Supporting Information

A Palladium/Norbornene Cooperative Catalysis to Access Tetrahdrophanthalenes and Indanes with a Quaternary Center

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1. General information.

All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere or in the argon-filled glove box. Unless noted otherwise, all solvents were dried by JC Meyer Solvent Drying System. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or basic solution of KMnO₄ or acidic solution of p-anisaldehyde and heat as a developing agent. All NMR spectra were recorded on a Bruker spectrometer at 400 MHz (¹H NMR), 100 MHz (¹³C NMR), 376 MHz (¹⁹F NMR) and were calibrated using residual undeuterated solvent as an internal reference (CDCl₃ @ 7.26 ppm ¹H NMR, 77.16 ppm ¹³C NMR; CD₃OD @ 3.31 ppm ¹H NMR, 49.0 ppm ¹³C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad. Gas chromatography (GC) were recorded on Agilent 7890 instrument and the biphenyl as internal standard. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Enantiomeric ratio (ee) values were determined by chiral HPLC (Agilent 1260) with chiral OJ-H column with n-hexane and i-PrOH as solvents.
2. Optimization of reaction conditions.

Table S1. Optimization of reaction conditions.\textsuperscript{a}

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<tr>
<th>Entry</th>
<th>[Pd]</th>
<th>Ligand</th>
<th>[NBE]</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield [%]\textsuperscript{e}</th>
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<td>MeCN</td>
<td>84 (81)\textsuperscript{h}</td>
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</table>

\textsuperscript{a}The reaction was performed on 0.1 mmol scale. \textsuperscript{b}50 mol% was applied. \textsuperscript{c}with 5 mol% [Pd(C\textsubscript{3}H\textsubscript{5})Cl\textsubscript{2}], and 11 mol% ligand. \textsuperscript{d}with 20 mol% [Pd], and 22 mol% ligand. \textsuperscript{e}GC yield with
biphenyl as an internal standard. \(^a\) Result of pure endo-type 5-norbornene-2-carboxylic acid in parentheses. \(^b\) 2.5 equivalents of K\(_2\)CO\(_3\) were applied. \(^h\) Isolated yield in parentheses.


NBE derivatives N\(^1\), N\(^4\), N\(^5\) were commercially available and were used without further purification. N\(^2\),\(^1\) N\(^3\) and N\(^6\)\(^6\) were known compounds and were synthesized by reported procedures.

4. Preparation of aryl iodides.

Aryl iodides 1a to 1f, 1j to 1p, 1t to 1w, 1h were commercially available and were used without further purification. Aryl iodides 1g,\(^4\) 1i,\(^5\) 1q\(^6\) and 1r\(^6\) were known compounds and were synthesized by reported procedures.

*tert*-butyl (6-chloro-2, 3-dihydro-1\(H\)-inden-5-yl)carbamate (S1)

\[
\text{BocHN} \quad \text{NCS (1.1 eq.)} \quad \text{MeCN, 65 °C, 2 h} \quad \text{BocHN} \quad \text{Cl}
\]

\(N\)-Chlorosuccinimide (734 mg, 5.5 mmol, 1.1 eq.) was added to a solution of *tert*-butyl (2,3-dihydro-1\(H\)-inden-5-yl)carbamate (known compound, prepared according to the reported literature\(^7\)) (1.17 g, 5.0 mmol, 1.0 eq.) in dry MeCN (20 mL), then the reaction mixture was heated to 65 °C and stirred for 2 h. The mixture was cooled to r.t. and transferred to a separatory funnel containing saturated aqueous solution of NaHCO\(_3\). The aqueous portion was extracted with EtOAc (3 × 50 mL) and the combined organic layers were washed with brine (30 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to give the desired product S1 (967 mg, 73% yield).

**Physical state:** yellow solid;

**Melting point:** 74–76 °C;

\(R_f = 0.60\) (silica gel, PE:EtOAc = 5:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)):

\[\delta 7.99 \text{ (s, 1H)}, \quad 7.17 \text{ (s, 1H)}, \quad 6.93 \text{ (brs, 1H)}, \quad 2.88 - 2.81 \text{ (m, 4H)}, \quad 2.09 - 2.02 \text{ (m, 2H)}, \quad 1.53 \text{ (s, 9H)};\]
**\[^{13}\text{C}\]** NMR (100 MHz, CDCl\(_3\)): δ 152.8, 144.2, 139.6, 132.9, 124.6, 119.8, 116.0, 80.9, 33.0, 32.5, 28.4, 25.9.

**HRMS** (ESI-TOF): calc’d for C\(_{14}\)H\(_{18}\)ClINaO\(_2\) [M+Na\(^+\)] 290.0918, found 290.0917.

**tert-butyl (6-chloro-1-oxo-2,3-dihydro-1\(^H\)-inden-5-yl)carbamate (S2)**

A stirred solution of **tert-butyl (6-chloro-2,3-dihydro-1\(^H\)-inden-5-yl)carbamate (S1)** (1.6 g, 6.0 mmol, 1.0 eq.) in glacial AcOH (20 mL) was cooled to 0 °C, and a solution of CrO\(_3\) (1.5 g, 15.0 mmol, 2.5 eq.) in AcOH/H\(_2\)O (4:1, 10 mL) was added slowly, then ice-bath was removed, warmed to r.t. and stirred for 6 h. The reaction mixture was diluted with water (20 mL), transferred to a separatory funnel and carefully neutralized by addition of a saturated solution of NaHCO\(_3\) and extracted with EtOAc (3 × 50 mL). The organic layers were washed with brine (30 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1 to 5:1) to give the desired product **S2** (1.51 g, 85% yield).

**Physical state:** light yellow solid;

**Melting point:** 162–164 °C;

\(R_f = 0.30\) (silica gel, PE:EtOAc = 5:1);

**\(^1\text{H}\)** NMR (400 MHz, CDCl\(_3\)): δ 8.37 (s, 1H), 7.73 (s, 1H), 7.33 (brs, 1H), 3.10 – 3.07 (m, 2H), 2.70 – 2.67 (m, 2H), 1.55 (s, 9H);

**\[^{13}\text{C}\]** NMR (100 MHz, CDCl\(_3\)): δ 204.8, 155.4, 152.0, 140.5, 131.9, 124.4, 121.8, 115.7, 82.2, 36.7, 28.3, 25.9.

**HRMS** (ESI-TOF): calc’d for C\(_{14}\)H\(_{16}\)ClINaO\(_3\) [M+Na\(^+\)] 304.0711, found 304.0717.

**5-amino-6-chloro-2, 3-dihydro-1\(^H\)-inden-1-one (S3)**

S5
A cooled solution of tert-butyl (6-chloro-1-oxo-2, 3-dihydro-1H-inden-5-yl)carbamate (S2) (1.60 g, 5.7 mmol) in DCM (40 mL) at 0 °C was treated with trifluoroacetic acid (2.4 mL) and stirred at r.t. for 6 h. The mixture was neutralized by saturated aqueous solution of NaHCO₃, and removed most of the DCM, extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 2:1) to give the desired product S3 (940 mg, 90% yield).

**Physical state**: light yellow solid;

**Melting point**: 201–203 °C;

*RF* = 0.50 (silica gel, PE:EtOAc = 1:1);

**1H NMR** (400 MHz, CDCl₃): δ 7.68 (s, 1H), 6.73 (s, 1H), 4.63 (brs, 2H), 3.00–2.97 (m, 2H), 2.65–2.62 (m, 2H);

**13C NMR** (100 MHz, CDCl₃): δ 204.2, 155.9, 148.6, 128.5, 125.3, 119.6, 110.7, 36.6, 25.5;

**HRMS** (ESI-TOF): calc’d for C₉H₈ClNNaO [M+Na⁺] 204.0187, found 204.0189.

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**6-chloro-5-iodo-2, 3-dihydro-1H-inden-1-one (S4)**

![Chemical Structure](image)

*t*-Butyl nitrite (36 µL, 0.3 mmol, 1.5 eq.) and iodine (50.7 mg, 0.2 mmol, 1.0 eq.) in dry MeCN (3 mL) were added to a solution of 5-amino-6-chloro-2,3-dihydro-1H-inden-1-one (S3) (36.0 mg, 0.2 mmol, 1.0 eq.) in dry MeCN (10 mL) at r.t.. The mixture was heated to 60 °C and stirred for 1 h under argon. A saturated aqueous solution of sodium thiosulfate was added and the solution was concentrated in vacuo to remove most of the MeCN. The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 5:1) to give the desired product S4 (33 mg, 55% yield).

**Physical state**: yellow solid;

**Melting point**: 137–139 °C;

*RF* = 0.80 (silica gel, PE:EtOAc = 2:1);
$^1$H NMR (400 MHz, CDCl$_3$): δ 8.07 (s, 1H), 7.77 (s, 1H), 3.10 – 3.07 (m, 2H), 2.71 – 2.68 (m, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 204.9, 153.7, 138.8, 138.6, 138.2, 123.6, 107.0, 36.6, 25.0;

HRMS (APCI-TOF): calc’d for C$_9$H$_7$ClIO [M+H$^+$] 292.9225, found 292.9224.

6-chloro-5-iodo-2, 3-dihydrospiro[indene-1, 2'-[1, 3]dioxolane] (1s)

To a solution of 6-chloro-5-iodo-2,3-dihydro-1H-inden-1-one (S4) (117 mg, 0.4 mmol, 1.0 eq.) in benzene (10 mL) were added ethylene glycol (497 μL, 8 mmol, 20 eq.), tosic acid (76 mg, 0.4 mmol, 1.0 eq.) and trimethoxymethane (219 μL, 2 mmol, 5.0 eq.), the mixture was heated to 50 °C and stirred for 6 h. Then the reaction mixture was diluted with EtOAc (20 mL) and neutralized with saturated aqueous solution of NaHCO$_3$, separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE: EtOAc = 20:1) to give the desired product 1s (117 mg, 77% yield).

Physical state: white solid;

Melting point: 112–114 °C;

$R_f$ = 0.45 (silica gel, PE:EtOAc = 5:1);

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (s, 1H), 7.41 (s, 1H), 4.19 – 4.13 (m, 2H), 4.11 – 4.05 (m, 2H), 2.89 (t, $J$ = 6.9 Hz, 2H), 2.28 (t, $J$ = 6.9 Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 144.4, 143.9, 136.9, 136.7, 123.9, 116.4, 99.4, 65.5, 37.4, 27.7.

HRMS (ESI-TOF): calc’d for C$_{11}$H$_{10}$ClINaO$_2$ [M+Na$^+$] 358.9306, found 358.9310.

methyl 2, 6-bis(benzyloxy)-3-iodobenzoate (1x)
BnBr (2.2 g, 13.2 mmol, 2.2 eq.) was added to a suspension of methyl 2,6-dihydroxy-3-iodobenzoate (known compound, prepared according to the reported literature) (1.76 g, 6.0 mmol, 1.0 eq.) and K$_2$CO$_3$ (1.8 g, 13.2 mmol, 2.2 eq.) in DMF (30 mL). The mixture was stirred overnight at r.t., then diluted with water (30 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 30:1) to give the desired product 1x (1.99 g, 70% yield).

Physical state: white solid;

Melting point: 107–109 ºC;

$R_f$ = 0.45 (silica gel, PE:EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, $J$ = 8.8 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.42 – 7.30 (m, 8H), 6.58 (d, $J$ = 8.8 Hz, 1H), 5.12 (s, 2H), 5.05 (s, 2H), 3.83 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.9, 156.9, 156.0, 140.6, 136.6, 136.2, 128.7, 128.5, 128.4, 128.1, 127.0, 120.6, 111.1, 81.3, 76.7, 70.8, 52.8;

HRMS (ESI-TOF): calc’d for C$_{22}$H$_{19}$INaO$_4$ [M+Na$^+$] 497.0220, found 497.0223.

5-hydroxy-6-iodo-2, 2-dimethyl-4H-benzo[d][1,3]dioxin-4-one$^9$ (S5)

To a mixture of 5-hydroxy-2, 2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (prepared according to the reported literature$^{10}$) (971 mg, 5 mmol, 1.0 eq.) and silver trifluoroacetate (1.16 g, 5.25 mmol, 1.05 eq.) in CHCl$_3$ (75 mL) was added a solution of I$_2$ (1.33 g, 5.25 mmol, 1.05 eq.) in CHCl$_3$ (100 mL) dropwise at -20 ºC. After stirring for 10 h, the reaction mixture was filtered through a thin pad of celite, eluted with CHCl$_3$ (20.0 mL), and 10% aqueous solution of Na$_2$S$_2$O$_3$ was added to the filtrate at 0 ºC. The product was extracted with CHCl$_3$ (3 × 30 mL), and the combined organic layers were washed with saturated aqueous solution of NaHCO$_3$, brine, and dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 30:1) to give the aryl iodide S5 (1.17 g, 73%).

Physical state: white solid;
Melting point: 127–129 ºC;  
$R_f$ = 0.45 (silica gel, PE:EtOAc = 10:1);  
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.16 (s, 1H), 7.85 (dd, $J = 8.7, 1.8$ Hz, 1H), 6.34 (dd, $J = 8.6, 1.3$ Hz, 1H), 1.76 (s, 6H);  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.0, 160.1, 156.0, 146.7, 109.7, 107.9, 99.6, 75.0, 25.7;  
HRMS (ESI-TOF): calc’d for C$_{10}$H$_{10}$IO$_4$ [M+H$^+$] 320.9618, found 320.9617.

5-(benzyloxy)-6-iodo-2, 2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (1y)

BnBr (918 mg, 5.4 mmol) was added to a suspension of 5-hydroxy-6-iodo-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (S5) (1.05 g, 3.6 mmol, 1.5 eq.) and K$_2$CO$_3$ (746 mg, 5.4 mmol, 1.5 eq.) in DMF (20 mL). The mixture was stirred overnight at r.t., then diluted with water (20 mL) and extracted with EtOAc (3 × 20 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 30:1) to give the desired product 1y (1.14 g, 78% yield).  
Physical state: white solid;  
Melting point: 100–102 ºC;  
$R_f$ = 0.40 (silica gel, PE:EtOAc = 10:1);  
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J = 8.7$ Hz, 1H), 7.69 – 7.66 (m, 2H), 7.42 – 7.33 (m, 3H), 6.60 (d, $J = 8.7$ Hz, 1H), 5.12 (s, 2H), 1.69 (s, 6H);  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.4, 157.8, 157.3, 145.6, 136.1, 129.5, 128.6, 128.6, 115.4, 109.4, 105.9, 85.7, 76.0, 25.7;  
HRMS (ESI-TOF): calc’d for C$_{17}$H$_{15}$INaO$_4$ [M+Na$^+$] 432.9907, found 432.9908.

5. Preparation of functionalized alkylating reagents.  

(E)-6-bromo-3-methylhex-2-en-1-ol (2a) and (Z)-6-bromo-3-methylhex-2-en-1-ol (2a’)

S9
The (E)-6-bromo-3-methylhex-2-en-1-ol (2a) and (Z)-6-bromo-3-methylhex-2-en-1-ol (2a') were synthesized following the reported procedure.\textsuperscript{11}

\textbf{(E)-6-iodo-3-methylhex-2-en-1-ol (2a'')}

To a stirred suspension of NaI (7.49 g, 50 mmol, 10.0 eq.) in acetone (30 mL) was added (2a) (966 mg, 5.0 mmol, 1.0 eq.). The mixture was refluxed at 65 °C overnight. After completion, water and Et\textsubscript{2}O were added to the mixture and the organic layer was separated. The aqueous layer was extracted with Et\textsubscript{2}O (3 × 20 mL). The combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 5:1) to give the desired product 2a'' (1.20 g, 99% yield).

\textbf{Physical state}: yellow oil;

\textit{R} \textsubscript{f} = 0.22 (silica gel, PE:EtOAc = 5:1);

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 5.48 – 5.43 (m, 1H), 4.15 (d, \textit{J} = 6.8 Hz, 2H), 3.16 (t, \textit{J} = 6.9 Hz, 2H), 2.12 (t, \textit{J} = 7.4 Hz, 2H), 1.98 – 1.90 (m, 2H), 1.67 (s, 3H), The \textsuperscript{1}H NMR matched the data reported in the literature.\textsuperscript{12}

\textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 137.7, 124.7, 59.4, 40.0, 31.4, 16.3, 6.5;

\textbf{HRMS} (ESI-TOF): calc’d for C\textsubscript{7}H\textsubscript{13}INaO [M+Na\textsuperscript{+}] 262.9903, found 262.9902.

\textbf{(E)-7-bromo-4-methylhept-3-en-1-ol (2b)}
To a suspension of 3-triphenylphosphoniumpropanol bromide (1.6 g, 4.0 mmol, 1.0 eq.) in dry THF (20 mL) at -20 °C was added n-BuLi (5.0 mL, 1.6 M in hexane, 8.0 mmol, 2.0 eq.), the resulted orange solution was continuing stirred for 10 min, then TMSCl (0.42 mL, 4.8 mmol, 1.2 eq.) was added. 5 min later, a solution of 5-bromopentan-2-one (0.99 g, 6.0 mmol, 1.5 eq.) in THF (12 mL) was added dropwise, and the mixture was warmed to r.t., and stirred for another 3 h, then quenched with water, concentrated in vacuo. The resulted residue was dissolved in THF (10 mL), a solution of H₂SO₄ (25 mL, 5%) was added, the solution was stirred at 35 °C for 8 h, then concentrated in vacuo. The crude oil was purified by column chromatography on silica gel (PE:EtOAc = 5:1) to give the alcohol 2b as an inseparable E,Z isomer (≈ 1:1) (286 mg, 39% yield).

