Supporting Information

Direct Coupling of $sp^3$ Carbon of Alkanes with $\alpha,\beta$-Unsaturated Carbonyl Compounds Using Copper/Hydroperoxides System

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General Information:

Tert-butyl hydroperoxide and ferrous acetate were purchased from Admas-beta and were used as received. Other reagents and solvents were purchased from TCI, J&K Chemical, Alfa Aesar or Energy Chemical and were used as received.

Thin layer chromatography was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating. Flash column chromatography was performed using Merck silica gel 60 with analytical grade solvents as eluents.

$^1$H NMR and $^{13}$C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Corresponding chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d ($\delta=7.26$, singlet). Multiplicities were given as: s = single, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet. Values of coupling constant are reported as $J$ in Hz. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer.

CAUTION: We have never encountered any safety issue in working with or handling the compounds described in this work. Nonetheless, extra precaution should be taken when working with mixture of peroxides and metal salts or metals will cause explosion. It is noteworthy to avoid exposing neat peroxides with heating, too.
Optimization of reaction conditions:

Table 1. Effect of solvent on the reaction of phenyl vinylketone with cyclohexane\textsuperscript{a,b}

\[
\begin{array}{ccc}
1 \text{a} & \text{1BuOOH} & 3 \text{a} \\
\end{array}
\]

\[
\xrightarrow{\text{CuO (5 mol\%)}}
\]

\[
\begin{array}{ccc}
\text{solvent} & \text{100 °C} \\
\end{array}
\]

<table>
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<tr>
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<td>Acetone</td>
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<td>4</td>
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<td>5</td>
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\textsuperscript{a}Unless otherwise noted, typical reaction conditions: phenyl vinylketone (1a, 0.50 mmol), TBHP (2, 2.0 mmol, 70% solution in water), cyclohexane (3a, 50 equiv), solvent (1.0 mL), 100 °C, 5 h, under N\textsubscript{2}. \textsuperscript{b}Reported yields were based on 1a and determined by \textsuperscript{1}H NMR using CH\textsubscript{2}Br\textsubscript{2} as internal standard.

Table 2. Effect of temperature and reaction time on the reaction of phenyl vinylketone with cyclohexane\textsuperscript{a,b}

\[
\begin{array}{ccc}
1 \text{a} & \text{1BuOOH} & 3 \text{a} \\
\end{array}
\]

\[
\xrightarrow{\text{CuO (5 mol\%)}}
\]

\[
\begin{array}{ccc}
\text{MeCN} & \text{t (h), T (°C)} \\
\end{array}
\]

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<th>entry</th>
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<th>time (h)</th>
<th>yield (%)</th>
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<td>4</td>
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</tr>
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<tr>
<td>10</td>
<td>120</td>
<td>1</td>
<td>59</td>
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Unless otherwise noted, typical reaction conditions: phenyl vinylketone (1a, 0.50 mmol), TBHP (2, 2.0 mmol, 70% solution in water), cyclohexane (3a, 50 equiv), MeCN (1.0 mL), under N₂. Reported yields were based on 1a and determined by ¹H NMR using CH₂Br₂ as internal standard.

<table>
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<th>MeCN (mL)</th>
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<td>FeBr₂</td>
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<td>trace</td>
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<tr>
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<td>Fe(OAc)₂</td>
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<td>65 (57 %)</td>
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<tr>
<td>14</td>
<td>CuOAc</td>
<td>1.0</td>
<td>50</td>
<td>trace</td>
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Unless otherwise noted, typical reaction conditions: phenyl vinyl ketone (1a, 0.50 mmol), TBHP (2, 2.0 mmol, 70% solution in water), 120 °C, 0.5 h, under N₂. Reported yields were based on 1a and determined by ¹H NMR using CH₂Br₂ as internal standard. Isolated yield. TBHP (2.0 mmol, 5.5 M in decane).

General procedure for the synthesis of phenyl vinylketone (GP1) and its spectral data:

To a stirred solution of 3-chloropropiophenone (15.0 g, 89.0 mmol, 1.0 equiv) in chloroform (200 mL) was added dropwise triethylamine (30.0 mL, 214 mmol, 2.4 equiv) for 5 min under atmosphere of nitrogen. The reaction mixture was stirred during 12 h followed by washing with 0.1 N HCl aq., distilled water, saturated NaHCO₃ aq., and brine. The organic layer was dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash
chromatography with EtOAc/PE = 2:100 to give corresponding product as pale yellow oil in 92% yield. The analytical data are in accordance with the literature.\textsuperscript{1}

\[ \text{H NMR (400 MHz, Chloroform-d): } \delta 8.00 – 7.89 (m, 2H); 7.64 – 7.53 (m, 1H); 7.53 – 7.41 (m, 2H); 7.16 (dd, \textit{J} = 17.1, 10.6 Hz, 1H); 6.44 (dd, \textit{J} = 17.1, 1.7 Hz, 1H); 5.93 (dd, \textit{J} = 10.5, 1.7 Hz, 1H). \]

\[ \text{C NMR (101 MHz, Chloroform-d): } \delta 191.04, 137.28, 132.97, 132.39, 130.16, 128.69, 128.61 \]

\textit{HRMS (ESI):} C\textsubscript{9}H\textsubscript{9}O [M+H]\textsuperscript{+}: Calculated: 133.0653; found: 133.0655

**General procedure for the synthesis of \( \alpha,\beta \)-unsaturated ketones (GP2) and their spectral data:**\textsuperscript{1,2}

\[
\begin{align*}
\text{R} = \text{Alkyl group} \\
\text{or Aryl group} \\
\text{Cl} \quad \text{Me-N-O-Me} \quad \text{Cl} \\
\text{CH}_2\text{Cl}_2, 25 \degree \text{C} \quad \text{BrMg} \quad \text{THF, 0 \degree \text{C}} \\
\end{align*}
\]

To a stirred suspension of \( N \)-methoxy methylamine hydrochloride salt (1.05 equiv) in DCM (5.0 mL/1.0 mmol acylhalide) at 0 \degree C was slowly added triethylamine (2.1 equiv). Corresponding acylhalide (1.0 equiv) was then added dropwise to the solution. The temperature was monitored at all stages and kept at 0\degree C. The solution was then allowed to warm to room temperature and stirred for three hours before quenching the reaction with HCl (aq., 1.0 N). The phases were separated and the aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 10 mL). The combined organic phases were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and then the solvent was removed in vacuo to afford the Weinreb amide. This crude amide was used in next step without further purification.

To a stirred solution of Weinreb amide (1.0 equiv) in dry THF (5.0 mL/1.0 mmol Weinreb amide) was added dropwise vinyl magnesium bromide (1.0 M in THF, 1.2 equiv) for 15 min at 0 \degree C under atmosphere of argon. After stirred at 0\degree C for 10 min, the reaction mixture was allowed to warm up to room temperature and was stirred for 3 h. The reaction mixture was quenched with HCl (aq., 1.0 N), and extracted with diethyl ether (3 x 10 mL). The combined organic layer was dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated under reduced pressure. The residue was purified by flash chromatography with diethyl ether/PE to afforded the \( \alpha,\beta \)-unsaturated carbonyl compounds.

