Supporting Information

Free-Radical Anti-Markovnikov Hydroalkylation of Unactivated Alkenes with Simple Alkanes

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General Information
¹H and ¹³C NMR spectra were recorded on a Bruker advance III 400 spectrometer in CDCl₃ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. All products were identified by ¹H and ¹³C NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Aldrich, Acros Organics, Adamas, J&K Chemicals or TCI and used without further purification.
Typical procedure
A mixture of alkene (1 equiv., 0.10 mmol), CuF$_2$ (5 mol %, 0.005 mmol), DCP (3 eq, 0.30 mmol) and alkanes (5 mL) was heated under reflux at 110 °C (measured temperature of the oil bath) for 16 h. After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.

Competing Kinetic Isotope Effect (KIE) Experiment:

raw material conversion 33%  
$^1$H NMR  
$K_{H}/K_{D} = 11.5/1$
**Note:** The value of $k_H/k_D$ was calculated from the $^1$H NMR spectra above which should be the mixture of compound a and b (the KIE scheme). The sum of the integral of a and b at chemical shift 4.28 – 4.32 was integrated as 2.00 (both a and b keep the same hydrogen). Compound a has 4 hydrogen atoms at chemical shift 1.31 - 1.40, while b has no H atoms. The amount of a could be defined as 0.92(3.67 / 4 = 0.92), on the other hand, the sum of a and b is 1.00, so the amount of b is 0.08 (1.00 - 0.92 = 0.08). As a result, $k_H/k_D$=0.92 / 0.08 =11.5.

**Physical data and references for the following products**

All known compounds are determined by $^1$H NMR and $^{13}$C NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

**References:**

Physical data for the following products:

1. 5-cyclohexylpentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

![Chemical Structure of 5-cyclohexylpentyl 4-chlorobenzoate]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 8.4 Hz, 2H), 7.41 (d, $J$ = 8.4 Hz, 2H), 4.30 (t, $J$ = 6.8 Hz, 3H), 1.79 – 1.62 (m, 7H), 1.40 – 1.31 (m, 4H), 1.25 – 1.08 (m, 6H), 0.89 – 0.84 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.8, 139.2, 130.9, 128.6, 65.4, 37.6, 37.3, 33.4, 28.7, 26.7, 26.5, 26.4, 26.3.

HRMS (ESI, m/z): Calculated for C$_{18}$H$_{25}$ClO$_2$ (M+H)$^+$ 309.1616, found 309.1625

2. 3-cyclohexylpropyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

![Chemical Structure of 3-cyclohexylpropyl 4-bromobenzoate]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J$ = 8.4 Hz, 2H), 7.58 (d, $J$ = 8.4 Hz, 2H), 4.28 (t, $J$ = 6.8 Hz, 2H), 1.80 – 1.64 (m, 7H), 1.33 – 1.08 (m, 6H), 0.93 – 0.84 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.9, 131.6, 131.1, 129.4, 127.9, 65.8, 37.3, 33.6, 33.3, 26.6, 26.3, 26.0.

HRMS (ESI, m/z): Calculated for C$_{16}$H$_{21}$BrO$_2$ (M+Na)$^+$ 347.0617, found 347.0609

3. 4-cyclohexylbutyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
1H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 4.30 (t, J = 6.8 Hz, 2H), 1.77 – 1.63 (m, 7H), 1.46 – 1.39 (m, 2H), 1.24 – 1.11 (m, 6H), 0.91 – 0.85 (m, 2H).

13C NMR (100 MHz, CDCl₃): δ 165.9, 131.6, 131.1, 129.4, 127.9, 65.4, 37.5, 37.1, 33.3, 28.9, 26.7, 26.4, 23.2.

HRMS (ESI, m/z): Calculated for C₁₇H₂₃BrO₂ (M+Na)⁺ 361.0774, found 361.0768.

4. 5-cyclohexylpentyl 4-bromobenzoate
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

1H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 4.30 (t, J = 6.8 Hz, 2H), 1.79 – 1.59 (m, 7H), 1.44 – 1.31 (m, 4H), 1.22 – 1.08 (m, 6H), 0.89 – 0.84 (m, 2H).