Physical state: colorless oil;

Rᵣ = 0.40 (silica gel, PE:EtOAc = 5:1);

¹H NMR (400 MHz, CDCl₃): δ 5.23 – 5.18 (m, 1H), 3.63 (t, J = 6.5 Hz, 2H), 3.41 – 3.36 (m, 2H), 2.34 – 2.26 (m, 2H), 2.22 – 2.14 (m, 2H), 2.00 – 1.92 (m, 2H), 1.72 – 1.64 (m, 3H, Z+E);

¹³C NMR (100 MHz, CDCl₃): δ 137.0, 136.8, 122.4, 121.4, 62.7, 62.6, 38.1, 33.7, 33.5, 31.6 (2C), 31.1, 30.9, 30.3, 23.5, 16.2;


(E)-5-bromo-3-methylpent-2-en-1-ol (2c)

The (E)-5-bromo-3-methylpent-2-en-1-ol (2c) (known compound) was synthesized following the reported procedure.²³

(E)-6-bromo-4-methylhex-3-en-1-ol (2d)

The (E)-6-bromo-4-methylhex-3-en-1-ol (2d) (known compound) was synthesized
following the reported literature.\textsuperscript{13}

\textbf{(E)-6-bromo-1-methoxy-3-methylhex-2-ene (2A)}

\[
\begin{align*}
\text{Br} & \quad \text{Me} & \quad \text{OH} & \quad \text{TMSCHN}_2 (2.0 \text{ eq.}) & \quad \text{HBF}_4 (1.0 \text{ eq.}) & \quad \text{DCM, 0} \sim 20^\circ \text{C} & \quad \text{Br} & \quad \text{Me} & \quad \text{OMe}\n\end{align*}
\]

(Trimethylsilyl)diazomethane (2 M in hexanes, 0.1 mL, 0.2 mmol, 1.0 eq.) was added dropwise to a stirred mixture of (E)-6-bromo-3-methylhex-2-en-1-ol (2a) (38.6 mg, 0.2 mmol, 1.0 eq.) and aqueous fluoroboric acid (48\%, 36.6 mg, 0.2 mmol, 1.0 eq.) in DCM (0.65 mL) at 0 \(^\circ\)C, then warmed to r.t. for 20 min. Second portion of (Trimethylsilyl)diazomethane (0.05 mL, 0.1 mmol, 0.5 eq.) was added with stirring at r.t. for another 20 min. Third portion of (Trimethylsilyl)diazomethane (0.05 mL, 0.1 mmol, 0.5 eq.) was added with stirring at r.t. for additional 30 min. Water (5.0 mL) was added to quench the reaction. The mixture was extracted with DCM (3 \(\times\) 5 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), concentrated \textit{in vacuo} and the residue was purified by column chromatography on silica gel (PE:EtOAc = 20:1) to give the ether 2A (25 mg, 60\% yield).

\textbf{Physical state: colorless oil;}  
\textit{Rf} = 0.60 (silica gel, PE:EtOAc = 20:1);

\[\text{\textsuperscript{1}H NMR} (400 \text{MHz, CDCl}_3): \delta 5.41 - 5.37 (m, 1H), 3.93 (d, J = 6.7 \text{ Hz, 2H}), 3.39 (t, J = 6.7 \text{ Hz, 2H}), 3.33 (s, 3H), 2.18 (t, J = 7.1 \text{ Hz, 2H}), 2.00 - 1.96 (m, 2H), 1.67 (s, 3H);\]

\[\text{\textsuperscript{13}C NMR} (100 \text{MHz, CDCl}_3): \delta 138.6, 122.1, 69.0, 58.1, 37.9, 33.4, 30.7, 16.5;\]

\[\text{HRMS (ESI-TOF): calc'd for C}_8\text{H}_{15}\text{BrNaO [M+Na}\text{]}^+ 229.0198, \text{found 229.0195.}\]

\textbf{(E)-6-bromo-3-methylhex-2-enal (S6)}

\[
\begin{align*}
\text{Br} & \quad \text{Me} & \quad \text{OH} & \quad \text{DMP (1.2 \text{ eq.})} & \quad \text{DCM, r.t.} & \quad \text{Br} & \quad \text{Me} & \quad \text{O}\n\end{align*}
\]

A mixture of (E)-6-bromo-3-methylhex-2-en-1-ol (2a) (580 mg, 3.0 mmol, 1.0 eq.) and Dess-Martin periodinane (1.53 g, 3.6 mmol, 1.2 eq.) in DCM (5 mL) was stirred at r.t. for 2 h. Saturated aqueous solution of NaHCO\(_3\) (2 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted with DCM (3 \(\times\) 10 mL). The combined organic layers were
washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to give the aldehyde S6 (479 mg, 84% yield).

**Physical state**: pale oil;

$R_f = 0.50$ (silica gel, PE:EtOAc = 3:1);

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.00 (d, $J = 7.9$ Hz, 1H), 5.90 (dq, $J = 7.9$, 1.3 Hz, 1H), 3.41 (t, $J = 6.5$ Hz, 2H), 2.40 – 2.36 (m, 2H), 2.18 (d, $J = 1.3$ Hz, 3H), 2.10 – 2.03 (m, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.2, 161.9, 127.9, 38.8, 32.6, 30.0, 17.8;

HRMS (ESI-TOF): calc’d for C$_7$H$_{11}$BrNaO [M+Na$^+$] 212.9885, found 212.9883.

**Typical procedure for the reaction of aldehyde (S6) with Grignard reagent to prepare 2f-2h.**

To a stirred solution of (E)-6-bromo-3-methylhex-2-enal (S6) in dry THF was added Grignard reagent (1.2 eq.) at 0 °C under argon. The mixture was then warmed to r.t.. After completion, saturated aqueous solution of NH$_4$Cl was added to the mixture. The organic layer was separated, aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated in vacuo. The residue was purified by column chromatography to give the desired secondary alcohol.

(E)-7-bromo-4-methylhept-3-en-2-ol (2B)

Following the typical procedure, aldehyde (S6) (191.1 mg, 1.0 mmol, 1.0 eq.), and methyl magnesium bromide (3 M in Et$_2$O, 1.2 mmol, 1.2 eq.) were used. Column chromatography on silica gel (PE:EtOAc = 10:1) to give the desired product 2B (179 mg, 87% yield).

**Physical state**: yellow oil;

$R_f = 0.30$ (silica gel, PE:EtOAc = 3:1);
\( ^1 \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \): 5.25 (dq, \( J = 8.4, 1.3 \) Hz, 1H), 4.65 – 4.31 (m, 1H), 3.38 (td, \( J = 6.7, \) 0.8 Hz, 2H), 2.16 – 2.10 (m, 2H), 2.00 – 1.93 (m, 2H), 1.67 (d, \( J = 1.4 \) Hz, 3H), 1.23 (d, \( J = 6.3 \) Hz, 3H);

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \): 135.8, 130.3, 64.8, 37.7, 33.4, 30.7, 23.8, 16.5;

HRMS (ESI-TOF): calc’d for C\(_8\)H\(_{15}\)BrNaO [M+Na\(^+\)] 229.0198, found 229.0197.

\((E)-10\text{-bromo-7-methyldec-6-en-5-ol (2C)}\)

Following the typical procedure, aldehyde (S6) (95.6 mg, 0.5 mmol, 1.0 eq.), and butylmagnesium chloride (2 M in THF, 0.6 mmol, 1.2 eq.) were used. Column chromatography on silica gel (PE:EtOAc = 10:1) to give the desired product 2C (112 mg, 90% yield).

Physical state: yellow oil;

\( R_f = 0.52 \) (silica gel, PE:EtOAc = 3:1);

\( ^1 \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \): 5.22 – 5.19 (m, 1H), 4.34 (dt, \( J = 8.6, \) 6.6 Hz, 1H), 3.38 (td, \( J = 6.7, 2.9 \) Hz, 2H), 2.17 – 2.12 (m, 2H), 2.00 – 1.93 (m, 2H), 1.67 (d, \( J = 1.4 \) Hz, 3H), 1.63 – 1.54 (m, 1H), 1.46 – 1.39 (m, 2H), 1.35 – 1.19 (m, 4H), 0.89 (t, \( J = 6.9 \) Hz, 3H);

\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \): 136.6, 129.3, 68.7, 37.9, 37.5, 33.4, 30.7, 27.7, 22.8, 16.6, 14.2;

HRMS (ESI-TOF): calc’d for C\(_{11}\)H\(_{21}\)BrKO [M+K\(^+\)] 271.0668, found 271.0669.

\( (E)-9\text{-bromo-6-methylnona-1,5-dien-4-ol (2D)}\)

Following the typical procedure, aldehyde (S6) (152.9 mg, 0.8 mmol, 1.0 eq.), and allylmagnesium bromide (1 M in THF, 0.96 mmol, 1.2 eq.) were used. Column chromatography on silica gel (PE:EtOAc = 10:1) to give the desired product 2D (172 mg, 92% yield).

Physical state: yellow oil;

\( R_f = 0.50 \) (silica gel, PE:EtOAc = 3:1);
**1H NMR** (400 MHz, CDCl₃) δ 5.84 – 5.74 (m, 1H), 5.26 – 5.23 (m, 1H), 5.17 – 5.10 (m, 2H), 4.44 – 4.39 (m, 1H), 3.38 (td, J = 6.7, 3.3 Hz, 2H), 2.32 – 2.23 (m, 2H), 2.19 – 2.11 (m, 2H), 2.01 – 1.93 (m, 2H), 1.69 (d, J = 1.3 Hz, 3H);

**13C NMR** (100 MHz, CDCl₃) δ 137.0, 134.4, 128.3, 118.3, 67.7, 42.4, 37.8, 33.3, 30.7, 16.7;


6-bromohexan-3-one (S7)

To a 50 mL of oven-dried flask equipped with a magnetic stir bar was charged with 4-bromobutanoic acid (835 mg, 5.0 mmol, 1.11 eq.) and DCM (15 mL), then oxalyl chloride (0.85 mL, 10.0 mmol, 2.22 eq.) and a catalytic amount of DMF (18 mg, 0.25 mmol, 0.05 eq.) were added at 0 °C. The mixture was stirred at r.t. under argon for 6 h, then solvent was removed in vacuo, the resulted crude product was dissolved in THF (15 mL), and CuI (901 mg, 4.7 mmol, 1.05 eq.) was added to the solution. The mixture was cooled to -78 °C, and ethyl magnesium bromide (1.5 mL, 3 M in Et₂O, 4.5 mmol, 1.0 eq.) was added dropwise. The reaction was allowed to slowly warm to 0 °C overnight. The reaction mixture was then quenched with saturated aqueous solution of NH₄Cl, extracted with Et₂O (3 × 20 mL), washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 100:1) to give 6-bromohexan-3-one (S7) (524 mg, 65% over two steps) as a colorless oil. **1H NMR** (600 MHz, CDCl₃) δ 3.44 (t, J = 6.4 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 2.44 (q, J = 7.4 Hz, 2H), 2.11 (p, J = 6.8 Hz, 2H), 1.06 (t, J = 7.4 Hz, 3H). The **1H NMR** matched the data reported in the literature.¹⁴

**ethyl (E)-6-bromo-3-ethylhex-2-enoate (S8)**

To a 50 mL of oven-dried flask equipped with a magnetic stir bar was charged with sodium hydride (94 mg, 2.35 mmol, 1.2 eq.) and dry THF (8 mL), then triethyl phosphonoacetate (526 mg, 2.35 mmol, 1.2 eq.) was added dropwise at 0 °C, and the mixture was stirred at 0 °C for 30 min,
then a solution of 6-bromohexan-3-one (S7) (350 mg, 1.95 mmol, 1.0 eq.) in THF (5 mL) was added dropwise. The reaction mixture was stirred overnight at 0 °C under argon. The reaction was diluted with Et₂O (5 mL), water (5 mL) was added, and the organic layer was separated, the aqueous layer was extracted with Et₂O (3 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and then concentrated in vacuo. Purified by column chromatography on silica gel (PE:EtOAc = 100:1) to give the desired E isomer S8 (102 mg, 21% yield) together with undesired Z isomer (100 mg, 21% yield).

**Physical state:** colorless oil;

\( R_f = 0.80 \) (silica gel, PE:EtOAc = 20:1);

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta 5.63 \) (t, \( J = 1.1 \) Hz, 1H), 4.14 (q, \( J = 7.1 \) Hz, 2H), 3.41 (t, \( J = 6.5 \) Hz, 2H), 2.61 (q, \( J = 7.5 \) Hz, 2H), 2.33 - 2.29 (m, 2H), 2.06 – 1.99 (m, 2H), 1.27 (t, \( J = 7.1 \) Hz, 3H), 1.08 (t, \( J = 7.5 \) Hz, 3H);

\(^13\)C NMR (100 MHz, CDCl₃) \( \delta 166.3, 163.7, 115.8, 59.7, 36.1, 33.0, 30.5, 25.3, 14.4, 13.1 \);


\((E)-6\)-bromo-3-ethylhex-2-en-1-ol (2E)

![Chemical structure](image)

A solution of ethyl \((E)-6\)-bromo-3-ethylhex-2-enoate (S8) (102 mg, 0.41 mmol, 1.0 eq.) in dry THF (3 mL) was cooled to −78 °C, then diisobutylaluminium hydride (1 M solution in hexane, 1.0 mL, 1.0 mmol, 2.5 eq.) was added dropwise. The reaction mixture was stirred at −78 °C for 3 h under argon, and then allowed to warm to 0 °C. Et₂O (3 mL) and saturated potassium sodium tartrate solution (3 mL) were added. The mixture was stirred at r.t. for another 30 min, and the organic layer was separated, the aqueous layer was extracted with Et₂O (3 × 5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to give the product 2E (81 mg, 95% yield).

**Physical state:** colorless oil;

\( R_f = 0.25 \) (silica gel, PE:EtOAc = 10:1);
**1H NMR** (400 MHz, CDCl$_3$) δ 5.40 (t, $J = 6.9$ Hz, 1H), 4.17 (d, $J = 6.9$ Hz, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 2.21 – 2.17 (m, 2H), 2.08 (q, $J = 7.6$ Hz, 2H), 2.01 – 1.94 (m, 2H), 0.99 (t, $J = 7.6$ Hz, 3H);

**13C NMR** (100 MHz, CDCl$_3$) δ 143.9, 124.1, 59.1, 34.7, 33.6, 31.0, 23.5, 13.8;


4-bromo-1-phenylbutan-1-one (S9)

![Chemical structure of 4-bromo-1-phenylbutan-1-one (S9)](image)

To a solution of 4-bromobutanenitrile (740 mg, 5.0 mmol, 1.0 eq.) and dry Et$_2$O (15 mL) in a 50 mL of Schlenk flask was added phenylmagnesium bromide (3 M solution in Et$_2$O, 1.7 mL, 5.0 mmol, 1.0 eq.) dropwise at 0 °C, then the reaction mixture was stirred at r.t. for 15 h. The mixture was cooled to 0 °C, and stirred rapidly with hydrochloric acid (1 M, 5 mL) for 1 h. The organic layer was separated, the aqueous layer was extracted with Et$_2$O (3 × 20 mL). The combined organic layers were washed with saturated aqueous solution of NaHCO$_3$, brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 100:1) to give the ketone S9 (574 mg, 51% yield) as a colorless oil. **1H NMR** (600 MHz, CDCl$_3$) δ 7.98 (d, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 3.56 (t, $J = 6.3$ Hz, 2H), 3.19 (t, $J = 6.9$ Hz, 2H), 2.34 – 2.30 (m, 2H). The **1H NMR** matched the data reported in the literature.$^{15}$

**ethyl (E)-6-bromo-3-phenylhex-2-enoate (S10)**

![Chemical structure of ethyl (E)-6-bromo-3-phenylhex-2-enoate (S10)](image)

To a 50 mL of oven-dried flask equipped with a magnetic stir bar was charged with sodium hydride (121 mg, 3.03 mmol, 1.2 eq.) and dry THF (10 mL), then triethyl phosphonoacetate (680 mg, 3.03 mmol, 1.2 eq.) was added dropwise at 0 °C, and the mixture was stirred at 0 °C for 30
min. Then a solution of 4-bromo-1-phenylbutan-1-one (S9) (574 mg, 2.53 mmol, 1.0 eq.) in THF (5 mL) was added dropwise. The reaction mixture was stirred overnight at 0 °C under argon. The reaction was diluted with Et₂O (5 mL), and water (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and then concentrated in vacuo. Purified by column chromatography on silica gel (PE:EtOAc = 100:1) to give the desired E isomer S10 (205 mg, 27% yield) together with undesired Z isomer (100 mg, 13% yield).

**Physical state**: colorless oil;

\[ R_f = 0.75 \text{ (silica gel, PE:EtOAc = 20:1);} \]

**1H NMR** (400 MHz, CDCl₃) \( \delta 7.46 – 7.43 \) (m, 2H), \( 7.40 – 7.37 \) (m, 3H), 6.09 (s, 1H), 4.21 (q, \( J = 7.1 \) Hz, 2H), 3.43 (t, \( J = 6.8 \) Hz, 2H), 3.32 – 3.19 (m, 2H), 2.08 – 1.93 (m, 2H), 1.32 (t, \( J = 7.1 \) Hz, 3H);

**13C NMR** (100 MHz, CDCl₃) \( \delta 166.5, 158.7, 140.7, 129.3, 128.8, 126.8, 118.3, 60.2, 33.6, 32.1, 29.9, 14.5; \)

**HRMS (ESI-TOF)**: calc’d for C\textsubscript{14}H\textsubscript{17}BrNaO\textsubscript{2} [M+Na\textsuperscript{+}] 319.0304, found 319.0307.

(E)-6-bromo-3-phenylhex-2-en-1-ol (2F)

A solution of ethyl (E)-6-bromo-3-phenylhex-2-enoate (S10) (205 mg, 0.69 mmol, 1.0 eq.) in dry THF (5 mL) was cooled to –78 °C, then diisobutylaluminium hydride (1 M solution in hexane, 1.7 mL, 1.7 mmol, 2.5 eq.) was added dropwise. The reaction mixture was stirred at –78 °C for 3 h under argon, and then allowed to warm to 0 °C. Et₂O (5 mL) and saturated potassium sodium tartrate solution (5 mL) were added. The mixture was stirred at r.t. for another 30 min, and the organic layer was separated, the aqueous layer was extracted with Et₂O (3 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to give the product 2F (169 mg, 96% yield).

