Supporting Information

Facile Access to 1,3-Diketones by Gold(I)-Catalyzed Regioselective Hydration of Ynones

<table>
<thead>
<tr>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General information</td>
<td>S2</td>
</tr>
<tr>
<td>2. Optimization of solvent</td>
<td>S2</td>
</tr>
<tr>
<td>3. Synthesis and characterization data of 1,3-diketones</td>
<td>S3</td>
</tr>
<tr>
<td>4. Gram-scale reactions</td>
<td>S11</td>
</tr>
<tr>
<td>5. Synthesis of enolether 3a</td>
<td>S12</td>
</tr>
<tr>
<td>6. References</td>
<td>S12</td>
</tr>
<tr>
<td>7. Copies of $^1$H and $^{13}$C NMR spectra for compounds 2 and 3a</td>
<td>S14</td>
</tr>
</tbody>
</table>
1. **General Information**

All commercially available reagents were used without further purification. Analytical TLC was performed on glass-backed plates pre-coated with silica gel, which were visualized by UV fluorescence ($\lambda_{\text{max}} = 254$ nm) and/or by staining with 1% w/v KMnO$_4$ in 0.5 M aqueous K$_2$CO$_3$. $^1$H NMR and $^{13}$C NMR spectra were measured on a 500 MHz spectrometer ($^1$H: 500 MHz, $^{13}$C: 125 MHz), using CDCl$_3$ or d$_6$-DMSO as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. All $^1$H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm (CHCl$_3$) or the signals at 0.00 ppm (TMS). All $^{13}$C NMR spectra were reported in ppm relative to residual CHCl$_3$ (77.0 ppm) and were obtained with $^1$H-decoupling. Data for $^1$H NMR are described as following: chemical shift ($\delta$ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sep, septet; m, multiplet; br, broad signal), coupling constant (Hz), integration. Data for $^{13}$C NMR are described in terms of chemical shift ($\delta$ in ppm). High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on X4 melting point apparatus and uncorrected.

Ynones are prepared from known literature procedure$^1$.

2. **Table S1** Optimization of solvent for the synthesis of 1,3-diketone 2a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Isolated yield of 2a</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>98%</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>Not detected</td>
</tr>
<tr>
<td>3</td>
<td>1,4-dioxane</td>
<td>90%</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$CN</td>
<td>Not detected</td>
</tr>
</tbody>
</table>
3. General procedure for the Gold(I)-Catalyzed Synthesis of 1,3-Diketones

To a 10 mL Schlenk tube equipped with a stirring bar was charged with PPh₃AuCl (0.005 mmol), AgOTf (0.006 mmol), ynone 1 (0.2 mmol), methanol (2 mL), and H₂O (2 mmol) sequentially without any protection. The reaction was then stirred at room temperature for 12h (open to the air, monitored by TLC). Upon completion the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: PE / EA) to afford the 1,3-diketone products 2.

All the 1,3-diketone products are in keto-enol equilibrium, and the enol forms are contained as the majority as indicated in the parentheses. Characterization data of enol form of each product are shown below.

From the copies of the NMR spectra we could observe very small amount of the keto forms in all cases, which are in very low ratio and some of the peaks are overlapped with those of the enol forms. According to suggestions of the reviewer and editor, we have indicated signals of the minor keto form with asterisk. For the same compound prepared from different precursors, the names of the precursors are given in corresponding spectra.

**1-phenylheptane-1,3-dione (2a)**: Light brown oil (39.4 mg, 98%). (PE/EA = 80/1)
**1H NMR (500 MHz, CDCl₃):** δ = 0.95 (t, J = 7.5 Hz, 3H), 1.36 – 1.46 (m, 2H), 1.63 – 1.73 (m, 2H), 2.43 (t, J = 7.5 Hz, 2H), 6.17 (s, 1H), 7.42 - 7.48 (m, 2H), 7.51 (tt, J = 7.5, 1.5 Hz, 1H), 7.85 – 7.91 (m, 2H), 16.19 (br, 1H) ppm;
**13C NMR (125 MHz, CDCl₃):** δ = 13.8, 22.4, 27.9, 39.0, 96.1, 127.0, 128.6, 132.2, 135.2, 183.5, 196.9 ppm;
**HRMS (ESI):** calcd for C₁₃H₁₇O₂ [M+H]⁺ 205.1229, found 205.1219.