13C NMR (100 MHz, CDCl₃): δ 165.9, 131.6, 131.1, 129.4, 127.9, 65.4, 37.6, 37.3, 33.4, 28.7, 26.7, 26.5, 26.4, 26.3.

HRMS (ESI, m/z): Calculated for C₁₈H₂₅BrO₂ (M+Na)⁺ 375.0930, found 375.0937.

5. 6-cyclohexylhexyl 4-bromobenzoate
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 4.30 (t, $J = 6.8$ Hz, 2H), 1.79 – 1.62 (m, 7H), 1.45 – 1.37 (m, 2H), 1.35 – 1.28 (m, 4H), 1.22 – 1.11 (m, 6H), 0.88 – 0.80 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.9, 131.6, 131.1, 129.4, 127.9, 65.4, 37.6, 37.4, 33.4, 29.6, 28.6, 26.7, 26.7, 26.4, 26.0.

HRMS (ESI, m/z): Calculated for C$_{19}$H$_{27}$BrO$_2$ (M+Na)$^+$ 389.1087, found 389.1079.

6. 3-cyclohexylpropyl 4-fluorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 (dd, $J = 8.8, 5.6$ Hz, 2H), 7.11 (t, $J = 8.8$ Hz, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 1.80 – 1.64 (m, 6H), 1.34 – 1.08 (m, 7H), 0.94 – 0.86 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.0, 165.7 (d, $J = 127.2$ Hz), 132.0 (d, $J = 9.3$ Hz), 126.8 (d, $J = 2.9$ Hz), 115.4 (d, $J = 22.0$ Hz), 65.6, 37.3, 33.6, 33.3, 26.6, 26.3, 26.0.

HRMS (ESI, m/z): Calculated for C$_{16}$H$_{21}$FO$_2$ (M+Na)$^+$ 287.1418, found 287.1429.

7. 3-cyclohexylpropyl benzoate

A colorless liquid light yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 – 8.03 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.42 (m, 2H), 4.30 (t, $J = 6.8$ Hz, 2H), 1.81 – 1.64 (m, 6H), 1.36 – 1.13 (m, 7H), 0.96 – 0.86 (m, 2H).
**8. 6-cyclohexylhexyl benzoate**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

![Structure of 6-cyclohexylhexyl benzoate]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 4.31 (t, $J = 7.6$ Hz, 2H), 1.80 – 1.58 (m, 7H), 1.47 – 1.40 (m, 2H), 1.36 – 1.27 (m, 4H), 1.22 – 1.11 (m, 6H), 0.90 – 0.80 (m, 2H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 166.7, 132.8, 130.5, 129.5, 128.3, 65.2, 37.6, 37.4, 33.4, 29.6, 28.7, 26.7, 26.4, 26.1.

**HRMS (ESI, m/z):** Calculated for C$_{19}$H$_{28}$O$_2$ (M+Na)$^+$ 311.1982, found 311.1974.

**9. 4-cyclohexylbutyl 4-methoxybenzoate**

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

![Structure of 4-cyclohexylbutyl 4-methoxybenzoate]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ 7.99 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 4.27 (t, $J = 6.8$ Hz, 2H), 3.86 (s, 3H), 1.76 – 1.64 (m, 7H), 1.47 – 1.39 (m, 2H), 1.26 – 1.11 (m, 6H), 0.92 – 0.80 (m, 2H).

**$^{13}$C NMR (100 MHz, CDCl$_3$):** δ 166.4, 163.2, 131.5, 122.9, 113.5, 67.1, 64.8, 55.4, 37.5, 37.1, 33.3, 29.0, 26.7, 26.4, 23.3.