**Physical state**: colorless oil;
$R_f = 0.30$ (silica gel, PE:EtOAc = 5:1); 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.26 (m, 5H), 5.94 (t, $J = 6.9$ Hz, 1H), 4.40 (d, $J = 6.9$ Hz, 2H), 3.35 (t, $J = 6.3$ Hz, 2H), 2.73 (t, $J = 7.3$ Hz, 2H), 1.93 – 1.86 (m, 2H), 1.52 (b.r.s, 1H); 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.5, 141.3, 128.7, 128.6, 127.6, 126.6, 59.7, 33.6, 31.1, 27.9; 

HRMS (ESI-TOF): calc’d for C$_{12}$H$_{15}$BrNaO [M+Na$^+$] 277.0198, found 277.0197.

(E)-6-bromohex-2-en-1-ol (2G)

\[
\begin{align*}
\text{Br} & \quad \text{CO}_2\text{Et} \quad \text{DIBAL-H} \quad \text{THF, -78 °C} \quad \text{Br} \quad \text{OH} \\
\text{Br} & \quad \text{CO}_2\text{Et} \quad \text{DIBAL-H} \quad \text{THF, -78 °C} \quad \text{Br} \quad \text{OH} \\
\end{align*}
\]

The (E)-6-bromohex-2-en-1-ol 2G (known compound) was synthesized following the reported procedure.$^{16}$

(E)-7-bromohept-2-en-1-ol (2H)

\[
\begin{align*}
\text{Br} & \quad \text{CN} \quad \text{DIBAL-H} \quad \text{Toluene, -78 °C} \quad \text{Br} \quad \text{O} \\
\text{Br} & \quad \text{CN} \quad \text{DIBAL-H} \quad \text{THF, -78 °C} \quad \text{Br} \quad \text{OH} \\
\end{align*}
\]

The (E)-7-bromohept-2-en-1-ol 2H (known compounds) was synthesized following the reported procedure.$^{16,17}$

methyl (E)-3-(3-bromopropoxy)acrylate (S11)

\[
\begin{align*}
\text{Br} & \quad \text{OH} \quad + \quad \equiv \text{CO}_2\text{Me} \quad \text{N-methylmorpholine (1.0 eq.)} \quad \text{DCM, r.t.} \quad \text{Br} \quad \text{O} \quad \equiv \text{CO}_2\text{Me} \\
\end{align*}
\]

To a stirred solution of the 3-bromopropan-1-ol (5.0 mmol, 695.0 mg, 1.0 eq.) in dry DCM (20 mL) was added N-methylmorpholine (5.0 mmol, 506 mg, 1.0 eq.) and methylpropiolate (5.5 mmol, 463 mg, 1.1 eq.) at r.t. and stirred until the completion of the reaction. The reaction mixture
was extracted with DCM (3 × 15 mL), and the combined organic layers were washed with saturated aqueous solution of NaHCO₃, brine, and dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EtOAc = 20:1) to give the product S11 (1.1 g, 99% yield)

**Physical state:** colorless oil;

\[ R_f = 0.6 \] (silica gel, PE:EtOAc = 10:1);

\(^1\text{H NMR} \) (400 MHz, CDCl₃): \( \delta 7.59 \) (d, \( J = 12.6 \) Hz, 1H), \( 5.24 \) (d, \( J = 12.6 \) Hz, 1H), \( 3.99 \) (t, \( J = 5.8 \) Hz, 2H), \( 3.70 \) (s, 3H), \( 3.50 \) (t, \( J = 6.3 \) Hz, 2H), \( 2.26 - 2.20 \) (m, 2H);

\(^1\text{C NMR} \) (100 MHz, CDCl₃) \( \delta 168.2, 162.2, 96.7, 68.2, 51.3, 31.8, 29.3 \);

**HRMS** (ESI-TOF): calc’d for C₇H₁₁BrNaO₃ [M+Na⁺] 244.9784, found 244.9782.

\((E)-3-(3\text{-bromopropoxy})\text{prop-2-en-1-ol (2I)}\)

A solution of S11 (892.4 mg, 4.0 mmol, 1.0 eq.) in dry THF (40 mL) was stirred under argon and cooled to −78°C, then diisobutylaluminium hydride (1 M solution in hexane, 9.6 mL, 9.6 mmol, 2.4 eq.) was added dropwise. The resulting mixture was stirred at −78 °C for 2 h, then allowed to warm to 0 °C. Upon completion of the reaction, saturated potassium sodium tartrate solution (15 mL) and Et₂O (20 mL) were added. The mixture was stirred at r.t. for 30 min, and the organic layer was separated. The aqueous layer was extracted with Et₂O (3 × 15 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and then concentrated in vacuo, purified by column chromatography on silica gel (PE:EtOAc = 3:1) to give the alcohol 2I (750 mg, 96% yield).

**Physical state:** colorless oil;

\[ R_f = 0.3 \] (silica gel, PE:EtOAc = 3:1);

\(^1\text{H NMR} \) (400 MHz, CDCl₃): \( \delta 6.52 \) (d, \( J = 12.6 \) Hz, 1H), \( 5.05 \) (dt, \( J = 12.7, 7.4 \) Hz, 1H), \( 4.07 - 4.05 \) (m, 2H), \( 3.84 \) (t, \( J = 5.8 \) Hz, 2H), \( 3.51 \) (t, \( J = 6.4 \) Hz, 2H), \( 2.22 - 2.16 \) (m, 2H), \( 1.61 \) (s, 1H).

\(^1\text{C NMR} \) (100 MHz, CDCl₃) \( \delta 150.1, 103.1, 66.5, 60.9, 32.2, 30.0 \);

**HRMS** (ESI-TOF): calc’d for C₆H₁₁BrNaO₂ [M+Na⁺] 216.9835, found 216.9838.
6. Typical procedure for the synthesis of compound 3.

To a 25 mL of oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Pd(C₅H₃)Cl]₂ (3.7 mg, 0.01 mmol, 0.05 eq.), XPhos (10.5 mg, 0.022 mmol, 0.11 eq.), K₂CO₃ (69.1 mg, 0.5 mmol, 2.5 eq.), and dry MeCN (1 mL). After stirring for about 15 min at r.t. under argon, a solution of aryl iodide 1 (0.24 mmol, 1.2 eq.), alkylating reagent 2 (0.2 mmol, 1.0 eq.), 5-norbornene-2-carboxylic acid N₄ (5.5 mg, 0.04 mmol, 0.2 eq.) in dry MeCN (1 mL) was added, then heated to 70 °C and stirred for 5-24 h. The reaction was monitored by TLC, after completion of the reaction, the mixture was cooled to r.t., filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated in vacuo. The residue was directly purified by column chromatography on silica gel or purified by PTLC to give the desired product.

7. Characterization data for compounds 3.

2-(4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)acetaldehyde (3aa)

**Physical state:** colorless oil;

**Yield:** 81%;

R_f = 0.44 (silica gel, PE:EtOAc = 10:1);

^1H NMR (400 MHz, CDCl₃): δ 9.36 (dd, J = 3.5, 2.4 Hz, 1H), 8.32 (d, J = 8.7 Hz, 1H), 7.81 (dd, J = 8.1, 1.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.51 - 7.47 (m, 1H), 7.43 - 7.39 (m, 1H), 7.19 (d, J
= 8.3 Hz, 1H), 3.44 (dd, \( J = 16.0, 2.4 \text{ Hz}, 1H \)), 3.03 – 2.91 (m, 2H), 2.87 (dd, \( J = 16.0, 3.6 \text{ Hz}, 1H \)), 2.05 – 1.94 (m, 1H), 1.93 – 1.85 (m, 3H), 1.80 (s, 3H);

\(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 203.4, 136.4, 136.3, 133.9, 131.6, 129.9, 128.8, 127.7, 125.8, 125.5, 124.4, 54.8, 42.2, 37.1, 32.8, 28.7, 18.8;

\text{HRMS (ESI-TOF)}: \text{calc'd for C}_{17}\text{H}_{18}\text{NaO} \ [\text{M+Na}^+] \ 261.1250, \text{found} \ 261.1254.

3-(4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)propanal (3ab)

\text{Physical state}: \text{light yellow oil};

\text{Yield}: 68%;

\( R_f = 0.40 \) (silica gel, PE:EtOAc = 20:1);

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta \) 9.58 (t, \( J = 1.6 \text{ Hz}, 1H \)), 8.34 (d, \( J = 8.7 \text{ Hz}, 1H \)), 7.79 (dd, \( J = 8.0, 1.7 \text{ Hz}, 1H \)), 7.60 (d, \( J = 8.3 \text{ Hz}, 1H \)), 7.46 – 7.36 (m, 2H), 7.17 (d, \( J = 8.4 \text{ Hz}, 1H \)), 2.98 – 2.87 (m, 2H), 2.78 – 2.71 (m, 1H), 2.31 – 2.22 (m, 1H), 2.13 – 2.06 (m, 1H), 1.95 – 1.81 (m, 4H), 1.73 – 1.67 (m, 4H);

\(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta \) 202.7, 137.2, 136.6, 133.7, 132.4, 129.6, 128.8, 127.2, 125.5, 125.3, 124.3, 40.7, 40.3, 38.0, 34.0, 33.1, 28.6, 19.1;

\text{HRMS (ESI-TOF)}: \text{calc'd for C}_{18}\text{H}_{20}\text{NaO} \ [\text{M+Na}^+] \ 275.1406, \text{found} \ 275.1406.

2-(8-ethyl-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ba)

\text{Physical state}: \text{colorless oil};

\text{Yield}: 73%;

\( R_f = 0.68 \) (silica gel, PE:EtOAc = 20:1);
\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}): δ 9.52 (t, \(J = 3.0\) Hz, 1H), 7.12 – 7.06 (m, 2H), 6.96 – 6.93 (m, 1H), 3.08 (dd, \(J = 16.1, 2.7\) Hz, 1H), 2.93 – 2.77 (m, 4H), 2.62 (dd, \(J = 16.1, 3.2\) Hz, 1H), 1.96 – 1.88 (m, 1H), 1.81 – 1.74 (m, 3H), 1.55 (s, 3H), 1.26 (t, \(J = 7.5\) Hz, 3H);
\textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}): δ 203.7, 143.1, 139.5, 137.9, 129.4, 128.0, 126.4, 55.0, 42.0, 37.0, 32.7, 29.0, 27.4, 19.2, 16.7;
\textbf{HRMS} (ESI-TOF): calc’d for C\textsubscript{15}H\textsubscript{20}NaO [M+Na\textsuperscript{+}] 239.1406, found 239.1412.

2-(8-isopropyl-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ca)

\textbf{Physical state}: colorless oil;
\textbf{Yield}: 60%;
\(R_f = 0.48\) (silica gel, PE:EtOAc = 20:1);
\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}): δ 9.53 (dd, \(J = 3.3, 2.5\) Hz, 1H), 7.18 (dd, \(J = 7.8, 1.7\) Hz, 1H), 7.12 (t, \(J = 7.5\) Hz, 1H), 6.95 – 6.92 (m, 1H), 3.54 – 3.47 (m, 1H), 3.08 (dd, \(J = 16.2, 2.5\) Hz, 1H), 2.83 (t, \(J = 6.2\) Hz, 2H), 2.64 (dd, \(J = 16.2, 3.3\) Hz, 1H), 1.94 – 1.86 (m, 1H), 1.80 – 1.75 (m, 3H), 1.57 (s, 3H), 1.26 (t, \(J = 6.6\) Hz, 6H);
\textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}): δ 203.8, 148.4, 138.7, 137.8, 128.0, 126.5, 126.2, 55.1, 42.3, 36.8, 32.9, 30.3, 29.1, 25.2, 24.3, 19.2;
\textbf{HRMS} (ESI-TOF): calc’d for C\textsubscript{16}H\textsubscript{22}NaO [M+Na\textsuperscript{+}] 253.1563, found 253.1564.

2-(1-methyl-8-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3da)

\textbf{Physical state}: colorless oil;
\textbf{Yield}: 63%;
\(R_f = 0.55\) (silica gel, PE:EtOAc = 10:1);
**1H NMR** (400 MHz, CDCl₃): δ 9.48 (dd, J = 3.0, 2.1 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.17 – 7.09 (m, 3H), 6.84 (dd, J = 6.8, 2.3 Hz, 1H), 2.97 – 2.93 (m, 2H), 2.51 (dd, J = 16.8, 2.1 Hz, 1H), 2.17 (dd, J = 16.8, 3.0 Hz, 1H), 1.95 – 1.77 (m, 3H), 1.64 – 1.56 (m, 1H), 1.33 (s, 3H);

**13C NMR** (100 MHz, CDCl₃): δ 203.9, 144.8, 142.4, 139.8, 137.7, 130.9, 130.4, 129.8, 129.6, 128.0, 127.4, 127.1, 125.4, 54.8, 40.7, 37.2, 32.0, 30.8, 18.9;


2-(8-fluoro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ea)

![3ea](image)

**Physical state:** light brown oil;

**Yield:** 78%;

**RF** = 0.71 (silica gel, PE:EtOAc = 20:1);

**1H NMR** (400 MHz, CDCl₃): δ 9.57 – 9.56 (m, 1H), 7.11 – 7.06 (m, 1H), 6.90 – 6.1 (m, 2H), 3.13 (ddd, J = 15.6, 2.3, 1.2 Hz, 1H), 2.82 – 2.71 (m, 2H), 2.61 (ddd, J = 15.6, 3.4, 1.4 Hz, 1H), 1.91 – 1.85 (m, 1H), 1.81 – 1.71 (m, 3H), 1.47 (d, J = 1.1 Hz, 3H);

**13C NMR** (100 MHz, CDCl₃): δ 203.3, 161.9 (d, J = 246.1 Hz), 140.1 (d, J = 4.9 Hz), 129.2 (d, J = 11.7 Hz), 127.4 (d, J = 9.9 Hz), 125.5 (d, J = 2.7 Hz), 113.9 (d, J = 24.5 Hz), 54.3 (d, J = 6.2 Hz), 38.7, 35.4 (d, J = 1.9 Hz), 30.9 (d, J = 2.7 Hz), 28.2 (d, J = 3.7 Hz), 19.4;

**19F NMR** (376 MHz, CDCl₃) δ –110.3;

**HRMS** (ESI-TOF): calc’d for C₁₃H₁₅FNaO [M+Na⁺] 229.0999, found 229.1006.

2-(8-chloro-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3fa)

![3fa](image)

**Physical state:** colorless oil;

**Yield:** 64%;

**RF** = 0.45 (silica gel, PE:EtOAc = 20:1);
\[ \text{H NMR (400 MHz, CDCl} \text{3): } \delta \text{ 9.51 (dd, } J = 3.2, 2.2 \text{ Hz, 1H), 7.20 – 7.17 (m, 1H), 7.06 – 6.99 (m, 2H), 3.65 (dd, } J = 16.2, 2.2 \text{ Hz, 1H), 2.84 – 2.80 (m, 2H), 2.65 (dd, } J = 16.2, 3.2 \text{ Hz, 1H), 1.97 – 1.88 (m, 1H), 1.80 – 1.71 (m, 3H), 1.58 (s, 3H); } \]

\[ \text{C NMR (100 MHz, CDCl} \text{3): } \delta \text{ 203.1, 140.7, 138.7, 133.8, 130.0, 129.1, 127.2, 53.3, 40.9, 37.2, 32.4, 26.9, 19.1; } \]

\[ \text{HRMS (ESI-TOF): calc'd for C}_{13}\text{H}_{15}\text{ClNaO} [M+Na}^{+}] \text{ 245.0704, found 245.0710.} \]

2-(8-(benzyloxy)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ga)

\begin{center}
\text{Physical state: colorless oil;}
\text{Yield: 71%;}
\text{R}_f = 0.55 \text{ (silica gel, PE:EtoAc = 10:1);}
\end{center}

\[ \text{H NMR (400 MHz, CDCl} \text{3): } \delta \text{ 9.47 (dd, } J = 3.6, 2.3 \text{ Hz, 1H), 7.45 – 7.35 (m, 5H), 7.09 (t, } J = 7.9 \text{ Hz, 1H), 6.79 – 6.74 (m, 2H), 5.07 (s, 2H), 3.34 (dd, } J = 15.5, 2.4 \text{ Hz, 1H), 2.78 (t, } J = 6.1 \text{ Hz, 2H), 2.46 (dd, } J = 15.5, 3.6 \text{ Hz, 1H), 1.85 – 1.68 (m, 4H), 1.47 (s, 3H); } \]

\[ \text{C NMR (100 MHz, CDCl} \text{3): } \delta \text{ 204.7, 157.4, 139.6, 137.4, 130.0, 128.8, 128.2, 127.8, 127.0, 122.8, 109.9, 70.4, 54.1, 40.4, 35.9, 31.7, 27.4, 19.4; } \]

\[ \text{HRMS (ESI-TOF): calc'd for C}_{20}\text{H}_{22}\text{NaO}_2 [M+Na}^{+}] \text{ 317.1512, found 317.1514.} \]

2-(1,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ha)

\begin{center}
\text{Physical state: light brown oil;}
\text{Yield: 65%;}
\text{R}_f = 0.49 \text{ (silica gel, PE:EtoAc = 10:1);}
\end{center}
**1H NMR** (400 MHz, CDCl₃): δ 9.50 (t, J = 3.0 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.96 – 6.94 (m, 2H), 3.15 (dd, J = 16.2, 3.2 Hz, 1H), 2.85 – 2.82 (m, 2H), 2.53 (dd, J = 16.2, 2.8 Hz, 1H), 2.49 (s, 3H), 2.04 – 1.94 (m, 1H), 1.86 – 1.76 (m, 3H), 1.50 (s, 3H);  
**13C NMR** (100 MHz, CDCl₃): δ 203.4, 140.0, 138.0, 136.3, 131.2, 128.4, 126.3, 54.1, 41.7, 37.0, 32.3, 27.9, 23.8, 19.3; 

**Physical state:** light yellow oil;  
**Yield:** 75%;  
**Rf** = 0.45 (silica gel, PE:EtOAc = 20:1);

**1H NMR** (400 MHz, CDCl₃): δ 9.74 (t, J = 1.6 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.94 – 6.92 (m, 2H), 2.80 – 2.77 (m, 2H), 2.49 – 2.32 (m, 2H), 2.45 (s, 3H), 2.15 – 2.07 (m, 1H), 1.82 – 1.72 (m, 4H), 1.57 – 1.53 (m, 1H), 1.41 (s, 3H);  
**13C NMR** (100 MHz, CDCl₃): δ 202.8, 140.8, 138.5, 136.8, 130.9, 128.3, 125.8, 40.3, 39.8, 38.0, 32.6 (2C), 27.8, 23.5, 19.4; 

**Physical state:** colorless oil;  
**Yield:** 51%;  
**Rf** = 0.72 (silica gel, PE:EtOAc = 10:1);
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.45 (dd, $J = 3.6$, 2.1 Hz, 1H), 7.30 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H), 7.04 (dd, $J = 7.3$, 1.5 Hz, 1H), 4.93 (d, $J = 12.2$ Hz, 1H), 4.77 (d, $J = 12.2$ Hz, 1H), 3.17 (dd, $J = 16.1$, 2.1 Hz, 1H), 2.84 (t, $J = 6.4$ Hz, 2H), 2.51 (dd, $J = 16.2$, 3.5 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.85 – 1.76 (m, 2H), 1.75 – 1.69 (m, 1H), 1.49 (s, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.0, 139.5, 139.3, 137.8, 129.9, 129.3, 126.4, 64.4, 55.4, 41.5, 36.9, 32.2, 29.3, 26.1, 19.1, 18.5, -4.9, -5.0;

HRMS (ESI-TOF): calc’d for C$_{20}$H$_{32}$NaO$_2$Si [M+Na$^+$] 355.2064, found 355.2060.

