Photochemical Oxidation of Benzylic Primary and Secondary Alcohols utilizing Air as the Oxidant

Nikolaos F. Nikitas, Dimitrios Ioannis Tzaras, Ierasia Triandafillidi and Christoforos G. Kokotos*

Laboratory of Organic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Greece

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General Remarks

Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F254 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F254). Visualization of the developed chromatogram was performed by fluorescence quenching, using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. 1H, 19F and 13C NMR spectra were recorded on Varian® Mercury (200 MHz, 188 MHz and 50 MHz, respectively or Bruker 400 MHz) and are internally referenced to residual solvent signals. Data for 1H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant and assignment. Data for 19F NMR are reported in terms of chemical shift (δ ppm) and are internally referenced to trifluoroacetic acid. Data for 13C NMR are reported in terms of chemical shift (δ ppm). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T.: 0.25 μm, I.D.: 0.25 mm, L: 30 m, Tmax: 350 °C, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used as the light source for the quantum yield measurements and the UV-Vis data. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies.
Optimization of the Reaction Conditions for the Photochemical Oxidation of Benzyl Alcohol

Table S1. Catalyst screening for the photochemical oxidation of 1a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst (mol%)</th>
<th>Time (h)</th>
<th>Yield 2a (%)(^a)</th>
<th>Yield 2A (%)(^a)</th>
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<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>20</td>
<td>18</td>
<td>32</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>20</td>
<td>18</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Eosin Y 3c</td>
<td>5</td>
<td>18</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>3d</td>
<td>20</td>
<td>18</td>
<td>6</td>
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<tr>
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<td>3e</td>
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<td>18</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>3f</td>
<td>20</td>
<td>18</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>3g</td>
<td>20</td>
<td>18</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>3h</td>
<td>20</td>
<td>18</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>3i</td>
<td>20</td>
<td>18</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>10(^b)</td>
<td>3i</td>
<td>20</td>
<td>19</td>
<td>55</td>
<td>45</td>
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<tr>
<td>11</td>
<td>3i</td>
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<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>0</td>
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</tr>
<tr>
<td>13(^c)</td>
<td>3i</td>
<td>20</td>
<td>14</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Yield determined by \(^1\)H-NMR. [b] Increasing of reaction time from 18 to 19 h leads to lower yield, due to the overoxidation to benzoic acid. [c] Reaction kept in dark.
Table S2. Solvent screening for the photochemical oxidation of 1a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>MeCN</td>
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</tr>
<tr>
<td>2</td>
<td>H$_2$O</td>
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<tr>
<td>3</td>
<td>DMF</td>
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<tr>
<td>4</td>
<td>CH$_2$Cl$_2$</td>
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<tr>
<td>5</td>
<td>Toluene</td>
<td>26</td>
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<tr>
<td>6</td>
<td>THF</td>
<td>0</td>
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<tr>
<td>7</td>
<td>Acetone</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>MeOH</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>MeCN/DMSO</td>
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</tr>
<tr>
<td><strong>10</strong></td>
<td><strong>DMSO</strong></td>
<td><strong>85</strong></td>
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Mechanistic Scavengers of the Reaction Conditions for the Photochemical of Benzyl Alcohol

Table S3. Quencher screening for the photochemical oxidation of 1a.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Quencher</th>
<th>Notes</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BHT (1.0)</td>
<td>Radical Scavenger</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>TEMPO (1.0)</td>
<td>Radical Scavenger</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>NaN₃ (1.0)</td>
<td>Singlet Oxygen Scavenger</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>DABCO (1.0)</td>
<td>Singlet Oxygen Scavenger</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>2,2,6,6-tetramethylpiperidine (1.0)</td>
<td>Singlet Oxygen Scavenger</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Benzoquinone (1.0)</td>
<td>Superoxide Radical Anion Scavenger</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Ar atmosphere</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>Sunlight</td>
<td>48</td>
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</tbody>
</table>
Synthesis of Starting Materials

1-Phenylbut-3-en-1-ol (1v)\(^1\)

![Chemical Structure](image)

To a flame-dried round-bottom flask, Mg (3.0 equiv., 73 mg, 3.00 mmol), I\(_2\) (catalytic amount) and dry THF (2 mL) were added. The reaction mixture was degassed and a cold bath was added. To the ice cold solution, allyl bromide (3.0 equiv., 363 mg, 3.00 mmol) was added dropwise. After warming at room temperature, the reaction mixture was stirred for 1 h. Then, benzaldehyde (1.0 equiv., 106 mg, 1.00 mmol) was added dropwise and the reaction mixture was left stirring overnight. The reaction mixture was quenched slowly with saturated aq. NH\(_4\)Cl (10 mL) and extracted with AcOEt (3 x 10 mL). The organic layers were combined, washed with saturated aq. NH\(_4\)Cl (2 x 10 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed \textit{in vacuo}. The crude mixture was purified by column chromatography on silica gel (Pet. Ether/AcOEt 8:2), to obtain the desired alcohol 1u; Colorless oil; 72% yield; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.38-7.25 (5H, m, ArH), 5.98-5.67 (1H, m, =CH), 5.22-5.06 (2H, m, 2 x =CH\_H), 4.75-4.64 (1H, m, CHPh), 2.56-2.44 (2H, m, CH\(_2\)), 2.36 (1, s, OH); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 143.7, 134.2, 127.9, 127.0, 125.6, 117.3, 73.0, 43.2; MS 149 [M+H]\(^+\).
General Procedure for the Synthesis of Compounds 1u, 1w-1y

To a flame-dried round-bottom flask, commercially available Grignard reagent (1.5 equiv.) and dry THF (1 mL) were added. The reaction mixture was degassed and a cold bath was added. To the ice cold solution, benzaldehyde (1.0 equiv., 106 mg, 1.00 mmol) was added dropwise and the reaction mixture was left stirring overnight at room temperature. The reaction mixture was quenched slowly with saturated aq. NH₄Cl (10 mL) and extracted with AcOEt (3 x 10 mL). The organic layers were combined and washed with saturated aq. NH₄Cl (2 x 10 mL), dried over Na₂SO₄ and the solvent was removed in vacuo. The crude mixture was purified by column chromatography on silica gel, to obtain the desired alcohols.

1,3-Diphenylpropan-1-ol (1u)

Yellow oil; 80% yield; ¹H NMR (200 MHz, CDCl₃) δ: 7.36-7.31 (4H, m, ArH), 7.32-7.29 (4H, m, ArH), 7.27-7.15 (2H, m, ArH), 4.71-4.67 (1H, q, J = 5.4 Hz, OCH), 2.76-2.67 (2H, m, CH₂), 2.15-2.04 (2H, m, CH₂), 1.9 (1H, br s, OH); ¹³C NMR (50 MHz, CDCl₃) δ: 144.7, 141.6, 128.7, 128.6, 128.5, 127.7, 126.1, 126.0, 74.0, 49.6, 32.2; MS (ESI) m/z 213 [M+H]⁺.