**1-(4-methoxyphenyl)prop-2-en-1-one:**

The title compound was prepared according to GP2 using 4-methoxybenzoyl chloride (854 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE =

S5
10:100 as yellow oil (663 mg, 4.1 mmol, 82% yield). The analytical data are in accordance with the literature.

\[ \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-d): } \delta 8.02 - 7.92 \text{ (m, 2H), 7.17 (dd, } J = 17.1, 10.5 \text{ Hz, 1H), 7.01 - 6.88 \text{ (m, 2H), 6.42 (dd, } J = 17.1, 1.8 \text{ Hz, 1H), 5.87 (dd, } J = 10.5, 1.8 \text{ Hz, 1H), 3.88 \text{ (s, 3H)}} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, Chloroform-d): } \delta 189.23, 163.55, 132.15, 131.02, 130.23, 129.21, 113.85, 55.48 \]

\[ \text{HRMS (ESI): } C_{10}H_{11}O_2 [M+H]^+ \text{ Calculated: 163.0759; found: 163.0760} \]

**1-(4-fluorophenyl)prop-2-en-1-one**

![Structural formula of 1-(4-fluorophenyl)prop-2-en-1-one]

The title compound was prepared according to GP2 using 4-fluorobenzoyl chloride (791 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (465 mg, 3.1 mmol, 63% yield). The analytical data are in accordance with the literature.

\[ \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-d): } \delta 8.06 - 7.94 \text{ (m, 2H), 7.24 - 7.08 \text{ (m, 3H), 6.44 (dd, } J = 17.1, 1.6 \text{ Hz, 1H), 5.94 \text{ (dd, } J = 10.6, 1.7 \text{ Hz, 1H)}} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, Chloroform-d): } \delta 189.37, 165.70 \text{ (d, } J = 254.7 \text{ Hz), 133.61 \text{ (d, } J = 3.0 \text{ Hz), 132.00, 131.31 \text{ (d, } J = 9.3 \text{ Hz), 130.33, 115.76 \text{ (d, } J = 21.8 \text{ Hz)}} \]

\[ \text{HRMS (ESI): } C_{9}H_{8}O_{2} [M+H]^+ \text{ Calculated: 151.0559; found: 151.0554} \]

**1-(4-chlorophenyl)prop-2-en-1-one**

![Structural formula of 1-(4-chlorophenyl)prop-2-en-1-one]

The title compound was prepared according to GP2 using 4-chlorobenzoyl chloride (878 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (484 mg, 2.9 mmol, 58% yield). The analytical data are in accordance with the literature.

\[ \text{\textsuperscript{1}H NMR (400 MHz, Chloroform-d): } \delta 7.90 \text{ (dd, } J = 8.6, 2.1 \text{ Hz, 2H), 7.46 \text{ (dd, } J = 8.6, 2.0 \text{ Hz, 2H), 7.12 \text{ (ddd, } J = 17.1, 10.6, 2.1 \text{ Hz, 1H), 6.45 \text{ (dd, } J = 17.1, 2.4 \text{ Hz, 1H), 5.96 \text{ (ddd, } J = 10.6, 2.4, 1.5 \text{ Hz, 1H)}} \]

\[ \text{\textsuperscript{13}C NMR (101 MHz, Chloroform-d): } \delta 189.74, 139.47, 135.56, 131.93, 130.65, 130.09, 128.96 \]
HRMS (ESI): C₉H₈OCl [M+H]^+ : Calculated: 167.0264; found: 167.0265

1-(3-bromophenyl)prop-2-en-1-one

The title compound was prepared according to GP2 using 3-bromobenzoyl chloride (1099 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (833 mg, 3.9 mmol, 79% yield). The analytical data are in accordance with the literature.³

¹H NMR (400 MHz, Chloroform-d): δ 8.11 – 8.04 (m, 1H), 7.86 (ddd, J = 7.8, 1.6, 1.0 Hz, 1H), 7.70 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.37 (td, J = 7.9, 0.4 Hz, 1H), 7.10 (dd, J = 17.1, 10.6 Hz, 1H), 6.46 (dd, J = 17.1, 1.6 Hz, 1H), 5.98 (dd, J = 10.5, 1.6 Hz, 1H)

¹³C NMR (101 MHz, Chloroform-d): δ 189.64, 139.02, 135.82, 131.92, 131.71, 131.06, 130.21, 127.18, 122.95


1-(3-chlorophenyl)prop-2-en-1-one

The title compound was prepared according to GP2 using 3-chlorobenzoyl chloride (876 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (607 mg, 3.7 mmol, 73% yield). The analytical data are in accordance with the literature.³

¹H NMR (400 MHz, Chloroform-d): δ 7.82 (ddd, J = 2.1, 1.6, 0.5 Hz, 1H), 7.72 (ddd, J = 7.7, 1.7, 1.1 Hz, 1H), 7.45 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.33 (td, J = 7.9, 0.5 Hz, 1H), 7.01 (dd, J = 17.1, 10.6 Hz, 1H), 6.36 (dd, J = 17.1, 1.6 Hz, 1H), 5.88 (dd, J = 10.6, 1.6 Hz, 1H)

¹³C NMR (101 MHz, Chloroform-d): δ 188.63, 137.77, 133.90, 131.86, 130.89, 129.95, 128.92, 127.70, 125.70

HRMS (ESI): C₉H₈OCl [M+H]^+ : Calculated: 167.0264; found: 167.0264

1-(2-chlorophenyl)prop-2-en-1-one
The title compound was prepared according to GP2 using 2-chlorobenzoyl chloride (876 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (465 mg, 2.8 mmol, 56% yield).

\[ \text{\textsuperscript{1}H NMR} \ (400 \text{ MHz, Chloroform-}d) : \delta \ 7.40 - 7.29 \ (m, 3H), 7.29 - 7.23 \ (m, 1H), 6.69 \ (dd, J = 17.5, 10.5 \text{ Hz, 1H}), 6.07 \ (dd, J = 17.5, 1.0 \text{ Hz, 1H}), 5.98 \ (dd, J = 10.5, 1.0 \text{ Hz, 1H}) \]

\[ \text{\textsuperscript{13}C NMR} \ (101 \text{ MHz, Chloroform-}d) : \delta \ 193.26, 137.15, 135.15, 130.96, 130.48, 130.32, 129.26, 128.29, 125.69 \]

HRMS (ESI): \text{C}_{9}\text{H}_{8}\text{OCl} [M+H]^+ : Calculated: 167.0264; found: 167.0263

1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one

The title compound was prepared according to GP2 using 4-trifluoromethylbenzoyl chloride (1039 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (602 mg, 3.0 mmol, 61% yield).

\[ \text{\textsuperscript{1}H NMR} \ (400 \text{ MHz, Chloroform-}d) : \delta \ 7.96 \ (dt, J = 7.9, 0.9 \text{ Hz, 2H}), 7.68 \ (dt, J = 8.1, 0.7 \text{ Hz, 2H}), 7.05 \ (dd, J = 17.2, 10.6 \text{ Hz, 1H}), 6.39 \ (dd, J = 17.2, 1.5 \text{ Hz, 1H}), 5.95 \ (dd, J = 10.6, 1.5 \text{ Hz, 1H}) \]

\[ \text{\textsuperscript{13}C NMR} \ (101 \text{ MHz, Chloroform-}d) : \delta \ 190.22, 140.04, 134.23 \ (q, J = 32.7 \text{ Hz}), 131.75 \ (d, J = 61.1 \text{ Hz}), 128.96, 125.67 \ (q, J = 3.8 \text{ Hz}), 124.94, 122.23 \]

