2,2-Diiododimedone: a mild electrophilic iodinating agent for the selective synthesis of α-iodoketones from allylic alcohols

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General Information:
All iridium-catalyzed reactions were carried out in closed glass-vials under an atmosphere of air. Air and moisture sensitive reactions were carried out in oven-dried glassware, under an atmosphere of dry nitrogen. Iridium-catalyzed reactions were run under air. Reagents were used as obtained from commercial suppliers without further purification. 2-methyltetrahydrofuran (2-MeTHF) was used as obtained from supplier (>97%). Flash chromatography was carried out on 60 Å (35-70 μm) silica gel (Acros Kieselgel 60) using pentane, mixtures pentane / EtOAc or mixtures pentane / Et₂O as eluent. Analytical TLC was performed on aluminum-backed plates (1.5 Å~ 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 5% KMnO₄ in 95% basified water (w/v). Melting points were recorded in a metal block and are uncorrected.

¹H NMR spectra were recorded at 400 MHz or 500 MHz; ¹³C NMR spectra were recorded at 100 MHz or 125 MHz on a Bruker Advance spectrometer. ¹H and ¹³C NMR chemical shifts (δ) are reported in ppm from tetramethylsilane using the residual solvent resonance (CHCl₃: δH 7.26 and CDCl₃: δC 77.0). Coupling constants (J) are given in Hz. High resolution mass spectra (HRMS) were recorded on Bruker microTOF ESI-TOF mass spectrometer. NMR yields and/or conversions were calculated using 1 equiv. of 2,3,5,6-tetrachloronitrobenzene as internal standard.

Anisole 4a, N,N-dimethylaniline 4b, oct-1-en-3-ol (1a), (E)-oct-2-en-1-ol (1n), cinnamyl alcohol (1o) and [Cp*IrCl₂]₂ were used as obtained from suppliers without further purification. [Cp*Ir(H₂O)₃]SO₄ and [(Cp*Ir)(OH)₃]OH·11H₂O were synthesized as described in the literature.¹ 1-Pivaloyl-1H-indole 4c and allylic alcohols 1b,d,e,g,i,j,k,l were synthesized according to literature procedures.
Synthesis of (E)-6,10-dimethylundeca-3,9-dien-2-one (1g):

(+/-)-Citronellal (5 g, 14 mmol, 1.2 equiv.), (2-oxopropyl)-triphenylphosponium chloride (2.44 g, 17 mmol, 1.5 equiv.) and K$_2$CO$_3$ (2.11 g, 11.75 mmol, 1 equiv.) were dissolved in dry toluene (100 mL) under inert atmosphere and stirred at 80 °C overnight. After that time, the reaction was quenched with aq. NH$_4$Cl (sat., 50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic phases were dried with MgSO$_4$ and evaporated under vacuum. The resulting crude product was taken for the next reaction without further purification.

(E)-6,10-Dimethylundeca-3,9-dien-2-one (1.2 g, 6.18 mmol, 1 equiv.) was dissolved in dry MeOH (25 mL) under an inert atmosphere and cooled to 0 °C. NaBH$_4$ was then added (352 mg, 9.28 mmol, 1.5 equiv.) and the reaction was stirred for 2 h. The solvent was reduced under vacuum and the crude mixture was dissolved in EtOAc (25 mL). H$_2$O (25 mL) was added and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over MgSO$_4$ and the solvent reduced under vacuum. The resulting product was purified by column chromatography using petroleum ether / EtOAc (9:1) mixture as eluent. Allylic alcohol 1g was isolated as a colorless oil (780 mg, 68% yield).

$^1$H NMR (400 MHz, CDCl$_3$, mixture of diastereoisomers ca. 1:1) δ 5.64–5.56 (m, 1H(both diast.)), 5.53–5.47 (m, 1H(both diast.)), 5.10–5.06 (m, 1H(both diast.)), 4.26 (p, $^3$J(1H,1H) = 6.5 Hz, 1H(both diast.)), 2.07–1.92 (m, 3H(both diast.)), 1.89–1.81 (m, 1H(both diast.)), 1.67 (s, 3H(both diast.)), 1.60 (s, 3H(both diast.)), 1.53–1.44 (m, 1H(both diast.)), 1.37–1.28 (m, 1H(both diast.)), 1.25 (d, $^3$J(1H,1H) = 6.5 Hz, 3H(both diast.)), 1.19–1.09 (m, 1H(both diast.)), 0.86 (d, $^3$J(1H,1H) = 6.4 Hz, 3H(both diast.)); $^{13}$C NMR (100 MHz, CDCl$_3$, mixture of diastereoisomers) δ 135.5, 131.2, 129.50, 129.47, 124.8, 68.9, 39.5, 36.65, 36.60, 32.5, 25.7, 25.5, 23.5, 19.4, 19.3, 17.6; HRMS (ESI): m/z calcd for [C$_{13}$H$_{24}$O+Na$^+$]: 219.1719; found: 219.1711.
Synthesis and characterization of 2,2-diiodo-dimedone (2):

To a solution of dimedone (8.1 g, 54.89 mmol) in 1,4-dioxane (200 mL) in a 2 L bottom flask, a solution of iodine monochloride (19.4 g, 119.5 mmol, 2.1 equiv.) in 1,4-dioxane (100 mL) was added dropwise over 20 min. The reaction was stirred for 2 h at room temperature. Water was added (1 L) and a yellow-orange solid precipitated. The solid was filtered off and washed with a mixture of H₂O / 1,4-dioxane (4 : 1, 10 x 100 mL) (the solid should be washed until the mother liquids are colorless), following by H₂O (10 x 100 mL) in order to remove the traces of acids. The solid was dried under reduced pressure (0.2 mmHg), to obtain the title compound as a yellow solid (16.12 g, 41.13 mmol, 75%). The product is stable overnight at room temperature under a air atmosphere, however, it decomposes over the days. It should be kept at room temperature under vacuum, or in an atmosphere of air at −16 °C. m.p. 143-145 °C (decomp.).