**1-o-tolylheptane-1,3-dione (2b)**: Light brown oil (41.3 mg, 98%). (PE/EA = 40/1)
**1H NMR (500 MHz, CDCl₃):** δ = 0.94 (t, J = 7.5 Hz, 3H), 1.35 – 1.45 (m, 2H), 1.63 – 1.69 (m, 2H), 2.39 (t, J = 7.5 Hz, 2H), 2.49 (s, 3H), 5.84 (s, 1H), 7.22 (d, J = 7.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H) 7.30 – 7.35 (m, 1H), 7.44 – 7.48 (m, 1H), 16.00 (br, 1H) ppm;
**13C NMR (125 MHz, CDCl₃):** δ = 13.8, 20.6, 22.4, 27.9, 38.7, 100.1, 125.7, 128.2, 130.5, 131.3, 136.2, 137.0, 188.2, 196.2 ppm.
HRMS (ESI): calcd for C_{14}H_{19}O_{2} [M+H]^+ 219.1385, found 219.1376.

1-(2-ethoxyphenyl)heptane-1,3-dione (2c): White solid (47.0 mg, 93%). Mp: 39-41°C. (PE/EA = 100/1)
(enol form) \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 0.94 (t, J = 7.5 Hz, 3H), 1.36 – 1.44 (m, 2H), 1.49 (t, J = 7.0 Hz, 3H), 1.62 – 1.71 (m, 2H), 2.40 (t, J = 7.5 Hz, 2H), 4.12 (q, J = 7.0 Hz, 2H), 6.56 (s, 1H), 6.93 (d, J = 8.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 16.21 (br, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ = 13.8, 14.7, 22.3, 27.9, 39.2, 64.3, 101.3, 112.5, 120.6, 124.4, 130.2, 132.7, 157.8, 181.2, 197.5 ppm;

1-(4-methoxyphenyl)heptane-1,3-dione (2d): colorless oil (47.5 mg, 99%). (PE/EA = 40/1)
(enol form) \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 0.94 (t, J = 7.5 Hz, 3H), 1.36 – 1.44 (m, 2H), 1.61 – 1.71 (m, 2H), 2.39 (t, J = 7.5 Hz, 2H), 3.85 (s, 3H), 6.10 (s, 1H), 6.93 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 2H), 16.35 (br, 1H) ppm;
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ = 13.8, 22.4, 28.1, 38.4, 55.4, 95.1, 113.9, 129.1, 131.1, 163.0, 184.3, 194.8 ppm;
HRMS (ESI): calcd for C\(_{14}\)H\(_{19}\)O\(_3\) [M+H]^+ 235.1334, found 235.1326.

1-(4-fluorophenyl)heptane-1,3-dione (2e): Pale yellow oil (40.8 mg, 90%). (PE/EA = 100/1)
(enol form) \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 0.95 (t, J = 7.5 Hz, 3H), 1.35 – 1.46 (m, 2H), 1.62 – 1.72 (m, 2H), 2.42 (t, J = 7.5 Hz, 2H), 6.12 (s, 1H), 7.07 – 7.16 (m, 2H), 7.86 – 7.93 (m, 2H), 16.19 (br, 1H) ppm;
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ = 13.8, 22.4, 28.0, 38.7, 95.7, 115.7 (d, J = 21.8 Hz), 129.4 (d, J = 9.0 Hz), 131.5 (d, J = 3.0 Hz), 165.3 (d, J = 252.0 Hz), 183.1, 196.1 ppm;
\(^{19}\)F NMR (471 MHz, CDCl\(_3\)) δ = -106.7 ppm;
HRMS (ESI): calcd for C\(_{13}\)H\(_{16}\)FO\(_2\) [M+H]^+ 223.1134, found 223.1123.
1-(naphthalen-1-yl)heptane-1,3-dione (2f): Light brown oil (52.0 mg, > 99%). (PE/EA = 40/1)  
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 0.95 (t, $J = 7.5$ Hz, 3H), 1.38 – 1.46 (m, 2H), 1.65 – 1.71 (m, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 6.02 (s, 1H), 7.46 – 7.70 (m, 3H), 7.71 (dd, $J = 7.0$, 1.0 Hz, 1H), 7.87 (d, $J = 7.5$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 8.46 (d, $J = 8.0$ Hz, 1H), 16.15 (s, 1H) ppm;  
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 13.8, 22.4, 27.9, 38.5, 101.0, 124.7, 125.6, 126.3, 126.9, 127.1, 128.5, 130.2, 131.5, 133.8, 134.5, 188.4, 195.7 ppm;  
HRMS (ESI): calcd for C$_{17}$H$_{19}$O$_2$ [M+H]$^+$ 255.1385, found 255.1380.