HRMS (ESI): \text{C}_{10}\text{H}_{8}\text{OF}_{3} [M+H]^+ : Calculated: 201.0527; found: 201.0521

4-acryloylbenzonitrile

The title compound was prepared according to GP2 using 4-cyanobenzoyl chloride (828 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE =1:10 as white solid (612 mg, 3.9 mmol, 77% yield).

\[ \text{\textsuperscript{1}H NMR} \ (400 \text{ MHz, Chloroform-}d) : \delta \ 8.09 - 7.94 \ (m, 2H), 7.88 - 7.72 \ (m, 2H), 7.11 \ (dd, J = 17.2, 10.6 \text{ Hz, 1H}), 6.48 \ (dd, J = 17.2, 1.4 \text{ Hz, 1H}), 6.05 \ (dd, J = 10.6, 1.3 \text{ Hz, 1H}) \]

\[ \text{\textsuperscript{13}C NMR} \ (101 \text{ MHz, Chloroform-}d) : \delta \ 189.76, 140.42, 132.49, 131.91, 131.75, 129.04, 117.90, \]
HRMS (ESI): C_{10}H_{11}NO [M+H]^+ : Calculated: 158.0606; found: 158.0602

1-(naphthalen-2-yl)prop-2-en-1-one

The title compound was prepared according to GP2 using 2-naphthoyl chloride (956 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as white solid (638 mg, 3.5 mmol, 70% yield). The analytical data are in accordance with the literature.\(^3\)

\(^1\)H NMR (400 MHz, Chloroform-d): δ 8.51 – 8.43 (m, 1H), 8.04 (dd, J = 8.6, 1.8 Hz, 1H), 8.01 – 7.84 (m, 3H), 7.53–7.64 (m, 2H), 7.33 (dd, J = 17.1, 10.6 Hz, 1H), 6.51 (dd, J = 17.1, 1.7 Hz, 1H), 5.98 (dd, J = 10.6, 1.7 Hz, 1H)

\(^13\)C NMR (101 MHz, Chloroform-d): δ 190.85, 135.56, 134.61, 132.49, 132.38, 130.41, 130.10, 129.54, 128.61, 128.51, 127.82, 126.82, 124.44

HRMS (ESI): C_{13}H_{11}O [M+H]^+ : Calculated: 183.0810; found: 183.0806

1-(thiophen-2-yl)prop-2-en-1-one

The title compound was prepared according to GP2 using 2-thiophencarbonyl chloride (732 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 3:100 as yellow oil (399 mg, 2.9 mmol, 58% yield).

\(^1\)H NMR (400 MHz, Chloroform-d): δ 7.84 – 7.64 (m, 2H), 7.17 (dd, J = 4.9, 3.8 Hz, 1H), 7.09 (dd, J = 17.0, 10.4 Hz, 1H), 6.51 (dd, J = 17.0, 1.6 Hz, 1H), 5.89 (dd, J = 10.5, 1.6 Hz, 1H)

\(^13\)C NMR (101 MHz, Chloroform-d): δ 182.43, 144.58, 134.28, 132.41, 131.88, 129.44, 128.24

HRMS (ESI): C_{7}H_{7}OS [M+H]^+ : Calculated: 139.0218; found: 139.0215

undec-1-en-3-one

The title compound was prepared according to GP2 using nonanoyl chloride (883 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 2:100 as yellow oil (421 mg, 2.5 mmol, 51% yield).
\(^1\)H NMR (400 MHz, Chloroform-\(d\)): \(\delta\) 6.28 (dd, \(J = 17.6, 10.5\) Hz, 1H), 6.14 (dd, \(J = 17.6, 1.3\) Hz, 1H), 5.74 (dd, \(J = 10.5, 1.3\) Hz, 1H), 2.58 – 2.46 (m, 2H), 1.62 – 1.46 (m, 2H), 1.31 – 1.12 (m, 11H), 0.88 – 0.74 (m, 3H)

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)): \(\delta\) 201.08, 136.58, 127.78, 39.65, 31.80, 29.36, 29.25, 29.12, 24.01, 22.62, 14.06

HRMS (ESI): \(\text{C}_{11}\text{H}_{21}\text{O}\) [M+H]^+ : Calculated: 169.1592; found: 169.1590

1-phenylbut-3-en-2-one

The title compound was prepared according to GP2 using phenyl acetyl chloride (774 mg, 5.0 mmol, 1.0 equiv) and was obtained after column chromatography with diethyl ether/PE = 2:100 as yellow oil (612 mg, 4.2 mmol, 84% yield). The analytical data are in accordance with the literature.\(^1\)

\(^1\)H NMR (400 MHz, Chloroform-\(d\)): \(\delta\) 7.39 – 7.30 (m, 2H), 7.30 – 7.18 (m, 4H), 6.41 (dd, \(J = 17.6, 10.2\) Hz, 1H), 6.31 (dd, \(J = 17.5, 1.4\) Hz, 1H), 5.83 (dd, \(J = 10.2, 1.4\) Hz, 1H), 3.88 (s, 2H)

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)): \(\delta\) 197.69, 135.59, 134.04, 129.46, 129.00, 128.72, 127.00, 47.19

HRMS (ESI): \(\text{C}_{10}\text{H}_{11}\text{O}\) [M+H]^+ : Calculated: 147.0810; found: 147.0808

General procedure for the synthesis of 1,1,1-trichlorobut-3-en-2-one (GP3) and its spectral data:

To a stirred suspension of \(N\)-methoxy methylamine hydrochloride salt (1.05 equiv) in DCM (40 mL) at 0 °C was slowly added triethylamine (2.1 equiv). Trichlorocetyl chloride (1823 mg, 10.0 mmol, 1.0 equiv) was then added dropwise to the solution. The temperature was monitored at all stages and kept below 4 °C. The solution was then allowed to warm to room temperature and stirred for three hours before quenching the reaction with HCl (aq., 1.0 N). The phases were separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) for three times. The combined organic phases were dried over Na\(_2\)SO\(_4\), filtered and then the solvent was removed in vacuo to afford the Weinreb amide. This crude amide was used in next step without further purification.

To a stirred solution of Weinreb amide (1.0 equiv) in dry THF (6.0 mL/1.0 mmol Weinreb amide) was added dropwise vinyl magnesium bromide (1.0 M in THF, 1.2 equiv) for 15 min at 0 °C under atmosphere of argon. After stirred at 0°C for 30 min, the reaction mixture was quenched with HCl (aq., 1.0 N), and extracted with diethyl ether (3 x 20 mL). The combined organic layer was dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The residue was purified by flash chromatography with diethyl ether/PE = 3:100 to afford the 1,1,1-trichlorobut-3-en-2-
one colorless oil (396 mg, 2.3 mmol, 23% yield).