1-Phenylheptan-1-ol (1w)

Colorless oil; 82% yield; ¹H NMR (200 MHz, CDCl₃) δ: 7.36–7.27 (5H, m, ArH), 4.68-4.65 (1H, m, OCH), 1.85-1.66 (3H, m, CH₂ and OH), 1.45-1.25 (8H, m, 4 x CH₂), 0.87
(3H, t, J = 6.8 Hz, CH₃); $^{13}$C NMR (50 MHz, CDCl₃) δ: 145.1, 128.6, 127.6, 126.0, 74.9, 39.3, 31.9, 29.3, 26.0, 22.8, 14.2; MS (ESI) m/z 193 [M+H]$^+$. 

1-Phenylundecan-1-ol (1x)

Colorless oil; 70% yield; $^1$H NMR (200 MHz, CDCl₃) δ: 7.56–7.22 (5H, m, ArH), 4.69-4.61 (1H, m, OCH), 1.93-1.66 (3H, m, CH₂ and OH), 1.47-1.11 (16H, m, 8 x CH₂), 0.86 (3H, t, J = 6.5 Hz, CH₃); $^{13}$C NMR (50 MHz, CDCl₃) δ: 144.9, 128.5, 128.4, 125.7, 74.7, 39.1, 31.9, 29.6, 29.5, 29.3, 25.8, 25.6, 24.4, 22.3, 14.1; MS (ESI) m/z 249 [M+H]$^+$. 

1-Phenyltridecan-1-ol (1y)

Colorless oil; 75% yield; $^1$H NMR (200 MHz, CDCl₃) δ: 7.39-7.21 (5H, m, ArH), 4.61 (1H, t, J = 6.6 Hz, OCH), 2.32 (1H, br s, OH), 1.84-1.61 (2H, m, CH₂), 1.40-1.17 (20H, m, 10 x CH₂), 0.91 (3H, t, J = 6.3 Hz, CH₃); $^{13}$C NMR (50 MHz, CDCl₃) δ: 144.9, 128.3, 127.3, 125.8, 74.5, 39.0, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 25.8, 22.7, 14.1; MS (ESI) m/z 277 [M+H]$^+$. 


1-(4-Nitrophenyl)ethanol (1o)\(^6\)

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

To an ice-cold solution of 1-(4-nitrophenyl)ethenone (1.0 equiv., 169 mg, 1.00 mmol) in absolute ethanol (5 mL), sodium borohydride (1.0 equiv., 38 mg, 1.00 mmol) was added slowly. After the addition, the reaction mixture was left at room temperature for 2 h. The reaction mixture was quenched with 5% aq. HCl (5 mL) and extracted with AcOEt (2 x 10 mL). The organic layers were combined, washed with brine (10 mL), dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo}. The crude mixture was purified by column chromatography on silica gel, to obtain the desired alcohol. Yellow oil; 87% yield; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 8.30-8.01 (2H, m, ArH), 7.51 (2H, d, \(J = 8.5\) Hz, ArH), 4.99 (1H, q, \(J = 6.5\) Hz, OCH), 2.45 (1H, s, OH), 1.49 (3H, d, \(J = 6.5\) Hz, CH\(_3\)); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 153.2, 147.1, 126.1, 123.7, 69.4, 25.5; MS (ESI) m/z 168 [M+H]\(^+\).

1-Phenylpropan-1,3-diol (1ah)\(^7\)

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

To a flame-dried round-bottom flask, commercially available vinyl magnesium bromide 1M in THF (1.5 equiv., 1.50 mL, 1.50 mmol) and dry THF (1 mL) were added. The reaction mixture was degassed and a cold bath was added. To the ice cold solution, benzaldehyde (1.0 equiv., 106 mg, 1.00 mmol) was added dropwise and the reaction mixture was left stirring overnight at room temperature. The reaction mixture was quenched slowly with saturated aq. NH\(_4\)Cl (10 mL) and extracted with AcOEt (3 x 10 mL). The organic layers were combined and washed with saturated aq. NH\(_4\)Cl (2 x 10 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed \textit{in vacuo}. The crude mixture was purified by column chromatography on silica gel, to obtain the desired vinyl alcohol.
Colorless oil; 83% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.34-7.26 (5H, m, ArH), 6.10-6.02 (1H, m, CH=), 5.38-5.33 (1H, m, CHO), 5.22-5.19 (2H, m, =CHH); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 142.5, 140.2, 128.6, 127.8, 126.3, 115.1, 76.7; MS (ESI) m/z 135 [M+H]$^+$.

To an ice-cold solution of vinyl alcohol (1.0 equiv., 152 mg, 1.00 mmol) in dry THF (2 mL), solution of borane in THF 1M (3.0 equiv., 6.0 mL, 6.00 mmol) was added dropwise and the reaction mixture was left stirring for 18h at room temperature. The reaction mixture was cooled to 0 $^\circ$C and a solution of NaOH (4.0 equiv., 160 mg, 4.00 mmol) in water (2 mL) and hydrogen peroxide solution (4.0 equiv., 0.2 mL) were added dropwise subsequently. After the addition, the reaction mixture was left stirring for 2h. The reaction mixture was extracted with AcOEt (3 x 10 mL). The organic layers were combined and dried over Na$_2$SO$_4$ and the solvent was removed in vacuo. The crude mixture was purified by column chromatography on silica gel to obtain the desired alcohol. Colorless oil; 60% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.43-7.28 (5H, m, ArH), 5.02-4.92 (1H, m, CHO), 3.87 (2H, t, $J = 5.6$ Hz, CH$_2$OH), 2.11-1.87 (2H, m, CH$_2$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 144.4, 128.6, 127.7, 125.7, 74.6, 61.6, 40.5; MS (ESI) m/z 153 [M+H]$^+$.