2-(7-fluoro-1,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ja)

**Physical state:** light brown oil;

**Yield:** 72%;

$R_f = 0.55$ (silica gel, PE:EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.49 (t, $J = 2.9$ Hz, 1H), 6.93 – 6.89 (m, 1H), 6.85 – 6.80 (m, 1H), 3.15 (dd, $J = 16.3$, 3.1 Hz, 1H), 2.78 (t, $J = 6.0$ Hz, 2H), 2.56 (dd, $J = 16.3$, 2.8 Hz, 1H), 2.36 (d, $J = 3.2$ Hz, 3H), 1.98 – 1.89 (m, 1H), 1.82 – 1.72 (m, 3H), 1.50 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.8, 160.6 (d, $J = 240.3$ Hz), 141.8 (d, $J = 1.9$ Hz), 133.2 (d, $J = 3.4$ Hz), 128.7 (d, $J = 9.1$ Hz), 123.1 (d, $J = 14.6$ Hz), 113.2 (d, $J = 24.5$ Hz), 54.1, 41.5, 37.3 (d, $J = 2.1$ Hz), 31.8, 27.9, 19.3, 13.8 (d, $J = 9.6$ Hz);

$^9$F NMR (377 MHz, CDCl$_3$) $\delta$ –115.5;

HRMS (ESI-TOF): calc’d for C$_{14}$H$_{17}$FNaO [M+Na$^+$] 243.1156, found 243.1160.

2-(6-fluoro-1,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ka)

**Physical state:** colorless oil;
Yield: 70%;

\( R_f = 0.35 \) (silica gel, PE:EtOAc = 10:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 9.49 \) (t, \( J = 3.0 \) Hz, 1H), 6.68 – 6.64 (m, 2H), 3.12 (dd, \( J = 16.3, 3.3 \) Hz, 1H), 2.83 – 2.79 (m, 2H), 2.51 (dd, \( J = 16.3, 2.7 \) Hz, 1H), 2.47 (s, 3H), 2.00 – 1.95 (m, 1H), 1.83 – 1.73 (m, 3H), 1.46 (s, 3H);

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 203.0, 160.4 \) (d, \( J = 244.9 \) Hz), 140.4 (d, \( J = 7.3 \) Hz), 138.8 (d, \( J = 7.5 \) Hz), 135.7 (d, \( J = 3.1 \) Hz), 117.6 (d, \( J = 20.4 \) Hz), 114.1 (d, \( J = 19.3 \) Hz), 54.1, 41.6, 36.6, 32.6 (d, \( J = 1.6 \) Hz), 28.0, 23.8 (d, \( J = 1.5 \) Hz), 19.0;

\(^19\)F NMR (376 MHz, CDCl\(_3\)) \( \delta -118.8 \).

HRMS (ESI-TOF): calc’d for C\(_{14}\)H\(_{17}\)FNaO \([M+Na]^+\) 243.1156, found 243.1161.

2-(6-bromo-1,8-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3la)

Physical state: light brown oil;

Yield: 59%;

\( R_f = 0.66 \) (silica gel, PE:EtOAc = 5:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta 9.50 \) (t, \( J = 2.9 \) Hz, 1H), 7.09 (s, 1H), 3.11 (d, \( J = 16.3, 3.2 \) Hz, 1H), 2.82 – 2.79 (m, 2H), 2.52 (dd, \( J = 16.3, 2.6 \) Hz, 1H), 2.45 (s, 3H), 2.02 – 1.92 (m, 1H), 1.82 – 1.72 (m, 3H), 1.46 (s, 3H);

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 202.7, 140.3, 139.1, 138.6, 133.6, 130.9, 119.9, 53.9, 41.3, 36.8, 32.2, 27.8, 23.5, 19.0 \);

HRMS (ESI-TOF): calc’d for C\(_{14}\)H\(_{17}\)BrNaO \([M+Na]^+\) 303.0355, found 303.0354.

2-(1,8-dimethyl-6-nitro-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ma)

Physical state: colorless oil;
Yield: 85%;

$R_f = 0.49$ (silica gel, PE:EtOAc = 5:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.53 (t, $J = 2.6$ Hz, 1H), 7.80 – 7.77 (m, 2H), 3.22 (dd, $J = 16.8$, 2.9 Hz, 1H), 2.93 (t, $J = 6.4$ Hz, 2H), 2.62 (dd, $J = 16.8$, 2.2 Hz, 1H), 2.57 (s, 3H), 2.07 – 2.02 (m, 1H), 1.87 – 1.76 (m, 3H), 1.49 (s, 3H);  

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.3, 148.0, 145.5, 139.9, 138.2, 125.2, 122.8, 53.9, 41.0, 37.4, 32.5, 27.5, 24.0, 18.8;  

HRMS (ESI-TOF): calc’d for C$_{14}$H$_{17}$NNaO$_3$ [M+Na$^+$] 270.1101, found 270.1105.

methyl 4,5-dimethyl-5-(2-oxoethyl)-5,6,7,8-tetrahydroanaphthalene-2-carboxylate (3na)

Physical state: colorless oil;  
Yield: 83%;  

$R_f = 0.61$ (silica gel, PE:EtOAc = 5:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.48 (t, $J = 2.8$ Hz, 1H), 7.61 – 7.59 (m, 2H), 3.88 (s, 3H), 3.17 (dd, $J = 16.4$, 3.0 Hz, 1H), 2.88 (t, $J = 6.3$ Hz, 2H), 2.58 – 2.53 (m, 4H), 2.05 – 1.95 (m, 1H), 1.85 – 1.74 (m, 3H), 1.49 (s, 3H);  

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.4, 167.2, 145.4, 138.4, 136.6, 131.9, 129.4, 127.7, 53.9, 52.1, 41.4, 37.3, 32.3, 27.7, 23.8, 19.1;  

HRMS (ESI-TOF): calc’d for C$_{16}$H$_{20}$NaO$_3$ [M+Na$^+$] 283.1305, found 283.1306.

tert-butyl (4-chloro-5-methyl-5-(2-oxoethyl)-5,6,7,8-tetrahydroanaphthalen-2-yl)carbamate (3oa)

Physical state: colorless oil;  
Yield: 61%;
$R_f = 0.23$ (silica gel, PE:EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.50 (dd, $J = 3.3, 2.2$ Hz, 1H), 7.05 (s, 1H), 6.40 (s, 1H), 3.60 (dd, $J = 16.1, 2.2$ Hz, 1H), 2.77 (t, $J = 6.4$ Hz, 2H), 2.59 (dd, $J = 16.1, 3.3$ Hz, 1H), 1.93 – 1.84 (m, 1H), 1.78 – 1.68 (m, 3H), 1.54 (s, 3H), 1.50 (s, 9H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.3, 152.6, 141.2, 137.0, 134.1, 133.1, 119.8, 118.3, 53.4, 40.9, 36.8, 32.7, 28.4, 28.1, 27.1, 19.2;

HRMS (ESI-TOF): calc’d for C$_{18}$H$_{24}$ClINaO$_3$ [M+Na$^+$] 360.1337, found 360.1335.

2-(9-bromo-4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)acetaldehyde (3pa)

Physical state: light yellow solid;
Melting point: 94–96 ºC
Yield: 60%;

$R_f = 0.30$ (silica gel, PE:EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.37 (dd, $J = 3.4, 2.4$ Hz, 1H), 8.33 – 8.27 (m, 2H), 7.56 – 7.49 (m, 3H), 3.40 (dd, $J = 16.1, 2.5$ Hz, 1H), 3.01 – 2.91 (m, 2H), 2.87 (dd, $J = 16.1, 3.4$ Hz, 1H), 2.05 – 1.98 (m, 1H), 1.92 – 1.84 (m, 3H), 1.78 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 202.7, 137.2, 136.7, 133.1, 132.6, 131.9, 128.9, 126.3, 126.0, 125.8, 122.3, 54.8, 42.1, 37.0, 32.5, 28.8, 18.6;

HRMS (ESI-TOF): calc’d for C$_{17}$H$_{17}$BrNaO [M+Na$^+$] 339.0355, found 339.0359.

2-(9-methyl-2,3,6,7,8,9-hexahydro-1H-cyclopenta[a]naphthalen-9-yl)acetaldehyde (3qa)

Physical state: colorless oil;
Yield: 58%;

$R_f = 0.73$ (silica gel, PE:EtOAc = 10:1);
**1H NMR** (400 MHz, CDCl₃): δ 9.51 (t, J = 3.0 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 3.13 – 3.03 (m, 2H), 2.96 – 2.89 (m, 1H), 2.83 – 2.79 (m, 4H), 2.52 (dd, J = 15.9, 2.9 Hz, 1H), 2.12 – 1.91 (m, 3H), 1.85 – 1.74 (m, 3H), 1.45 (s, 3H);

**13C NMR** (100 MHz, CDCl₃): δ 203.7, 143.7, 141.5, 138.3, 135.1, 128.5, 122.8, 53.9, 40.0, 36.8, 35.2, 32.4, 31.5, 27.9, 26.2, 19.6;


2-(4-methyl-1,2,3,4,5,6,7,8-octahydrophenanthren-4-yl)acetaldehyde (3ra)

[Diagram of 3ra]

**Physical state**: colorless oil;

**Yield**: 53%;

R<sub>f</sub> = 0.55 (silica gel, PE:EtOAc = 20:1);

**1H NMR** (400 MHz, CDCl₃): δ 9.49 (t, J = 3.0 Hz, 1H), 6.90 (s, 2H), 3.16 (dd, J = 16.3, 3.1 Hz, 1H), 2.96 (dt, J = 14.6, 5.0 Hz, 1H), 2.83 – 2.65 (m, 5H), 2.55 (dd, J = 16.4, 2.8 Hz, 1H), 1.98 – 1.93 (m, 1H), 1.87 – 1.68 (m, 7H), 1.53 (s, 3H);

**13C NMR** (100 MHz, CDCl₃): δ 203.7, 139.3, 137.3, 137.1, 135.2, 127.9, 127.6, 54.6, 42.5, 36.9, 32.3, 30.1, 29.2, 28.3, 22.8, 21.9, 19.3;


2-(5-chloro-6-methyl-1,2,6,7,8,9-hexahydrospiro[cyclopenta[a]naphthalene-3,2’-[1,3]dioxolan]-6-yl)acetaldehyde (3sa)

[Diagram of 3sa]

**Physical state**: colorless oil;

**Yield**: 75%;

R<sub>f</sub> = 0.35 (silica gel, PE:EtOAc = 10:1);
\textbf{\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}):} \(\delta\) 9.48 (dd, \(J = 3.4, 2.2\) Hz, 1H), 7.21 (s, 1H), 4.20 – 4.14 (m, 2H), 4.12 – 4.04 (m, 2H), 3.63 (dd, \(J = 16.1, 2.3\) Hz, 1H), 2.82 – 2.54 (m, 5H), 2.31 – 2.28 (m, 2H), 1.94 – 1.87 (m, 1H), 1.81 – 1.70 (m, 3H), 1.57 (s, 3H);

\textbf{\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}):} \(\delta\) 203.2, 141.8, 140.9, 139.5, 137.0, 132.7, 124.3, 116.9, 65.5, 65.3, 53.1, 40.6, 37.3, 36.9, 28.7, 27.4, 26.8, 18.5;

\textbf{HRMS (ESI-TOF):} calc’d for \(C_{18}H_{21}ClNaO_3\) [M+Na\(^+\)] 343.1071, found 343.1073.

2-(7-(benzyloxy)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ta)

According to the typical procedure, (\textit{E})-6-iodo-3-methylhex-2-en-1-ol (2a\(^{**}\)) was used instead of (\textit{E})-6-bromo-3-methylhex-2-en-1-ol (2a), and [Pd(C\textsubscript{3}H\textsubscript{5})Cl\textsubscript{2} (7.4 mg, 0.02 mmol), XPhos (21 mg, 0.044 mmol) were used.

\textbf{Physical state:} colorless oil; 
\textbf{Yield:} 53%;

\(R_f = 0.51\) (silica gel, PE:EtOAc = 10:1);

\textbf{\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}):} \(\delta\) 9.54 (dd, \(J = 3.6, 2.4\) Hz, 1H), 7.45 – 7.37 (m, 4H), 7.34 – 7.30 (m, 1H), 7.01 (d, \(J = 8.4\) Hz, 1H), 6.89 (d, \(J = 2.6\) Hz, 1H), 6.77 (dd, \(J = 8.4, 2.6\) Hz, 1H), 5.03 (s, 2H), 2.77 (dd, \(J = 15.2, 2.5\) Hz, 1H), 2.72 (t, \(J = 6.1\) Hz, 2H), 2.53 (dd, \(J = 15.2, 3.5\) Hz, 1H), 1.88 – 1.71 (m, 3H), 1.75 – 1.70 (m, 1H), 1.38 (s, 3H);

\textbf{\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}):} \(\delta\) 203.5, 157.2, 143.7, 137.2, 130.5, 129.2, 128.7, 128.1, 127.7, 113.4, 112.7, 70.3, 56.2, 36.8, 36.6, 30.8, 29.6, 19.6;

\textbf{HRMS (ESI-TOF):} calc’d for \(C_{20}H_{22}NaO_2\) [M+Na\(^+\)] 317.1512, found 317.1503.

2-(7-((tert-butyldiphenylsilyl)oxy)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetaldehyde (3ua)
According to the typical procedure, \((E)-6\)-iodo-3-methylhex-2-en-1-ol \((2a'')\) was used instead of \((E)-6\)-bromo-3-methylhex-2-en-1-ol \((2a)\).