1-(furan-2-yl)heptane-1,3-dione (2g): Pale yellow oil (29.6 mg, 76%). (PE/EA = 100/1)  
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 0.94 (t, $J = 7.5$ Hz, 3H), 1.34 – 1.43 (m, 2H), 1.62 – 1.68 (m, 2H), 2.42 (t, $J = 7.5$ Hz, 2H), 6.07 (s, 1H), 6.54 (dd, $J = 3.5$, 1.5 Hz, 1H), 7.15 (d, $J = 3.5$ Hz, 1H), 7.56 (d, $J = 1.0$ Hz, 1H), 15.56 (s, 1H) ppm;  
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 13.8, 22.3, 28.1, 37.7, 95.4, 112.4, 115.4, 145.8, 150.7, 176.2, 193.0 ppm;  

1-(thiophen-2-yl)heptane-1,3-dione (2h): Light brown oil (40.8 mg, 93%). (PE/EA = 80/1)  
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 0.94 (t, $J = 7.5$ Hz, 3H), 1.34 – 1.43 (m, 2H), 1.61 – 1.70 (m, 2H), 2.36 (t, $J = 7.5$ Hz, 2H), 6.01 (s, 1H), 7.12 (dd, $J = 5.0$, 4.0 Hz, 1H), 7.59 (dd, $J = 5.0$, 1.0 Hz, 1H), 7.69 (dd, $J = 4.0$, 1.0 Hz, 1H), 15.69 (br, 1H) ppm;  
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 13.7, 22.3, 28.2, 37.2, 95.7, 128.1, 130.0, 132.1, 141.8, 181.8, 190.8 ppm;  
HRMS (ESI): calcd for C$_{11}$H$_{15}$O$_2$S [M+H]$^+$ 211.0793, found 211.0789.

(E)-1-phenylnon-1-ene-3,5-dione (2i): Pale yellow solid (40.7 mg, 86%). Mp: 39-41°C. (PE/EA = 80/1)  
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 0.94 (t, $J = 7.5$ Hz, 3H), 1.34 – 1.43 (m, 2H), 1.60 –
1.68 (m, 2H), 2.40 (t, J = 7.5, 2H), 5.65 (s, 1H), 6.48 (d, J = 16.0, Hz, 1H), 7.33 – 7.42 (m, 3H), 7.49 – 7.54 (m, 2H), 7.59 (d, J = 16.0 Hz, 1H), 15.41 (br, 1 H) ppm; 

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 13.8, 22.4, 27.6, 40.03, 100.6, 123.0, 127.9, 128.9, 129.8, 135.1, 139.5, 177.0, 201.1 ppm; 

HRMS (ESI): calcd for C$_{15}$H$_{19}$O$_2$ [M+H]$^+$ 231.1385, found 231.1387.

2,2-dimethylnonane-3,5-dione (2j): colorless oil (26.5 mg, 72%). (PE/EA = 100/1) 

(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.93 (t, J = 7.5 Hz, 3H), 1.17 (s, 9H), 1.31 – 1.40 (m, 2H), 1.56 – 1.63 (m, 2H), 2.31 (t, J = 7.5, 2H). 5.59 (s, 1H), 15.84 (br, 1H) ppm; 

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 13.8, 22.4, 27.3, 27.9, 38.6, 39.1, 95.0, 195.6, 200.4 ppm; 

HRMS (ESI): calcd for C$_{11}$H$_{21}$O$_2$ [M+H]$^+$ 185.1542, found 185.1536.