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{Cl} & \quad = \\
\end{align*}
\]

\[^1\text{H} \text{ NMR} \, (400 \, \text{MHz}, \text{Chloroform}-d): \delta \, 7.06 \, (\text{dd}, \, J = 17.0, \, 10.4 \, \text{Hz}, \, 1\, \text{H}), \, 6.76 \, (\text{dd}, \, J = 17.0, \, 1.3 \, \text{Hz}, \, 1\, \text{H}), \, 6.15 \, (\text{dd}, \, J = 10.4, \, 1.3 \, \text{Hz}, \, 1\, \text{H})
\]

\[^{13}\text{C} \text{ NMR} \, (101 \, \text{MHz}, \text{Chloroform}-d): \delta \, 131.91, \, 21.88, \, 102.36, \, 83.21
\]

\text{HRMS (ESI)}: \text{C}_4\text{H}_4\text{OCl}_3 \, [\text{M+H}]^+ : \text{Calculated: 172.9328; found: 172.9327}

**General procedure for the synthesis of \(\alpha\)-peroxy carbonyl compounds (4a-n, 5a-d, 5f) (GP4) and their spectral data:**

To a mixture of copper(I) acetate (5 mol%, 3.1 mg) in 1.0 mL of MeCN, the \(\alpha,\beta\)-unsaturated carbonyl compound (0.5 mmol, 1 equiv) and TBHP (70% solution in water, 2.0 mmol, 4 equiv) were added dropwise under nitrogen atmosphere at room temperature. Alkane (50 equiv) was then added to the reaction mixture. The reaction mixture was stirred at 120 °C for 30 min. After cooling to room temperature, the crude product was afforded after evaporation of the solvent in vacuo and ready to be purified by column chromatography with diethyl ether/PE.

**General procedure for the synthesis of \(\alpha\)-peroxy ketones (5e) (GP5) and their spectral data:**

To a mixture of copper(I) acetate (5 mol%, 3.1 mg) and in 1.0 mL of MeCN, the \(\alpha,\beta\)-unsaturated carbonyl compound (0.5 mmol, 1 equiv) and TBHP (70% solution in water, 2.0 mmol, 4 equiv) were added dropwise under nitrogen atmosphere at room temperature. Alkane (5 mmol, 10 equiv.) in 3.0 mL of benzene was then added to the reaction mixture. The reaction mixture was stirred at 120 °C for 30 min. After cooling to room temperature, the crude product was afforded after evaporation of the solvent in vacuo and ready to be purified by column chromatography with diethyl ether/PE.

**General procedure for the synthesis of \(\alpha\)-peroxy ketones (4o) (GP6) and the spectral data:**

To a mixture of copper(I) acetate (5 mol%, 3.1 mg) in 1.0 mL of MeCN, the \(\alpha,\beta\)-unsaturated carbonyl compound (0.5 mmol, 1 equiv) and TBHP (70% solution in water, 2.0 mmol, 4 equiv) were added dropwise under nitrogen atmosphere at room temperature. Alkane (50 equiv) was then added to the reaction mixture. The reaction mixture was stirred at 100 °C for 10 min. After cooling to room temperature, the crude product was afforded after evaporation of the solvent in vacuo and ready to be purified by column chromatography with diethyl ether/PE.

4a. 2-\((\text{tert-buty}l\text{peroxy})\)-3-cyclohexyl-1-phenylpropan-1-one
4a was synthesized according to the GP4 using phenyl vinylketone (66.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (85.5 mg, 0.28 mmol, 57% yield).

\(^1^H\) NMR (400 MHz, Chloroform-d): \(\delta 8.12 – 8.04\) (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 5.21 (dd, \(J = 9.3, 4.0\) Hz, 1H), 1.93 – 1.84 (m, 1H), 1.79 – 1.62 (m, 5H), 1.62 – 1.49 (m, 2H), 1.21 (s, 12H), 1.02 – 0.87 (m, 2H)

\(^1^3^C\) NMR (101 MHz, Chloroform-d): \(\delta 199.66, 135.50, 132.98, 128.90, 128.41, 84.00, 80.63, 38.50, 34.53, 33.84, 32.85, 26.39, 26.35, 26.18, 26.06\)

HRMS (ESI): C\(_{19}\)H\(_{29}\)O\(_3\) [M+H\(^+\)] : Calculated: 305.2117; found: 305.2116

4b. 2-(tert-butylperoxy)-3-cyclohexyl-1-(4-methoxyphenyl)propan-1-one

4b was synthesized according to the GP4 using 1-(4-Methoxyphenyl)propenone (81.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (94.7 mg, 0.28 mmol, 57% yield).

\(^1^H\) NMR (400 MHz, Chloroform-d): \(\delta 8.10\) (d, \(J = 9.0\) Hz, 2H), 6.93 (d, \(J = 8.9\) Hz, 2H), 5.16 (dd, \(J = 9.3, 4.1\) Hz, 1H), 3.87 (s, 3H), 1.87 (d, \(J = 12.4\) Hz, 1H), 1.79 – 1.61 (m, 5H), 1.60 – 1.47 (m, 2H), 1.21 (s, 12H), 1.02 – 0.82 (m, 2H)

\(^1^3^C\) NMR (101 MHz, Chloroform-d): \(\delta 198.05, 163.43, 131.29, 128.42, 113.60, 84.08, 80.57, 55.40, 38.74, 34.52, 33.84, 32.89, 26.41, 26.38, 26.18, 26.07\)

HRMS (ESI): C\(_{20}\)H\(_{31}\)O\(_4\) [M+H\(^+\)] : Calculated: 335.2222; found: 335.2229

4c. 2-(tert-butylperoxy)-3-cyclohexyl-1-(4-(trifluoromethyl)phenyl)propan-1-one

4c was synthesized according to the GP4 using 1-(4-(trifluoromethyl)phenyl)propenone (100.1 mg,
0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (104.3 mg, 0.28 mmol, 56% yield).

\( ^1\text{H NMR} (400 \text{ MHz, Chloroform-}d) \): \( \delta \) 8.14 (dt, \( J = 8.0, 0.9 \text{ Hz, 2H} \), 7.67 – 7.61 (m, 2H), 5.03 (dd, \( J = 9.3, 4.2 \text{ Hz, 1H} \), 1.77 (dd, \( J = 12.9, 2.6 \text{ Hz, 1H} \), 1.54-1.70 (m, 5H), 1.53 – 1.40 (m, 2H), 1.12 (s, 13H), 0.81-0.94 (m, 2H).

\( ^{13}\text{C NMR} (101 \text{ MHz, Chloroform-}d) \): \( \delta \) 199.21, 138.09, 134.14 (q, \( J = 32.5 \text{ Hz, 2H} \), 129.38, 125.38 (q, \( J = 3.8 \text{ Hz, 2H} \), 123.65 (d, \( J = 272.6 \text{ Hz, 2H} \), 85.06, 80.92, 38.31, 34.49, 33.77, 32.81, 26.32, 26.28, 26.15, 26.02

\text{HRMS (ESI)}: C_{19}H_{27}O_3Na [M+Na]^+ \text{ Calculated: 395.1810; found: 395.1814}

4d. 1-(3-bromophenyl)-2-(tert-butylperoxy)-3-cyclohexylpropan-1-one

\( 4d \) was synthesized according to the GP4 using 1-(3-bromophenyl)propenone (105.5 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (114.7 mg, 0.30 mmol, 60% yield).