**Physical state:** colorless oil;

**Yield:** 48%;

\(R_f = 0.59\) (silica gel, PE:EtOAc = 10:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.16 (dd, \(J = 4.0, 2.0\) Hz, 1H), 7.71 (td, \(J = 8.1, 1.5\) Hz, 4H), 7.45 – 7.33 (m, 6H), 6.86 (d, \(J = 8.1\) Hz, 1H), 6.67 (dd, \(J = 8.3, 2.5\) Hz, 1H), 6.52 (d, \(J = 2.5\) Hz, 1H), 2.66 – 2.56 (m, 2H), 2.32 (dd, \(J = 15.0, 2.1\) Hz, 1H), 2.15 (dd, \(J = 15.1, 4.0\) Hz, 1H), 1.74 – 1.63 (m, 3H), 1.61 – 1.55 (m, 1H), 1.12 (s, 9H), 1.07 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.7, 153.9, 142.9, 135.6, 133.2, 133.1, 130.3, 130.1, 130.0, 129.1, 127.9, 118.1, 117.6, 56.1, 36.6, 36.2, 30.6, 29.6, 26.7, 19.6, 19.6;

**HRMS (ESI-TOF):** calc’d for C\(_{29}\)H\(_{34}\)NaO\(_2\)Si [M+Na\(^+\)] 465.2220, found 465.2215.

2-(1-methoxy-8-methyl-5,6,7,8-tetrahydroisoquinolin-8-yl)acetaldehyde (3va)

**Physical state:** colorless oil;

**Yield:** 62%;

\(R_f = 0.26\) (silica gel, PE:EtOAc = 10:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.52 (dd, \(J = 3.6, 2.1\) Hz, 1H), 7.87 (d, \(J = 5.1\) Hz, 1H), 6.62 (d, \(J = 5.2\) Hz, 1H), 3.93 (s, 3H), 3.22 (dd, \(J = 15.5, 2.2\) Hz, 1H), 2.69 (t, \(J = 6.2\) Hz, 2H), 2.56 (dd, \(J = 15.6, 3.6\) Hz, 1H), 1.88 – 1.82 (m, 1H), 1.79 – 1.69 (m, 3H), 1.42 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.6, 161.9, 149.0, 143.5, 124.4, 118.8, 53.6, 53.1, 39.2, 34.8, 30.8, 26.6, 18.7;

**HRMS (ESI-TOF):** calc’d for C\(_{13}\)H\(_{17}\)NNaO\(_2\) [M+Na\(^+\)] 242.1151, found 242.1151.
2-(1-methyl-1,2,3,4-tetrahydrophenanthridin-1-yl)acetaldehyde (3wa)

Physical state: colorless oil;
Yield: 65%;
$R_f = 0.19$ (silica gel, PE:EtOAc = 3:1);
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.43 (dd, $J = 3.2$, 2.5 Hz, 1H), 9.05 (s, 1H), 8.24 (dd, $J = 8.9$, 1.1 Hz, 1H), 7.94 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.52 (t, $J = 7.5$ Hz, 1H), 3.32 (dd, $J = 16.0$, 2.5 Hz, 1H), 3.16 – 3.13 (m, 2H), 2.92 (dd, $J = 16.1$, 3.3 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.98 – 1.88 (m, 3H), 1.76 (s, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 202.4, 151.7, 151.6, 134.5, 130.0, 129.6 (2C), 128.4, 125.7, 124.7, 54.4, 41.1, 37.0, 34.9, 28.4, 18.7;
HRMS (ESI-TOF): calc’d for C$_{16}$H$_{18}$NO [M+H$^+$] 240.1383, found 240.1386.

methyl 1,3-bis(benzyloxy)-8-methyl-8-(2-oxoethyl)-5,6,7,8-tetrahydronaphthalene-2-carboxylate (3xa)

Physical state: light yellow solid;
Melting point: 120–122 ºC
Yield: 88%;
$R_f = 0.65$ (silica gel, PE:EtOAc = 5:1);
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.49 (dd, $J = 3.5$, 2.3 Hz, 1H), 7.43 – 7.29 (m, 10H), 6.48 (s, 1H), 5.10 – 5.13 (m, 4H), 3.75 (s, 3H), 3.18 (dd, $J = 15.5$, 2.3 Hz, 1H), 2.74 (t, $J = 6.0$ Hz, 2H), 2.46 (dd, $J = 15.5$, 3.5 Hz, 1H), 1.82 – 1.70 (m, 3H), 1.68 – 1.61 (m, 1H), 1.40 (s, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.4, 167.6, 156.3, 154.7, 141.8, 136.8, 128.7, 128.6, 128.2, 127.9, 127.6, 127.4, 127.0, 115.8, 108.6, 75.7, 70.5, 54.4, 52.6, 40.1, 35.8, 32.4, 28.7, 19.1;
HRMS (ESI-TOF): calc’d for C$_{29}$H$_{30}$NaO$_5$ [M+Na$^+$] 481.1985, found 481.1990.
methyl-1,3-bis(benzyloxy)-8-methyl-8-(3-oxopropyl)-5,6,7,8-tetrahydronaphthalene-2-carboxylate (3xb)

Physical state: light yellow oil;  
Yield: 61%;  
$R_f = 0.60$ (silica gel, PE:EtOAc = 4:1);  
$^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 9.59 (t, $J = 2.0$ Hz, 1H), 7.42 – 7.31 (m, 10H), 6.46 (s, 1H), 5.07 (s, 2H), 5.04 (s, 2H), 3.73 (s, 3H), 2.71 (t, $J = 5.7$ Hz, 2H), 2.41 – 2.33 (m, 1H), 2.21 – 2.15 (m, 2H), 1.78 – 1.61 (m, 4H), 1.51 – 1.45 (m, 1H), 1.33 (s, 3H);  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 203.3, 167.7, 156.6, 154.4, 142.1, 137.1, 136.9, 128.6, 128.5, 128.1, 127.9, 127.5, 127.0, 115.8, 108.5, 75.8, 70.5, 52.6, 40.4, 38.5, 36.9, 32.9, 32.6, 28.4, 19.2;  
HRMS (ESI-TOF): calc’d for C$_{30}$H$_{32}$NaO$_5$ [M+Na$^+$] 495.2142, found 495.2147.

2-(5-(benzyloxy)-2,2,6-trimethyl-4-oxo-6,7,8,9-tetrahydro-4$H$-naphtho[2,3-][1,3]dioxin-6-yl)acetaldehyde (3ya)

Physical state: colorless oil;  
Yield: 76%;  
$R_f = 0.49$ (silica gel, PE:EtOAc = 4:1);  
$^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 9.47 (dd, $J = 3.1$, 2.1 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.42 – 7.33 (m, 3H), 6.49 (t, $J = 1.0$ Hz, 1H), 5.16 (d, $J = 10.2$ Hz, 1H), 5.02 (d, $J = 10.2$ Hz, 1H), 3.27 (dd, $J = 15.9$, 2.2 Hz, 1H), 2.77 (t, $J = 6.2$ Hz, 2H), 2.50 (dd, $J = 15.9$, 3.1 Hz, 1H), 1.82 – 1.70 (m, 8H), 1.66 – 1.60 (m, 2H), 1.41 (s, 3H);  
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 203.6, 160.7, 158.9, 155.1, 149.0, 136.4, 129.9, 128.7 (2C), 128.5,
112.4, 105.3, 105.1, 54.3, 39.7, 35.9, 32.7, 28.3, 26.1, 25.2, 18.8;

**HRMS (ESI-TOF):** calc’d for C_{24}H_{26}NaO_{5} [M+Na^+] 417.1672, found 417.1670.

2-(1-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-yl)acetaldehyde (3ac)

![Structure of 3ac](image.png)

**Physical state:** light yellow oil;

**Yield:** 56%;

$R_f$ = 0.45 (silica gel, PE:EtOAc = 20:1);

$^1$H NMR (600 MHz, CDCl$_3$): δ 9.60 (t, $J = 3.0$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 3.10 – 3.02 (m, 3H), 2.95 (dd, $J = 15.1$, 3.5 Hz, 1H), 2.39 – 2.19 (m, 1H), 1.70 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.3, 142.1, 141.2, 133.9, 129.8, 129.7, 128.7, 126.2, 124.7, 123.7, 123.2, 53.9, 48.0, 40.1, 30.9, 27.8;

**HRMS (ESI-TOF):** calc’d for C$_{16}$H$_{16}$NaO [M+Na^+] 247.1093, found 247.1096.

3-(1-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-yl)propanal (3ad)

![Structure of 3ad](image.png)

**Physical state:** colorless oil;

**Yield:** 60%;

$R_f$ = 0.46 (silica gel, PE:EtOAc = 20:1);

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.64 (t, $J = 1.4$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.48 – 7.39 (m, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 3.10 – 2.96 (m, 2H), 2.48 – 2.41 (m, 2H), 2.27 – 2.13 (m, 3H), 2.05 – 1.98 (m, 1H), 1.61 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 202.7, 142.4, 141.6, 133.7, 130.3, 129.5, 128.3, 126.0, 124.6, 123.7, 123.2, 49.4, 40.6, 39.3, 33.2, 31.1, 28.1;
**HRMS** (ESI-TOF): calc’d for C_{17}H_{18}NaO [M+Na^+] 261.1250, found 261.1256.

2-(1,7-dimethyl-2,3-dihydro-1H-inden-1-yl)acetaldehyde (3bc)

![Chemical structure of 3bc](image)

**Physical state:** light yellow oil;

**Yield:** 46%;

\( R_f = 0.50 \) (silica gel, PE:EtOAc = 20:1);

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta 9.67 \) (t, \( J = 3.0 \) Hz, 1H), 7.11 – 7.05 (m, 2H), 6.95 (d, \( J = 7.0 \) Hz, 1H), 2.97 – 2.83 (m, 2H), 2.82 – 2.71 (m, 2H), 2.39 (s, 3H), 2.24 – 2.17 (m, 1H), 2.03 – 1.96 (m, 1H), 1.46 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta 203.3, 146.0, 143.5, 133.5, 129.7, 127.4, 122.9, 52.9, 47.2, 39.8, 30.2, 26.2, 19.7; \)

**HRMS** (ESI-TOF): calc’d for C_{13}H_{16}NaO [M+Na^+] 211.1093, found 211.1098.

2-(7-ethyl-1-methyl-2,3-dihydro-1H-inden-1-yl)acetaldehyde (3cc)

![Chemical structure of 3cc](image)

**Physical state:** light yellow oil;

**Yield:** 50%;

\( R_f = 0.45 \) (silica gel, PE:EtOAc = 20:1);

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta 9.67 \) (t, \( J = 3.0 \) Hz, 1H), 7.18 – 7.04 (m, 1H), 7.07 – 7.04 (m, 2H), 2.97 – 2.84 (m, 2H), 2.82 – 2.68 (m, 4H), 2.23 – 2.17 (m, 1H), 2.04 – 1.96 (m, 1H), 1.50 (s, 3H), 1.27 (t, \( J = 7.5 \) Hz, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta 203.3, 145.5, 143.6, 140.1, 127.6, 127.5, 122.6, 53.7, 47.3, 40.0, 30.2, 27.2, 25.0, 15.6; \)

**HRMS** (ESI-TOF): calc’d for C_{14}H_{18}NaO [M+Na^+] 225.1250, found 225.1252.
2-(7-fluoro-1-methyl-2,3-dihydro-1H-inden-1-yl)acetaldehyde (3dc)

**Physical state:** light yellow oil;
**Yield:** 41%;
**$R_f = 0.40$** (silica gel, PE:EtOAc = 20:1);

**$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 9.71 (t, $J = 3.0$ Hz, 1H), 7.18 – 7.13 (m, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.84 (t, $J = 9.5$ Hz, 1H), 3.04 – 2.89 (m, 2H), 2.86 – 2.78 (m, 2H), 2.21 – 2.13 (m, 1H), 2.08 – 2.00 (m, 1H), 1.47 (s, 3H);

**$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 202.8, 159.7 (d, $J = 245.2$ Hz), 146.4 (d, $J = 6.1$ Hz), 134.6 (d, $J = 14.6$ Hz), 129.3 (d, $J = 7.6$ Hz), 120.8 (d, $J = 3.3$ Hz), 113.9 (d, $J = 21.2$ Hz), 53.3 (d, $J = 2.1$ Hz), 46.1 (d, $J = 2.4$ Hz), 39.3, 31.0 (d, $J = 1.6$ Hz), 26.5 (d, $J = 1.7$ Hz);

**$^{19}$F NMR** (376 MHz, CDCl$_3$): $\delta$ –121.1;

**HRMS** (ESI-TOF): calc’d for C$_{12}$H$_{13}$FNaO [M+Na$^+$] 215.0843, found 215.0854.

2-(7-chloro-1-methyl-2,3-dihydro-1H-inden-1-yl)acetaldehyde (3ec)

**Physical state:** light yellow oil;
**Yield:** 42%;
**$R_f = 0.45$** (silica gel, PE:EtOAc = 20:1);

**$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 9.66 (dd, $J = 3.3$, 2.1 Hz, 1H), 7.15 – 7.10 (m, 3H), 3.09 (dd, $J = 15.6$, 2.1 Hz, 1H), 3.00 – 2.89 (m, 2H), 2.85 (dd, $J = 15.6$, 3.3 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.05 – 1.98 (m, 1H), 1.49 (s, 3H);

**$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 202.8, 146.0, 144.5, 130.5, 128.8, 128.5, 123.7, 52.4, 47.7, 39.2, 30.4, 25.8;

**HRMS** (ESI-TOF): calc’d for C$_{12}$H$_{13}$ClNaO [M+Na$^+$] 231.0547, found 231.0555.
2-(7-methoxy-1-methyl-2,3-dihydro-1H-inden-1-yl)acetaldehyde (3fc)

Physical state: colorless oil;
Yield: 45%;

$R_f = 0.40$ (silica gel, PE:EtOAc = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.65 (dd, $J = 3.8, 2.2$ Hz, 1H), 7.18 – 7.13 (m, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.69 (d, $J = 8.1$ Hz, 1H), 3.81 (s, 3H), 2.99 – 2.83 (m, 3H), 2.75 (dd, $J = 15.0, 3.8$ Hz, 1H), 2.13 – 2.06 (m, 1H), 2.01 – 1.94 (m, 1H), 1.43 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.4, 156.4, 145.1, 135.3, 128.8, 117.5, 108.8, 55.1, 53.1, 46.4, 39.6, 30.6, 26.0;

HRMS (ESI-TOF): calc’d for C$_{13}$H$_{16}$NaO $[M+Na^+]$ 227.1043, found 227.1049.

methyl 4,6-bis(benzyloxy)-3-methyl-3-(2-oxoethyl)-2,3-dihydro-1H-indene-5-carboxylate (3gc)

Physical state: colorless oil;
Yield: 55%;

$R_f = 0.60$ (silica gel, PE:EtOAc = 4:1);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.61 (dd, $J = 3.4, 2.2$ Hz, 1H), 7.44 – 7.33 (m, 10H), 6.62 (s, 1H), 5.10 – 5.04 (m, 4H), 3.82 (s, 3H), 2.96 – 2.81 (m, 2H), 2.79 – 2.65 (m, 2H), 2.13 – 2.05 (m, 1H), 1.99 – 1.93 (m, 1H), 1.39 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 203.6, 167.7, 156.9, 153.4, 147.6, 136.8 (2C), 132.7, 128.7, 128.6, 128.3, 127.9, 127.8, 126.9, 116.0, 104.8, 76.1, 70.8, 53.3, 52.7, 46.3, 39.4, 31.2, 27.1;

HRMS (ESI-TOF): calc’d for C$_{28}$H$_{28}$NaO$_5$ [M+Na$^+$] 467.1829, found 467.1834.
2-(5-(benzyloxy)-2,2,6-trimethyl-4-oxo-4,6,7,8-tetrahydroindeno[5,6-\textit{d}][1,3]dioxin-6-yl)acetaldehyde (3hc)

**Physical state:** colorless oil;

**Yield:** 44%;

\(R_f = 0.55\) (silica gel, PE:EtOAc = 4:1);

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)):\(\delta\) 9.57 (dd, \(J = 3.0, 2.1\) Hz, 1H), 7.53 – 7.50 (m, 2H), 7.41 – 7.34 (m, 3H), 6.58 (s, 1H), 5.18 (d, \(J = 10.3\) Hz, 1H), 5.02 (d, \(J = 10.4\) Hz, 1H), 2.93 – 2.86 (m, 2H), 2.81 – 2.67 (m, 2H), 2.12 – 2.04 (m, 1H), 1.98 – 1.91 (m, 1H), 1.74 (s, 6H), 1.36 (s, 3H);

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)):\(\delta\) 202.9, 159.0, 157.6, 157.5, 154.6, 136.6, 135.2, 128.9, 128.7, 128.5, 108.7, 105.3, 105.2, 53.2, 46.3, 38.8, 31.4, 26.9, 25.9, 25.4;

**HRMS** (ESI-TOF): calc’d for C\(_{23}\)H\(_{24}\)NaO\(_5\) [M+Na\(^+\)] 403.1516, found 403.1518.

\((E)-4-(2\text{-methoxyvinyl})-4\text{-methyl-1,2,3,4-tetrahydrophanenthrene } ((E)-3A)\)

**Physical state:** colorless oil;

**Yield:** 52%;

\(R_f = 0.70\) (silica gel, PE:EtOAc = 20:1);

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)):\(\delta\) 8.44 – 8.41 (m, 1H), 7.76 – 7.72 (m, 1H), 7.59 (d, \(J = 9.0\) Hz, 1H), 7.39 – 7.32 (m, 2H), 7.17 (d, \(J = 8.4\) Hz, 1H), 6.14 (d, \(J = 13.0\) Hz, 1H), 5.16 (d, \(J = 13.0\) Hz, 1H), 3.47 (s, 3H), 2.92 (t, \(J = 6.2\) Hz, 2H), 1.91 – 1.73 (m, 4H), 1.66 (s, 3H);

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)):\(\delta\) 147.5, 138.0, 135.5, 133.7, 132.1, 128.8, 128.5, 128.1, 127.0, 124.4, 124.2, 115.4, 56.2, 44.2, 38.2, 32.5, 28.8, 18.7;

**HRMS** (ESI-TOF): calc’d for C\(_{18}\)H\(_{20}\)NaO [M+Na\(^+\)] 275.1406, found 275.1411.
(Z)-4-(2-methoxyvinyl)-4-methyl-1,2,3,4-tetrahydrophenanthrene ((Z)-3A)

Physical state: colorless oil;
Yield: 29%;
$R_f = 0.74$ (silica gel, PE:EtOAc = 20:1);
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.49 – 8.46 (m, 1H), 7.77 – 7.74 (m, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.41 – 7.33 (m, 2H), 7.16 (d, $J = 8.3$ Hz, 1H), 5.76 (d, $J = 6.8$ Hz, 1H), 4.81 (d, $J = 6.8$ Hz, 1H), 3.43 (s, 3H), 3.01 – 2.85 (m, 2H), 2.12 – 1.99 (m, 2H), 1.88 – 1.80 (m, 2H), 1.79 (s, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.1, 140.3, 134.2, 133.6, 131.9, 128.9, 128.6, 127.3, 126.4, 124.2, 124.1, 118.8, 59.7, 40.7, 38.7, 32.4, 28.5, 19.3;
HRMS (ESI-TOF): calc’d for C$_{18}$H$_{20}$NaO [M+Na$^+$] 275.1406, found 275.1411.