1-(4-Methoxyphenyl)-2,2-dimethylpropan-1-ol (1aj)$^8$

To a flame-dried round-bottom flask, 4-bromoanisole (2.0 equiv., 374 mg, 2.00 mmol), magnesium (2.0 equiv., 48 mg, 2.00 mmol), zinc dust (2.0 equiv., 130 mg, 2.00 mmol) and dry THF (2 mL) were added. The reaction mixture was degassed and placed under argon atmosphere. A solution of trimethylacetaldehyde (1.0 equiv., 86 mg, 1.00 mmol) in dry THF (1 mL) was added dropwise and the reaction mixture was left stirring overnight at room temperature. The reaction mixture was quenched slowly with saturated aq.
NH₄Cl (10 mL) and extracted with AcOEt (3 x 10 mL). The organic layers were combined and washed with saturated aq. NH₄Cl (2 x 10 mL), dried over Na₂SO₄ and the solvent was removed in vacuo. The crude mixture was purified by column chromatography on silica gel, to obtain the desired alcohol. Colorless oil; 85% yield; ¹H NMR (200 MHz, CDCl₃) δ: 7.25-7.17 (2H, d, J = 8.7 Hz, ArH), 6.86-6.80 (2H, d, J = 8.7 Hz, ArH), 4.30 (1H, s, CH), 3.77 (3H, s, OCH₃), 2.24 (1H, br s, OH), 0.89 (9H, s, 3 x CH₃); ¹³C NMR (50 MHz, CDCl₃) δ: 158.6, 134.3, 128.5, 122.8, 81.8, 55.0, 35.5, 25.8; MS (ESI) m/z 165 [M+H]⁺.
General Procedure for the Photochemical Oxidation of Benzyl Alcohols to Aldehydes

\[
\begin{align*}
\text{R}_1^1\text{OH} & \rightarrow \text{R}_1^1\text{H} \\
\text{1a-j} & \rightarrow \text{2a-j}
\end{align*}
\]

Scheme S1. General procedure for the photochemical synthesis of aldehydes.

In an open glass vial containing thioxanthene-9-one 3h (8.5 mg, 0.04 mmol) in DMSO (0.6 mL), benzyl alcohol (0.20 mmol) was added. The vial was left stirring under household bulb irradiation (2 x 80W household lamps, see photos below) for 14 h. The desired product was isolated after purification by column chromatography.

General Procedure for the Photochemical Oxidation of Secondary Alcohols to Ketones

\[
\begin{align*}
\text{OH} & \rightarrow \text{O} \\
\text{R}_1\text{R}_2 & \rightarrow \text{R}_1\text{R}_2
\end{align*}
\]

Scheme S2. General procedure for the photochemical synthesis of ketones.
In an open glass vial containing thioxanthene-9-one 3i (2.1 mg-8.5 mg, 0.01-0.04 mmol) in DMSO (0.6 mL), secondary alcohol (0.20 mmol) was added. The vial was left stirring under household bulb irradiation (2 x 80W household lamps, see Figure S1) for 18 h. The desired product was isolated after purification by column chromatography.

Figure S1. A: 2 x 80W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. B: Beginning of the reaction.
Benzaldehyde (2a)$^9$

![Benzaldehyde (2a)](image)

Colorless oil; 85% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 10.08 (1H, s, CHO), 7.98-7.91 (2H, m, ArH), 7.69 (1H, m, ArH), 7.59 (2H, m, ArH); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 191.9, 136.0, 134.0, 129.2, 128.5; MS (ESI) m/z 107 [M+H]$^+$. 

4-Methoxybenzaldehyde (2b)$^{10}$

![4-Methoxybenzaldehyde (2b)](image)

Colorless oil; 65% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 9.89 (1H, s, CHO), 7.84 (2H, d, $J = 8.7$ Hz, ArH), 7.01 (2H, m, $J = 8.7$ Hz, ArH), 3.90 (3H, s, OCH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 190.9, 164.7, 132.0, 130.0, 114.4, 55.6; MS (ESI) m/z 137 [M+H]$^+$. 

3,4-Dimethoxybenzaldehyde (2c)$^{11}$

![3,4-Dimethoxybenzaldehyde (2c)](image)

White solid; mp: 40-42 °C (lit. mp: 41-42 °C$^{11}$); 60% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 9.83 (1H, s, ArH), 7.43 (1H, dd, $J = 8.2$ and 1.9 Hz, ArH), 7.38 (1H, d, $J = 1.9$ Hz, ArH), 6.96 (1H, d, $J = 8.2$ Hz, ArH), 3.94 (3H, s, OCH$_3$), 3.91 (3H, s, OCH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 190.9, 154.5, 149.7, 130.2, 126.9, 110.5, 109.0, 56.2, 56.1; MS (ESI) m/z 167 [M+H]$^+$. 


2-Methoxybenzaldehyde (2d)\textsuperscript{12}

![Image of 2-Methoxybenzaldehyde (2d)]

Colorless oil; 46% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 10.48 (1H, s, CHO), 7.84 (1H, dd, \(J = 7.6\) and 2.0 Hz, ArH), 7.56 (1H, ddd, \(J = 8.5, 7.6\) and 2.0 Hz, ArH), 7.03 (1H, t, \(J = 7.6\) Hz, ArH), 7.00 (1H, d, \(J = 8.5\) Hz, ArH), 2.68 (3H, s, OCH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 190.0, 162.0, 136.1, 128.7, 125.0, 120.8, 111.8, 55.8; MS (ESI) m/z 137 [M+H]\textsuperscript{+}.

2-Chlorobenzaldehyde (2e)\textsuperscript{13}

![Image of 2-Chlorobenzaldehyde (2e)]

Yellow oil; 33% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 10.50 (1H, s, CHO), 7.93 (1H, dd, \(J = 7.7\) and 1.5 Hz, ArH), 7.54 (1H, ddd, \(J = 7.9, 7.7\) and 1.5 Hz, ArH), 7.46 (1H, d, \(J = 7.9\) Hz, ArH), 7.40 (1H, t, \(J = 7.7\) Hz, ArH); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 189.9, 138.0, 135.1, 132.4, 130.6, 129.4, 127.3; MS (ESI) m/z 141 [M+H]\textsuperscript{+}.

4-Bromobenzaldehyde (2f)\textsuperscript{14}

![Image of 4-Bromobenzaldehyde (2f)]

White solid; mp: 54-56 °C (lit. mp: 55-57 °C\textsuperscript{14b}); 70% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 9.99 (1H, s, CHO), 7.76 (2H, d, \(J = 8.4\) Hz, ArH), 7.69 (2H, d, \(J = 8.4\) Hz, ArH); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 191.1, 135.1, 132.5, 131.0, 129.8; MS (ESI) m/z 186 [M+H]\textsuperscript{+}.
2-Formylbenzonitrile (2g)\textsuperscript{14}

White solid; mp: 98-100 °C (lit. mp: 97-99 °C\textsuperscript{14b}); 47% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 10.09 (1H, s, CHO), 8.00 (2H, d, \(J = 8.3\) Hz, ArH), 7.85 (2H, d, \(J = 8.3\) Hz, ArH); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 190.8, 138.7, 132.9, 129.9, 117.8, 117.5; MS (ESI) m/z 132 [M+H]\textsuperscript{+}.