\( ^1\text{H NMR} (400 \text{ MHz, Chloroform-}d) \): \( \delta \) 8.25 (t, \( J = 1.8 \text{ Hz, 1H} \), 8.03 (ddd, \( J = 7.8, 1.6, 1.0 \text{ Hz, 1H} \), 7.68 (ddd, \( J = 8.0, 2.1, 1.1 \text{ Hz, 1H} \), 7.33 (t, \( J = 7.9 \text{ Hz, 1H} \), 5.08 (dd, \( J = 9.3, 4.2 \text{ Hz, 1H} \), 1.89 – 1.81 (m, 1H), 1.79 – 1.61 (m, 5H), 1.61 – 1.47 (m, 2H), 1.31 – 1.11 (m, 12H), 1.03 – 0.88 (m, 2H)

\( ^{13}\text{C NMR} (101 \text{ MHz, Chloroform-}d) \): \( \delta \) 198.61, 137.08, 135.78, 132.08, 129.97, 127.53, 122.67, 84.67, 80.80, 38.33, 34.48, 33.77, 32.78, 26.36, 26.33, 26.16, 26.04

\text{HRMS (ESI)}: C_{19}H_{27}O_3BrNa [M+Na]^+ \text{ Calculated: 405.1041; found: 405.1036}

4e. 2-(tert-butylperoxy)-1-(4-chlorophenyl)-3-cyclohexylpropan-1-one

\( 4e \) was synthesized according to the GP4 using 1-(4-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (97.9 mg, 0.29 mmol, 58% yield).

\( ^1\text{H NMR} (400 \text{ MHz, Chloroform-}d) \): \( \delta \) 8.09 – 8.03 (m, 2H), 7.46 – 7.40 (m, 2H), 5.09 (dd, \( J = 9.3, 4.2 \text{ Hz, 1H} \), 1.84 (d, \( J = 12.4 \text{ Hz, 1H} \), 1.78 – 1.59 (m, 5H), 1.59 – 1.45 (m, 2H), 1.20 (s, 12H), 1.01
- 0.86 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d): $\delta$ 198.76, 139.41, 133.63, 130.51, 128.71, 84.76, 80.80, 38.48, 34.50, 33.79, 32.84, 26.37, 26.36, 26.16, 26.04

HRMS (ESI): $\text{C}_{2}\text{H}_{2}\text{O}_{3}\text{ClNa}$ $[\text{M+Na}]^+$: Calculated: 361.1546; found: 361.1544

4f. 2-(tert-butyloperoxy)-3-cyclohexyl-1-(4-fluorophenyl)propan-1-one

![Chemical Structure](image)

4f was synthesized according to the GP4 using 1-(4-fluorophenyl)propenone (75.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (99.3 mg, 0.31 mmol, 62% yield).

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.15 (dd, $J = 9.0, 5.5$ Hz, 2H), 7.12 (dd, $J = 9.0, 8.4$ Hz, 2H), 5.10 (dd, $J = 9.3, 4.2$ Hz, 1H), 1.90 – 1.81 (m, 1H), 1.80 – 1.61 (m, 5H), 1.60 – 1.47 (m, 2H), 1.31 – 1.12 (m, 12H), 1.01 – 0.87 (m, 2H)

$^{13}$C NMR (101 MHz, Chloroform-d): $\delta$ 198.28, 166.92, 164.38, 131.75 (q, $J = 9.2$ Hz), 115.47 (d, $J = 21.7$ Hz), 84.69, 80.73, 38.52, 34.51, 33.79, 32.84, 26.36, 26.33, 26.16, 26.04

HRMS (ESI): $\text{C}_{1}\text{H}_{2}\text{O}_{3}\text{F}$ [M+H]$: Calculated: 323.2022; found: 323.2021

4g. 2-(tert-butyloperoxy)-1-(3-chlorophenyl)-3-cyclohexylpropan-1-one

![Chemical Structure](image)

4g was synthesized according to the GP4 using 1-(3-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (113.1 mg, 0.33 mmol, 67% yield).

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.09 (t, $J = 1.9$ Hz, 1H), 7.98 (dt, $J = 7.9, 1.4$ Hz, 1H), 7.53 (dd, $J = 8.0, 2.3, 1.1$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 1H), 5.09 (dd, $J = 9.3, 4.0$ Hz, 1H), 1.90 – 1.81 (m, 1H), 1.79 – 1.61 (m, 5H), 1.60 – 1.47 (m, 2H), 1.32 – 1.11 (m, 12H), 1.03 – 0.88 (m, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d): $\delta$ 198.71, 136.87, 134.62, 132.87, 129.70, 129.14, 127.09, 84.67, 80.80, 38.35, 34.48, 33.78, 32.78, 26.36, 26.25, 26.16, 26.04

HRMS (ESI): $\text{C}_{1}\text{H}_{2}\text{O}_{3}\text{ClNa}$ [M+Na]$: Calculated: 361.1546; found: 361.1546
4h. 2-(tert-butylperoxy)-1-(2-chlorophenyl)-3-cyclohexylpropan-1-one

![Chemical structure](image)

4h was synthesized according to the GP4 using 1-(2-chlorophenyl)propanone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (119.3 mg, 0.35 mmol, 71% yield).

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d\text{): } \delta 7.60 \ (\text{ddd, } J = 7.5, 1.8, 0.5 \text{ Hz, } 1\text{H}), 7.41 \ (\text{ddd, } J = 8.0, 1.6, 0.5 \text{ Hz, } 1\text{H}), 7.39 – 7.34 \ (m, 1\text{H}), 7.33 – 7.28 \ (m, 1\text{H}), 5.04 \ (\text{dd, } J = 9.0, 4.4 \text{ Hz, } 1\text{H}), 1.87 – 1.79 \ (m, 1\text{H}), 1.76 – 1.59 \ (m, 6\text{H}), 1.58 – 1.45 \ (m, 1\text{H}), 1.16 \ (s, 12\text{H}), 1.02 – 0.84 \ (m, 2\text{H})\]

\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d\text{): } \delta 203.29, 138.05, 131.24, 130.32, 129.36, 126.30, 84.99, 80.59, 37.15, 34.32, 33.89, 32.64, 26.40, 26.25, 26.21, 26.08\]

HRMS (ESI): C_{19}H_{27}O_3ClNa [M+Na]^+: Calculated: 361.1546; found: 361.1552

4i. 4-(2-(tert-butylperoxy)-3-cyclohexylpropanoyl)benzonitrile

![Chemical structure](image)

4i was synthesized according to the GP4 using 1-(4-cyanophenyl)propanone (78.6 mg, 0.5 mmol, 1 equiv) and isolated as white solid after purification by flash column chromatography (103.7 mg, 0.31 mmol, 63% yield).