1-cyclohexylheptane-1,3-dione (2k): Light brown oil (34.9 mg, 86%). (PE/EA = 100/1) 

(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.92 (t, J = 7.5 Hz, 3H), 1.27 – 1.39 (m, 6H), 1.55 – 1.62 (m, 2H), 1.66 – 1.87 (m, 6H), 2.16 (tt, J = 11.5, 3.5 Hz, 1H), 2.29 (t, J = 7.0 Hz, 2H). 5.48 (s, 1H), 15.65 (br, 1H) ppm; 

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 13.8, 22.4, 25.8, 25.9, 27.9, 29.6, 38.4, 46.5, 97.3, 195.4, 197.3 ppm. 

HRMS (ESI): calcd for C$_{13}$H$_{23}$O$_2$ [M+H]$^+$ 211.1698, found 211.1699.

1-[(3r,5r,7r)-Adamantan-1-yl]heptane-1,3-dione (2l): Light brown oil(51.0 mg, 97%). (PE/EA = 100/1) 

(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.92 (t, J = 7.5 Hz, 3H), 1.32 – 1.40 (m, 2H), 1.56 – 1.63 (m, 2H), 1.65 – 1.76 (m, 6H), 1.82 (d, J = 2.5 Hz, 6H), 2.04 (s, 3H), 2.31 (t, J = 7.5 Hz, 2H), 5.54 (s, 1H), 15.92 (br, 1H) ppm; 

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 13.8, 22.4, 27.9, 28.1, 36.6, 38.8, 39.0, 40.8, 94.8, 196.8, 198.8 ppm; 

HRMS (ESI): calcd for C$_{17}$H$_{27}$O$_2$ [M+H]$^+$ 263.2011, found 263.2002.
1-phenylbutane-1,3-dione (2m): White solid. From 4-phenylbut-3-yn-2-one (29.5 mg, 0.20 mmol), (14.2 mg, 43%), or from 1-phenylbut-2-yn-1-one (26.1 mg, 0.18 mmol), (23.5 mg, 80%). Mp: 57-59°C. (PE/EA = 80/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 2.20$ (s, 3H), 6.18 (s, 1H), 7.42 - 7.48 (m, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.86 – 7.90 (m, 2H), 16.15 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.8$, 96.7, 127.0, 128.6, 132.2, 134.9 , 183.4, 193.7 ppm;
HRMS (ESI): calcd for C$_{10}$H$_{13}$O$_2$ [M+H]$^+$ 163.0759, found 163.0756.

1-phenylpentane-1,3-dione (2n): colorless oil (26.4 mg, 74%). (PE/EA = 100/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.22$ (t, $J = 7.5$ Hz, 3H), 2.47 (q, $J = 7.5$ Hz, 2H), 6.18 (s, 1H), 7.41 – 7.48 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.85 – 7.91 (m, 2H), 16.12 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 9.7$, 32.4, 95.4, 126.9, 128.7, 132.1, 135.1, 183.1, 198.0 ppm;
HRMS (ESI): calcd for C$_{11}$H$_{13}$O$_2$ [M+H]$^+$ 177.0916, found 177.0908.

4,4-Dimethyl-1-phenylpentane-1,3-dione (2o): Light brown oil. From 4,4-dimethyl-1-phenylpent-2-yn-1-one (36.6 mg, 0.20 mmol), (38.6 mg, 96%), or from 4,4-dimethyl-1-phenylpent-1-yn-3-one (36.7 mg, 0.20 mmol), (26.7 mg, 66%). (PE/EA = 40/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.26$ (s, 9H), 6.30 (s, 1H), 7.42 – 7.48 (m, 2H), 7.52 (tt, $J = 7.5$, 1.5 Hz, 1H), 7.87 – 7.91 (m, 2H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 27.4$, 39.9, 92.1, 127.0, 128.6, 132.1, 135.6, 184.6, 202.9 ppm;
HRMS (ESI): calcd for C$_{13}$H$_{17}$O$_2$ [M+H]$^+$ 205.1229, found 205.1229.