**HRMS (ESI, m/z):** Calculated for C$_{18}$H$_{26}$O$_3$ (M+H)$^+$ 291.1955, found 291.1967.
10. 5-cyclohexylpentyl 3-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\[
\begin{align*}
&\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.01 (t, J = 2.0 \text{ Hz, } 1\text{H}), 7.94 - 7.91 (m, 1\text{H}), 7.52 \\
&(\text{ddd, } J = 8.0, 2.0, 1.2 \text{ Hz, } 1\text{H}), 7.38 (t, J = 8.0\text{Hz, } 1\text{H}), 4.32 (t, J = 6.8 \text{ Hz, } 2\text{H}), 1.80 - \\
&1.63 (m, 7\text{H}), 1.45 - 1.32 (m, 4\text{H}), 1.23 - 1.08 (m, 6\text{H}), 0.90 - 0.79 (m, 2\text{H}).
\end{align*}
\]

\[\text{HRMS (ESI, m/z): Calculated for C}_{18}\text{H}_{25}\text{ClO}_2 (M+H)^{+} 309.1616, \text{ found } 309.1612.\]

11. 3-cyclohexylpropyl [1,1'-biphenyl]-4-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\[
\begin{align*}
&\text{H NMR (400 MHz, CDCl}_3\text{): } \delta 8.11 (d, J = 8.4 \text{ Hz, } 2\text{H}), 7.67 - 7.62 (m, 4\text{H}), 7.47 \\
&(t, J = 7.6 \text{ Hz, } 2\text{H}), 7.39 (t, J = 7.6 \text{ Hz, } 1\text{H}), 4.32 (t, J = 6.8 \text{ Hz, } 2\text{H}), 1.83 - 1.65 (m, \\
&7\text{H}), 1.37 - 1.11 (m, 6\text{H}), 0.96 - 0.87 (m, 2\text{H}).
\end{align*}
\]

\[\text{HRMS (ESI, m/z): Calculated for C}_{22}\text{H}_{26}\text{O}_2 (M+H)^{+} 323.2006, \text{ found } 323.2001.\]

12. 6-cyclohexylhexyl 2,4,6-trimethylbenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)
1H NMR (400 MHz, CDCl3): δ 6.85 (s, 2H), 4.30 (t, J = 6.8 Hz, 2H), 2.29 (s, 6H), 2.28 (s, 3H), 1.76 – 1.63 (m, 7H), 1.44 – 1.37 (m, 2H), 1.30 – 1.11 (m, 10H), 0.88 – 0.80 (m, 2H).

13C NMR (100 MHz, CDCl3): δ 170.3, 139.1, 134.9, 131.2, 128.3, 65.0, 37.6, 37.4, 33.4, 29.5, 28.6, 26.7, 26.4, 26.1, 21.1, 19.7.

HRMS (ESI, m/z): Calculated for C22H34O2 (M+H)+ 331.2632, found 331.2628.

13. 5-cyclohexylpentyl 4-(N,N-dipropylsulfamoyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

1H NMR (400 MHz, CDCl3): δ 8.15 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 4.34 (t, J = 6.8 Hz, 2H), 3.11 – 3.07 (m, 4H), δ 1.81 – 1.74 (m, 2H), 1.70 – 1.62 (m, 5H), 1.59 – 1.50 (m, 4H), 1.45 – 1.32 (m, 4H), 1.25 – 1.11 (m, 8H), 0.86 (t, J = 7.2 Hz, 6H).

13C NMR (100 MHz, CDCl3): δ 165.3, 144.1, 133.8, 130.1, 126.9, 65.8, 49.9, 37.6, 37.3, 33.4, 28.6, 26.7, 26.5, 26.4, 26.3, 21.9 11.1.

HRMS (ESI, m/z): Calculated for C24H39NO4S (M+H)+ 438.2673, found 438.2666.

14. 3-cyclohexylpropyl benzo[d][1,3]dioxole-5-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
**1H NMR (400 MHz, CDCl₃):** δ 7.65 (dd, J = 8.0, 1.6 Hz, 1H), 7.46 (d, J = 1.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.03 (s, 2H), 4.25 (t, J = 6.8 Hz, 2H), 1.78 – 1.63 (m, 7H), 1.33 – 1.12 (m, 6H), 0.95 – 0.85 (m, 2H).

**13C NMR (100 MHz, CDCl₃):** δ 166.0, 151.5, 147.7, 125.2, 124.6, 109.5, 107.9, 101.7, 65.4, 37.4, 33.7, 33.3, 26.6, 26.3, 26.1.