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d\text{): } \delta 8.30 – 8.14 \ (m, 2\text{H}), 7.76 \ (d, J = 8.4 \text{ Hz, } 2\text{H}), 5.06 \ (\text{dd, } J = 9.3, 4.2 \text{ Hz, } 1\text{H}), 1.88 – 1.79 \ (m, 1\text{H}), 1.79 – 1.62 \ (m, 5\text{H}), 1.47-1.61 \ (m, 2\text{H}), 1.18 \ (s, 12\text{H}), 1.05 – 0.85 \ (m, 2\text{H})\]

\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d\text{): } \delta 199.05, 138.47, 132.17, 129.49, 118.05, 116.08, 85.32, 81.00, 38.22, 34.48, 33.73, 32.77, 26.30, 26.24, 26.12, 26.00\]

HRMS (ESI): C_{20}H_{27}NO_3Na [M+Na]^+: Calculated: 352.1889; found: 352.1889

4j. 2-(tert-butylperoxy)-3-cyclohexyl-1-(thiophen-2-yl)propan-1-one

![Chemical structure](image)
4j was synthesized according to the GP4 using 1-(2-thienyl)propenone (69.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (84.2 mg, 0.27 mmol, 55% yield).

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.03 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.65 (dd, $J = 4.9, 1.1$ Hz, 1H), 7.14 (dd, $J = 5.0, 3.8$ Hz, 1H), 4.92 (dd, $J = 9.4, 4.2$ Hz, 1H), 1.90 – 1.81 (m, 1H), 1.80 – 1.62 (m, 6H), 1.61 – 1.47 (m, 2H), 1.33 – 1.12 (m, 14H), 1.01 – 0.84 (m, 3H)

$^{13}$C NMR (101 MHz, Chloroform-d): $\delta$ 193.46, 140.76, 133.79, 133.42, 127.84, 85.73, 80.90, 39.08, 33.83, 32.82, 26.40, 26.38, 26.17, 26.04

HRMS (ESI): C$\text{$_17$H$_{27}$O$_3$}$ [M+H]$^+$ : Calculated: 311.1681; found: 311.1680

4k. 2-(tert-butyperoxy)-3-cyclohexyl-1-(naphthalen-2-yl)propan-1-one

4k was synthesized according to the GP4 using 1-(2-naphthyl)propenone (91.1 mg, 0.5 mmol, 1 equiv) and isolated as white solid after purification by flash column chromatography (109.6 mg, 0.31 mmol, 62% yield).

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.73 – 8.64 (m, 1H), 8.12 (dd, $J = 8.6, 1.7$ Hz, 1H), 8.00 – 7.93 (m, 1H), 7.91 – 7.82 (m, 2H), 7.63 – 7.50 (m, 2H), 5.33 (dd, $J = 9.3, 4.2$ Hz, 1H), 1.91 (ddt, $J = 12.4, 3.5, 1.7$ Hz, 1H), 1.84 – 1.52 (m, 7H), 1.32 – 1.13 (m, 12H), 0.90-0.93 (m, 2H)

$^{13}$C NMR (101 MHz, Chloroform-d): $\delta$ 199.57, 135.58, 132.74, 132.52, 130.77, 129.74, 128.45, 128.20, 127.73, 126.61, 124.71, 84.28, 80.68, 38.70, 34.58, 33.86, 32.90, 26.45, 26.41, 26.21, 26.10

HRMS (ESI): C$_{23}$H$_{38}$O$_3$Na [M+Na]$^+$ : Calculated: 377.2093; found: 377.2100

4l. 3-(tert-butyperoxy)-4-cyclohexyl-1-phenylbutan-2-one

4l was synthesized according to the GP4 using 1-benzylpropenone (73.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (87.0 mg, 0.27 mmol, 55% yield).

$^1$H NMR (400 MHz, Chloroform-d): $\delta$ 7.31 (dd, $J = 8.0, 6.5$ Hz, 2H), 7.28 – 7.17 (m, 3H), 4.43 (dd,
$J = 9.4, 4.4 \text{ Hz}, 1H)$, 3.98 ($d, J = 1.7 \text{ Hz}, 2H)$, 1.80 – 1.57 (m, 5H), 1.53 – 1.31 (m, 3H), 1.09-1.30 (m, 12H), 1.03 – 0.80 (m, 2H).

$^{13}C \text{ NMR (101 MHz, Chloroform-d): } \delta 210.36, 134.36, 129.92, 128.37, 126.68, 86.64, 80.94, 43.77, 37.64, 34.20, 33.84, 32.69, 26.43, 26.37, 26.19, 26.06$

HRMS (ESI): $C_{20}H_{30}O_3 \text{ [M+Na]^+}$: Calculated: 341.2093; found: 341.2088

4m. benzyl 2-(tert-butylperoxy)-3-cyclohexylpropionate

4m was synthesized according to the GP4 using benzyl acrylate (81.1 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (89.2 mg, 0.27 mmol, 54% yield).

$^1H \text{ NMR (400 MHz, Chloroform-d): } \delta 7.42 – 7.28 (m, 5H), 5.22 (d, J = 4.3 \text{ Hz}, 2H), 4.54 (dd, J = 8.5, 5.5 \text{ Hz}, 1H), 1.79 – 1.56 (m, 6H), 1.46-1.55 (m, 1H), 1.44 – 1.32 (m, 1H), 1.23 (s, 12H), 0.95 – 0.82 (m, 2H).

$^{13}C \text{ NMR (101 MHz, Chloroform-d): } \delta 172.27, 135.89, 128.45, 128.14, 128.13, 80.83, 80.71, 66.30, 37.89, 34.09, 33.55, 32.94, 26.35, 26.33, 26.11, 26.04$

HRMS (ESI): $C_{20}H_{31}O_4 \text{ [M+H]^+}$: Calculated: 335.2222; found: 335.2219

4n. 2-(tert-butylperoxy)-1-cyclohexylundecan-3-one

4n was synthesized according to the GP4 using undec-1-en-3-one (84.1 mg, 0.5 mmol, 1 equiv) and isolated as yellow oil after purification by flash column chromatography (86.6 mg, 0.25 mmol, 51% yield).

$^1H \text{ NMR (400 MHz, Chloroform-d): } \delta 4.32 (dd, J = 9.3, 4.4 \text{ Hz}, 1H), 2.76 – 2.50 (m, 2H), 1.79 (d, J = 12.8 \text{ Hz}, 1H), 1.75 – 1.64 (m, 3H), 1.58 (s, 2H), 1.49 – 1.39 (m, 2H), 1.36 – 1.16 (m, 24H), 0.95 – 0.83 (m, 5H)

$^{13}C \text{ NMR (101 MHz, Chloroform-d): } \delta 213.52, 86.73, 80.67, 37.63, 36.73, 34.21, 33.87, 32.74, 31.85, 29.42, 29.29, 29.18, 26.38, 26.20, 26.06, 23.04, 22.66, 14.10$

HRMS (ESI): $C_{21}H_{41}O_3 \text{ [M+H]^+}$: Calculated: 341.3056; found: 341.3048
4o. 2-(tert-butylperoxy)-3-cyclohexyl-1-trichloromethylpropan-1-one

4o was synthesized according to the GP6 using 1-trichloromethylpropenone (86.7 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (89.1 mg, 0.26 mmol, 52% yield).