1-cyclohexyl-3-phenylpropane-1,3-dione (2p): White solid (41.2 mg, 89%). Mp: 48-49°C. (PE/EA = 100/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.19 – 1.37$ (m, 4H), 1.42 – 1.50 (m, 2H), 1.80 – 1.96 (m, 4H), 2.32 (tt, $J = 11.5$, 3.5 Hz, 1H), 6.18 (s, 1H), 7.40 – 7.46 (m, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.84 – 7.90 (m, 2H), 16.30 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.8$, 25.8, 29.6, 47.3, 94.4, 127.0, 128.5, 132.1, 135.4, 184.3, 199.8 ppm;
HRMS (ESI): calcd for C$_{15}$H$_{19}$O$_2$ [M+H]$^+$ 231.1380, found 231.1355.
1-{(3r,5r,7r)-Adamantan-1-yl}-3-phenylpropane-1,3-dione (2q): White solid (46.9 mg, 90%). M.p.: 48-50 °C. (PE/EA = 40/1)
(enol form) 1H NMR (500 MHz, CDCl3): δ = 1.76 (q, J = 12.5 Hz, 6H), 1.91 (d, J = 2.5 Hz, 6H), 2.08 (s, 3H), 6.26 (s, 1H), 7.41 – 7.48 (m, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.86 – 7.94 (m, 2H) ppm;
13C NMR (125 MHz, CDCl3): δ = 28.1, 36.6, 39.1, 41.6, 91.9, 127.0, 128.5, 132.0, 135.9, 185.5, 201.4 ppm;

1-(furan-2-yl)-3-phenylpropane-1,3-dione (2r): yellow solid (35.8 mg, 84%). Mp: 67-69 °C. (PE/EA = 40/1)
(enol form) 1H NMR (500 MHz, CDCl3): δ = 6.58 (dd, J = 3.5, 1.5 Hz, 1H), 6.76 (s, 1H), 7.24 (dd, J = 3.5, 0.5 Hz, 1H), 7.42 – 7.50 (m, 2H), 7.53 (tt, J = 7.5, 1.5 Hz, 1H), 7.61 (dd, J = 1.5, 0.5 Hz, 1H), 7.91 – 7.99 (m, 2H), 16.19 (br, 1H) ppm;
13C NMR (125 MHz, CDCl3): δ = 92.7, 112.6, 115.7, 127.0, 128.6, 132.3, 134.7, 146.0, 151.1, 177.5, 182.6 ppm;

1-(2-ethoxyphenyl)-3-phenylpropane-1,3-dione (2s): Pale yellow solid (51.1 mg, 95%). Mp: 85-86 °C. (PE/EA = 80/1)
(enol form) 1H NMR (500 MHz, CDCl3): δ = 1.55 (t, J = 7.0 Hz, 3H), 4.16 (q, J = 7.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 1H), 7.01 – 7.08 (m, 1H), 7.33 (s, 1H), 7.40 – 7.48 (m, 3H), 7.52 (tt, J = 7.5, 1.5 Hz, 1H), 7.93 – 7.99 (m, 2H), 8.00 (dd, J = 8.0, 1.5 Hz, 1H) ppm;
13C NMR (125 MHz, CDCl3): δ = 14.9, 64.3, 98.6, 112.6, 120.7, 124.6, 127.1, 128.6, 130.3, 132.1, 133.1, 136.2, 158.1, 183.5, 186.0 ppm;

1-(2-ethoxyphenyl)-3-phenylpropane-1,3-dione (2t): yellow solid (47.6 mg, 99%). Mp: 85-86 °C.
(lit. Mp 80–82 °C). (PE/EA = 80/1)

(enol form) \(^1\)H NMR \( (500 \text{ MHz}, \text{CDCl}_3)\): \(\delta = 2.42 \text{ (s, 3H)}, \ 6.82 \text{ (s, 1H)}, \ 7.28 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, \ 7.44 – 7.50 \text{ (m, 2H)}, \ 7.53 \text{ (t, } J = 7.5 \text{ Hz, 1H)}, \ 7.89 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, \ 7.94 – 8.00 \text{ (m, 2H) ppm;}

\(^{13}\)C NMR \( (125 \text{ MHz, CDCl}_3)\): \(\delta = 21.6, \ 92.8, \ 127.1, \ 127.2, \ 128.6, \ 129.4, \ 132.3, \ 132.9, \ 135.6, \ 143.2, \ 185.1, \ 186.0 \text{ ppm;}

HRMS (ESI): calcd for C\(_{16}\)H\(_{15}\)O\(_2\) [M+H]\(^+\) 239.1072, found 239.1070.