**HRMS (ESI, m/z):** Calculated for C₁₇H₂₂O₄(M+H)⁺ 291.1591, found 291.1588.

**15. 3-cyclohexylpropyl nicotinate**
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

**1H NMR (400 MHz, CDCl₃):** δ 9.25 (s, 1H), 8.80 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 4.33 (t, J = 6.8 Hz, 2H), 1.82 – 1.64 (m, 7H), 1.35 – 1.13 (m, 6H), 0.94 – 0.83 (m, 2H).

**13C NMR (100 MHz, CDCl₃):** δ 165.4, 153.2, 150.9, 137.0, 123.3, 65.9, 37.3, 33.6, 33.3, 26.6, 26.3, 26.0.

**HRMS (ESI, m/z):** Calculated for C₁₅H₂₁NO₂ (M+H)⁺ 248.1645, found 248.1646.

**16. 3-cyclohexylpropyl picolinate**
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.77 – 8.76 (m, 1H), 8.12 (d, \(J = 7.6\) Hz, 1H), 7.84 (td, \(J = 7.6, 1.6\) Hz, 1H), 7.47 (ddd, \(J = 7.6, 4.8, 1.2\) Hz, 1H), 4.39 (t, \(J = 6.8\) Hz, 2H), 1.87 – 1.79 (m, 2H), 1.74 – 1.62 (m, 5H), 1.34 – 1.11 (m, 6H), 0.93 – 0.84 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 165.3, 149.9, 148.4, 136.9, 126.7, 125.0, 66.4, 37.3, 33.4, 33.3, 26.6, 26.3, 26.1.

HRMS (ESI, m/z): Calculated for C\(_{15}\)H\(_{21}\)NO\(_2\) (M+H\(^+\)) 248.1645, found 248.1640.

17. 4-cyclohexylbutyl 4-methylbenzenesulfonate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate =100/1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.79 (d, \(J = 8.4\) Hz, 2H), 7.34 (d, \(J = 8.4\) Hz, 2H), 4.02 (t, \(J = 6.8\)Hz, 2H), 2.45 (s, 3H), 1.68 – 1.57 (m, 7H), 1.32 – 1.05 (m, 8H), 0.84 – 0.74 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 144.6, 133.2, 129.8, 127.9, 70.7, 37.4, 36.7, 33.2, 29.1, 26.6, 26.3, 22.6, 21.6.

HRMS (ESI, m/z): Calculated for C\(_{17}\)H\(_{26}\)O\(_3\)S (M+Na\(^+\)) 333.1495, found 333.1499.

18. 2-(4-cyclohexylbutyl)isoindoline-1,3-dione

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.84 (dd, \(J = 5.6, 3.2\) Hz, 2H), 7.70 (dd, \(J = 5.6, 3.2\) Hz, 2H), 3.67 (t, \(J = 7.2\) Hz, 2H), 1.68 – 1.60 (m, 7H), 1.37 – 1.29 (m, 2H), 1.22 – 1.10 (m, 6H), 0.88 – 0.80 (m, 2H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 168.5, 133.8, 132.2, 123.1, 38.1, 37.5, 37.0, 33.3, 28.9, 26.7, 26.4, 24.2.
HRMS (ESI, m/z): Calculated for C_{18}H_{23}NO_{2} (M+H)^+ 286.1802, found 286.1798.

19. 2-(5-cyclohexylpentyl)isoindoline-1,3-dione
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)

\[ \text{\textbf{1H NMR (400 MHz, CDCl}_3\textbf{)}}: \delta 7.87 - 7.80 (m, 2H), 7.70 (dd, J = 5.2, 2.8 Hz, 2H), 3.67 (t, J = 7.2 Hz, 2H), 1.68 - 1.45 (m, 8H), 1.31 - 0.98 (m, 9H), 0.87 - 0.79 (m, 2H).
\]

\[ \text{\textbf{13C NMR (100 MHz, CDCl}_3\textbf{)}}: \delta 168.5, 133.8, 132.2, 123.1, 38.1, 37.5, 37.3, 33.4, 33.1, 28.6, 27.2, 26.7, 26.4.
\]

HRMS (ESI, m/z): Calculated for C_{19}H_{25}NO_{2} (M+H)^+ 300.1958, found 300.1952.

