo.

We conducted control experiments to understand the role of the enol in this reaction by using TMS-2a. In the case of TMS-2a, the yield was similar to that using 2a (99% yield). These results suggest the enol form of 2a might be a potential intermediate in this reaction.

f) Control experiments with non-racemic cobalt complex

![Chemical reaction diagram]

We also tested the non-racemic cobalt complexes (R,R)-[Co]-3 and (R,R)-[Co]-5 to explore asymmetric induction. Although the enantioselectivities with both catalysts were poor, slight asymmetric inductions were observed. These results suggest that the cobalt catalyst interacts with the substrate during the C–C bond formation and that the reaction does not proceed via free radical or achiral cation intermediates.

(R,R)-[Co]-3 as catalyst: HPLC analysis (AD, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm) indicated 57:42 e.r. tR (major) = 12.50 min, tR (minor) = 13.66 min.
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\[(R,R)-[\text{Co}]-5\] as catalyst: HPLC analysis (AD, Hexane/IPA = 95/5, 0.8 mL/min, 254 nm) indicated 57:42 e.r. tR (major) = 13.45 min, tR (minor) = 15.12 min.
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g) Control experiments with α-Fluorinated-1,3-diketone

As for the possibility of electrophilic fluorination of the β-diketone 2 under this Co-catalyzed transformation, the reaction mixture within 30 min was studied under \(^{19}\text{F}-\text{NMR}\) analysis, and no fluorinated intermediate was observed except for the fluorine signal of the oxidant 3a. We also used the presynthesized α-fluorinated 1,3-diactone 12 to conduct the reaction under standard conditions, notably, the desired product 7j was not observed.
h) Control experiments

Control experiments showed that no product was formed in the absence of catalysts and silane. The reaction in the absence of ligand also provided the desired product in very low yields (<15% yield).
VI. Reference


VII. $^1$H, $^{13}$C, $^{19}$F Spectra of New Compounds
\[ \text{dr} = 1:1 \]
dr = 1:1

dr = 1:1.4
dr = 1:1.4