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\begin{array}{c}
\text{O} \\
\text{O} \\
\text{F}
\end{array}
\]

1-(4-fluorophenyl)-3-phenylpropane-1,3-dione (2u): Pale yellow solid. Mp: 81-83°C. From 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one (44.8 mg, 0.20 mmol), (45.7 mg, 94%), or from 3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one (44.3 mg, 0.20 mmol), (42.3 mg, 88%). (PE/EA = 80/1)

(enol form) \(^1\)H NMR \( (500 \text{ MHz, CDCl}_3)\): \(\delta = 6.79 \text{ (s, 1H)}, \ 7.18 – 7.15 \text{ (m, 2H)}, \ 7.43 – 7.51 \text{ (m, 2H)}, \ 7.55 \text{ (t, } J = 7.5, 1.5 \text{ Hz, 1H)}, \ 7.95 – 8.03 \text{ (m, 4H) ppm;}

\(^{13}\)C NMR \( (125 \text{ MHz, CDCl}_3)\): \(\delta = 92.82, \ 115.8(d, J = 21.8 \text{ Hz}), \ 127.1, \ 128.7, \ 129.6 (d, J = 9.1 \text{ Hz}), \ 132.0 (d, J = 3.0 \text{ Hz}), \ 132.5, \ 135.3, \ 165.4 (d, J = 252.4 \text{ Hz}), \ 185.0, \ 185.1 \text{ ppm;}

\(^{19}\)F NMR \( (471 \text{ MHz, CDCl}_3)\): \(\delta = -106.2 \text{ ppm;}

HRMS (ESI): calcd for C\(_{15}\)H\(_{12}\)FO\(_2\) [M+H]\(^+\) 243.0821, found 243.0816.

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\text{O} \\
\text{O} \\
\text{F}
\end{array}
\]

1-(naphthalen-2-yl)-3-phenylpropane-1,3-dione (2v): white solid (52.0 mg, 95%). Mp: 101-103°C. (PE/EA = 80/1)

(enol form) \(^1\)H NMR \( (500 \text{ MHz, CDCl}_3)\): \(\delta = 6.97 \text{ (s, 1H)}, \ 7.45 – 7.60 \text{ (m, 5H)}, \ 7.83 – 7.91 \text{ (m, 2H)}, \ 7.92 – 8.04 \text{ (m, 4H)}, \ 8.51 \text{ (s, 1H) ppm;}

\(^{13}\)C NMR \( (125 \text{ MHz, CDCl}_3)\): \(\delta = 93.4, \ 123.2, \ 126.8, \ 127.2, \ 127.7, \ 128.1, \ 128.3, \ 128.7, \ 129.3, \ 132.4, \ 132.7, \ 132.8, \ 135.3, \ 135.6, \ 185.5, \ 185.7 \text{ ppm;}

HRMS (ESI): calcd for C\(_{19}\)H\(_{15}\)O\(_2\) [M+H]\(^+\) 275.1072, found 275.1071.

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1,3-diphenylpropane-1,3-dione (2w): White solid (92%, 41.5 mg): Mp: 77-78°C. (Lit. 76–77 °C). (PE/EA = 80/1)

(enol form) \(^1\)H NMR \( (500 \text{ MHz, CDCl}_3)\): \(\delta = 6.85 \text{ (s, 1H)}, \ 7.45 – 7.52 \text{ (m, 4H)}, \ 7.55 \text{ (tt, } J = 7.5, 1.5 \text{ Hz, 2H)}, \ 7.93 – 8.00 \text{ (m, 4H) ppm;}

\(^{13}\)C NMR \( (125 \text{ MHz, CDCl}_3)\): \(\delta = 93.2, \ 127.2, \ 128.7, \ 132.4, \ 135.6, \ 185.8 \text{ ppm;}