20. 1-((6-cyclohexylhexyl)oxy)-4-methoxybenzene
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate =100/1)

\[ \text{\textbf{1H NMR (400 MHz, CDCl}_3\textbf{)}}: \delta 6.83 (s, 4H), 3.90 (t, J = 6.8 Hz, 2H), 3.77 (s, 3H), 1.78 - 1.62 (m, 7H), 1.47 - 1.40 (m, 2H), 1.33 - 1.11 (m, 10H), 0.89 - 0.81 (m, 2H).
\]

\[ \text{\textbf{13C NMR (100 MHz, CDCl}_3\textbf{)}}: \delta 153.6, 153.3, 115.4, 114.6, 68.7, 55.7, 37.6, 37.5, 33.4, 29.7, 29.4, 26.8, 26.7, 26.4, 26.0.
\]

HRMS (ESI, m/z): Calculated for C_{19}H_{30}O_{2} (M+H)^+ 291.2319, found 291.2313.

21. 6-cyclohexylhexan-1-ol
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)
\[ HO-\text{structure} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{): } \delta 3.64 (t, J = 6.4 \text{ Hz}, 2\text{H}), 1.70 – 1.53 (m, 7\text{H}), 1.36 – 1.27 (m, 5\text{H}), 1.22 – 1.11 (m, 7\text{H}), 0.89 – 0.80 (m, 2\text{H}). \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 63.1, 37.6, 37.4, 33.4, 32.8, 29.7, 26.8, 26.7, 26.4, \]

\[ \text{MS(EI): } m/z \text{%: 41(39.3), 55(100.0), 82(78.5), 96(73.8), 109(20.8), 166(5.5).} \]

22. 2-(6-cyclohexylhexyl)oxirane

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\[ \text{structure} \]

\[^1^H\text{NMR (400 MHz, CDCl}_3\text{): } \delta 2.95 – 2.85 (m, 1\text{H}), 2.73 (t, J = 4.4 \text{ Hz}, 1\text{H}), 2.45 (dd, J = 4.8, 2.8 \text{ Hz}, 1\text{H}), 1.69 – 1.62 (m, 5\text{H}), 1.52 – 1.41 (m, 4\text{H}), 1.34 – 1.10 (m, 12\text{H}), 0.88 – 0.79 (m, 2\text{H}). \]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta 52.4, 47.1, 37.7, 37.5, 33.4, 32.5, 29.9, 29.5, 26.8, 26.7, 26.4, \]

\[ \text{HRMS (ESI, m/z): Calculated for } C_{14}H_{26}O (M+H)^{+} \text{211.2056, found 211.2049.} \]

23. 

(8R,9S,13S,14S)-3-((5-cyclohexylpentyloxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.19 (d, $J = 8.4$ Hz, 1H), 6.71 (dd, $J = 8.4$, 2.8 Hz, 1H), 6.64 (d, $J = 2.4$ Hz, 1H), 3.92 (t, $J = 6.4$ Hz, 2H), 2.91 – 2.87 (m, 2H), 2.50 (dd, $J = 18.8$, 8.4 Hz, 1H), 2.42 – 2.37 (m, 1H), 2.30 – 2.22 (m, 1H), 2.19 – 1.94 (m, 5H), 1.79 – 1.31 (m, 14H), 1.23 – 1.12 (m, 7H), 0.91 – 0.85 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 220.9, 157.2, 137.7, 131.8, 126.3, 114.6, 112.1, 68.0, 50.5, 48.0, 44.0, 38.4, 37.6, 37.4, 35.9, 33.4, 31.6, 29.7, 29.4, 26.8, 26.6, 26.6, 26.4, 26.4, 25.9, 21.6, 13.9.

HRMS (ESI, m/z): Calculated for C$_{29}$H$_{43}$O$_2$(M+H)$^+$ 423.3258, found 423.3254.

24. 3-cyclohexylcyclopentyl)methyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 4.21 – 4.16 (m, 2H), 1.93 – 1.59 (m, 8H), 1.48 – 1.39 (m, 1H), 1.33 – 0.99 (m, 8H), 0.95 – 0.86 (m, 2H).