4-Nitrobenzaldehyde (2h)\textsuperscript{14b,15}

White solid; mp: 101-104 °C (lit. mp: 103-106 °C\textsuperscript{14b}); 23% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 10.18 (1H, s, CHO), 8.41 (2H, d, \(J = 8.6\) Hz, ArH), 8.09 (2H, d, \(J = 8.6\) Hz, ArH); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 190.3, 151.2, 140.1, 130.5, 124.3; MS (ESI) m/z 152 [M+H]\textsuperscript{+}.

4-Hydroxybenzaldehyde (2i)\textsuperscript{14b,16}

White solid; mp: 110-113 °C (lit. mp: 113-116 °C\textsuperscript{14b}); 14% yield; \textsuperscript{1}H NMR (200 MHz, DMSO-d\textsubscript{6}) \(\delta\): 10.59 (1H, s, CHO), 9.78 (1H, br s, OH), 7.75 (2H, d, \(J = 8.4\) Hz, ArH), 6.93 (2H, d, \(J = 8.4\) Hz, ArH); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 190.9, 163.4, 132.1, 128.5, 115.9; MS (ESI) m/z 123 [M+H]\textsuperscript{+}.
(E)-3-Phenylpropenal (2j)

\[
\begin{align*}
\text{Colorless oil; 36\% yield; }^1\text{H NMR (200 MHz, CDCl}_3\text{) }\delta: & \ 9.67 (1\text{H, d, } J = 7.7 \text{ Hz, CHO}), \\
& \ 7.56-7.38 (6\text{H, m, 5 x ArH and } =\text{CH}), \\
& \ 6.68 (1\text{H, dd, } J = 16.0 \text{ and } 7.7 \text{ Hz, } =\text{CH}); \\
^1\text{C NMR (50 MHz, CDCl}_3\text{) }\delta: & \ 193.5, 152.6, 133.8, 131.1, 128.9, 128.3; \\
\text{MS (ESI) m/z } & \ 133 \ [M+H]^+.
\end{align*}
\]

Acetophenone (2k)

\[
\begin{align*}
\text{Colorless oil; 91\% yield; }^1\text{H NMR (200 MHz, CDCl}_3\text{) }\delta: & \ 7.96-7.92 (2\text{H, m, ArH}), \\
& \ 7.55-7.44 (3\text{H, m, ArH}), \\
& \ 2.59 (3\text{H, s, CH}_3); \\
^1\text{C NMR (50 MHz, CDCl}_3\text{) }\delta: & \ 198.1, 137.0, 133.1, 128.5, 128.3, 26.6; \\
\text{MS (ESI) m/z } & \ 121 \ [M+H]^+.
\end{align*}
\]

1-(p-Tolyl)ethanone (2l)

\[
\begin{align*}
\text{Colorless oil; 97\% yield; }^1\text{H NMR (200 MHz, CDCl}_3\text{) }\delta: & \ 7.86 (2\text{H, d, } J = 8.1 \text{ Hz, ArH}), \\
& \ 7.25 (2\text{H, d, } J = 8.1 \text{ Hz, ArH}), \\
& \ 2.57 (3\text{H, s, CH}_3), \\
& \ 2.41 (3\text{H, s, CH}_3); \\
^1\text{C NMR (50 MHz, CDCl}_3\text{) }\delta: & \ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6; \\
\text{MS (ESI) m/z } & \ 135 \ [M+H]^+.
\end{align*}
\]
1-(4-Bromophenyl)ethanone (2m)\(^{19}\)

White solid; m.p. 51-53 °C (lit. mp: 50-52 °C\(^{19}\)); 98% yield; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.82 (2H, d, \(J = 8.4\) Hz, ArH), 7.61 (2H, d, \(J = 8.4\) Hz, ArH), 2.57 (3H, s, CH\(_3\)); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 197.1, 135.9, 132.0, 130.0, 128.4, 26.7; MS (ESI) m/z 199 [M+H]\(^+\).

1-(4-Methoxyphenyl)ethanone (2n)\(^{19,20}\)

White solid; m.p.: 35-37 °C (lit. mp: 36-38 °C\(^{19}\)); 95% yield; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.95 (2H, d, \(J = 8.4\) Hz, ArH), 6.94 (2H, d, \(J = 8.4\) Hz, ArH), 3.87 (3H, s, OCH\(_3\)), 2.56 (3H, s, CH\(_3\)); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 197.0, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5; MS (ESI) m/z 151 [M+H]\(^+\).

1-(4-Fluorophenyl)ethanone (2o)\(^{13}\)

Yellow oil; 98% yield; \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.96 (2H, m, ArH), 7.11 (2H, tt, \(J = 8.7\) and 2.0 Hz, ArH), 2.57 (3H, s, CH\(_3\)); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\): 196.4, 165.7 (d, \(J = 255\) Hz), 133.5 (d, \(J = 3.0\) Hz), 130.9 (d, \(J = 9.4\) Hz), 115.6 (d, \(J = 21.9\) Hz), 26.4; MS (ESI) m/z 139 [M+H]\(^+\).
1-([1,1'-Biphenyl]-4-yl)ethanone (2p)\textsuperscript{21}

White solid; mp: 115-117 °C (lit. mp: 118-120 °C\textsuperscript{21b}); 92% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 8.03 (2H, d, \(J = 8.7\) Hz, ArH), 7.68 (2H, d, \(J = 8.7\) Hz, ArH), 7.64-7.61 (2H, m, ArH), 7.47 (2H, t, \(J = 7.3\) Hz, ArH), 7.40 (1H, t, \(J = 7.3\) Hz, ArH), 2.63 (3H, s, CH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 197.9, 154.9, 140.0, 135.9, 129.1, 129.0, 128.3, 127.4, 127.3, 26.8; MS (ESI) m/z 197 [M+H]\textsuperscript{+}.

1-(4-Nitrophenyl)ethanone (2q)\textsuperscript{20}

Yellow solid; mp: 75-77 °C (lit. mp: 79-81 °C\textsuperscript{20b}); 37% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 8.34 (2H, d, \(J = 8.6\) Hz, ArH), 8.12 (2H, d, \(J = 8.6\) Hz, ArH), 2.68 (3H, s, CH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 196.5, 150.5, 141.5, 129.5, 124.0, 27.2; MS (ESI) m/z 166 [M+H]\textsuperscript{+}.