HRMS (ESI): calcd for C\(_{15}\)H\(_{13}\)O\(_2\) [M+H]\(^+\) 225.0916, found 225.0913.
1-(4-Methoxyphenyl)-3-phenylpropane-1,3-dione (2x): white solid (45.7 mg, 90%). Mp: 130-132°C. (Lit. 127−128 °C). (PE/EA = 40/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 6.79 (s, 1H), 6.97 (d, $J = 9.0$ Hz, 2H), 7.43 − 7.51 (m, 2H), 7.53 (tt, $J = 7.5, 1.5$ Hz, 1H), 7.90 − 7.98 ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$) δ = 55.4, 92.4, 114.0, 127.0, 128.2, 128.6, 129.3, 132.1, 135.6, 163.3, 184.0, 186.2 ppm;
HRMS (ESI): calcd for C$_{16}$H$_{15}$O$_3$ [M+H]$^+$ 255.1021, found 255.1018.

1-cyclopropyl-3-phenylpropane-1,3-dione (2y): White solid (35.9 mg, 94%). Mp: 38-40°C. (PE/EA = 40/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 0.94 − 1.00 (m, 2H), 1.16 − 1.22 (m, 2H), 1.80 (tt, $J = 8.0, 3.5$ Hz, 1H), 6.28 (s, 1H), 7.40 − 7.46 (m, 2H), 7.50 (tt, $J = 7.5, 1.5$ Hz, 1H), 7.83- 7.88 ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 10.6, 19.3, 54.9, 96.1, 126.7, 128.5, 131.9, 134.5, 178.5, 200.23 ppm;
HRMS (ESI): calcd for C$_{12}$H$_{13}$O$_2$ [M+H]$^+$ 189.0916, found 189.0911.

1,3-bis(4-fluorophenyl)propane-1,3-dione (2z): Pale yellow solid (43.2 mg, 83%). Mp: 118-120°C. (PE/EA = 100/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): δ = 6.74 (s, 1H), 7.13 − 7.19 ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 92.5, 115.8 (d, $J = 21.8$ Hz), 129.6 (d, $J = 9.1$ Hz), 131.71 (d, $J = 2.8$ Hz), 165.5 (d, $J = 252.5$ Hz), 184.5 ppm;
$^{19}$F NMR (471 MHz, CDCl$_3$): δ = -106.1 ppm;
HRMS (ESI): calcd for C$_{15}$H$_{11}$F$_2$O$_2$ [M+H]$^+$ 261.0727, found 261.0718.
1,3-bis(4-methoxyphenyl)propane-1,3-dione (2A): White solid (49.3 mg, 87%). Mp: 118-120°C. (PE/EA = 20/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 3.87$ (s, 6H), 6.72 (s, 1H), 6.97 (d, $J = 9.0$ Hz, 4H), 7.95 (d, $J = 9.0$ Hz, 4H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 55.4$, 91.5, 113.9, 128.2, 129.1, 163.0, 184.6 ppm;
HRMS (ESI): calcd for C$_{17}$H$_{17}$O$_4$ [M+H]$^+$ 285.1127, found 285.1128.

1-cyclohexyl-4,4-dimethylpentane-1,3-dione (2B): Light brown oil (36.0 mg, 85%). (PE/EA = 100/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.17$ (s, 9H), 1.16 – 1.34 (m, 4H), 1.36 – 1.46 (m 2H), 1.62 – 1.92 (m, 4H), 2.19 (tt, $J = 11.5$, 3.5 Hz, 1H), 5.60 (s, 1H), 15.96 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 25.8$, 27.4, 29.6, 39.2, 45.0, 93.3, 198.5, 201.2 ppm;
HRMS (ESI): calcd for C$_{13}$H$_{23}$O$_2$ [M+H]$^+$ 211.1698, found 211.1691.