$^{13}$C NMR (100 MHz, cdcl$_3$): $\delta$ 165.9, 139.2, 130.9, 129.0, 128.6, 69.4, 45.3, 43.5, 38.4, 34.9, 33.1, 32.1, 32.0, 31.9, 30.8, 29.5, 29.3, 28.3, 26.6, 26.4.

HRMS (ESI, m/z): Calculated for C$_{19}$H$_{25}$ClO$_2$ (M+Na)$^+$ 343.1435, found 343.1429.

25. 6-cyclopentylhexyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.97\) (d, \(J = 8.8\) Hz, 2H), 7.41 (d, \(J = 8.8\) Hz, 2H), 4.30 (t, \(J = 6.8\) Hz, 2H), 1.80 – 1.67 (m, 5H), 1.62 – 1.30 (m, 9H), 1.10 – 1.02 (m, 2H), 0.91 – 0.83 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 165.8, 139.2, 130.9, 128.6, 65.4, 40.1, 36.1, 32.7, 28.7, 28.4, 26.3, 25.2\).

HRMS (ESI, m/z): Calculated for C\(_{17}\)H\(_{23}\)ClO\(_2\) (M+H\(^+\)) 295.1459, found 295.1454.

26. 5-cycloheptylpentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.97\) (d, \(J = 8.4\) Hz, 2H), 7.41 (d, \(J = 8.4\) Hz, 2H), 4.30 (t, \(J = 6.8\) Hz, 2H), 1.79 – 1.72 (m, 2H), 1.70 – 1.53 (m, 4H), 1.50 – 1.30 (m, 10H), 1.25 – 1.10 (m, 4H), 0.94 – 0.83 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 165.8, 139.2, 130.9, 128.9, 128.6, 65.4, 39.2, 38.0, 34.6, 28.7, 28.5, 27.0, 26.5, 26.3\).

HRMS (ESI, m/z): Calculated for C\(_{19}\)H\(_{27}\)ClO\(_2\) (M+H\(^+\)) 323.1772, found 323.1781.

27. 5-cyclooctylpentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.98\) (d, \(J = 8.8\) Hz, 2H), 7.40 (d, \(J = 8.8\) Hz, 2H), 4.31 (t, \(J = 6.8\) Hz, 2H), 1.79 – 1.72 (m, 2H), 1.66 – 1.58 (m, 7H), 1.52 – 1.31 (m, 10H), 1.28 – 1.18 (m, 4H).
$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.8, 130.9, 128.6, 125.5, 65.4, 38.1, 37.1, 32.4, 28.7, 27.3, 27.1, 26.3, 25.5.

HRMS (ESI, m/z): Calculated for C$_{20}$H$_{29}$ClO$_2$ (M+H)$^+$ 337.1929, found 337.1938.

28. 5-(1-methylcyclopentyl)pentyl 4-chlorobenzoate
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 1.81 – 1.72 (m, 2H), 1.62 – 1.55 (m, 3H), 1.43 – 1.26 (m, 10H), 0.95 (dd, $J = 6.8$, 3.2 Hz, 1H), 0.91 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.8, 139.2, 130.9, 129.0, 128.7, 65.5, 42.4, 42.0, 39.4, 28.8, 27.0, 26.0, 25.1, 24.5.

HRMS (ESI, m/z): Calculated for C$_{18}$H$_{25}$ClO$_2$ (M+H)$^+$ 309.1616, found 309.1606.

29. 5-(1-methylcyclohexyl)pentyl 4-chlorobenzoate
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 1.81 – 1.62 (m, 4H), 1.42 – 1.30 (m, 6H), 1.23 – 1.20 (m, 6H), 0.91 – 0.85 (m, 2H), 0.84 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.8, 139.2, 130.9, 129.0, 128.7, 65.5, 37.9, 32.5, 29.7, 28.8, 27.1, 26.6, 23.0, 22.1.

HRMS (ESI, m/z): Calculated for C$_{19}$H$_{27}$ClO$_2$ (M+H)$^+$ 323.1772, found 323.1781.
30. Regio-isomers of n-hexane product

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3)\]: $\delta$ 7.98 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 2H), 1.76 (dt, $J = 14.0$, 6.8 Hz, 2H), 1.45 – 1.29 (m, 11H), 1.19 – 1.04 (m, 2H), 0.88 – 0.81 (m, 6H).