1-(2-Bromophenyl)ethanone (2r)\textsuperscript{22}

Colorless oil; 39% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 7.61 (1H, d, \(J = 7.9\) Hz, ArH), 7.46 (1H, dd, \(J = 7.6\) and 1.8 Hz, ArH), 7.40-7.34 (1H, m, ArH), 7.32-7.27 (1H, m, ArH), 2.63 (3H, s, CH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 201.6, 141.5, 134.0, 131.9, 129.0, 127.6, 119.0, 30.4; MS (ESI) m/z 199 [M+H]\textsuperscript{+}.
1-(Napthalen-2-yl)ethanone (2s)$^{23}$

![Chemical Structure: 1-(Napthalen-2-yl)ethanone](image)

Colorless oil; 35% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 8.39 (1H, s, ArH), 7.99 (1H, d, $J = 8.4$ Hz, ArH), 7.89 (1H, d, $J = 8.4$ Hz, ArH), 7.82-7.80 (2H, m, ArH), 7.57-7.48 (2H, m, ArH), 2.67 (3H, s, CH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 198.0, 135.5, 134.4, 132.5, 130.2, 129.5, 128.4, 128.4, 127.8, 126.8, 123.8, 26.6; MS (ESI) m/z 171 [M+H]$^+$.  

Benzophenone (2t)$^{18,20b}$

![Chemical Structure: Benzophenone](image)

White solid; mp: 46-48 °C (lit. mp: 47-49 °C$^{20b}$); 96% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.81 (4H, d, $J = 7.8$ Hz, ArH), 7.60 (2H, t, $J = 7.8$ Hz, ArH), 7.49 (4H, t, $J = 7.8$ Hz, ArH); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 196.7, 137.6, 132.2, 130.0, 128.2; MS (ESI) m/z 183 [M+H]$^+$.  

1,3-Diphenylprop-2-yn-1-one (2u)$^{24}$

![Chemical Structure: 1,3-Diphenylprop-2-yn-1-one](image)

Colorless solid; mp: 45-47 °C (lit. mp: 48-51 °C$^{24b}$); 78% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 8.21 (2H, d, $J = 7.6$ Hz, ArH), 7.64 (2H, d, $J = 7.6$ Hz, ArH), 7.59 (1H, t, $J = 7.6$ Hz, ArH), 7.50-7.36 (5H, m, ArH); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 178.0, 136.9, 133.1, 130.9, 129.6, 128.7, 127.2, 120.1, 93.2, 87.0; MS (ESI) m/z 207 [M+H]$^+$. 
1,3-Diphenylpropan-1-one (2v)\textsuperscript{25}

\begin{center}
\includegraphics[width=0.2\textwidth]{13-Diphenylpropan-1-one.png}
\end{center}

Colorless solid; mp: 68-70 °C (lit. mp: 69-70 °C\textsuperscript{25b}); 82% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 7.94 (2H, d, \(J = 7.8\) Hz, ArH), 7.52 (1H, t, \(J = 6.8\) Hz, ArH), 7.43 (2H, t, \(J = 7.8\) Hz, ArH), 7.32-7.15 (5H, m, ArH), 3.27 (2H, t, \(J = 7.8\) Hz, CH\textsubscript{2}), 3.06 (2H, t, \(J = 7.8\) Hz, CH\textsubscript{2}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 199.1, 141.2, 136.7, 133.0, 128.5, 128.4, 128.3, 127.9, 126.0, 40.3, 30.0; MS (ESI) m/z 211 [M+H]\textsuperscript{+}.

1-Phenyl-3-en-1-one (2w)\textsuperscript{26}

\begin{center}
\includegraphics[width=0.2\textwidth]{1-Phenyl-3-en-1-one.png}
\end{center}

Colorless oil; 96% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 7.99-7.93 (2H, m, ArH), 7.60-7.52 (1H, m, ArH), 7.50-7.42 (2H, m, ArH), 6.16-6.02 (1H, m, =CH), 5.26-5.16 (2H, m, =CH\textsubscript{2}), 3.79-3.72 (2H, m, CH\textsubscript{2}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 198.2, 136.7, 133.3, 131.2, 128.8, 128.4, 118.9, 43.6; MS (ESI) m/z 147 [M+H]\textsuperscript{+}.

1-Phenylheptan-1-one (2x)\textsuperscript{27}

\begin{center}
\includegraphics[width=0.2\textwidth]{1-Phenylheptan-1-one.png}
\end{center}

Colorless oil; 55% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 7.98 (2H, m, ArH), 7.57 (1H, m, ArH), 7.47 (2H, m, ArH), 2.98 (2H, t, \(J = 7.2\) Hz, CH\textsubscript{2}), 1.75 (2H, m, CH\textsubscript{2}), 1.45-1.37 (6H, m, 2 x CH\textsubscript{2}), 0.88 (3H, t, \(J = 7.2\) Hz, CH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 200.6, 137.1, 132.9, 128.1, 38.6, 31.7, 29.1, 24.4, 22.6, 14.1; MS (ESI) m/z 191 [M+H]\textsuperscript{+}.
1-Phenylundecan-1-one (2y)

Yellow oil; 51% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.98-7.96 (2H, m, ArH), 7.57-7.56 (1H, m, ArH), 7.48-7.45 (2H, m, ArH), 2.97 (2H, t, $J = 7.5$ Hz, CH$_2$), 1.74 (2H, m, CH$_2$), 1.27 (14H, m, 7 x CH$_2$), 0.89 (3H, t, $J = 6.8$ Hz, CH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 200.5, 137.2, 132.8, 128.8, 128.0, 38.5, 31.8, 29.5, 29.3, 24.3, 22.6, 14.0; MS (ESI) m/z 247 [M+H]$^+$. 

1-Phenyltridecan-1-one (2z)

Colorless oil; 66% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.87 (2H, d, $J = 7.5$ Hz, ArH), 7.45 (1H, t, $J = 7.5$ Hz, ArH), 7.35 (2H, m, ArH), 2.86 (2H, t, $J = 7.2$ Hz, CH$_2$), 1.71-1.57 (2H, m, CH$_2$), 1.36-1.04 (18H, m, 9 x CH$_2$), 0.79 (3H, t, $J = 6.5$ Hz, CH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 200.5, 137.1, 132.8, 128.5, 128.0, 38.6, 32.0, 29.7, 29.7, 29.6, 29.5, 29.4, 24.4, 22.7, 14.1; MS (ESI) m/z 275 [M+H]$^+$. 

9H-Xanthen-9-one (2aa)

Colorless solid; mp: 172-174 °C (lit. mp: 173-174 °C$^{30}$); 97% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 8.37 (2H, dd, $J = 8.0$ and 1.8 Hz, ArH), 7.76 (2H, ddd, $J = 8.5$, 7.1 and 1.8 Hz, ArH), 7.53 (2H, dd, $J = 8.5$ and 1.0, ArH), 7.41 (2H, ddd, $J = 8.0$, 7.1 and 1.0 Hz, ArH);
$^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 177.5, 156.1, 134.0, 126.8, 123.9, 121.9, 118.0; MS (ESI) m/z 197 [M+H]$^+$. 