¹H NMR (400 MHz, CDCl₃): δ 3.08 (s, 4H), 0.97 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 196.8, 45.9, 31.2, 27.3, 18.7; HRMS (ESI): m/z calcd for C₈H₁₁O₂I₂: 392.8843 [M+H]⁺; found: 392.8840.
Table S1. Optimization of the iodination of anisole by 2.[a]

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Additive (equiv.)</th>
<th>Time (h)</th>
<th>Yield [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et$_2$O</td>
<td>-</td>
<td>16</td>
<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>-</td>
<td>16</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>-</td>
<td>16</td>
<td>&lt;1</td>
</tr>
<tr>
<td>4</td>
<td>trifluoroethanol</td>
<td>-</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Hexafluoroisopropanol (HFIP)</td>
<td>-</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>HFIP</td>
<td>BF$_3$-Et$_2$O (1)</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>HFIP</td>
<td>FeCl$_3$ (0.1)</td>
<td>2</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8[c]</td>
<td>HFIP</td>
<td>FeCl$_3$-H$_2$O (0.1)</td>
<td>2</td>
<td>&gt;99(82)</td>
</tr>
</tbody>
</table>

[a] Reactions were performed on a 0.5 mmol scale. [4a] = 0.1 M. 4a and the additive were dissolved in the corresponding solvent under argon. 2,2-Diiodo-dimedone (1.2 equiv.) were used. [b] Yield determined by $^1$H NMR spectroscopy using 2,3,5,6-tetrachloronitrobenzene as internal standard, isolated yield in parentheses. [c] Under an atmosphere of air.
Table S2. Optimization of the iridium-catalyzed isomerization / iodination of oct-1-en-3-ol (1a) by 2.[a]

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvents (v/v)</th>
<th>Conversion [%][b]</th>
<th>3a/6a [%][b][c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[IrCp*Cl2]2</td>
<td>Dioxane / H2O 1:1</td>
<td>99</td>
<td>46/53</td>
</tr>
<tr>
<td>2</td>
<td>[IrCp*Cl2]2</td>
<td>Dioxane / H2O 5:1</td>
<td>23</td>
<td>10/13</td>
</tr>
<tr>
<td>3</td>
<td>[IrCp*Cl2]2</td>
<td>THF / H2O 1:1</td>
<td>86</td>
<td>58/28</td>
</tr>
<tr>
<td>4</td>
<td>[IrCp*Cl2]2</td>
<td>THF / H2O 5:1</td>
<td>51</td>
<td>42/9</td>
</tr>
<tr>
<td>5</td>
<td>[IrCp*Cl2]2</td>
<td>Acetone / H2O 1:1</td>
<td>&gt;99</td>
<td>36/64</td>
</tr>
<tr>
<td>6</td>
<td>[IrCp*Cl2]2</td>
<td>Acetone / H2O 5:1</td>
<td>80</td>
<td>52/28</td>
</tr>
<tr>
<td>7</td>
<td>[IrCp*(H2O)2]SO4</td>
<td>Acetone / H2O 2:1</td>
<td>78</td>
<td>50/28</td>
</tr>
<tr>
<td>8</td>
<td>[IrCp*(H2O)2]SO4</td>
<td>Acetone / H2O 2:1</td>
<td>87</td>
<td>59/28</td>
</tr>
<tr>
<td>9</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>Acetone / H2O 2:1</td>
<td>89</td>
<td>65/24</td>
</tr>
<tr>
<td>10</td>
<td>[IrCp*Cl2]2</td>
<td>2-MeTHF / H2O 1:1</td>
<td>96</td>
<td>85/11</td>
</tr>
<tr>
<td>11</td>
<td>[IrCp*(H2O)2]SO4</td>
<td>2-MeTHF / H2O 1:1</td>
<td>99</td>
<td>93/6</td>
</tr>
<tr>
<td>16</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 2:1</td>
<td>86</td>
<td>79/7/-</td>
</tr>
<tr>
<td>17</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 2:1</td>
<td>92</td>
<td>88/-</td>
</tr>
<tr>
<td>18</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 2:1</td>
<td>92</td>
<td>88/-</td>
</tr>
<tr>
<td>19</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 2:1</td>
<td>70</td>
<td>69/1/-</td>
</tr>
<tr>
<td>20</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 2:1</td>
<td>70</td>
<td>72/-</td>
</tr>
<tr>
<td>21</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 5:1</td>
<td>95</td>
<td>91/4</td>
</tr>
<tr>
<td>22</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 5:1</td>
<td>99</td>
<td>95/4</td>
</tr>
<tr>
<td>23</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 20:1</td>
<td>94</td>
<td>89/5</td>
</tr>
<tr>
<td>24</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF / H2O 20:1</td>
<td>97</td>
<td>93/4</td>
</tr>
<tr>
<td>25</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF</td>
<td>87</td>
<td>76/11</td>
</tr>
<tr>
<td>26</td>
<td>[(IrCp*2)(OH)2]OH 11H2O</td>
<td>2-MeTHF</td>
<td>66</td>
<td>54/12</td>
</tr>
</tbody>
</table>

[a] Unless otherwise noted: The reaction were run on a 0.5 mmol scale of 1a; [1a] = 0.1 M; catalyst loading: 2 mol% of Ir; room temperature; 1.2 equiv. of 2,2-diiododimedone were used; Reaction time 16 h. [b] Determined by 1H NMR spectroscopy using 2,3,5,6-tetraclorobenzene as internal standard after quenching with an aqueous solution of Na2S2O3. [c] Octan-3-one was not formed. [d] 1 mol% of Ir was used. [e] 0.6 equiv. of 2. [f] 0.2 equiv. of 2.

The solvent mixture is a critical parameter in this reaction. The mixture of solvents 2-MeTHF / H2O was shown to be essential to afford the corresponding α-iodoketones in good yields while minimizing the amount of byproduct 6a. The replacement of 2-MeTHF by other organic solvents (i.e. dioxane, THF or acetone) failed to provide the product in good yields and the amount of 6a increased (entries 1-9). This could be due to the formation of a biphasic system using the mixture 2-MeTHF / H2O, where acid species formed by the decomposition of 2,2-diiododimedone stay in the aqueous phase and the allylic alcohol in the organic phase. Over the different mixtures of 2-MeTHF / H2O evaluated, the optimal was found to be 2:1 (entry 18).
Table S3. Control experiments of the iridium-catalyzed isomerization / iodination of oct-1-en-3-ol (1a) by 2.^[a]

![Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Allylic alcohol</th>
<th>2</th>
<th>1a/2/3a (%)^[b]</th>
<th>6a/2' (%)^[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>&gt;95/-/-</td>
<td>-/-</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>-/-38/-</td>
<td>-/-43</td>
</tr>
<tr>
<td>3</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>96/84/-</td>
<td>2/10</td>
</tr>
<tr>
<td>4^[c]</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>6/15/87</td>
<td>7/78</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>-/nd/94</td>
<td>6/nd</td>
</tr>
</tbody>
</table>

^[a] Unless otherwise noted: The reaction were run on a 0.5 mmol scale of 1a; [1a] = 0.1 M; catalyst loading: 2 mol% of Ir; room temperature; 1.2 equiv. of 2,2-diiodo-dimedone were used; Reaction time 16 h. [b] Determined by 1H NMR spectroscopy using 2,3,5,6-tetrachloronitrobenzene as internal standard without quenching with an aqueous solution of Na2S2O3. [c] The catalyst and 2 were stirred for 4 h before the addition of the allylic alcohol. nd = not determined.