\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3)\]: $\delta$ 165.8, 139.2, 130.9, 129.0, 128.6, 65.4, 38.6, 36.9, 36.7, 35.6, 33.1, 32.7, 29.7, 29.3, 28.7, 26.7, 26.5, 26.4, 25.8, 23.0, 19.8, 19.7, 14.5, 14.2, 10.8, 1.0.

HRMS (ESI, m/z): Calculated for C$_{18}$H$_{27}$ClO$_2$ (M+H)$^+$ 311.1772, found 311.1774.

31. 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3)\]: $\delta$ 3.62 – 3.55 (m, 1H), 2.09 – 1.99 (m, 2H), 1.80 – 1.68 (m, 2H), 1.56 – 1.41 (m, 6H), 1.34 – 1.16 (m, 6H), 1.12 (s, 12H).

\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3)\]: $\delta$ 81.7, 59.6, 40.3, 32.9, 26.0, 25.1, 17.3.

HRMS (ESI, m/z): Calculated for C$_{15}$H$_{30}$NO (M+H)$^+$: 240.3967, found: 240.3970.

32. 3,3',5,5'-tetra-tert-butyl-1-cyclohexyl-4'-hydroxy-[1,1'-biphenyl]-4(1H)-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.02 (s, 1H), 6.66 (s, 1H), 5.09 (s, 1H), 2.04 (tt, $J = 11.6, 2.8$ Hz, 1H), 1.71 (dd, $J = 30.0, 12.8$ Hz, 5H), 1.41 (s, 18H), 1.26 (s, 18H), 1.14 – 1.03 (m, 2H), 0.96 – 0.87 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 186.9, 152.2, 146.1, 145.4, 135.7, 132.2, 123.4, 50.2, 46.0, 34.9, 34.6, 30.3, 29.6, 28.4, 27.0, 26.6.

HRMS (ESI, m/z): Calculated for C$_{34}$H$_{52}$O$_2$ (M+ Na)$^+$ 515.3860, found 515.3855.

Copies of the $^1$H NMR, $^{13}$C NMR
$^1$H NMR

$^{13}$C NMR

$^2$H NMR
2\textsuperscript{13}C NMR

3\textsuperscript{1}H NMR
3. $^{13}$C NMR

4. $^1$H NMR
4-$^{13}$C NMR

5-$^1$H NMR
5.$^{13}$C NMR

6.$^1$H NMR
6-$^{13}$CNMR

7-$^1$H NMR
7-$^{13}$C NMR

8-$^1$H NMR
8. $^{13}$C NMR

9. $^1$H NMR
9. $^{13}$C NMR

10. $^1$H NMR
10. $^{13}$C NMR

11. $^1$H NMR
11-\textsuperscript{13}C NMR

12-\textsuperscript{1}H NMR
$^{13}$C NMR

$^1$H NMR
14\(^{13}\)C NMR

15\(^1\)H NMR
15. $^{13}$C NMR

16. $^1$H NMR
16. $^{13}$C NMR

17. $^1$H NMR
17. $^{13}$C NMR

18. $^1$H NMR
18. $^{13}$C NMR

19. $^1$H NMR
19. $^{13}$C NMR

20. $^1$H NMR
20. $^{13}$C NMR

21. $^1$H NMR
21. $^{13}$C NMR

22. $^1$H NMR
22. $^{13}$C NMR

23. $^1$H NMR
23. $^{13}$C NMR

24. $^1$H NMR
24 $^{13}$C NMR

25 $^1$H NMR
25-\textsuperscript{13}C NMR

26-\textsuperscript{1}H NMR
27. $^{13}$C NMR

28. $^1$H NMR
28. $^{13}$C NMR

29. $^1$H NMR
29. $^{13}$C NMR

30. $^1$H NMR
$^{30}_{13}$C NMR

$^{31}_{1}$H NMR
31. $^{13}$C NMR

32. $^1$H NMR
$^{32}$C NMR