**Pentan-2-one (2ab)$^{31}$**

![](image)

Colorless oil; 49% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 2.38 (2H, t, $J = 7.2$ Hz, COCH$_2$), 2.13 (3H, s, COCH$_3$), 1.53 (2H, sept, $J = 7.4$ Hz, CH$_2$), 0.89 (3H, t, $J = 7.4$ Hz, CH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 209.3, 45.6, 24.8, 24.3, 13.6; MS (ESI) m/z 87 [M+H]$^+$. 

**Cyclopentanone (2ac)$^{32}$**

![](image)

Colorless oil; 50% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 2.16-2.13 (4H, m, CH$_2$), 1.96-1.93 (4H, m, CH$_2$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 220.5, 38.2, 23.1; MS (ESI) m/z 85 [M+H]$^+$. 

**Cyclohexanone (2ad)$^{32}$**

![](image)

Colorless oil; 89% yield; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 2.34 (4H, t, $J = 5.0$ Hz, 2 x CH$_2$), 1.89-1.84 (4H, m, 2 x CH$_2$), 1.75-1.71 (2H, m, CH$_2$); $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 212.0, 41.9, 26.9, 24.9; MS (ESI) m/z 99 [M+H]$^+$. 
2-Methylcyclohexanone (2ae)\textsuperscript{33}

![2-Methylcyclohexanone](image)

Colorless oil; 65% yield; \( ^1H \text{NMR} (200 \text{ MHz, } \text{CDCl}_3) \delta: 2.39-2.31 \text{ (3H, m, COCH and CH}_2\text{CO)}, 2.09 \text{ (2H, m, CH}_2\text{)}, 1.86-1.64 \text{ (3H, m, 3 x CH}_3\text{H)}, 1.39 \text{ (1H, m, CH}_3\text{H)}, 1.02 \text{ (3H, d, } J = 6.6 \text{ Hz, CH}_3\text{); } ^{13}C \text{ NMR (50 MHz, CDCl}_3\text{) } \delta: 213.3, 45.4, 41.9, 36.3, 28.0, 25.3, 14.8; \text{ MS (ESI) } m/z 113 \text{ [M+H]}^+ \).

1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (2af)\textsuperscript{34}

![1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one](image)

Colorless solid; mp: 173-175 °C (lit. mp: 172-174 °C\textsuperscript{34}); 55% yield; \( ^1H \text{NMR} (200 \text{ MHz, CDCl}_3) \delta: 2.36 \text{ (1H, dd, } J = 18.3 \text{ and 3.8 Hz, COCH}_3\text{H)}, 2.09 \text{ (1H, t, } J = 4.7 \text{ Hz, CH)}, 2.00-1.90 \text{ (1H, m, CH}_3\text{H)}, 1.85 \text{ (1H, d, } J = 18.3 \text{ Hz, COCH}_3\text{H)}, 1.68 \text{ (1H, td, } J = 13.2 \text{ and 3.8 Hz, CH}_3\text{H)}, 1.45-1.30 \text{ (2H, m, 2 x CH}_3\text{H)}, 0.96 \text{ (3H, s, CH}_3\text{), 0.92 \text{ (3H, s, CH}_3\text{), 0.84 \text{ (3H, s, CH}_3\text{); } ^{13}C \text{ NMR (50 MHz, CDCl}_3\text{) } \delta: 219.7, 57.7, 46.7, 43.2, 43.0, 29.9, 27.0, 19.7, 19.1, 9.2; \text{ MS (ESI) } m/z 153 \text{ [M}^+\text{]};

(2S, 5R)-Menthone (2ag)\textsuperscript{14b,35}

![Menthone](image)

Colorless oil; 70% yield; \([\alpha]_D^{20} = -33.0 \text{ (c 1.0, CHCl}_3\text{) (lit. } [\alpha]_D^{20} = -27.5^{14b}); \text{ } ^1H \text{NMR (200 MHz, CDCl}_3\text{) } \delta: 2.35 \text{ (1H, ddd, } J = 12.9, 3.9 \text{ and 2.2 Hz, COCH)}, 2.19-1.78 \text{ (6H,
m, 2 x CH and 2 x CH₂), 1.45-1.28 (2H, m, CH₂), 1.01 (3H, d, J = 6.3 Hz, CH₃), 0.91 (3H, d, J = 6.8 Hz, CH₃), 0.86 (3H, d, J = 6.8 Hz, CH₃); ¹³C NMR (50 MHz, CDCl₃) δ: 212.6, 56.1, 51.0, 35.6, 34.1, 28.0, 26.1, 22.4, 21.4, 18.9; MS (ESI) m/z 155 [M+H]⁺.

3-Hydroxy-1-phenylpropan-1-one (2ah)

![Image of 3-Hydroxy-1-phenylpropan-1-one](image)

Colorless oil; 70% yield; ¹H NMR (200 MHz, CDCl₃) δ: 7.93-7.91 (2H, m, ArH), 7.56-7.54 (1H, m, ArH), 7.44-7.40 (2H, m, ArH), 4.03 (2H, t, J = 5.4 Hz, OCH₂), 3.22 (2H, t, J = 5.4 Hz, CH₂), 2.89 (1H, br s, OH); ¹³C NMR (50 MHz, CDCl₃) δ: 200.5, 136.7, 133.6, 128.7, 128.1, 58.1, 40.4; MS (ESI) m/z 151 [M+H]⁺.

(10R, 13R)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)-4,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (2ai)

![Image of (10R, 13R)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)-4,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one](image)

White solid; mp: 127-129 °C (lit. mp: 126-128 °C³⁶c); 63% yield; ¹H NMR (400 MHz, CDCl₃) δ: 5.72-5.66 (1H, s, =CH), 2.46-2.23 (4H, m, 2 x CH₂), 2.08-1.97 (2H, m, CH₂), 1.89-1.80 (2H, m, 2 x CH), 1.73-0.82 (35H, m, 5 x CH₃, 8 x CH₂, 4 x CH); ¹³C NMR (100 MHz, CDCl₃) δ: 199.6, 171.7, 123.7, 56.1, 55.9, 53.8, 42.4, 39.6, 39.5, 38.6, 36.1, 35.7, 35.7, 35.6, 34.0, 32.9, 32.1, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 18.6, 17.3; [α]²⁰D = -6.0 (c 0.5, CHCl₃) (lit. [α]²⁰D = -5.0³⁶d); MS (ESI) m/z 385 [M+H]⁺.
1-(4-Methoxyphenyl)-2,2-dimethylpropan-1-one (2aj)\textsuperscript{37}

Pale yellow oil; 68% yield; \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}) \(\delta\): 7.84 (2H, d, \(J = 8.8\) Hz, ArH), 6.89 (2H, d, \(J = 8.8\) Hz, ArH), 3.84 (3H, s, OCH\textsubscript{3}), 1.36 (9H, s, 3 x CH\textsubscript{3}); \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \(\delta\): 205.7, 161.7, 130.5, 129.7, 113.0, 54.9, 43.5, 28.0; MS (ESI) m/z 193 [M+H]\textsuperscript{+}. 
Determination of the Quantum Yield

Determination of the photon flux of the lamps

A 0.006M solution of potassium ferrioxalate was prepared by dissolving 120 mg of potassium ferrioxalate hydrate in 40 mL of 0.05M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 10 mg of phenanthroline and 2.25 g of sodium acetate in 250 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark. To determine the photon flux of the lamps, 2.0 mL of the solution of potassium ferrioxalate was placed in a cuvette, its UV-Vis absorbance was recorded (absorbance of interest at 510 nm) and was irradiated for 90 seconds at the lamps. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was allowed to rest for 1 h (complete coordination of ferrous ions to phenanthroline). The absorbance of the solution was then measured at 510 nm.

The fraction of light absorbed (f) by this solution was calculated, using this absorbance (A):

\[ f = 1 - 10^{-A} = 1 - 10^{-4.9987} = 0.9999 \]

In order to measure the photon flux, the mol of Fe²⁺ are required:

\[
\text{Mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.00235 \text{ L} \times 0.382}{1.0 \text{ cm} \times 11.100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 8.09 \times 10^{-8} \text{ mol}
\]

In this equation, V is the total volume of the solution after addition of the phenanthroline (0.00235 L), ΔA is the difference in the absorbance at 510 nm between the irradiated and the non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11.100 L mol⁻¹ cm⁻¹). The photon flux then calculated:
In this equation, \( \Phi \) is the quantum yield of the ferrioxalate actinometer,\(^{38} \) \( t \) is the time of the irradiation (90 seconds), and \( f \) is the fraction of the light absorbed at the lamps (that is calculated above). Thus, the photon flux of the spectrophotometer was calculated to be \( 6.66 \times 10^{-10} \) einstein s\(^{-1} \).

**Determination of the quantum yield**

\[
\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.062 \times 10^{-3} \text{ mol}}{6.66 \times 10^{-10} \text{ einstein s}^{-1} \times 7800 \text{ s} \times 0.9999} = 12
\]

An open cuvette was charged with 1-phenylethanol (24.4 mg, 0.20 mmol), thioxanthen-9-one (8.50 mg, 0.04 mmol) in DMSO (0.6 mL). The sample was stirred and then irradiated under CFL irradiation for 7800 s (2 h and 10 min). After irradiation, the solvent was removed and the yield of the product was determined by \(^1\)H NMR (31%). The quantum yield was determined with the following equation:

\[
\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{0.062 \times 10^{-3} \text{ mol}}{6.66 \times 10^{-10} \text{ einstein s}^{-1} \times 7800 \text{ s} \times 0.9999} = 12
\]
Fluorescence Quenching Studies

After irradiation of thioxanthen-9-one (10^{-3} M in DMSO) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added benzyl alcohol, no significant decrease in the fluorescence was observed.

Figure S2. Fluorescence quenching of excited thioxanthen-9-one by benzyl alcohol in DMSO.

Figure S3. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by benzyl alcohol in DMSO.
After irradiation of thioxanthen-9-one (10^{-3} M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added benzyl alcohol, no significant decrease in the fluorescence was observed.

Figure S4. Fluorescence quenching of excited thioxanthen-9-one by benzyl alcohol in MeCN.

Figure S5. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by benzyl alcohol in MeCN.
After irradiation of thioxanthen-9-one (10^{-3} M in DMSO) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added benzhydrol, no significant decrease in the fluorescence was observed.

![Figure S6. Fluorescence quenching of excited thioxanthen-9-one by benzhydrol in DMSO.](image)

![Figure S7. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by benzhydrol in DMSO.](image)
After irradiation of thioxanthen-9-one ($10^{-3}$M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added benzhydrol, no significant decrease in the fluorescence was observed.

**Figure S8.** Fluorescence quenching of excited thioxanthen-9-one by benzhydrol in MeCN.

**Figure S9.** Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by benzhydrol in MeCN.
After irradiation of thioxanthen-9-one ($10^{-3}\text{M}$ in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added Tempo, a constant decrease in the fluorescence was observed.

Figure S10. Fluorescence quenching of excited thioxanthen-9-one by Tempo in MeCN.

Figure S11. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by Tempo in MeCN.
After irradiation of thioxanthen-9-one (10^{-3} M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added NaN₃, a constant decrease in the fluorescence was observed.

![Fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN.](image1)

Figure S12. Fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN.

![Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN.](image2)

Figure S13. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN.
After irradiation of thioxanthen-9-one (10^{-3} M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added Tempo, in the absence of oxygen, a similar decrease in the fluorescence was observed, as under air. This indicates that TEMPO quenches the catalyst both under oxygen or argon.

Figure S14. Fluorescence quenching of excited thioxanthen-9-one by Tempo in MeCN under argon.

Figure S15. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by Tempo in MeCN under argon.
After irradiation of thioxanthen-9-one (10^{-3} M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Increasing the amount of the added NaN₃ in the absence of oxygen, no significant decrease in the fluorescence was observed. This indicates that NaN₃ quenches the catalyst only under oxygen and not under argon. This result, in conjunction with the next one, postulates that NaN₃ quenches singlet oxygen and not thioxanthenone directly (oxygen quenches thioxanthenone generating singlet oxygen).

Figure S16. Fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN under argon.

Figure S17. Stern-Volmer plot for the fluorescence quenching of excited thioxanthen-9-one by NaN₃ in MeCN under argon.
After irradiation of thioxanthen-9-one (10^{-3} M in MeCN) at 312 nm, its fluorescence was measured at 450 nm. Bubbling of oxygen in the cuvette containing thioxanthenone in MeCN, causes a constant decrease of the fluorescence, which is caused by the quench of the catalyst by the oxygen, forming singlet oxygen.

Figure S18. Fluorescence quenching of excited thioxanthen-9-one by oxygen bubbling.
Mechanistic Studies

In order to determine the species that actually does the oxidation, a series of experiments were performed. First of all, we examined the origin of the oxidation of DMSO to dimethylsulfone. A stirring solution containing DMSO (0.6 mL, 8.40 mmol) and aqueous hydrogen peroxide (30%) (1 mL, 9.70 mmol) (Scheme S4) was monitored by GC-MS for 2 h. GC-MS analysis of the reaction mixture revealed a 50% conversion of the starting compound to dimethylsulfone. This experiment shows that hydrogen peroxide, which is generated from the photochemical reaction, is enough to oxidize the solvent, DMSO, to the previously detected by-product dimethylsulfone.

Scheme S4. Oxidation of DMSO to dimethyl sulfone by hydrogen peroxide.

Then, the origin of hydrogen peroxide was explored. A mixture of DMSO (0.6 mL, 8.40 mmol) with thioxanthenone (8.5 mg, 0.04 mmol) was irradiated (2 x 80W CFL lamps) and monitored by GC-MS (Scheme S5). Indeed, even in the first 4 h of irradiation, the production of dimethylsulfone was detected by GC-MS. This verifies that \( \text{H}_2\text{O}_2 \), that oxidizes DMSO, derives from the photochemical excitation of thioxanthenone, which is quenched by air, to singlet oxygen. Singlet oxygen is known to produce hydrogen peroxide.

Scheme S5. Control experiment, irradiation of DMSO in the presence of thioxanthenone.
Another plausible scenario would be that hydrogen peroxide can oxidize the substrate to the corresponding aldehyde or ketone. To a stirring solution of 1-phenyl-ethanol (24.4 mg, 0.20 mmol) in acetonitrile (0.6 mL), hydrogen peroxide 30% w/w (0.5 mL, 4.90 mmol) was added and the reaction mixture was left stirring at r.t. overnight (Scheme S6). No product could be detected by GC-MS, so we can safely assume that hydrogen peroxide is not strong enough, in order to oxidize the alcohol to the corresponding ketone. Thus, another oxygen species (and not hydrogen peroxide) is responsible for the oxidation of the alcohols.

\[
\text{Scheme S6. Control experiment, oxidation of 1-phenylethanol by hydrogen peroxide.}
\]

In order to provide a greener and environmentally friendly protocol, we performed the oxidation of alcohols under sunlight. The sunlight experiments were performed in Athens, Greece, on the roof of the Department of Chemistry of the National and Kapodistrian University of Athens, (37°58'05.4"N 23°47'08.0"E).

To a stirring solution of 1-phenylethanol (24.4 mg, 0.20 mmol) and thioxanthenone (8.5 mg, 0.04 mmol) in DMSO (0.6 mL) was irradiated under sunlight for 5 h. GC-MS analysis of the reaction mixture revealed the formation of acetophenone in 85% yield (Scheme S7, A). Then, we tried to expand the sunlight experiments by using other alcohols. First, a stirring solution of benzyl alcohol (22.0 mg, 0.20 mmol) and thioxanthenone (8.5 mg, 0.04 mmol) in DMSO (0.6 mL) was irradiated under sunlight for 5 h. GC-MS analysis of the reaction mixture revealed the formation of 48% benzaldehyde and 31% benzoic acid. The problem of overoxidation cannot be bypassed, because the oxidation of benzaldehyde to benzoic acid does not need any catalyst to occur. (Scheme S7, B) Finally, a stirring solution of benzhydrol (37.0 mg, 0.20 mmol) and thioxanthenone (8.5 mg, 0.04 mmol) in DMSO (0.6 mL) was irradiated under sunlight for
5h. GC-MS analysis of the reaction mixture revealed the formation of benzophenone in 82% yield (Scheme S7, C).

Scheme S7. Sunlight-mediated oxidation of alcohols.
In order to better understand the mechanistic pathway after the excitation of the catalyst, we employed the published mechanistic study by Orfanopoulos et al., where they have evaluated the pathway of the photocatalytic oxidation of aryl alkanols to aldehydes and ketones. The different possible pathways are a HAT or a SET process. In order to distinguish between those two, they performed a series of experiments. Firstly, they repeated the oxidation reaction in the presence of TMB (1,3,5-trimethoxybenzene), which has a relatively low oxidation potential \( E_{(ox)}^{\text{TMB}} = +1.12 \, \text{eV vs SCE} \), while they employed 9,10-dicyanoanthracene as the photocatalyst, which is a typical example of a catalyst that proceeds through SET pathways (Scheme S8, A). Orfanopoulos and coworkers observed that the pathway, in the presence of TMB, was terminated and they did not observe any product of oxidation, which is indicative of a SET process. In our case, we repeated the reaction, in the presence of TMB, and after 18 h of irradiation, we observed the corresponding aldehyde 2a (Scheme S8, B). This result indicates that our protocol does not proceed through a SET pathway.

Scheme S8. Control experiment in the presence of 1,3,5-trimethoxybenzene.
Orfanopoulos et al. also performed the oxidation reaction of 1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol, using 9,10-dicyanoanthracene as the photocatalyst. This type of catalyst is known to work through SET paths. Due to its specific substitution, 1aj is rapidly subjected to a C\(_\alpha\)-C\(_\beta\) cleavage, after the Set event, leading to the formation of the corresponding aldehyde and carboxylic acid (Scheme S9, A). In correlation with the previous experiment, they received in 65\% yield of the corresponding aldehyde and only 25\% yield of the desired ketone 2aj, showing that their reaction proceeds through a SET pathway. Following their example, when we examined the photooxidation of 1aj, using thioxanthenone, the starting material was converted quantitatively to the final crude mixture. We identified the corresponding ketone as the major product in a mixture of the ketone, the aldehyde and the acid, in relative ratios of 68\%, 3\% and 29\%, respectively (Scheme S9, B). This results shows that we can safely assume that the mechanism does not follow a SET path, but mainly a HAT path. The next step of the mechanism is the formation of the peroxyacetal, which with further irradiation can be subjected to various rearrangements, leading to the desired product, but probably through additional rearrangements (such as the Hock rearrangement) can lead to products of C\(_\alpha\)-C\(_\beta\) cleavage.

Scheme S9. Comparison between Orfanopoulos et al. test experiment\(^8\) and ours.
As an additional mechanistic tool for the formation of radicals, we employed TEMPO as the radical trap. The reaction of secondary alcohol 1k with TEMPO scavenger was studied extensively by GC-MS and the intermediate compound 1k’ was detected and presented below, confirming the radical pathway of this method (Scheme S10). To a stirring solution of 1-phenylethanol (24.4 mg, 0.20 mmol), TEMPO (31.3 mg, 0.20 mmol) and thioxanthenone (8.5 mg, 0.04 mmol), in DMSO (0.6 mmol), in an open test tube, was irradiated for 18 h. Then, the crude reaction mixture was monitored by GC-MS, where the adduct of benzyl radical of 1-phenylethanol with TEMPO was detected.

Scheme S10. GC-MS trace of the crude reaction mixture of the photochemical oxidation of 1k with TEMPO, showing the formed adduct.

This result strongly indicates that in the reaction mixture, we have the formation of a benzyl radical, probably through a HAT process, since the SET pathway is not supported by our experiments.
References