1-(4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)propan-2-one (3B)

Physical state: light yellow oil;
Yield: 71%;
$R_f = 0.40$ (silica gel, PE:EtOAc = 20:1);
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (d, $J = 8.8$ Hz, 1H), 7.80 (dd, $J = 8.1$, 1.6 Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.41 – 7.37 (m, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 3.45 (d, $J = 15.4$ Hz, 1H), 3.10 (d, $J = 15.4$ Hz, 1H), 3.01 – 2.89 (m, 2H), 2.20 – 2.15 (m, 1H), 1.88 – 1.80 (m, 3H), 1.85 (s, 3H), 1.78 (s, 3H);
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.6, 137.8, 136.1, 133.9, 131.9, 129.8, 128.9, 127.2, 125.8, 125.1, 124.2, 54.4, 40.7, 37.8, 32.9, 32.0, 28.7, 19.0;
HRMS (ESI-TOF): calc’d for C$_{18}$H$_{20}$NaO [M+Na$^+$] 275.1406, found 275.1409.
1-(4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)hexan-2-one (3C)

**Physical state:** brown oil;

**Yield:** 45%;

$R_f = 0.50$ (silica gel, PE:EtOAc = 20:1);

$^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (d, $J = 8.7$ Hz, 1H), 7.79 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.59 (d, $J = 8.3$ Hz, 1H), 7.48 – 7.43 (m, 1H), 7.40 – 7.36 (m, 1H), 7.18 (d, $J = 8.3$ Hz, 1H), 3.39 (d, $J = 15.7$ Hz, 1H), 3.10 (d, $J = 15.7$ Hz, 1H), 3.01 – 2.88 (m, 2H), 2.22 – 2.08 (m, 3H), 1.87 – 1.77 (m, 3H), 1.77 (s, 3H), 1.38 – 1.31 (m, 2H), 1.14 – 1.04 (m, 2H), 0.77 (t, $J = 7.3$ Hz, 3H);

$^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta$ 210.7, 138.0, 136.0, 133.9, 131.8, 129.8, 128.9, 127.1, 125.9, 125.0, 124.1, 53.3, 44.4, 40.7, 37.8, 32.9, 28.6, 25.7, 22.3, 19.0, 13.9;

HRMS (ESI-TOF): calc’d for C$_{21}$H$_{26}$NaO [M+Na$^+$] 317.1876, found 317.1879.

(E)-1-(4-methyl-1,2,3,4-tetrahydrophenanthren-4-yl)pent-3-en-2-one (3D)

**Physical state:** light yellow oil;

**Yield:** 53%;

$R_f = 0.45$ (silica gel, PE:EtOAc = 20:1);

$^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 8.41 (d, $J = 8.4$ Hz, 1H), 7.80 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 1H), 7.49 – 7.44 (m, 1H), 7.40 – 7.36 (m, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 6.76 – 6.67 (m, 1H), 5.98 (dd, $J = 15.5$, 1.7 Hz, 1H), 3.32 (s, 2H), 3.00 – 2.89 (m, 2H), 2.19 – 2.14 (m, 1H), 1.86 – 1.77 (m, 9H);

$^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta$ 199.8, 142.1, 138.5, 135.8, 133.9, 133.1, 131.8, 129.7, 128.8, 127.2, 126.1, 125.0, 124.1, 50.4, 40.6, 38.0, 32.9, 28.5, 18.9, 18.3;
**HRMS (ESI-TOF):** calc’d for C_{20}H_{22}NaO [M+Na^+] 301.1563, found 301.1564.

**2-(4-ethyl-1,2,3,4-tetrahydrophenanthren-4-y)acetaldehyde (3E)**

![Chemical Structure of 3E]

**Physical state:** colorless oil;
**Yield:** 72%;
**R_f = 0.55** (silica gel, PE:EtOAc = 10:1);

**^1H NMR** (400 MHz, CDCl_3) δ 9.42 (dd, J = 3.7, 2.4 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.42 – 7.38 (m, 1H), 7.19 (d, J = 8.3 Hz, 1H), 3.42 (dd, J = 15.7, 2.5 Hz, 1H), 2.96 (t, J = 6.3 Hz, 2H), 2.84 (dd, J = 15.7, 3.7 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.21 – 2.09 (m, 2H), 1.94 – 1.78 (m, 3H), 0.78 (t, J = 7.5 Hz, 3H);

**^13C NMR** (100 MHz, CDCl_3) δ 203.8, 137.2, 135.4, 133.8, 132.0, 129.9, 128.8, 127.7, 125.6, 125.3, 124.4, 53.2, 40.8, 37.5, 32.8, 32.7, 18.8, 8.9;

**HRMS (ESI-TOF):** calc’d for C_{18}H_{20}NaO [M+Na^+] 275.1406, found 275.1414.

**2-(4-phenyl-1,2,3,4-tetrahydrophenanthren-4-y)acetaldehyde (3F)**

![Chemical Structure of 3F]

**Physical state:** colorless oil;
**Yield:** 67%;
**R_f = 0.55** (silica gel, PE:EtOAc = 20:1);

**^1H NMR** (400 MHz, CDCl_3) δ 8.98 (dd, J = 3.8, 1.8 Hz, 1H), 7.78 (dd, J = 8.1, 1.4 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.39 – 7.14 (m, 9H), 3.82 (dd, J = 15.3, 1.8 Hz, 1H), 3.26 (dd, J = 15.3, 3.8 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.25 – 2.18 (m, 1H), 2.14 – 2.09 (m, 1H), 1.80 – 1.71 (m, 2H);

**^13C NMR** (100 MHz, CDCl_3) δ 202.9, 149.3, 138.2, 133.9, 133.4, 131.3, 129.2, 128.6, 128.4, 128.1, 127.0, 126.2, 125.4, 124.6, 53.5, 45.0, 44.0, 32.3, 18.1;

**HRMS (ESI-TOF):** calc’d for C_{22}H_{20}NaO [M+Na^+] 323.1406, found 323.1406.
2-(1,2,3,4-tetrahydrophenanthren-4-yl)acetaldehyde (3G)

![Structure of 2-(1,2,3,4-tetrahydrophenanthren-4-yl)acetaldehyde (3G)](image)

**Physical state:** brown oil;

**Yield:** 81%;

\( R_f = 0.52 \) (silica gel, PE:EtOAc = 10:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.92 (dd, \( J = 2.0, 0.9 \) Hz, 1H), 7.88 (d, \( J = 8.4 \) Hz, 1H), 7.82 (dd, \( J = 8.1, 1.4 \) Hz, 1H), 7.64 (d, \( J = 8.3 \) Hz, 1H), 7.53 – 7.49 (m, 1H), 7.46 – 7.42 (m, 1H), 7.20 (d, \( J = 8.4 \) Hz, 1H), 4.25 – 4.20 (m, 1H), 2.96 – 2.93 (m, 2H), 2.89 – 2.81 (m, 2H), 1.99 – 1.86 (m, 4H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 201.9, 134.5, 133.5, 132.7, 131.3, 129.1, 128.3, 126.7, 126.4, 124.9, 122.4, 49.7, 30.0, 27.4, 27.2, 17.7;


2-(8,9,10,11-tetrahydro-7H-cyclohepta[\(a\)]naphthalen-11-yl)acetaldehyde (3H)

![Structure of 2-(8,9,10,11-tetrahydro-7H-cyclohepta[\(a\)]naphthalen-11-yl)acetaldehyde (3H)](image)

**Physical state:** light yellow oil;

**Yield:** 76%;

\( R_f = 0.55 \) (silica gel, PE:EtOAc = 10:1);

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.80 (dd, \( J = 2.7, 1.3 \) Hz, 1H), 8.18 (d, \( J = 8.7 \) Hz, 1H), 8.18 (dd, \( J = 8.1, 1.4 \) Hz, 1H), 7.64 (d, \( J = 8.3 \) Hz, 1H), 7.52 – 7.48 (m, 1H), 7.44 – 7.40 (m, 1H), 7.25 – 7.22 (m, 1H), 4.71 – 4.65 (m, 1H), 3.20 – 3.07 (m, 2H), 2.90 – 2.80 (m, 2H), 2.06 – 1.96 (m, 2H), 1.90 – 1.77 (m, 3H), 1.56 – 1.53 (m, 1H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 202.1, 139.6, 138.1, 132.9, 131.9, 130.2, 129.0, 127.3, 126.5, 124.8, 123.0, 46.4, 36.3, 32.3, 30.5, 27.6, 25.1;

HRMS (ESI-TOF): calc’d for C\(_{17}\)H\(_{18}\)NaO \([M+Na]^+\) 261.1250, found 261.1255.
2-(1,3,4,5-tetrahydronaphtho[1,2-c]oxepin-1-yl)acetaldehyde (3I)

Physical state: colorless oil;
Yield: 21%;
\( R_f = 0.40 \) (silica gel, PE:EtOAc = 20:1);
\(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.99 (dd, \( J = 2.8, 1.6 \) Hz, 1H), 7.86 – 7.83 (m, 2H), 7.73 (d, \( J = 8.3 \) Hz, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 1H), 7.24 (d, \( J = 8.4 \) Hz, 1H), 6.22 (dd, \( J = 9.7, 2.5 \) Hz, 1H), 4.03 – 3.98 (m, 1H), 3.66 – 3.58 (m, 2H), 3.16 – 3.10 (m, 1H), 2.87 – 2.83 (m, 1H), 2.65 – 2.60 (m, 1H), 2.28 – 2.18 (m, 1H), 1.83 – 1.74 (m, 1H);
\(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 201.3, 136.0, 133.0, 132.5, 130.4, 129.6, 129.2, 128.6, 126.8, 125.1, 122.1, 77.0, 64.4, 49.8, 30.3, 28.5;
HRMS (ESI-TOF): calc’d for C\(_{16}\)H\(_{16}\)NaO\(_2\) [M+Na\(^+\)] 263.1043, found 263.1039.

(E)-3-(2-(3-hydroxypropyl)naphthalen-1-yl)acrylaldehyde (3I')

Physical state: colorless oil;
Yield: 44%;
\( R_f = 0.35 \) (silica gel, PE:EtOAc = 3:1);
\(^1H\) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 9.89 (d, \( J = 7.8 \) Hz, 1H), 8.10 (d, \( J = 16.2 \) Hz, 1H), 8.01 (d, \( J = 8.3 \) Hz, 1H), 7.91 – 7.79 (m, 2H), 7.53 – 7.48 (m, 2H), 7.41 (d, \( J = 8.5 \) Hz, 1H), 6.59 (dd, \( J = 16.3, 7.8 \) Hz, 1H), 3.70 (t, \( J = 6.2 \) Hz, 2H), 2.95 (t, \( J = 7.8 \) Hz, 2H), 1.94 – 1.89 (m, 2H), 1.49 (brs, 1H);
\(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 194.0, 151.0, 138.4, 136.4, 132.4, 131.0, 130.1, 129.9, 128.6, 127.9, 127.1, 125.8, 124.7, 62.0, 34.0, 30.3;
HRMS (ESI-TOF): calc’d for C\(_{16}\)H\(_{16}\)NaO\(_2\) [M+Na\(^+\)] 263.1043, found 263.1046.
8. Experimental procedure for gram-scale synthesis of compound 3xa.

To a 100 mL of oven-dried round-bottom flask equipped with a magnetic stir bar was charged with \([\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2\) (73.2 mg, 0.2 mmol, 0.05 eq.), XPhos (208.9 mg, 0.44 mmol, 0.11 eq.), \(\text{K}_2\text{CO}_3\) (1382 mg, 10 mmol, 2.5 eq.), and dry MeCN (20 mL). After stirring for about 15 min at r.t. in an argon-filled glovebox, a solution of aryl iodide 1x (1.99 g, 4.2 mmol, 1.05 eq.), allyl alcohol 2a (772.4 mg, 4.0 mmol, 1.0 eq.), 5-Norbornene-2-carboxylic acid \(\text{N}^4\) (110.6 mg, 0.8 mmol, 0.2 eq.) in dry MeCN (10 mL) was added, then heated to 70 °C and stirred for 24 h. The reaction mixture was cooled to r.t., filtered through a thin pad of celite eluting with ethyl acetate (30.0 mL), and the combined filtrate was concentrated in vacuo. The residue was directly purified by column chromatography on silica gel (PE:EtOAc = 30:1) to give the compound 3xa (1.34 g, 73% yield) as a yellow solid.

9. Experimental procedure and characterization data for the synthesis of (±)-eptazocine.

2-(7-(benzyloxy)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-N-methylethan-1-amine (4)

To a mixture of methylamine hydrochloride (40.1 mg, 0.59 mmol, 5.0 eq.) and \(\text{NaBH}_3\text{CN}\) (14.9 mg, 0.24 mmol, 2.0 eq.) in MeOH (0.5 mL) was added a solution of the aldehyde 3ta (35 mg, 0.12 mmol, 1.0 eq.) in MeOH (2 mL) at r.t. under argon. The resulting mixture was stirred at r.t. for 12 h, then quenched with a saturated aqueous solution of \(\text{NaHCO}_3\) and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over \(\text{Na}_2\text{SO}_4\), and concentrated in vacuo. The residue was purified by column chromatography on silica gel (DCM:MeOH = 20:1) to give the product 4 (35 mg, 94% yield).
Physical state: white solid;

Melting point: 188–190 ºC;

\[ R_f = 0.61 \text{ (silica gel, DCM:MeOH = 10:1);} \]

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3): \delta 9.39 \text{ (s, 1H), 7.46 – 7.44 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 6.95 (d, } J = 8.4 \text{ Hz, 1H), 6.86 (d, } J = 2.6 \text{ Hz, 1H), 6.74 (dd, } J = 8.4, 2.6 \text{ Hz, 1H), 5.08 (m, 2H), 2.83 (td, } J = 12.4, 4.3 \text{ Hz, 1H), 2.68 – 2.56 (m, 3H), 2.51 (s, 3H), 2.34 (td, } J = 12.9, 4.5 \text{ Hz, 1H), 2.04 (td, } J = 12.8, 4.3 \text{ Hz, 1H), 1.77 – 1.65 (m, 3H), 1.61 – 1.55 (m, 1H), 1.26 (s, 3H). \]

\[ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3): \delta 157.3, 143.1, 137.4, 130.4, 129.4, 128.6, 127.9, 127.7, 113.3, 112.3, 70.0, 46.0, 38.3, 36.5, 35.4, 32.7, 31.2, 29.7, 19.6. \]

HRMS (ESI-TOF): calc’d for C\textsubscript{21}H\textsubscript{28}N\textsubscript{2}O \ [M+H\textsuperscript{+}] 310.2165, found 310.2167.

10-(benzyloxy)-1,4-dimethyl-1,2,3,4,5,6-hexahydro-7H-1,6-methanobenzo[e]azonin-7-one (5)

A solution of CrO\textsubscript{3} (35.5 mg, 0.355 mmol, 2.5 eq.) in H\textsubscript{2}O/HOAc (1:4, 1 mL) was added dropwise to a solution of amine 4 (44 mg, 0.142 mmol, 1.0 eq.) in HOAc (3 mL) at r.t., and the mixture was stirred for 2 h at the same temperature. When the substrate was disappeared, methanol (0.5 mL) was added, and the mixture was further stirred for 1 h. Then HCHO (37% aqueous solution, 0.155 mmol, 1.1 eq.) was added, and stirred for 16 h at 55 ºC. The solvent was concentrated \textit{in vacuo} to give the residue, which was dissolved in water (3.0 ml) and neutralized with 10% aqueous solution of KOH, extracted with Et\textsubscript{2}O (3 \times 5 mL), the combined organic layers were washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, and concentrated \textit{in vacuo}. The residue was purified by column chromatography on silica gel (DCM:MeOH = 30:1) to give the compound 5 (34 mg, 71% yield).

Physical state: white solid;

Melting point: 175–177 ºC;

\[ R_f = 0.45 \text{ (silica gel, DCM:MeOH = 10:1);} \]
1H NMR (400 MHz, CDCl₃): δ 8.02 (d, J = 8.5 Hz, 1H), 7.43 – 7.32 (m, 5H), 6.96 – 6.92 (m, 2H), 5.11 (s, 2H), 3.54 (dd, J = 12.7, 8.4 Hz, 1H), 3.13 (d, J = 12.7 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.70 – 2.60 (m, 2H), 2.56 (s, 3H), 2.52 – 2.36 (m, 2H), 2.27 – 2.21 (m, 1H), 1.68 – 1.63 (m, 1H), 1.48 (s, 3H);
13C NMR (100 MHz, CDCl₃): δ 199.1, 164.0, 152.6, 135.9, 130.1, 128.8, 128.5, 127.7, 125.8, 113.5, 111.5, 70.3, 60.5, 53.2, 47.0, 44.0, 42.3, 36.2, 36.0, 29.9;

1,4-dimethyl-2,3,4,5,6,7-hexahydro-1H-1,6-methanobenzo[e]azonin-10-ol (±-eptazocine)

![Chemical structure of 1,4-dimethyl-2,3,4,5,6,7-hexahydro-1H-1,6-methanobenzo[e]azonin-10-ol (±-eptazocine)](image)

A solution of the ketone 5 (30 mg, 0.09 mmol, 1.0 eq.) in ethanol (2.0 mL) containing 5 μL of 70% HClO₄ and 30% weight of Pd/C (10%) was hydrogenated at an initial pressure of 40 atm at 65 °C for 24 h. The Pd/C was removed by filtration, and the solution was concentrated in vacuo, the residue was dissolved in water and neutralized with 10% aqueous solution of NaOH, extracted with Et₂O (3 × 5 mL), the combined organic layers were dried over Na₂SO₄, and concentrated in vacuo, the residue was purified by PTLC (DCM:MeOH = 6:1) to give the desired compound (±)-eptazocine (18 mg, 90% yield).

Physical state: colorless oil;

Rᶠ = 0.42 (silica gel, DCM:MeOH = 7:1);
1H NMR (600 MHz, Methanol-d₄): δ 6.88 (d, J = 8.2 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 6.56 (dd, J = 8.3, 2.5 Hz, 1H), 3.08 (t, J = 12.1 Hz, 1H), 2.77 (dd, J = 15.4, 4.4 Hz, 1H), 2.67 (d, J = 13.1 Hz, 1H), 2.45 (td, J = 8.0, 4.4 Hz, 1H), 2.36 (d, J = 15.4 Hz, 1H), 2.24 (s, 3H), 2.21 (dd, J = 13.8, 3.3 Hz, 1H), 1.86 (dd, J = 13.5, 7.2 Hz, 1H), 1.80 – 1.68 (m, 4H), 1.23 (s, 3H);
13C NMR (100 MHz, Methanol-d₄): δ 156.8, 145.4, 132.2, 127.4, 114.4, 113.6, 64.9, 60.1, 46.5, 41.6, 37.8, 37.3, 33.9, 30.8;
A solution of (±)-eptazocine (18 mg, 0.08 mmol, 1.0 eq.) in 40% HBr (1.0 ml) was stirred at r.t. for 1 h, then water and other volatile materials were evaporated in vacuo to obtain the HBr salt of (±)-eptazocine (23 mg, 91% yield).

**Physical state:** white solid;

**Melting point:** 267–269 °C;

$R_f = 0.41$ (silica gel, DCM:MeOH = 7:1);

$^1$H NMR (400 MHz, Methanol-d$_4$): $\delta$ 6.97 (d, $J = 8.3$ Hz, 1H), 6.75 (d, $J = 2.6$ Hz, 1H), 6.64 (dd, $J = 8.3$, 2.5 Hz, 1H), 3.71 – 3.63 (m, 1H), 3.37 – 3.30 (m, 1H), 2.92 – 2.87 (m, 1H), 2.82 (s, 3H), 2.73 – 2.62 (m, 3H), 2.51 (d, $J = 16.2$ Hz, 1H), 2.17 – 2.11 (m, 1H), 2.10 – 2.05 (m, 1H), 1.99 – 1.92 (m, 2H), 1.34 (s, 3H);

$^{13}$C NMR (100 MHz, Methanol-d$_4$): $\delta$ 157.7, 143.4, 132.7, 125.8, 115.5, 113.6, 63.6, 59.8, 47.6, 43.4, 40.8, 37.2, 36.4, 33.1, 28.7.
Table S2. $^1$H NMR data comparison between synthetic (±)-eptazocine•HBr and authentic (−)-eptazocine•HBr sample

<table>
<thead>
<tr>
<th></th>
<th>Synthetic (±)-eptazocine•HBr (Methanol-d$_4$, 400 MHz)</th>
<th>Authentic (−)-eptazocine•HBr sample (Methanol-d$_4$, 400 MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.97 (d, $J = 8.3$ Hz, 1H)</td>
<td>6.97 (d, $J = 8.3$ Hz, 1H)</td>
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<tr>
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<td>6.75 (d, $J = 2.5$ Hz, 1H)</td>
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<tr>
<td>6.64 (dd, $J = 8.3$, 2.5 Hz, 1H)</td>
<td>6.64 (dd, $J = 8.3$, 2.5 Hz, 1H)</td>
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<tr>
<td>3.71 – 3.63 (m, 1H)</td>
<td>3.74 – 3.67 (m, 1H)</td>
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<tr>
<td>3.37 – 3.30 (m, 1H)</td>
<td>3.38 – 3.33 (m, 1H)</td>
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<td>2.92 – 2.87 (m, 1H)</td>
<td>2.92 – 2.87 (m, 1H)</td>
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<td>2.82 (s, 3H)</td>
<td>2.85 (s, 3H)</td>
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<tr>
<td>2.73 – 2.62 (m, 3H)</td>
<td>2.74 – 2.65 (m, 3H)</td>
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<tr>
<td>2.51 (d, $J = 16.2$ Hz, 1H)</td>
<td>2.51 (d, $J = 15.9$ Hz, 1H)</td>
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<tr>
<td>2.17 – 2.11 (m, 1H)</td>
<td>2.18 – 2.13 (m, 1H)</td>
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<td>2.09 – 2.04 (m, 1H)</td>
<td>2.10 – 2.05 (m, 1H)</td>
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<tr>
<td>1.99 – 1.92 (m, 2H)</td>
<td>1.99 – 1.91 (m, 2H)</td>
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<tr>
<td>1.34 (s, 3H)</td>
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**Table S3.** $^{13}$C NMR data comparison between synthetic (±)-eptazocine•HBr and authentic (−)-eptazocine•HBr sample

<table>
<thead>
<tr>
<th></th>
<th>Synthetic (±)-eptazocine•HBr (Methanol-d$_4$, 100 MHz)</th>
<th>Authentic (−)-eptazocine•HBr sample (Methanol-d$_4$, 100 MHz)</th>
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<tr>
<td></td>
<td>28.7</td>
<td>28.7</td>
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10. Experimental procedure and characterization data for the transformations of 3xa.

methyl 1,3-bis(benzyloxy)-8-(2-hydroxyethyl)-8-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylate (7)

NaBH₄ (0.06 mmol, 1.2 eq.) was added to a solution of aldehyde 3xa (23 mg, 0.05 mmol, 1.0 eq.) in MeOH (1.00 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. DCM (1.50 mL) and saturated aqueous solution of NH₄Cl (1.00 mL) were added and the mixture was stirred for further 30 min at r.t.. The mixture was then extracted with DCM (3 × 5 mL), and the organic layers were combined, dried over Na₂SO₄, filtered, concentrated in vacuo, and the residue was purified by PTLC (PE:EtOAc = 5:1) to give the product 7 (20 mg, 87% yield).

Physical state: pale oil;
Yield: 87%;

\( R_f = 0.40 \) (silica gel, PE:EtOAc = 5:1);

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 – 7.28 (m, 10H), 6.45 (s, 1H), 5.06 (s, 4H), 3.73 (s, 3H), 7.55 – 7.42 (m, 2H), 2.70 (t, \( J = 6.2 \) Hz, 2H), 2.35 – 2.28 (m, 1H), 1.85 – 1.77 (m, 1H), 1.76 – 1.66 (m, 4H), 1.54 – 1.48 (m, 1H), 1.33 (s, 3H);

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 167.8, 156.8, 154.2, 141.9, 137.3, 137.0, 129.1, 128.6, 128.1, 127.9, 127.6, 127.0, 115.9, 108.6, 75.9, 70.4, 60.5, 52.6, 43.9, 39.4, 36.1, 32.7, 28.9, 19.4;

**HRMS** (ESI-TOF): calc’d for C\(_{29}\)H\(_{33}\)O\(_5\) [M+H\(^+\)] 461.2323, found 461.2330.

2-(6,8-bis(benzyloxy)-7-(methoxycarbonyl)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetic acid (8)

![Chemical Structure]

To a stirred solution of the aldehyde 3\(\text{xa}\) (23 mg, 0.05 mmol, 1.0 eq.) in acetone (2 mL) was added Jones reagent (0.5 mL) dropwise at 0 °C. After stirring for 15 min, isopropyl alcohol (0.5 mL) was added to quench the reaction. The solid byproduct was filtrated out with celite, then saturated aqueous solution of NH\(_4\)Cl (2 mL) was added, extracted with Et\(_2\)O (3 \( \times \) 5 mL), and the organic layers were combined, dried over Na\(_2\)SO\(_4\), filtered, concentrated in vacuo, and the residue was purified by PTLC (PE:EtOAc = 5:1) to give the product 8 (22 mg, 96% yield).

**Physical state:** yellow oil;

**Yield:** 96%;

\( R_f = 0.30 \) (silica gel, PE: EtOAc = 5:1);

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 – 7.28 (m, 10H), 6.45 (s, 1H), 5.06 (s, 4H), 3.71 (s, 3H), 2.97 (d, \( J = 14.6 \) Hz, 1H), 2.77 – 2.67 (m, 3H), 2.09 – 2.02 (m, 1H), 1.74 – 1.68 (m, 2H), 1.65 – 1.57 (m, 1H), 1.41 (s, 3H);

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)): \( \delta \) 177.7, 167.7, 156.5, 154.4, 141.9, 137.1, 137.0, 128.6, 128.5, 128.0, 127.9, 127.5, 127.0, 115.9, 108.6, 75.8, 70.4, 52.6, 45.0, 38.6, 36.2, 32.5, 28.2, 19.3;

**HRMS** (ESI-TOF): calc’d for C\(_{29}\)H\(_{30}\)NaO\(_6\) [M+Na\(^+\)] 497.1935, found 497.1937.
Methyl 8-allyl-1,3-bis(benzyloxycarbonyl)-8-methyl-5,6,7,8-tetrahydronaphtalene-2-carboxylate (9)

A stirred suspension of methyltriphenylphosphonium bromide (36 mg, 0.1 mmol, 2.0 eq.) in THF (0.5 mL) at 0 °C under argon was treated dropwise with n-BuLi (56 μL, 1.6 M in hexane, 0.09 mmol, 1.8 eq.) over 5 min. The resulting solution was stirred for 30 min. A solution of the aldehyde 3xa (23 mg, 0.05 mmol, 1.0 eq.) in THF (0.5 mL) was added dropwise. The cooling bath was removed and the mixture allowed to stirred at r.t. for 14 h. The mixture was then extracted with Et₂O (3 × 5 mL), and the organic layers were combined, dried over Na₂SO₄, filtered, concentrated in vacuo, and the residue was purified by PTLC (PE:EtOAc = 20:1) to give the product 9 (14 mg, 61% yield).

Physical state: colorless oil;

Yield: 61%;

R_f = 0.50 (silica gel, PE:EtOAc = 5:1);

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.44 – 7.28 (m, 10H), 6.45 (s, 1H), 5.64 – 5.53 (m, 1H), 5.08 – 5.04 (m, 4H), 4.94 – 4.88 (m, 2H), 3.72 (s, 3H), 2.81 – 2.75 (m, 1H), 2.70 (t, J = 6.3 Hz, 2H), 2.33 – 2.27 (m, 1H), 1.84 – 1.78 (m, 1H), 1.73 – 1.63 (m, 2H), 1.45 – 1.38 (m, 1H), 1.32 (s, 3H);

\(^1\)C NMR (100 MHz, CDCl₃) δ 167.8, 156.8, 154.1, 142.1, 137.5, 136.4, 129.9, 128.6, 128.5, 127.9, 127.3, 127.0, 116.9, 116.2, 108.6, 77.2, 75.8, 70.4, 52.5, 45.2, 38.3, 37.2, 32.8, 28.2, 19.2;


Methyl 1,3-bis(benzyloxycarbonyl)-8-(2-(dimethylamino)ethyl)-8-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylate (10)

To a mixture of NHMe₂ (2 M in THF, 0.25 mmol, 5.0 eq.) and NaBH₃CN (6 mg, 0.1 mmol, 2.0 eq.) in MeOH (0.5 mL) was added a solution of the aldehyde 3xa (23 mg, 0.05 mmol, 1.0 eq.)
in MeOH (1 mL) at r.t. under argon. The resulting mixture was stirred at r.t. for 12 h, then quenched with a saturated aqueous solution of NaHCO$_3$ and extracted with DCM (3 × 5 mL), the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by PTLC (DCM:MeOH = 10:1) to give the product 10 (22 mg, 90% yield).

**Physical state:** yellow oil;
**Yield:** 90%;
$R_f$ = 0.50 (silica gel, DCM:MeOH = 10:1);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.30 (m, 10H), 6.47 (s, 1H), 5.11 – 4.86 (m, 3H), 4.87 (d, $J$ = 10.6 Hz, 1H), 3.82 (d, $J$ = 0.7 Hz, 3H), 2.84 (td, $J$ = 12.4, 4.5 Hz, 1H), 2.71 – 2.68 (m, 2H), 2.58 (td, $J$ = 12.5, 4.4 Hz, 1H), 2.48 (s, 6H), 2.40 (td, $J$ = 12.2, 4.4 Hz, 1H), 1.84 – 1.64 (m, 4H), 1.59 – 1.55 (m, 1H), 1.36 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.6, 155.8, 154.7, 142.5, 136.7, 136.5, 128.9, 128.7, 128.6, 128.2, 128.0, 127.0, 126.7, 108.9, 76.1, 70.5, 54.8, 52.7, 38.6, 36.4, 34.7, 32.2, 29.8, 29.3, 19.0;

HRMS (ESI-TOF): calc’d for C$_{31}$H$_{38}$NO$_4$ [M+H$^+$] 488.2795, found 488.2803.

Methyl 2,8-dihydroxy-3a-methyl-2,3,3a,4,5,6-hexahydrobenzo[de]chromene-9-carboxylate (11)

Pd/C (10%) (10 mg) was added to a solution of the aldehyde 3xa (23 mg, 0.05 mmol, 1.0 eq.) in THF (1.0 mL), and the reaction was placed under a H$_2$ atmosphere (balloon). After 3 h, the reaction mixture was filtered through a plug of celite, which was further washed with THF (5.0 mL). The combined filtrates were concentrated in vacuo and the residue was purified by PTLC (PE:EtOAc = 3:1) to give the hemiacetal 11 and aldehyde 11’ as an unseparable mixture (11:11’ = 10:1, determined by $^1$H NMR) (12 mg, 86% yield).

**Physical state:** yellow oil;
**Yield:** 86%;
$R_f$ = 0.20 (silica gel, PE:EtOAc = 5:1);
Major component (8):
\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 11.11 (s, 1H), 6.37 – 6.34 (m, 1H), 5.93 – 5.89 (m, 1H), 3.93 (s, 3H), 3.44 – 3.38 (m, 1H), 2.82 – 2.63 (m, 2H), 2.19 (dd, \(J = 13.3, 5.1\) Hz, 1H), 1.97 – 1.91 (m, 1H), 1.84 – 1.77 (m, 1H), 1.75 – 1.69 (m, 1H), 1.56 – 1.50 (m, 1H), 1.47 – 1.39 (m, 1H), 1.21 (s, 3H);

\textbf{\textsuperscript{13}C NMR} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 171.4, 160.6, 153.3, 143.6, 120.2, 109.7, 101.4, 94.5, 52.5, 44.2, 36.9, 30.4, 29.2, 24.9, 17.7;

\textbf{HRMS} (ESI-TOF): calc'd for C\textsubscript{15}H\textsubscript{18}NaO\textsubscript{5} [M+Na\textsuperscript{+}] 301.1046, found 301.1047.
11. Preliminary asymmetric studies.

**Screening of chiral ligands**

![Chemical reactions and product structures]

**Typical procedure:** To a 25 mL of oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Pd(C₃H₅)Cl]₂ (3.7 mg, 0.01 mmol, 0.1 eq.), chiral ligand (0.022 mmol, 0.22 eq.), NBE (2.0 eq.), K₂CO₃ (2.5 eq.), MeCN (0.1 M), 70 °C, 24 h. GC yield with biphenyl as an internal standard.
eq.), K₂CO₃ (34.6 mg, 0.25 mmol, 2.5 eq.), and dry MeCN (0.5 mL). After stirring for about 15 min at r.t. under argon, a solution of 1-iodonaphthalene 1a (30.5 mg, 0.12 mmol, 1.2 eq.), (E)-6-bromo-3-methylhex-2-en-1-ol 2a (19.3 mg, 0.1 mmol, 1.0 eq.), norbornene (18.8 mg, 0.2 mmol, 2.0 eq.) in dry MeCN (0.5 mL) was added, then heated to 70 °C and stirred for 24 h. The reaction mixture was cooled to r.t., filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated in vacuo. The residue was directly purified by PTLC to give the desired product 3aa.

**Screening of NBE derivatives**

![Diagram of reaction](image)

Colorless oil, 36% yield, 62% ee (N⁶ as mediator). The ee was determined by HPLC (Daicel Chiralpak OJ-H column, n-hexane/i-PrOH, 95:5 v/v, flow rate 1.0 mL/min, λ = 230 nm, 25 °C). t (major) = 8.243 min; t (minor) = 9.811 min.
Racemic sample of 3aa

![Graph showing a peak with retention time, width, area, height, and area percentage.]

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<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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Enantioenriched sample of 3aa (N\textsuperscript{1} as mediator)

![Graph showing a peak with retention time, width, area, height, and area percentage.]

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<th>Area [%]</th>
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</table>
Enantioenriched sample of 3aa (N⁴ as mediator)

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<th>Type</th>
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<th>Area</th>
<th>%</th>
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Enantioenriched sample of 3aa (N⁴’ as mediator)

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Enantioenriched sample of 3aa (N^6 as mediator)

To a 25 mL of oven-dried Schlenk tube equipped with a magnetic stir bar was charged with [Pd(C_3H_5)Cl]_2 (3.7 mg, 0.01 mmol, 0.1 eq.), chiral ligand L_8 (20.3 mg, 0.04 mmol, 0.4 eq.), K_2CO_3 (34.6 mg, 0.25 mmol, 2.5 eq.), and dry MeCN (0.5 mL). After stirring for about 15 min at r.t. under argon, a solution of 1-iodonaphthalene 1a (30.5 mg, 0.12 mmol, 1.2 eq.), (E)-6-bromohex-2-en-1-ol 2G (17.9 mg, 0.1 mmol, 1.0 eq.), norbornene derivative N^6 (12.7 mg, 0.05 mmol, 0.5 eq.) in dry MeCN (0.5 mL) was added, then heated to 70 °C and stirred for 12 h. The reaction mixture was cooled to r.t., filtered through a thin pad of celite eluting with ethyl acetate (10 mL), and the combined filtrate was concentrated in vacuo. The residue was directly purified by PTLC to give the desired product 3G.

\[
\begin{align*}
\text{I} & + \text{Br} & \text{CHO} \\
\text{1a} & \text{2G} & \text{3G}
\end{align*}
\]

27% yield, 78% ee
Colorless oil, 27% yield, 78% ee. The ee was determined by HPLC (Daicel Chiralpak OJ-H column, n-hexane/i-PrOH, 95:5 v/v, flow rate 1.0 mL/min, λ = 230 nm, 25 ℃). t (major) = 8.165 min; t (minor) = 10.612 min.