[(IrCp*)2(OH)3]OH 11H2O is not able to react with allylic alcohol 1a under the reaction conditions in the absence of iodinating agent 2 (entry 1). Entries 2 and 4 suggests that the decomposition of 2 is mediated by [(IrCp*)2(OH)3]OH 11H2O. Allylic alcohol 1a does not react with the iodinating agent in the absence of the catalyst (entry 3). Entry 5 shows the optimal conditions for comparison purposes.
**General procedure for the iridium-catalyzed tandem isomerization / iodination of allylic alcohols:**

2,2-Diiodo-dimedone (2) (235 mg, 0.6 mmol, 1.2 equiv.) was dissolved in 2-MeTHF (3.3 mL) and H$_2$O (1.65 mL). The allylic alcohol (1) (0.5 mmol, 1 equiv.) and [(IrCp*)$_2$(OH)$_3$]OH 11H$_2$O (4.6 mg, 0.005 mmol, 1 mol%) were added to the mixture and the vial was closed. The reaction was stirred at room temperature for 16 h and subsequently quenched with an aqueous solution of Na$_2$S$_2$O$_3$ (1.5 mL) and extracted with Et$_2$O (3 x 2 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was reduced under pressure. The resulting crude was purified by column chromatography using petroleum ether / EtOAc (99:1) mixture as eluent.

**Synthesis and characterization of α-iodoketones 3a-m and α-iodoaldehydes 3n-r:**

**2-idoocanth-3-one (3a)**

![2-idoocanth-3-one](image)

The title compound was prepared from 1-Octenol-3-ol (144 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3a as a colorless oil (195 mg, 78%).

$^1$H NMR (400 MHz, CDCl$_3$): \(\delta\) 4.61 (q, $^3J(\text{H},\text{H}) = 6.8$ Hz, 1H), 2.89-2.83 (m, 1H), 2.63-2.58 (m, 1H), 1.88 (d, $^3J(\text{H},\text{H}) = 6.8$ Hz, 3H), 1.66-1.60 (m, 2H), 1.35-1.26 (m, 4H), 0.89 (t, $^3J(\text{H},\text{H}) = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): \(\delta\) 205.4, 38.6, 31.3, 24.9, 24.3, 22.5, 21.8, 14.0. HRMS (ESI): m/z calcd for C$_8$H$_{15}$OI+Na$^+$: 277.0060 [M+Na]$^+$; found: 277.0059.

**4-ethyl-2-idoocanth-3-one (3b)**

![4-ethyl-2-idoocanth-3-one](image)

The title compound was prepared from 4-ethylcoct-1-en-3-ol (156 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3b as a colorless oil (190 mg, 68%).

$^1$H NMR (400 MHz, CDCl$_3$, mixture of 2 diastereoisomers (d.r. = 1:1.3)): \(\delta\) 4.67 (q, $^3J(\text{H},\text{H}) = 6.8$ Hz, 1H (minor)), 4.66 ((q, $^3J(\text{H},\text{H}) = 6.8$ Hz, 1H (major)), 2.84-2.75 (m, 1H(both diast.)), 1.88 (d, $^3J(\text{H},\text{H}) = 6.8$ Hz, 3H (major)), 1.87 (d, $^3J(\text{H},\text{H}) = 6.8$ Hz, 3H (minor)), 1.80-1.70 (m, 1H(both diast.)), 1.58-1.18 (m, 7H(both diast.)), 0.91-0.84 (m, 6H(both diast.)). $^{13}$C NMR (100 MHz, CDCl$_3$, mixture of 2 diastereoisomers (d.r. = 1:1.3)): \(\delta\) 207.75, 207.72, 50.7, 50.3, 33.1, 30.2, 29.7, 29.6,
26.5, 25.5, 25.4, 24.2, 23.0, 22.9, 21.7, 21.6, 14.1, 14.0, 12.2, 11.7. **HRMS (ESI):** m/z calcd for C\textsubscript{10}H\textsubscript{10}I\textsubscript{2}O\textsubscript{2}Na\textsuperscript{+}: 305.0373 \[M+Na\]^+; found: 305.0362.

**4-ethyl-2-iodooctan-3-one (3c)**

![Chemical structure](BnO\(\begin{array}{c} \text{O} \end{array}\))

The title compound was prepared from 1-(benzyloxy)but-3-en-2-ol (178 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) afforded 3c as a colorless oil (225 mg, 74%).

\(^1\text{H NMR (400 MHz, CDCl}_3):\) δ 7.40–7.30 (m, 5H), 4.95 (q, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.9 Hz, 1H), 4.60 (s, 2H), 4.48 (d, 1\(^J\)\(^1\text{H},\text{H}^1\) = 16.6 Hz, 1H), 4.31 (d, 1\(^J\)\(^1\text{H},\text{H}^1\) = 16.6 Hz, 1H), 1.88 (d, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.9 Hz, 3H).

\(^13\text{C NMR (100 MHz, CDCl}_3):\) δ 203.3, 137.0, 128.6, 128.2, 128.1, 73.7, 71.6, 20.8, 18.8. **HRMS (ESI):** m/z calcd for C\textsubscript{11}H\textsubscript{13}IO\textsubscript{2}Na\textsuperscript{+}: 326.9852 \[M+Na\]^+; found: 326.9851.

**1-cyclohexyl-2-iodopropan-1-one (3d)**

![Chemical structure](C\(\begin{array}{c} \text{O} \end{array}\))

The title compound was prepared from 1-cyclohexylprop-2-en-1-ol (35 mg, 0.2 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) gave 3d as an oil (32 mg, 48%).

\(^1\text{H NMR (400 MHz, CDCl}_3):\) δ 4.72 (q, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.8 Hz, 1H), 2.83–2.76 (m, 1H), 1.87 (d, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.8 Hz, 3H), 1.76–1.72 (m, 5H), 1.35–1.17 (m, 5H). **HRMS (ESI):** m/z calcd for C\textsubscript{9}H\textsubscript{15}IO\textsuperscript{+}Na\textsuperscript{+}: 289.0060. \[M+Na\]^+; found: 289.0037.

**4-iodo-1-phenylpentan-3-one (3e)**

![Chemical structure](Ph\(\begin{array}{c} \text{O} \end{array}\))

The title compound was prepared from 5-phenylpent-1-en-3-ol (162 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) afforded 3e as a yellow oil (188 mg, 67%).

\(^1\text{H NMR (400 MHz, CDCl}_3):\) δ 7.32–7.25 (m, 2H), 7.23–7.19 (m, 3H), 4.53 (q, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.8 Hz, 1H), 3.25–3.18 (m, 1H), 2.99–2.86 (m, 3H), 1.85 (d, 3\(^J\)\(^1\text{H},\text{H}^1\) = 6.8 Hz, 3H). **HRMS (ESI):** m/z calcd for C\textsubscript{10}H\textsubscript{12}IO\textsuperscript{+}Na\textsuperscript{+}: 291.0072. \[M+Na\]^+; found: 291.0040.
CDCl₃): δ 204.4, 140.7, 128.7, 128.5, 126.4, 40.4, 30.9, 24.9, 21.6. HRMS (ESI): m/z calcd for C₁₁H₁₃IO+Na⁺: 310.9903 [M+Na]⁺; found: 310.9892.

(E)-4-iodo-2-methyl-1-phenylpent-1-en-3-one (3f)

The title compound was prepared from (E)-2-methyl-1-phenylpenta-1,4-dien-3-ol (174 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO₂; pentane / EtOAc, 99:1) afforded 3f as a yellow solid (190 mg, 64%). m.p. 70-72 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, 4J(¹H,H) = 1.5 Hz, 1H), 7.45–7.40 (m, 4H), 7.38–7.34 (m, 1H), 5.40 (q, 3J(¹H,H) = 7 Hz, 1H), 2.15 (d, 4J(¹H,H) = 1.5 Hz, 3H), 2.02 (d, 3J(¹H,H) = 7 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 197.2, 138.8, 135.6, 133.9, 130.0, 128.9, 128.6, 22.7, 17.9, 14.1. HRMS (ESI): m/z calcd for C₁十二H₁₃IO+Na⁺: 322.9912 [M+Na]⁺; found: 322.9903.

3-iodo-6,10-dimethylundec-9-en-2-one (3g)

The title compound was prepared from (E)-6,10-dimethylundeca-3,9-dien-2-ol (39 mg, 0.2 mmol) according to the general procedure. Purification by column chromatography (SiO₂; pentane / EtOAc, 99:1) gave 3g as an oil (22 mg, 34%).

¹H NMR (400 MHz, CDCl₃, mixture of 2 diastereoisomers (d.r. = 1:1)): δ 5.10-5.06 (m, 1H(both diast.)), 4.41 (t, 3J(¹H,H) = 7.5 Hz, 1H(both diast.)), 2.41 (s, 3H(both diast.)), 2.04-1.86 (m, 4H(both diast.)), 1.68 (s, 3H(both diast.)), 1.60 (s, 3H(both diast.)), 1.47-1.10 (m, 5H(both diast.)), 0.90-0.87 (m, 3H(both diast.)). ¹³C NMR (100 MHz, CDCl₃, mixture of 2 diastereoisomers (d.r. = 1:1)): δ 202.63, 202.61, 131.4, 124.6, 36.9, 36.7, 36.6, 36.4, 33.9, 33.7, 32.4, 32.2, 32.1, 25.97, 25.95, 25.8, 25.5, 25.4, 19.6, 19.4, 17.7. HRMS (ESI): m/z calcd for C₁₃H₂₃IO+Na⁺: 345.0686. [M+Na]⁺; found: 345.0689.

3-iodo-6-phenylhexan-2-one (3h)

The title compound was prepared from (E)-6-phenylhex-3-en-2-ol (176 nmol, 1 mmol) according to the general procedure. Purification by column chromatography (SiO₂; pentane / EtOAc, 99:1) afforded 3h as a colorless oil (199 mg, 66%).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31–7.26 (m, 2H), 7.21–7.16 (m, 3H), 4.45 (t, $^3$J($^1$H,$^1$H) = 7.4 Hz, 1H), 2.69–2.61 (m, 2H), 2.38 (s, 3H), 1.99–1.94 (m, 2H), 1.83–1.74 (m, 1H), 1.67–1.58 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.5, 141.5, 128.6, 128.5, 126.2, 35.2, 34.1, 33.1, 31.2, 26.1.

HRMS (ESI): m/z calcd for C$_{12}$H$_{15}$IO+Na$^+$: 325.0060 [M+Na]$^+$; found: 325.0070.

3-ido-4-phenylbutan-2-one (3i)

![Chemical Structure of 3i](attachment:image.png)

The title compound was prepared from (E)-4-phenylbut-3-en-2-ol (148 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3i as a yellow oil (125mg, 55%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32–7.25 (m, 3H), 7.19–7.17 (m, 2H), 4.72–4.68 (m, 1H), 3.48–3.43 (m, 1H), 3.22–3.17 (m, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.1, 138.9, 129.1, 128.8, 127.2, 40.8, 32.3, 26.8. HRMS (ESI): m/z calcd for C$_{10}$H$_{11}$IO+Na$^+$: 296.9747 [M+Na]$^+$; found:297.9745.

4-(4-chlorophenyl)-3-iodobutan-2-one (3j)

![Chemical Structure of 3j](attachment:image.png)

The title compound was prepared from (E)-4-(4-chlorophenyl)but-3-en-2-ol (180 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3j as a colorless oil (170 mg, 55%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29–7.26 (m, 2H), 7.14–7.11 (m, 2H), 4.68–4.64 (m, 1H), 3.42 (dd, $^1$J($^1$H,$^1$H) = 14.5 Hz, $^3$J($^1$H,$^1$H) = 8 Hz, 1H), 3.15 (dd, $^1$J($^1$H,$^1$H) = 14.5 Hz, $^3$J($^1$H,$^1$H) = 7 Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.8, 137.3, 133.1, 130.5, 128.9, 40.0, 31.7, 26.9. HRMS (ESI): m/z calcd for C$_{10}$H$_{10}$ClIO+Na$^+$: 330.9357 [M+Na]$^+$; found: 330.9350.

2-ido-1-phenylpropan-1-one (3k)

![Chemical Structure of 3k](attachment:image.png)

S10
The title compound was prepared from 1-phenylprop-2-en-1-ol (134 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3k as a colorless oil (189 mg, 72%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02–7.99 (m, 2H), 7.59–7.55 (m, 1H), 7.49–7.44 (m, 2H), 5.50 (q, $^3$$J$(H,$^1$H) = 6.7 Hz, 1H), 2.08 (d, $^3$$J$(H,$^1$H) = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.8, 133.7, 133.6, 128.83, 128.78, 22.2, 18.2.


2-iodo-1-(4-isobutylphenyl)propan-1-one (3l)

The title compound was prepared from 1-(4-isobutylphenyl)prop-2-en-1-ol (190 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3l as a colorless oil (230 mg, 74%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $^3$$J$(H,$^1$H) = 8.5 Hz, 2H), 7.24 (d, $^3$$J$(H,$^1$H) = 8.5 Hz, 2H), 5.48 (q, $^3$$J$(H,$^1$H) = 6.7 Hz, 1H), 2.54 (d, $^3$$J$(H,$^1$H) = 7.2 Hz, 2H), 2.07 (d, $^3$$J$(H,$^1$H) = 6.7 Hz, 3H), 1.91 (m, 1H), 0.92 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.5, 148.2, 131.3, 129.5, 128.7, 45.5, 30.1, 22.4, 22.1, 18.2.


1-(4-bromophenyl)-2-iodopropan-1-one (3m)

The title compound was prepared from 1-(4-bromophenyl)prop-2-en-1-ol (213, 1 mmol) according to the general procedure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 99:1) afforded 3m as a yellow solid (186 mg, 55%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $^3$$J$(H,$^1$H) = 8.5 Hz, 2H), 7.61 (d, $^3$$J$(H,$^1$H) = 8.7 Hz, 2H), 5.42 (q, $^3$$J$(H,$^1$H) = 6.7 Hz, 1H), 2.07 (d, $^3$$J$(H,$^1$H) = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.9, 132.5, 132.2, 130.3, 128.8, 22.0, 17.9.

2-iodooctanal (3n)

\[ \text{CH}_2=\text{CH}-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\text{CO} \]

The title compound was prepared from (E)-oct-2-en-1-ol (128 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) afforded 3n as a colorless oil (53 mg, 21%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 9.26 (d, \( \text{J}(1\text{H},1\text{H}) = 3.2 \text{ Hz}, 1\text{H} \)), 4.45 (ddd, \( \text{J}(1\text{H},1\text{H}) = 7.7 \text{ Hz}, \text{J}(1\text{H},1\text{H}) = 7.0 \text{ Hz}, \text{J}(1\text{H},1\text{H}) = 3.2 \text{ Hz}, 1\text{H} \)), 1.98-1.87 (m, 2H), 1.52-1.45 (m, 1H), 1.34-1.29 (m, 7H), 0.90-0.87 (m, 3H) \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 192.0, 36.9, 32.3, 31.6, 29.5, 28.7, 22.6, 14.1. HRMS (ESI): \( m/z \) calcd for C\textsubscript{8}H\textsubscript{15}IO\cdot\text{MeOH}+Na\textsuperscript{+}: 309.0322 \[ M+\text{MeOH}+\text{Na}\textsuperscript{+} \]; found: 309.0314.

2-iodo-3-phenylpropanal (3o)

\[ \text{Ph}-\text{CH}=-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\text{CO} \]

The title compound was prepared from (E)-3-phenylprop-2-en-1-ol (134 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) afforded 3o as a colorless oil (50 mg, 37%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 9.30 (d, \( \text{J}(1\text{H},1\text{H}) = 2.7 \text{ Hz}, 1\text{H} \)), 7.36-7.26 (m, 3H), 7.22-7.18 (m, 2H), 4.71 (td, \( \text{J}(1\text{H},1\text{H}) = 7.5, 2.7 \text{ Hz}, 1\text{H} \)), 3.50 (dd, \( \text{J}(1\text{H},1\text{H}) = 14.7, \text{J}(1\text{H},1\text{H}) = 7.5 \text{ Hz}, 1\text{H} \)), 3.21 (dd, \( \text{J}(1\text{H},1\text{H}) = 14.7, \text{J}(1\text{H},1\text{H}) = 7.5 \text{ Hz}, 1\text{H} \)). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 191.1, 138.2, 129.0, 128.9, 127.4, 38.6, 36.0. HRMS (ESI): \( m/z \) calcd for C\textsubscript{9}H\textsubscript{9}IO\cdot\text{H}_{2}O+Na\textsuperscript{+} : 300.9696 \[ M+\text{H}_{2}O+\text{Na}\textsuperscript{+} \]; found: 300.9695.

3-(4-chlorophenyl)-2-iodopropanal (3p)

\[ \text{ClPh}-\text{CH}=-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\text{CO} \]

The title compound was prepared from (E)-3-(4-chlorophenyl)prop-2-en-1-ol (168 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO\textsubscript{2}; pentane / EtOAc, 99:1) afforded 3p as a colorless oil (57 mg, 34%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 9.30 (d, \( \text{J}(1\text{H},1\text{H}) = 2.2 \text{ Hz}, 1\text{H} \)), 7.30-7.28 (m, 2H), 7.15-7.13 (m, 2H), 4.66 (td, \( \text{J}(1\text{H},1\text{H}) = 7.5, 2.2 \text{ Hz}, 1\text{H} \)), 3.46 (dd, \( \text{J}(1\text{H},1\text{H}) = 14.7, \text{J}(1\text{H},1\text{H}) = 7.5 \text{ Hz}, 1\text{H} \)), 3.16 (dd, \( \text{J}(1\text{H},1\text{H}) = 14.7, \text{J}(1\text{H},1\text{H}) = 7.5 \text{ Hz}, 1\text{H} \)). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 190.9, 136.7, 133.3,
130.5, 129.0, 37.8, 35.6. **HRMS (ESI):** m/z calcd for C_{9}H_{8}^{35}ClO-MeOH+Na⁺ : 348.9463 [M+MeOH+Na]⁺; found: 348.9472.

2-iodo-5-phenylpentanal (3q)

![2-iodo-5-phenylpentanal](image)

The title compound was prepared from (E)-5-phenylpent-2-en-1-ol (162 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO₂; pentane / EtOAc, 99:1) afforded 3p as a colorless oil (68 mg, 42%).

**¹H NMR (400 MHz, CDCl₃):** δ 9.25 (d, J(¹H,¹H) = 3 Hz, 1H), 7.31-7.28 (m, 2H), 7.22-7.17 (m, 3H), 4.47 (ddd, J(¹H,¹H) = 7.8, 6.8, 2.2 Hz, 1H), 2.72-2.62 (m, 2H), 2.03-1.66 (m, 4H). **¹³C NMR (100 MHz, CDCl₃):** δ 191.6, 141.3, 128.6, 128.5, 126.2, 36.6, 35.2, 31.7, 31.2. **HRMS (ESI):** m/z calcd for C_{11}H_{13}IO-MeOH+Na⁺ : 343.0165 [M+MeOH+Na]⁺; found: 343.0177.

4-(benzyloxy)-2-iodobutanal (3r)

![4-(benzyloxy)-2-iodobutanal](image)

The title compound was prepared from (Z)-4-(benzyloxy)but-2-en-1-ol (178 mg, 1 mmol) according to the general procedure. Purification by column chromatography (SiO₂; pentane / EtOAc, 99:1) afforded 3r as a colorless oil (70 mg, 23%).

**¹H NMR (400 MHz, CDCl₃):** δ 9.28 (d, J(¹H,¹H) = 2.7 Hz, 1H), 7.38-7.26 (m, 5H), 4.75 (ddd, J(¹H,¹H) = 7.8 Hz, J(¹H,¹H) = 6.7 Hz, J(¹H,¹H) = 2.7 Hz, 1H), 4.50 (s, 2H), 3.66-3.61 (m, 1H), 3.55-3.50 (m, 1H), 2.38-2.30 (m, 1H), 2.19-2.12 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 191.6, 138.0, 128.6, 128.0, 127.9, 73.4, 68.6, 33.7, 33.0. **HRMS (ESI):** m/z calcd for C_{11}H_{13}IO·H₂O+Na⁺ : 344.9958 [M+H₂O+Na]⁺; found: 344.9950.
Deuterium labelling studies:
Iridium-catalyzed isomerization / iodination of 1i-d

Deuterated allylic alcohol 2-d-(E)-4-phenylbut-3-en-2-ol (1i-d) (95% deuterium) (0.5 mmol) was reacted according to the general procedure using 1 mol% [(IrCp*)2(OH)3]OH 11H2O and 1.2 equiv. of 2,2-diodo-dimedone (16 h reaction time). 3i-d (79 mg, 58% isolated yield) was obtained as colorless oil after purification with column chromatography (SiO2: pentane / EtOAc, 99:1). 1H, 13C and HRMS showed 95% of deuterium content in 3i-d evidencing a 1,3-H shift pathway in these reaction conditions.

4-d-3-iodo-4-phenylbutan-2-one (3i-d)

1H NMR (400 MHz, CDCl3, mixture of 2 diastereoisomers (d.r. = 1:1)): δ 7.32–7.26 (m, 3H(both diast.)), 7.20–7.17 (m, 2H(both diast.)), 4.70 (d, 3J(1H,1H) = 7.7 Hz, 1H(both diast.)), 3.45–3.20 (m, 1H(both diast.)), 2.36 (s, 3H(one diast.)); 13C NMR (100 MHz, CDCl3, mixture of 2 diastereoisomers (d.r. = 1:1)): δ 202.1, 138.8, 129.1, 128.8, 127.2, 40.6 (t, 1J(1H,2H) = 19.9 Hz), 40.5 (t, 1J(1H,2H) = 19.9 Hz), 32.3, 32.1, 26.8. HRMS (ESI): m/z calcd for C10H10DIO+Na+: 297.9810 [M+Na]+; found: 297.9808

Crossover experiment between 1i-d and 1e

Deuterated allylic alcohol 2-d-(E)-4-phenylbut-3-en-2-ol (1i-d) (95% deuterium) (0.25 mmol) and allylic alcohol 5-phenylpent-1-en-3-ol (1e) were reacted according to the general procedure using 1 mol% [(IrCp*)2(OH)3]OH 11H2O and 1.2 equiv. of 2,2-diodo-dimedone (16 h reaction time). The mixture showed a 95% of deuterium content in 3i-d and no deuterium in 3e as determined by 1H, 13C and HRMS, suggesting an intramolecular process operating in this reaction.
General procedure for synthesis of iodoarenes using 2

2,2-Diiodo-dimedone (2) (235 mg, 0.6 mmol, 1.2 equiv.), the corresponding arene (0.5 mmol, 1 equiv.) and FeCl₃·H₂O (0.05 mmol, 10 mol%) were dissolved in HFIP (5 mL) and the mixture was stirred at room temperature under an air atmosphere for 2 h. The reaction was quenched by the addition of sat. aqueous solution of Na₂S₂O₅ (2 mL) and the product was extracted with CH₂Cl₂ (3x10 mL). The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure. The product was purified by column chromatography using petroleum ether / EtOAc (98:2) mixture as eluent.

Synthesis and characterization of iodoarenes 5a-c

1-iodo-4-methoxybenzene (5a)

The title compound was prepared from anisole 4a (108 µL, 1 mmol,) according to the general procedure affording 5a as a yellow solid (193 mg, 82%).

¹H NMR (400 MHz, CDCl₃): δ 7.64–7.53 (m, 2H), 6.78–6.66 (m, 2H), 3.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.5, 138.2, 116.4, 82.7, 55.3.

4-iodo-N,N-dimethylaniline (5b)

The title compound was prepared from N,N-dimethylaniline 4b (127 µL, 1 mmol) according to the general procedure affording 5b as a white solid (169 mg, 68%).

¹H NMR (400 MHz, CDCl₃): δ 7.56–7.42 (m, 2H), 6.60–6.45 (m, 2H), 2.94 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 150.0, 137.6, 114.7, 77.4, 40.4.

1-(3-iodo-1H-indol-1-yl)-2,2-dimethylpropan-1-one (5c)

The title compound was prepared from pivaloyl-1H-indole 4c (201 mg, 1 mmol) according to the general procedure affording 5c as a yellow solid (266 mg, 81%).

¹H NMR (400 MHz, CDCl₃): δ 8.53–8.47 (m, 1H), 7.88 (s, 1H), 7.47–7.35 (m, 3H), 1.55 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 176.2, 136.2, 131.0, 129.7, 126.2, 124.2, 121.2, 117.2, 67.3, 41.4, 28.7. HRMS (ESI): m/z calcd for C₁₃H₁₄NI+Na⁺: 350.0012 [M+Na⁺]; found: 349.9997.
Procedure for the synthesis and characterization of imidazole 7

α-iodoketone 6e (52 mg, 0.18 mmol, 1 equiv.) was dissolved in MeCN (2 mL). Benzamidine hydrochloride (35 mg, 0.225 mmol, 1.2 equiv.) and K$_2$CO$_3$ (31 mg, 0.225 mmol, 1.2 equiv.) were added and the reaction mixture was heated to reflux overnight. The reaction was subsequently quenched with H$_2$O (1.5 mL) and extracted with EtOAc (3 x 2 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was reduced under pressure. 4-methyl-5-phenethyl-2-phenyl-1H-imidazole (7) was isolated in 95% yield as a white oil/foam.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, $^3$J(H,$^1$H) = 7.0 Hz, 2H), 7.32−7.15 (m, 6H), 7.02 (d, $^3$J(H,$^1$H) = 7.0 Hz, 2H), 2.85−2.79 (m, 4H), 1.98 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.6, 141.7, 132.0, 130.7, 128.85, 128.85, 128.6, 127.9, 126.0, 125.0, 36.5, 28.0, 10.6.

HRMS (ESI): m/z calcd for C$_{18}$H$_{18}$N$_2$H$^+$: 263.1543 [M+H]$^+$; found: 263.1548.

One-pot synthesis and characterization of halohydrin 8 and synthesis of epoxide 9

2,2-Diiodo-dimedone (2) (92 mg, 0.24 mmol, 1.2 equiv.) was dissolved in 2-MeTHF (1.33 mL) and H$_2$O (0.66 mL). Allylic alcohol (1e) (33 mg, 0.2 mmol, 1 equiv.) and [(IrCp*)$_2$(OH)$_3$]OH 11H$_2$O (2 mg, 0.002 mmol, 1 mol%) were added to the mixture and the vial was closed and stirred at room temperature for 16 h. After that, MeOH (4 mL) was added and the mixture was cooled to −60 °C. NaBH$_4$ (20 mg, 0.5 mmol, 2.5 equiv.) was incorporated in small portions and the reaction stirred for 30 minutes at −60 °C. The volatiles were reduced under vacuum and the residue was then carefully quenched with H$_2$O (2 mL) and extracted with EtOAc (3 x 2 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was reduced under pressure. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 90:10) afforded 4-ido-1-phenylpentan-3-ol (8) with 59% isolated yield and a diastereomeric ratio of 93:7 (cis/trans).
1H NMR (400 MHz, CDCl₃, mixture of diastereoisomers (93:7)): δ 7.32–7.28 (m, 2H(both diast.)), 7.22–7.19 (m, 3H(both diast.)), 4.42–4.36 (m, 1H(minor)), 4.32–4.26 (m, 1H(major)), 2.89–2.68 (m, 2H(both diast.)), 1.96 (d, 3J(1H,1H) = 7.0 Hz, 3H(both diast.)), 1.88–1.82 (m, 2H(both diast.)), 1.76 (d, 3J(1H,1H) = 7.4 Hz, 1H(both diast.)).

13C NMR (100 MHz, CDCl₃ mixture of diastereoisomers (93:7)): δ 141.6, 128.62, 128.58, 126.2, 75.5, 40.4, 39.0, 31.9, 25.5.

HRMS (ESI): m/z calcd for C₁₁H₁₅IO+Na⁺: 313.0060 [M+Na⁺]; found: 313.0045.

Procedure for the synthesis and characterization of cyanoperoxide 10

α-iodoketone 3e (39 mg, 0.13 mmol, 1 equiv.) was dissolved in 2 mL of THF. KCN (22 mg, 0.337 mmol, 2.5 equiv.) and the reaction mixture was heated at 40 °C overnight. The volatiles were removed under vacuum and the crude was purified directly by column chromatography (SiO₂; pentane/CH₂Cl₂, 80:20 d.r.) to afford 74% isolated yield of cyanoperoxide 10 with a diastereomeric ratio of 80:20 (cis/trans).
(EtOAc, 90:10) affording 3-methyl-2-phenethyloxirane-2-carbonitrile (10) with 74% isolated yield and a diastereomeric ratio of 80:20.

$^{1}$H NMR (400 MHz, CDCl$_3$, mixture of diastereoisomers 80:20): $\delta$ 7.35–7.25 (m, 2H(both diast.)), 7.25–7.21 (m, 3H(both diast.)), 3.40 (q, $\delta^{1}$J(H,$^1$H) = 5.5 Hz, 1H(minor), 3.00–2.86 (m, 2H(both diast.)), 2.83 (q, $\delta^{1}$J(H,$^1$H) = 5.5 Hz, 1H(major), 2.24–2.11 (m, 1H(both diast.)), 1.98–1.92 (m, 1H(both diast.)), 1.41 (d, $\delta^{1}$J(H,$^1$H) = 5.5 Hz, 3H(major), 1.13 (d, $\delta^{1}$J(H,$^1$H) = 5.5 Hz, 3H(minor). $^{13}$C NMR (100 MHz, CDCl$_3$, mixture of diastereoisomers 80:20): $\delta$ 140.6, 139.6, 128.8, 128.80, 128.6, 128.5, 126.8, 126.7, 118.9, 117.3, 59.6, 59.5, 54.1, 52.0, 36.0, 31.4, 31.2, 30.4, 15.5, 12.8. HRMS (ESI): m/z calcd for C$_{12}$H$_{13}$NO$^+$ + Na$^+$: 210.0889 [M+Na]$^+$; found: 210.0887.

**Procedure for the synthesis and characterization of α-aminoketones 11-15**

![Chemical Structure](image)

The corresponding α-iodoketone (0.16 mmol, 1 equiv.) and the amine (0.486 mmol, 3 equiv.) were dissolved in 2 mL of 1,4 dioxane. The reaction mixture was stirred at room temperature overnight and then quenched with NaHCO$_3$ sat. aqueous solution and extracted with EtOAc. The organic phases were dried with MgSO$_4$ and the volatiles were removed under vacuum. The crude was purified by column chromatography (SiO$_2$; pentane / EtOAc, 90:10).

1-phenyl-4-(piperidin-1-yl)pentan-3-one (11)

![Chemical Structure](image)

The title compound was prepared from 3e (47 mg, 0.16 mmol) and piperidine (48 µL, 0.486 mmol), according to the procedure described above. Purification by column chromatography (SiO$_2$; pentane / EtOAc, 90:10) afforded 12 as a yellow oil (40 mg, 89%).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29–7.26 (m, 2H), 7.21–7.17 (m, 3H), 3.08 (q, $\delta^{1}$J(H,$^1$H) = 6.8 Hz, 1H), 2.99–2.85 (m, 4H), 2.41–2.29 (m, 4H), 1.57–1.49 (m, 4H), 1.43–1.39 (m, 2H), 1.06 (d, $\delta^{1}$J(H,$^1$H) = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 221.7, 141.6, 128.51, 128.46, 126.0, 69.8, 51.2, 40.8, 30.0, 26.4, 24.4, 10.0. HRMS (ESI): m/z calcd for C$_{16}$H$_{23}$NO$+$ : 246.1852 [M+H]$^+$; found: 246.1855.
4-(diethylamino)-1-phenylpentan-3-one (12)

The title compound was prepared from 3e (47 mg, 0.16 mmol) and diethylamine (50 µL, 0.486 mmol), according to the procedure described above. Purification by column chromatography (SiO2; pentane / EtOAc, 90:10) afforded 12 as an oil (20 mg, 51%).

1H NMR (400 MHz, CDCl3): δ 7.31–7.28 (m, 2H), 7.23–7.18 (m, 3H), 3.37 (q, $^3\nu^J(H,H) = 6.7$ Hz, 1H), 3.08–2.86 (m, 4H), 2.54–2.37 (m, 4H), 1.06–1.00 (m, 9H). 13C NMR (100 MHz, CDCl3): δ 213.2, 141.7, 128.53, 128.52, 126.1, 64.3, 44.4, 40.9, 30.3, 13.7, 8.5. HRMS (ESI): m/z calcd for C15H23NO+H⁺: 234.1852 [M+H⁺]; found: 234.1837.

1-phenyl-4-(4-(pyrimidin-2-yl)piperazin-1-yl)pentan-3-one (13)

The title compound was prepared from 3e (47 mg, 0.16 mmol) and 2-(piperazin-1-yl)pyrimidine (70 µL, 0.486 mmol), according to the procedure described above. Purification by column chromatography (SiO2; pentane / EtOAc, 90:10) afforded 13 as a yellow oil (40 mg, 73%).

1H NMR (400 MHz, CDCl3): δ 8.28 (d, $^3\nu^J(H,H) = 4.7$ Hz, 2H), 7.29–7.25 (m, 2H), 7.21–7.16 (m, 3H), 6.46 (t, $^3\nu^J(H,H) = 4.7$ Hz, 1H), 3.82–3.72 (m, 4H), 3.15 (q, $^3\nu^J(H,H) = 6.8$ Hz, 1H), 3.03–2.87 (m, 4H), 2.51–2.38 (m, 4H), 1.09 (d, $^3\nu^J(H,H) = 6.8$ Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 211.6, 161.7, 157.8, 141.4, 128.54, 128.52, 126.2, 110.0, 69.1, 49.7, 44.0, 40.9, 29.9, 10.4. HRMS (ESI): m/z calcd for C19H25NO+H⁺: 325.2023 [M+H⁺]; found: 325.2020.

3-(3,4-dihydroisoquinolin-2(1H)-yl)-6-phenylhexan-2-one (14)

The title compound was prepared from 3h (32 mg, 0.11 mmol) and tetrahydroisoquinoline (40 µL, 0.32 mmol), according to the procedure described above. Purification by column chromatography (SiO2; pentane / EtOAc, 90:10) afforded 14 as a yellow oil (25 mg, 77%).
\[ \text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.30-7.27 \text{ (m, 2H), 7.21-7.17 \text{ (m, 3H), 7.15-7.09 \text{ (m, 3H), 7.01-7.00 \text{ (m, 1H), 3.79 (d, } J^{(1}H,^{1}H) = 14.7 \text{ Hz, 1H), 3.68 (d, } J^{(1}H,^{1}H) = 14.7 \text{ Hz, 1H), 3.21-3.18 \text{ (m, 1H), 2.88-2.76 \text{ (m, 4H), 2.68-2.65 \text{ (m, 2H), 2.20 (s, 3H), 1.80-1.58 \text{ (m, 4H).}} \text{ ^{13}C NMR (100 MHz, CDCl}_3\text{):} \delta 210.3, 142.0, 134.9, 134.5, 128.9, 128.52, 128.47, 126.6, 126.2, 126.0, 125.8, 73.8, 52.7, 47.8, 36.0, 29.8, 28.4, 28.0, 25.7. \text{ HRMS (ESI):} m/z \text{ calcd for C}_{21}\text{H}_{25}\text{NO}^+H^+ : 308.2009 [M +H]^+; \text{ found: 308.2006.}} \]

**6-phenyl-3-thiomorpholinohexan-2-one (15)**

The title compound was prepared from 3h (32 mg, 0.11 mmol) and thiomorpholine (30 \( \mu \text{L, 0.32 mmol}), according to the procedure described above. Purification by column chromatography (SiO\(_2\); pentane / EtOAc, 90:10) afforded 15 as a yellow oil (26 mg, 88%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.29-7.26 \text{ (m, 2H), 7.20-7.15 \text{ (m, 3H), 3.05-3.01 \text{ (m, 1H), 2.80-2.78 \text{ (m, 4H), 2.63-2.60 \text{ (m, 6H), 2.16 (s, 3H), 1.70-1.50 \text{ (m, 4H).}} \text{ ^{13}C NMR (100 MHz, CDCl}_3\text{):} \delta 209.5, 142.1, 128.5, 128.5, 126.0, 74.8, 52.3, 36.0, 28.9, 28.7, 24.85, 24.85. \text{ HRMS (ESI):} m/z \text{ calcd for C}_{16}\text{H}_{23}\text{NOS}^+H^+ : 278.1573 [M +H]^+; \text{ found: 278.1584.}} \]

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$^1$H-NMR and $^{13}$C-NMR spectra of (E)-6,10-dimethylundeca-3,9-dien-2-ol (1g)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
$^1$H-NMR and $^{13}$C-NMR spectra of 2,2-diiodo-5,5-dimethylcyclohexane-1,3-dione 2,2-diiodo-5,5-dimethylcyclohexane-1,3-dione (2)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
**1H-NMR and 13C-NMR spectra of 1-(3-iodo-1H-indol-1-yl)-2,2-dimethylpropan-1-one**

(5c)

**1H NMR (400 Hz, CDCl₃)**

![1H NMR spectrum]

**13C NMR (100 Hz, CDCl₃)**

![13C NMR spectrum]
\(^1\text{H} \text{ and } {^{13}\text{C}}} \text{ NMR of } \alpha\text{-iodoketones 3a-j and } \alpha\text{-iodoaldehydes 3n-r

2-iodooctan-3-one (3a)

\(^1\text{H} \text{ NMR (400 Hz, CDCl}_3\)}

\(^{13}\text{C} \text{ NMR (100 Hz, CDCl}_3\)}
4-ethyl-2-iodooctan-3-one (3b)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-ethyl-2-iodooctan-3-one (3c)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
1-cyclohexyl-2-iodopropan-1-one (3d)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-iodo-1-phenylpentan-3-one (3e)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
(E)-4-iodo-2-methyl-1-phenylpent-1-en-3-one (3f)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
3-iodo-6,10-dimethylundec-9-en-2-one (3g)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
3-iodo-6-phenylhexan-2-one (3h)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
3-iodo-4-phenylbutan-2-one (3i)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-\textit{d}-3-iodo-4-phenylbutan-2-one (3i-\textit{d}_i)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-(4-chlorophenyl)-3-iodobutan-2-one (3j)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
2-iodooctanal (3n)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
2-iodo-3-phenylpropanal (3o)

\(^1\)H NMR (400 Hz, CDCl\(_3\))

\[^{13}\text{C NMR} (100 \text{ Hz, CDCl}_3)\]
3-(4-chlorophenyl)-2-iodopropanal (3p)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
2-iodo-5-phenylpentanal (3q)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-(benzyloxy)-2-iodobutanal (3r)

$^1$H NMR (400 Hz, CDCl$_3$)

$^1$C NMR (100 Hz, CDCl$_3$)
\[^1\text{H}\text{-NMR}\] and \[^{13}\text{C}\text{-NMR}\] spectra of 4-methyl-5-phenethyl-2-phenyl-1\(H\)-imidazole (7)

\[^1\text{H}\text{ NMR} (400 \text{ Hz, CDCl}_3)\]

\[^{13}\text{C}\text{ NMR} (100 \text{ Hz, CDCl}_3)\]

\(\text{HN-Ph}\)
**1H-NMR and 13C-NMR spectra of 4-iodo-1-phenylpentan-3-ol (8)**

### 1H NMR (400 Hz, CDCl$_3$)

- **OH**

### 13C NMR (100 Hz, CDCl$_3$)

- **[Chemical Shifts]**

S41
$^{1}$H-NMR and $^{13}$C-NMR spectra of 3-methyl-2-phenethyloxirane-2-carbonitrile (10)

$^{1}$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
$^{1}$H-NMR and $^{13}$C-NMR spectra of α-aminoketones 11-15

1-phenyl-4-(piperidin-1-yl)pentan-3-one (11)

$^{1}$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
4-(diethylamino)-1-phenylpentan-3-one (12)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
1-phenyl-4-(4-(pyrimidin-2-yl)piperazin-1-yl)pentan-3-one (13)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)
3-(3,4-dihydroisoquinolin-2(1H)-yl)-6-phenylhexan-2-one (14)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)

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S46
6-phenyl-3-thiomorpholinohexan-2-one (15)

$^1$H NMR (400 Hz, CDCl$_3$)

$^{13}$C NMR (100 Hz, CDCl$_3$)