1-[(3r,5r,7r)-Adamantan-1-yl]-4,4-dimethylpentane-1,3-dione (2C): White solid (51.1 mg, 97%). Mp: 86-87°C. (PE/EA = 100/1)
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.17$ (s, 9H), 1.67 - 1.77 (m, 6H), 1.83 (s, 6H), 2.04 (s, 3H), 5.68 (s, 1H), 16.25 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 27.4$, 28.1, 36.6, 39.1, 41.2, 90.5, 199.9, 202.7 ppm;
HRMS (ESI): calcd for C$_{17}$H$_{27}$O$_2$ [M+H]$^+$ 263.2011, found 263.2006.

2,2,6,6-tetramethylheptane-3,5-dione (2D): colorless oil (19.4 mg, 53%). (PE/EA = 200/1).
(enol form) $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 1.18$ (s, 18H), 5.73 (s, 1H), 16.16 (br, 1H) ppm;
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 27.4$, 39.4, 90.7, 201.45 ppm;
HRMS (ESI): calcd for C$_{11}$H$_{21}$O$_2$ [M+H]$^+$ 185.1542, found 185.1547.

Gram-scale reactions
To a 100 mL round bottom flask equipped with a stirring bar was charged with PPh$_3$AuCl (39.5 mg, 0.08 mmol), AgOTf (26.4 mg, 0.10 mmol), ynone 1a (1.493 g, 8.0 mmol), methanol (50 mL), and H$_2$O (1.73 mL, 1.73 g, 96.1 mmol) sequentially without any protection. The reaction was then stirred at room temperature for 18 h (open to the air, monitored by TLC). Upon completion the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: PE /EA=120/1) to afford the 1,3-diketone product 2a (1.5956 g, 96%).

To a 100 mL round bottom flask equipped with a stirring bar was charged with PPh$_3$AuCl (40.0 mg, 0.08 mmol), AgOTf (27.0 mg, 0.10 mmol), ynone 1w (1.6482 g, 8.0 mmol), methanol (50 mL), and H$_2$O (1.73 mL, 1.73 g, 96.1 mmol) sequentially without any protection. The reaction was then stirred at room temperature for 18 h (open to the air, monitored by TLC). Upon completion the solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: PE /EA=100/1) to afford the 1,3-diketone product 2w (1.5844 g, 88%).

**Synthesis of (E)-3-methoxy-1-phenylhept-2-en-1-one (3a)**

To an oven-dried 10 mL Schlenk tube equipped with a stirring bar was charged with PPh$_3$AuCl (2.5 mg, 0.005 mmol), AgOTf (1.8 mg, 0.007 mmol), ynone 1a (38.3 mg, 0.21 mmol), and dry methanol (2 mL) sequentially under N$_2$. The tube was then sealed and the reaction was stirred at room temperature for 18 h. Upon completion the solvent was removed under reduced pressure and the crude product was purified by Pre-TLC (eluent: PE/EA = 80/1) to afford the enolether 3a (36.7 mg, 82%).

$^1$H NMR (500 MHz, CDCl$_3$): δ = 0.93 (t, $J$ = 7.5 Hz, 3H), 1.36 – 1.45 (m, 2H), 1.56 – 1.64 (m, 2H), 2.85 (t, $J$ = 7.8 Hz, 2H), 3.76 (s, 3H), 6.11 (s, 1H), 7.43 (t, $J$ = 7.8 Hz, 2H), 7.49 (t, $J$ = 7.8 Hz, 1H), 7.90 (d, $J$ = 7.5 Hz, 2H) ppm;

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 13.9, 22.6, 29.6, 32.7, 55.5, 95.7, 127.6, 128.3, 131.6, 140.6, 178.6, 189.9 ppm;

HRMS (ESI): calcd for C$_{14}$H$_{19}$O$_2$ [M+H]$^+$ 219.1385, found 219.1383.
References:
From 4-phenylbut-3-yn-2-one
From 4-phenylbut-3-yn-2-one
From 4,4-dimethyl-1-phenylpent-1-yn-3-one
From 4,4-dimethyl-1-phenylpent-1-yn-3-one
From 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one

From 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one
From 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one
$^1$H NMR for 2m prepared from 1-phenylbut-2-yn-1-one (Table 3)
$^1$H NMR for 2o prepared from 4,4-dimethyl-1-phenylpent-2-yn-1-one (Table 3)

$^1$H NMR for 2u prepared from 3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one (Table 3)