Racemic sample of 3G
Enantioenriched sample of $3G$

12. X-ray crystallographic data for $3xa$ and $(-)$-eptazocine•HBr.

\[\text{Chemical Structures} \]

<table>
<thead>
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<th>Width</th>
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<th>Height</th>
<th>Area %</th>
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S63
**Table S4. Crystal data for 3xa**

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<tr>
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<tr>
<td><strong>Theta range for data collection</strong></td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
<td><strong>Completeness to theta = 24.69°</strong></td>
<td>98.1 %</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
<td>multi-scan / sadabs</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>4146 / 0 / 428</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.039</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R1 = 0.0496, wR2 = 0.1528</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0641, wR2 = 0.1674</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.270 and -0.230 e.Å⁻³</td>
</tr>
</tbody>
</table>
Table S5. Crystal data for (-)-eptazocine•HBr

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>CCDC 1568079</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C15H22BrNO</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C15H22BrNO</td>
</tr>
<tr>
<td>Formula weight</td>
<td>312.25</td>
</tr>
<tr>
<td>Temperature</td>
<td>296 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1211</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.5964(3) Å , α = 90°.</td>
</tr>
<tr>
<td></td>
<td>b = 16.0907(6) Å , β = 99.736(2)°.</td>
</tr>
<tr>
<td></td>
<td>c = 12.1098(5) Å , γ = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1458.88(10) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.422 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.807 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>648.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.20 x 0.20 mm³</td>
</tr>
<tr>
<td>Crystal color</td>
<td>colorless</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.71 to 37.69°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13≤h≤11, -27≤k≤27, -20≤l≤20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>64773</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15437 [R(int) = 0.0285]</td>
</tr>
<tr>
<td>Completeness to theta = 37.69°</td>
<td>99.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>multi-scan / sadabs</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>9304 / 1 / 331</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.011</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0374, wR2 = 0.0838</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0817, wR2 = 0.0963</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.001(4)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.780 and -0.610 e.Å⁻³</td>
</tr>
</tbody>
</table>
13. Reference.


14. NMR spectra of the new compounds.
\(^1\)H NMR Spectra of S1
$^{13}$C NMR Spectra of S1
$^1$H NMR Spectra of S2
$^{13}$C NMR Spectra of S2
$^1$H NMR Spectra of S3
$^{13}$C NMR Spectra of S3
$^1\text{H NMR Spectra of S4}$
$^{13}$C NMR Spectra of S4
$^1$H NMR Spectra of 1s

![NMR Spectra Image]
$^{13}\text{C}$ NMR Spectra of 1s
$^{1}$H NMR Spectra of 1x
$^{13}$C NMR Spectra of 1x
$^1$H NMR Spectra of S5
\[\text{\(^{13}\text{C NMR Spectra of S5}\)}\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{H}_3 \\
\text{O} & \quad \text{C} \quad \text{H}_3 \\
\text{I} & \quad \text{C} 
\end{align*}
\]
$^1$H NMR Spectra of 1y
$^{13}$C NMR Spectra of $1y$
$^1$H NMR Spectra of 2a''

![NMR spectrum graph]

- f1 (ppm) values: 1.03, 2.08, 2.11, 2.10, 2.12, 3.17
$^{13}$C NMR Spectra of 2a"
$^1$H NMR Spectra of 2b
$^{13}$C NMR Spectra of 2b

Br $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

Chemical shifts (ppm):
- 137.0
- 136.8
- 122.4
- 121.4
- 77.5
- 77.2
- 76.8
- 62.7
- 62.6
- 38.1
- 33.7
- 33.5
- 31.6
- 31.1
- 30.9
- 30.3
- 23.5
- 16.2

fl (ppm)
H NMR Spectra of 2A

\[ \text{Br} \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]

1H NMR Spectra of 2A
$^{13}$C NMR Spectra of 2A

![Chemical structure of 2A with NMR peaks labeled]

 peak positions (ppm): 16.5, 30.7, 33.4, 37.9, 58.1, 69.0, 72.7, 77.2, 77.5, 76.8, 69.0

Chemical formula: Br\(\text{CH}_3\)C=\(\text{CH}_2\)O\(\text{CH}_3\)
$^1$H NMR Spectra of S6
$^{13}$C NMR Spectra of S6

Br
\[\text{CH}_3\]
$^1$H NMR Spectra of 2B
$^{13}$C NMR Spectra of 2B

\[
\begin{align*}
\text{Br} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
16.5 & \quad 23.8 & \quad 30.7 & \quad 33.4 & \quad 37.7 & \quad 64.8 & \quad 76.8 \\
77.2 & \quad 77.5 & \quad 130.3 & \quad 135.8 & \quad 16.5 & \quad 23.8 & \quad 30.7 & \quad 33.4 & \quad 37.7 & \quad 64.8
\end{align*}
\]
$^1$H NMR Spectra of 2C

\[
\begin{array}{c}
\text{Br} \\
\text{CH}_3 \\
\text{OH} \\
\text{CH}_3
\end{array}
\]
$^{13}\text{C}$ NMR Spectra of 2C
$^1$H NMR Spectra of 2D

Br
\[
\text{CH}_3 \quad \text{OH}
\]
\[
\text{CH}_2
\]
$^{13}$C NMR Spectra of 2D
$^1$H NMR Spectra of S8

![H NMR Spectra of S8](image)
$^{13}$C NMR Spectra of S8

![Chemical Structure](image)

**Chemical Shifts (ppm):**
- 13.1
- 14.4
- 25.3
- 30.5
- 33.0
- 36.1
- 59.7
- 76.8
- 77.2
- 77.5
- 115.8
- 143.1
- 144.4
- 163.7
- 166.3

**Bonding:**
- Br
- C
- H
- O
- O
- C
- H
- O
- CH$_3$
$^1$H NMR Spectra of 2E
$^{13}$C NMR Spectra of 2E

![Carbon NMR Spectra of 2E](image)
$^{1}$H NMR Spectra of S10
$^{13}$C NMR Spectra of **S10**
$^1$H NMR Spectra of 2F

$\text{Br}$

$\text{O}$

$1 \text{H}$ NMR Spectra of 2F
$^{13}$C NMR Spectra of 2F
$^1$H NMR Spectra of S11

Br

O

O

C

H
$^{13}$C NMR Spectra of S11
$^1$H NMR Spectra of 2I

Br

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

$^1$H NMR Spectra of 2I
$^{13}$C NMR Spectra of 2I

![NMR Spectra Diagram]
$^1$H NMR Spectra of 3aa
$^{13}$C NMR Spectra of 3aa

![Chemical Structure of 3aa](image)

- **203.4 ppm**
- **136.4 ppm**
- **136.3 ppm**
- **133.9 ppm**
- **131.6 ppm**
- **129.9 ppm**
- **128.8 ppm**
- **127.7 ppm**
- **125.8 ppm**
- **125.5 ppm**
- **124.4 ppm**
- **77.5 ppm**
- **77.2 ppm**
- **76.8 ppm**
- **-54.8 ppm**
- **42.2 ppm**
- **37.1 ppm**
- **32.8 ppm**
- **28.7 ppm**
- **18.8 ppm**
$^1$H NMR Spectra of 3ab
$^{13}$C NMR Spectra of 3ab

![Chemical Structure Diagram](image)
$^1$H NMR Spectra of 3ba
$^{13}$C NMR Spectra of 3ba
$^{1}H$ NMR Spectra of 3ca
$^{13}$C NMR Spectra of 3ca

![Chemical Structure]

- C NMR Spectra of 3ca
$^1$H NMR Spectra of 3da

![NMR Spectra of 3da](image-url)
$^{13}$C NMR Spectra of 3da
$^1$H NMR Spectra of 3ea
$^{13}$C NMR Spectra of 3ea
$^{19}$F NMR Spectra of 3ea
$^1$H NMR Spectra of 3fa

![NMR Spectra of 3fa](image)
$^{13}$C NMR Spectra of 3fa

![Chemical structure of 3fa]

- $f_1 (ppm)$:
  - 77.5
  - 77.2
  - 76.8
  - 53.3
  - 40.9
  - 37.2
  - 32.4
  - 26.9
  - 19.1
  - 203.1
  - 140.7
  - 138.7
  - 133.8
  - 130.0
  - 129.1
  - 127.2
  - 130.0
  - 133.8
  - 130.0
  - 129.1
  - 127.2

fl (ppm)
$^1$H NMR Spectra of 3ga

The spectrum shows the chemical shifts of various protons in the molecule. The peaks at 0.94, 4.98, 1.98, 2.03, 0.99, 2.00, 1.03, 4.12, and 3.01 ppm indicate the presence of different types of hydrogens in the molecule.

The chemical structure of 3ga includes a phenyl ring, an ether group, and an aldehyde group, which can be observed in the spectrum.
$^{13}$C NMR Spectra of 3ga
$^1$H NMR Spectra of 3ha

\[ \text{Structure Image} \]
$^{13}$C NMR Spectra of 3ha

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{O} \\
\end{align*}
\]
$^1$H NMR Spectra of 3hb
$^{13}$C NMR Spectra of 3hb
$^{13}$C NMR Spectra of 3ia
$^1$H NMR Spectra of 3ja
$^{13}$C NMR Spectra of 3ja
$^{19}$F NMR Spectra of 3ja
$^1$H NMR Spectra of 3ka
$^{13}$C NMR Spectra of 3ka
\( ^{19}\text{F NMR Spectra of 3ka} \)
$^1$H NMR Spectra of 3la
$^{13}$C NMR Spectra of 3\textit{la}
$^{1}H$ NMR Spectra of 3ma
$^{13}$C NMR Spectra of 3ma
$^1$H NMR Spectra of 3na

![NMR Spectra of 3na]
\[ ^{13}\text{C} \text{ NMR Spectra of 3na} \]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{C} & \quad \text{H}_3\text{C} \\
\text{C} & \quad \text{H}_3\text{C} \\
\text{O} & \quad \text{C} \\
\text{O} & \quad \text{C}
\end{align*}
\]
$^1$H NMR Spectra of 3oa
$^{13}$C NMR Spectra of 3oa

![Chemical structure](attachment:chemical_structure.png)
$^1$H NMR Spectra of 3pa

![NMR Spectrum](image)
$^{13}$C NMR Spectra of 3pa
$^1$H NMR Spectra of 3qa

![Structural diagram of 3qa]
$^{13}$C NMR Spectra of 3qa
$^1$H NMR Spectra of 3ra

Chemical shifts:
- 0.93
- 1.95
- 3.01 (2x)
- 7.14
- 10.01

Structural formula:

```
H3C

H

\text{O}
```

Molecular formula:

C$_{13}$H$_{18}$O
$^{13}$C NMR Spectra of 3ra
$^1$H NMR Spectra of 3sa
$^{13}$C NMR Spectra of 3sa

![Chemical structure of 3sa]
$^1$H NMR Spectra of 3ta
$^{13}$C NMR Spectra of 3ta

![Chemical Structure](image)

### Key Observations
- Major peaks at 77.5, 77.2, 76.8, and 70.3 ppm.
- Other peaks at 143.7, 137.2, 130.5, 129.2, 128.7, 128.1, 127.7, 113.4, 112.7, 112.7, 112.7, and 56.2 ppm.
- Assignments consistent with the chemical structure shown.
$^1$H NMR Spectra of 3ua
$^{13}$C NMR Spectra of 3ua
$^1$H NMR Spectra of 3va

![NMR spectrum of 3va](image-url)
$^{13}$C NMR Spectra of 3va

![Chemical Structure](image)

- 203.6
- 161.9
- 149.0
- 143.5
- 124.4
- 118.8
- 77.5
- 77.2
- 76.8
- 53.1
- 53.6
- 39.2
- 34.8
- 30.8
- 26.6
- 18.7

fl (ppm)
$^1$H NMR Spectra of 3wa
$^{13}$C NMR Spectra of 3wa
$^1$H NMR Spectra of 3xa
$^{13}$C NMR Spectra of 3xa

![Chemical Structure](image)

**Chemical Shifts**
- 77.5
- 77.2
- 76.8
- 75.7
- 70.5
- 141.8
- 136.8
- 128.7
- 128.6
- 128.2
- 127.9
- 127.6
- 127.4
- 127.0
- 115.8
- 108.6
- 54.4
- 52.6
- 40.1
- 35.8
- 32.4
- 28.7
- 19.1

**Chemical Groups**
- MeO$_2$C
- BnO
- Me
- CHO
$^1$H NMR Spectra of 3xB
$^{13}$C NMR Spectra of 3xb
$^1$H NMR Spectra of 3ya

[Image of the 1H NMR spectrum with annotations for peaks at 0.97, 2.05, 3.08, 0.99, 1.00, 1.00, 0.97, 0.97, 8.37, 2.02, 3.01 ppm]
$^{13}$C NMR Spectra of 3ya

![Carbon NMR Spectra of 3ya](image)
$^1$H NMR Spectra of 3ac
$^{13}$C NMR Spectra of 3ac

![Chemical Structure](image)
$^1$H NMR Spectra of 3ad

![Chemical structure of 3ad](image)
$^{13}$C NMR Spectra of 3ad

![Chemical Structure](image)

The chemical structure shows a molecule with a benzene ring and an aldehyde group. The spectrum indicates the presence of various carbon signals at different ppm values, with peaks at 77.5, 77.2, 76.8, 142.4, 141.6, 133.7, 130.3, 129.5, 128.3, 126.9, 124.6, 123.7, 123.2, 49.4, 40.6, 39.3, 33.2, 31.1, and 28.1 ppm.
$^1$H NMR Spectra of 3bc

![Chemical structure of 3bc](image)

- **C(CH$_3$)$_3$**
- **H NMR Spectra of 3bc**

![NMR spectrum graph](image)
$^{13}$C NMR Spectra of 3bc

![NMR Spectrum Diagram](image-url)
^{1}H NMR Spectra of 3cc
$^{13}$C NMR Spectra of 3cc
$^1$H NMR Spectra of 3dc
$^{13}$C NMR Spectra of $3^\text{dc}$
$^{19}$F NMR Spectra of 3dc
$^1$H NMR Spectra of 3ec

\[
\begin{align*}
\text{Cl} & \quad \text{H}_3\text{C} \\
\text{H} & \quad \text{C} \\
\text{C} & \quad \text{H}_3 \\
\text{O} & \quad \text{H}
\end{align*}
\]
$^{13}\text{C} \text{ NMR Spectra of 3ec}$
$^1$H NMR Spectra of 3fc
$^{13}$C NMR Spectra of 3fc
$^1$H NMR Spectra of 3gc
$^{13}$C NMR Spectra of 3gc
$^1$H NMR Spectra of 3hc
$^{13}$C NMR Spectra of 3hc

![Chemical Structure Image]
$^1$H NMR Spectra of (E)-3A
$^{13}$C NMR Spectra of (E)-3A
$^1$H NMR Spectra of (Z)-3A
$^{13}\text{C}$ NMR Spectra of (Z)-3A

![Chemical Structure](image)
$^1$H NMR Spectra of 3B
$^{13}$C NMR Spectra of 3B

![Chemical structure of 3B with NMR peaks labelled](image)

- 208.6 ppm
- 19.0 ppm
- 28.7 ppm
- 32.0 ppm
- 32.9 ppm
- 37.8 ppm
- 40.7 ppm
- 54.4 ppm
- 76.8 ppm
- 77.2 ppm
- 77.5 ppm

fl (ppm): 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
$^1$H NMR Spectra of 3C
$^{13}$C NMR Spectra of 3C

- H3C
- CH3
- O

- 77.5
- 77.2
- 76.8

- 138.0
- 136.0
- 133.9
- 131.8
- 129.8
- 128.9
- 127.1
- 125.9
- 125.0
- 124.1

- 53.3
- 44.4
- 40.7
- 37.8
- 32.9
- 28.6
- 25.7
- 22.3
- 19.0
- 13.9

- 210.7
$^1$H NMR Spectra of 3D
$^{13}$C NMR Spectra of 3D
$^{1}{\text{H}}$ NMR Spectra of 3E
$^{13}$C NMR Spectra of 3E
$^1$H NMR Spectra of 3F
$^{13}$C NMR Spectra of $3F$
$^1$H NMR Spectra of 3G
$^{13}$C NMR Spectra of 3G

![Chemical Structure of 3G]
$^1$H NMR Spectra of 3H
$^{13}$C NMR Spectra of 3H
$^1$H NMR Spectra of 3I

The spectrum shows a series of peaks at various ppm values. The chemical shifts are indicated at specific positions on the graph, such as 0.90, 2.00, 1.00, 1.12, 1.05, 1.02, 0.93, 0.97, 2.08, 1.01, 1.04, 1.00, 1.04, and 1.07 ppm. The structure of the compound is depicted, showing the presence of aromatic and aliphatic regions, with the presence of an oxygen-bearing group and a double bond.
$^{13}$C NMR Spectra of 3I
$^1$H NMR Spectra of 31"
$^{13}$C NMR Spectra of $3I'$

![Chemical Structure](image)

### Key Peaks:
- $f_1 (ppm): 30.3, 34.0, 62.0, 76.8, 77.2, 77.5, 124.7, 125.8, 127.1, 127.9, 128.6, 129.9, 130.1, 130.8, 131.0, 132.4, 136.4, 138.4, 151.0, 194.0$

### Chemical Formula:

- $OH$

- $C$, $N$
$^1$H NMR Spectra of 4
$^{13}$C NMR Spectra of 4

![Chemical Structure Image]
$^1$H NMR Spectra of 5
$^{13}$C NMR Spectra of 5
$^1$H NMR Spectra of (±)-eptazocine
$^{13}$C NMR Spectra of (±)-eptazocine
$^1$H NMR Spectra of (±)-eptazocine•HBr
$^{13}$C NMR Spectra of (±)-eptazocine•HBr

(±)-eptazocine•HBr
$^1$H NMR Spectra of data comparison

Authentic (−)-eptazocine•HBr

Synthetic (±)-eptazocine•HBr
$^{13}$C NMR Spectra of data comparison

Synthetic (±)-eptazocine•HBr

Authentic (−)-eptazocine•HBr
$^1$H NMR Spectra of 7

![Chemical Structure Diagram]

 molt 1

NMR Spectra Figure
\(^{13}\text{C} \) NMR Spectra of 7

![Chemical Structure](image)

- C NMR Spectra of 7
$^1$H NMR Spectra of 8
$^{13}$C NMR Spectra of 8
$^1$H NMR Spectra of 9
$^{13}$C NMR Spectra of 9
$^1$H NMR Spectra of 10
$^{13}$C NMR Spectra of 10
$^1$H NMR Spectra of 11
$^{13}$C NMR Spectra of 11