\[\delta \text{ H NMR (400 MHz, Chloroform-} d\text{): } \delta \text{ 5.37 – 5.22 (m, 1H), 1.89 – 1.79 (m, 1H), 1.72 – 1.60 (m, 6H), 1.58 – 1.48 (m, 1H), 1.05-1.27 (m, 12H), 0.96 – 0.82 (m, 2H).}\]

\[\delta \text{ C NMR (101 MHz, Chloroform-} d\text{): } \delta \text{ 189.48, 95.01, 81.20, 78.78, 39.97, 34.61, 33.91, 32.39, 26.30, 26.23, 26.12, 25.93}\]

HRMS (ESI): C_{14}H_{23}O_{3}Cl_{3}Na [M+Na]^{+} : Calculated: 367.0610; found: 367.0613

5a. 2-(tert-butylperoxy)-1-(2-chlorophenyl)-3-cyclopentylpropan-1-one

5a was synthesized according to the GP4 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (106.5 mg, 0.33 mmol, 66% yield).

\[\delta \text{ H NMR (400 MHz, Chloroform-} d\text{): } \delta \text{ 7.55 – 7.51 (m, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.24 (td, J = 7.4, 1.6 Hz, 1H), 4.90 (dd, J = 9.1, 4.4 Hz, 1H), 2.03 – 1.89 (m, 1H), 1.83 – 1.62 (m, 4H), 1.61 – 1.41 (m, 4H), 1.09 (s, 11H).}\]

\[\delta \text{ C NMR (101 MHz, Chloroform-} d\text{): } \delta \text{ 201.98, 136.99, 130.33, 130.23, 129.24, 128.35, 125.29, 85.77, 79.65, 35.72, 34.90, 32.13, 31.41, 25.24, 24.16, 23.98}\]

HRMS (ESI): C_{18}H_{25}O_{3}ClNa [M+Na]^{+} : Calculated: 347.1390; found: 347.1387

5b. 2-(tert-butylperoxy)-1-(2-chlorophenyl)-3-cycloheptylpropan-1-one

5b was synthesized according to the GP4 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (131.7 mg, 0.37 mmol, 75% yield).
\( ^1H \text{ NMR} \) (400 MHz, Chloroform-\( d \)): \( \delta 7.55 - 7.50 \) (m, 1H), 7.35 - 7.32 (m, 1H), 7.29 (td, \( J = 7.9 \), 7.5, 1.8 Hz, 1H), 7.23 (td, \( J = 7.4 \), 1.6 Hz, 1H), 4.93 (dd, \( J = 7.8 \), 5.7 Hz, 1H), 1.76 - 1.61 (m, 3H), 1.61 - 1.55 (m, 3H), 1.55 - 1.44 (m, 3H), 1.44 - 1.28 (m, 4H), 1.04-1.17 (m, 11H)

\( ^{13}C \text{ NMR} \) (101 MHz, Chloroform-\( d \)): \( \delta 202.21, 137.03, 130.31, 130.19, 129.21, 128.32, 125.29, 84.52, 79.60, 36.70, 34.64, 32.64, 27.34, 27.26, 25.35, 25.23, 25.17

HRMS (ESI): \( \text{C}_{20}\text{H}_{29}\text{O}_3\text{ClNa} [\text{M+Na}]^+ \) : Calculated: 375.1703; found: 375.1707

5c. 2-(\text{tert-butylperoxy})-1-(2-chlorophenyl)-3-cyclooctylpropan-1-one

5c was synthesized according to the GP4 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (127.0 mg, 0.35 mmol, 70% yield).

\( ^1H \text{ NMR} \) (400 MHz, Chloroform-\( d \)): \( \delta 7.58 \) (dd, \( J = 7.5 \), 1.8 Hz, 1H), 7.41 (dd, \( J = 8.0 \), 1.5 Hz, 1H), 7.36 (td, \( J = 7.6 \), 1.8 Hz, 1H), 7.30 (td, \( J = 7.4 \), 1.5 Hz, 1H), 5.04 (dd, \( J = 7.8 \), 3.5 Hz, 1H), 1.96 (t, \( J = 3.2 \) Hz, 3H), 1.74 – 1.59 (m, 7H), 1.58 – 1.47 (m, 6H), 1.13 (s, 9H), 0.91 – 0.83 (m, 1H).

\( ^{13}C \text{ NMR} \) (101 MHz, Chloroform-\( d \)): \( \delta 203.29, 138.09, 131.31, 131.23, 130.24, 129.33, 126.30, 85.46, 80.58, 37.89, 33.53, 33.13, 31.49, 27.12, 27.06, 26.31, 26.27, 25.33, 25.24

HRMS (ESI): \( \text{C}_{21}\text{H}_{31}\text{O}_3\text{ClNa} [\text{M+Na}]^+ \) : Calculated: 389.1859; found: 389.1861

5d. 2-(\text{tert-butylperoxy})-1-(2-chlorophenyl)-4,4,5-trimethylhexan-1-one (a)
2-(\text{tert-butylperoxy})-1-(2-chlorophenyl)-5,6-dimethylheptan-1-one (b)

5d was synthesized according to the GP4 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (109.7 mg, 0.32 mmol, 65% yield).

\( ^1H \text{ NMR} \) (400 MHz, Chloroform-\( d \), 2 isomers): \( \delta 7.55 - 7.48 \) (m, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21-7.26 (m, 1H), 4.92 (dd, \( J = 8.1 \), 2.9 Hz, 0.92H, isomer a), 4.83 (dd, \( J = 8.6 \), 4.7 Hz, 0.08H, isomer b), 1.88 – 1.67 (m, 0.34H, isomer b), 1.67 – 1.57 (m, 1.76H, isomer a), 1.57-1.54 (m, 0.54H, isomer b), 1.54 – 1.46 (m, 0.98H, isomer a), 1.25 – 1.13 (m, 0.33H, isomer b), 1.09 (s, 0.78H, isomer b), 1.08 (d, \( J = 1.3 \) Hz, 0.82H, isomer b), 1.05 (s, 7.75H, isomer a), 1.01 – 519
0.95 (m, 0.62H, isomer b), 0.90 - 0.86 (m, 0.44H, isomer b), 0.82 (s, 2.72H, isomer a), 0.81 (s, 2.75H, isomer a), 0.78 (d, J = 6.8 Hz, 2.77H, isomer a), 0.73 (d, J = 6.9 Hz, 2.88H, isomer a)

$^{13}$C NMR (101 MHz, Chloroform-d): δ 202.45, 202.18, 137.01, 130.38, 130.35, 130.31, 130.23, 129.25, 129.21, 128.33, 128.19, 125.33, 125.28, 125.18, 87.17, 84.51, 83.46, 79.15, 38.72, 37.54, 35.03, 34.23, 33.47, 25.35, 25.22, 25.19, 23.96, 23.45, 22.21, 22.04, 16.49, 16.36, 9.24

HRMS (ESI): $C_{19}H_{29}O_3ClNa [M+Na]^+$ : Calculated: 363.1703; found: 363.1707

5e. 3-((3r,5r,7r)-adamantan-1-yl)-2-(tert-butyperoxy)-1-(2-chlorophenyl)propan-1-one (a)

5e was synthesized according to the GP6 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (116.7 mg, 0.30 mmol, 60% yield).

$^1$H NMR (400 MHz, Chloroform-d, 2 isomers): δ 7.58 (dd, J = 7.5, 1.8 Hz, 1H), 7.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.37 (dd, J = 7.2, 1.8 Hz, 1H), 7.30 (td, J = 7.4, 1.5 Hz, 1H), 5.04 (dd, J = 7.8, 3.5 Hz, 0.91H, isomer a), 4.98 (dd, J = 9.6, 3.6 Hz, 0.09H, isomer b), 1.92 – 1.99 (m, 3H), 1.75-1.47 (m, 13H), 1.13 (s, 9H), 0.83 – 0.89 (m, 1H)

$^{13}$C NMR (101 MHz, Chloroform-d): δ 203.48, 203.35, 138.04, 133.47, 131.40, 131.40, 131.33, 131.25, 130.26, 129.35, 129.26, 127.04, 126.31, 126.19, 85.72, 83.39, 80.62, 80.12, 43.95, 42.55, 40.73, 39.12, 38.20, 36.87, 32.96, 32.27, 31.30, 28.66, 26.40, 26.22

HRMS (ESI): $C_{23}H_{31}O_3ClNa [M+Na]^+$ : Calculated: 413.1859; found: 413.1864

5f. 2-(tert-butyperoxy)-1-(2-chlorophenyl)-4-cyclopentylbutan-1-one (a)

2-(tert-butyperoxy)-1-(2-chlorophenyl)-3-(1-methylcyclopentyl)propan-1-one (b)
2-(tert-butyperoxy)-1-(2-chlorophenyl)-3-(2-methylcyclopentyl)propan-1-one (c)
2-(tert-butyperoxy)-1-(2-chlorophenyl)-3-(3-methylcyclopentyl)propan-1-one (d)

5f was synthesized according to the GP4 using 1-(2-chlorophenyl)propenone (83.3 mg, 0.5 mmol, 1 equiv) and isolated as colorless oil after purification by flash column chromatography (130.7 mg, 0.39 mmol, 77% yield).
\[ ^1H \text{NMR} \ (400 \text{ MHz, Chloroform-}d, \ 4 \text{ isomers}): \delta \ 7.56 - 7.66 \text{ (m, 1H)}, \ 7.44 - 7.40 \text{ (m, 1H)}, \ 7.34 - 7.40 \text{ (m, 1H)}, \ 7.28 - 7.34 \text{ (m, 1H)}, \ 5.01 \text{ (dd, } J = 8.7, \ 2.8 \text{ Hz, 0.63H, isomer b)}, \ 4.98 - 4.92 \text{ (m, 0.33H, isomer c and d)}, \ 4.90 \text{ (dd, } J = 8.6, \ 4.7 \text{ Hz, 0.04H, isomer a)}, \ 2.24 - 1.84 \text{ (m, 1H)}, \ 1.85 - 1.68 \text{ (m, 2H)}, \ 1.67 - 1.55 \text{ (m, 3H)}, \ 1.56 - 1.46 \text{ (m, 1H)}, \ 1.46 - 1.35 \text{ (m, 2H)}, \ 1.30 - 1.07 \text{ (m, 10H)}, \ 1.03 \text{ (s, 1.84H, isomer b)}, \ 0.99 - 0.91 \text{ (m, 1H)} \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz, Chloroform-}d, \text{ major product}): \delta \ 203.37, \ 138.02, \ 131.28, \ 130.28, \ 129.37, \ 129.26, \ 126.22, \ 85.47, \ 80.23, \ 41.75, \ 41.59, \ 39.89, \ 39.73, \ 26.36, \ 26.06, \ 24.43, \ 23.95 \]

HRMS (ESI): \( \text{C}_{19}\text{H}_{27}\text{O}_{3}\text{Cl}_{3}\text{Na} [\text{M+Na}]^+ \): Calculated: 361.1546; found: 361.1549

6. methyl-2-(tert-butylperoxy)-3-cyclohexylpropanoate

In a screw cap vial, \( 4o \) (51.9 mg, 0.15 mmol) was dissolved in 3.0 mL of methanol and tetrahydrofuran (1:1) at 0 °C, to which \( \text{NaHCO}_3 \) (12.6 mg, 0.15 mmol) was added. The reaction mixture was allowed to stir at this temperature for 30 min. The solution was then diluted with cooled water, extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine and dried over \( \text{Na}_2\text{SO}_4 \). After evaporation of the solvent, the residue was purified by flash silica column chromatography with diethyl ether/PE to afford ester \( 6 \) (35.1 mg, pale yellow oil) in 90% yield.

\[ ^1H \text{NMR} \ (400 \text{ MHz, Chloroform-}d): \delta \ 4.44 \text{ (dd, } J = 8.8, \ 5.0 \text{ Hz, 1H}), \ 3.69 \text{ (s, 3H)}, \ 1.77 - 1.56 \text{ (m, 4H)}, \ 1.56 - 1.39 \text{ (m, 2H)}, \ 1.39 - 1.30 \text{ (m, 1H)}, \ 1.17 \text{ (s, 3H)}, \ 1.25 - 1.00 \text{ (m, 4H)}, \ 0.78 - 0.92 \text{ (m, 2H)} \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz, Chloroform-}d): \delta \ 172.91, \ 80.91, \ 80.74, \ 51.84, \ 38.03, \ 34.14, \ 33.63, \ 32.87, \ 26.33, \ 26.13, \ 26.02 \]

HRMS (ESI): \( \text{C}_{13}\text{H}_{22}\text{O}_{4}\text{Na} [\text{M+Na}]^+ \): Calculated: 281.1729; found: 281.1732

7. 3-cyclohexyl-2-hydroxy-4'-methoxypropiophenone

In a screw cap vial, \( 4b \) (133.7 mg, 0.4 mmol, 1 equiv) was dissolved in 2.0 mL of acetic acid, to which zinc dust (130.8 mg, 2.0 mmol, 5.0 equiv) was added. The reaction mixture was allowed to stir at 70 °C overnight. The reaction was diluted with ethyl acetate and washed with saturated sodium bicarbonate solution, brine and dried over magnesium sulphate. The organic layers were
evaporated in vacuo and the residue was purified by flash column chromatography with PE/EA to give 7 (80.4 mg, colorless oil) in 77% yield.

H NMR (400 MHz, Chloroform-d): \( \delta \) 7.81 (d, \( J = 8.9 \) Hz, 2H), 6.89 (d, \( J = 8.9 \) Hz, 2H), 5.01 (ddd, \( J = 10.4, 6.7, 2.3 \) Hz, 1H), 3.81 (s, 3H), 3.63 (d, \( J = 6.7 \) Hz, 1H), 2.05 – 1.97 (m, 1H), 1.73 – 1.47 (m, 6H), 1.33 – 1.15 (m, 3H), 1.03 – 1.15 (m, 1H), 0.77 – 0.97 (m, 2H)

C NMR (101 MHz, Chloroform-d): \( \delta \) 200.86, 164.05, 130.91, 126.30, 114.06, 70.73, 55.53, 44.28, 34.36, 34.34, 32.24, 26.52, 26.28, 26.08

HRMS (ESI): C_{16}H_{22}O_{3}Na [M+Na]^+ : Calculated: 285.1467; found: 285.1467

References: