Asymmetric Dearomative Synthesis of Polycyclic Compounds via Intramolecular Cyclopropanation of Naphthalenes

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1. Experimental Section

1.1 General Information

All commercial reagents were used as provided without further purification. The substrates 1 were prepared according to the literature.\(^{[1-2]}\) The reactions were monitored by thin layer chromatography (TLC) on silica gel GF254 coated 0.2 mm plates (Branch of Qingdao Haiyang Chemical plant). The product spots were visualized with UV and phosphomolybdic acid (PMA). Flash column chromatography were performed using silica gel (200-300 mesh, Branch of Qingdao Haiyang Chemical plant) and a gradient solvent system (EtOAc/n-hexane as eluent). \(^{1}\)H and \(^{13}\)C NMR spectra were recorded on either a Bruker Avance 300 spectrometer. Chemical shifts (δ) were measured with tetramethylsilane (TMS) as internal reference. High Resolution Mass Spectrometry (HR-MS) data were obtained on AB SCIEX TripleTOF 5600+ mass spectrometer. Enantiomeric excess (ee) was determined using Agilent 1260 Infinity II high-performance liquid chromatography (HPLC) with a UV detector (at appropriate wavelength).

1.2 General procedure for the preparation of substrates 1 \(^{[1-2]}\)

To a round-bottomed flask containing a Wittig reagent (1.8 equiv.) and sodium hydride (60%, 2.0 equiv.) was added THF/DMSO (4:1) at 0 °C. After stirred at room temperature for 30 mins, 1-naphthaldehydes (1.0 equiv.) was added to the reaction mixture at 0 °C and the reaction mixture was stirred at room temperature until the complete consumption of 1-naphthaldehydes as monitored by TLC analysis. Then the reaction was quenched with H\(_2\)O, extracted with EtOAc, washed with brine, dried with Na\(_2\)SO\(_4\), filtered and concentrated. The residue was purified by silica gel column chromatography to afford compound S0.

A round-bottom flask equipped with a magnetic stir bar was charged with S0, Pd/C (10 mg/1 mmol substrate) and EtOAc (5 mL/mmol). The reaction was stirred for 5 hours under balloon-pressure of hydrogen. Then the reaction mixture was filtered through a celite pad with EtOAc, dried with Na\(_2\)SO\(_4\), and concentrated under vacuo. The product S1 was used without chromatographic purification.

A 50-mL schlenk tube containing a magnetic stirring bar was dried with a heat-gun in vacuo and flushed with argon three times after cooling to room temperature. Ester S1 (1.0 equiv.), methyl benzoate (2.0 equiv.) and anhydrous THF were added and the resulting solution was
stirred at 0°C for 5 minutes. Then to the solution was slowly added LiMDS (1.0 M in THF, 2.0 equiv). The solution was stirred for 2 hours and then poured into sat. NH₄Cl aq. The resulting mixture was extracted two times with EtOAc, dried over Na₂SO₄, filtrated, and concentrated in vacuo to afford a yellow oil. The yellow oil was immediately was dissolved in MeCN (0.20 M). To the resulting solution were added p-acetamidobenzenesulfonyl azide (p-ABSA, 1.1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2.0 equiv.) at 0 °C. After stirring the mixture for 5 hours at room temperature, the reaction was diluted with EtOAc. The organics were washed with water and brine, dried over Na₂SO₄, filtrated and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding product.

1.3 General procedure for the intramolecular dearomatice cyclopropanation of naphthalenes

(1) General procedure for reaction condition screening

Catalyst (2 mol%) was added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then anhydrous solvent (0.5 mL, noted in Table S1) was added and the mixture was stirred under the indicated temperature for 15 minutes. Then substrate 1a or 1b (0.1 mmol, 1.0 equiv.) was dissolved in the same anhydrous solvent (1.5 mL, noted in Table S1). Then the solution was injected into the tube for 30 minutes by using a syringe pump. The reaction mixture was then stirred for the indicated temperature and time in Table S1. Upon completion, the reaction was warmed to ambient temperature. The mixture was concentrated by vacuum and the residue was purified by column chromatography on silica gel to give the corresponding product.

(2) General procedure for Rh₂(S-TBPTTL)₄-catalyzed intramolecular dearomatice cyclopropanation of naphthalenes

Rh₂(S-TBPTTL)₄ (2 mol%) was added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then 0.5 mL anhydrous toluene was added and the mixture was stirred under -50°C for 15 minutes. Then substrate 1 (0.1 mmol, 1.0 equiv.) was dissolved in 1.5 mL toluene. Then the solution was injected into the Schlenk tube for 30 minutes by using a syringe pump. The reaction mixture was then stirred under -50°C for 20 hours. Upon completion, the reaction was warmed to
ambient temperature. The mixture was concentrated by vacuum and the residue was purified by column chromatography on silica gel to give the corresponding product.

**Table S1.** Screening of catalyst and reaction conditions

| Entry | R   | Catalyst | solvent | T[°C] | % Yield | ee% |
|-------|-----|----------|---------|-------|---------|-----|
| 1     | Me  | Cat. 1   | DCM     | -78   | 88      | 39  |
| 2     | Me  | Cat. 2   | DCM     | -78   | 87      | 42  |
| 3     | Me  | Cat. 3   | DCM     | -78   | 89      | 45  |
| 4     | Me  | Cat. 4   | DCM     | -78   | 94      | 66  |
| 5     | Me  | Cat. 5   | DCM     | -78   | 94      | 45  |
| 6     | Me  | Cat. 6   | DCM     | -78   | 90      | 67  |
| 7     | Me  | Cat. 7   | DCM     | -78   | 90      | 78  |
| 8     | Me  | Cat. 8   | DCM     | -78   | 90      | 21  |
| 9     | Me  | Cat. 9   | DCM     | 0     | 0       |     |
| 10    | Me  | Cat. 10  | DCM     | 0     | 0       |     |
| 11    | tBu | Cat. 7   | DCM     | -78   | 46      | 90  |
| 12    | tBu | Cat. 7   | DCM     | -20   | 56      | 95  |
| 13    | tBu | Cat. 7   | DCM     | -50   | 64      | 97  |
| 14    | tBu | Cat. 7   | Hexane  | -50   | 46      | 93  |
| 15    | tBu | Cat. 7   | TBME    | -50   | 53      | 93  |
| 16    | tBu | Cat. 7   | Toluene | -50   | 80      | 99  |

![Diagram](image_url)

**Notes:**
- Reactions were conducted with 1a or 1b (0.1 mmol) and catalyst (2 mol%) in 2 mL solvent under Ar.
- Isolated yields.
- Determined by HPLC analysis.
1.4 Procedure for the synthesis of compound 4, 5, 6, 7 and 8

**Compound 4**

A dry 10 mL round-bottom flask equipped with a magnetic stir bar was charged with 2b (30 mg, 0.11 mmol), Pd(OH)$_2$ (2.3 mg, 0.017 mmol) and EtOAc (1 mL). The reaction was stirred for 6 h under balloon-pressure of hydrogen. Then the reaction was filtered through a celite pad with EtOAc, dried with Na$_2$SO$_4$, concentrated under vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product 4 as colorless liquid (26.2 mg, 88% yield, 94% ee).

**Compound 5**

A dry 10 mL round-bottom flask equipped with a magnetic stir bar was charged with 2b (30 mg, 0.11 mmol), Pd/C (5.5 mg) and EtOAc (1 mL). The reaction was stirred for 6 h under balloon-pressure of hydrogen. Then the reaction was filtered through a celite pad with EtOAc, dried with Na$_2$SO$_4$, concentrated under vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product 5 as colorless liquid (25.8 mg, 85%, 95% ee).

**Compound 6**

To a stirred solution of 2b (28.2 mg, 0.1 mmol, 1.0 equiv.) in CH$_3$OH (3.0 mL) was added NBS (26.7 mg, 0.15 mmol, 1.5 equiv.) at room temperature. After stirring for 2 h at 50 °C, the reaction was extracted with ethyl acetate (2×20 mL) and then washed with H$_2$O and brine, dried over Na$_2$SO$_4$ and concentrated in vacuum. The crude product was purified by flash column chromatography on silica gel to yield product 6 as white solid (28.4 mg, 93%, 95% ee).
Compound 7

To a round bottom flask were added 2b (84.6 mg, 0.3 mmol, 1.0 equiv.), MTO (CH$_3$O$_3$Re) (0.4 mg, 0.5 mol%), pyrazole (2.5 mg, 12 mol%), H$_2$O$_2$ (0.068 mL, 0.6 mmol, 2.0 equiv.) and DCM (2 mL). The resulting mixture was stirred at room temperature for 1 hour. When cooled to 0 °C, MnO$_2$ (2 mg) were added and the mixture was stirred at room temperature for 12 hours. Additional MTO (0.4 mg, 0.5 mol%) and H$_2$O$_2$ (0.068 mL, 0.6 mmol, 2.0 equiv.) were added. After 2b was consumed completely, the reaction mixture was quenched with Sat. aqueous NaHCO$_3$ and was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford product 7 as white solid (68.3 mg, 94%, 96% ee).

Compound 8

In a round-bottom flask, 25.4 mg of 2c (0.1 mmol, 1.0 equiv.) was dissolved in 4 mL of dry THF. Then 5.7 mg of LiAlH$_4$ (0.15 mmol, 1.5 equiv.) was added in portion at 0 °C. The mixture was stirred at room temperature for 3 hours inert atmosphere. The reaction was quenched by addition of 2 mL of 1 M HCl solution and was extracted with 2x10 mL of ethyl acetate. The organic phase was dried with anhydrous MgSO$_4$ and filtered. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford product 8 as white solid (19.1 mg, 90%, 91% ee).

2. Characterization Data of Compounds

2.1 Characterization data of substrates 1

methyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1a)

Yellow oil, 87% yield, $^1$H NMR (300 MHz, Chloroform-d) δ 8.01 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.50 (p, J = 6.7 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 6.9 Hz, 1H), 3.77 (s, 3H), 3.19 – 3.09 (t, J = 7.5 Hz, 2H), 2.45 (t, J = 7.5 Hz, 2H), 1.99 (p, J = 7.7 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.10, 137.48, 134.03, 131.83,
tert-butyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1b)

Yellow oil, 90% yield. \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 8.02 (d, \(J = 7.9\) Hz, 1H), 7.89 – 7.84 (m, 1H), 7.73 (d, \(J = 8.0\) Hz, 1H), 7.50 (p, \(J = 6.8\) Hz, 2H), 7.43 – 7.37 (m, 1H), 7.33 (d, \(J = 6.9\) Hz, 1H), 3.18 – 3.09 (t, \(J = 7.5\) Hz, 2H), 2.40 (t, \(J = 7.5\) Hz, 2H), 1.97 (p, \(J = 7.6\) Hz, 2H), 1.48 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(3\)) \(\delta\) 167.03, 137.56, 133.95, 131.77, 128.85, 126.84, 126.08, 125.89, 125.56, 125.51, 123.65, 81.17, 32.17, 28.63, 23.24.

HRMS (ESI+): Calculated for [C\(_{16}\)H\(_{16}\)N\(_2\)O\(_2\)Na]\(^+\) ([M+Na]\(^+\)]: 291.1104, Found: 291.1100.

ethyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1c)

Yellow oil, 88% yield, \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 8.01 (d, \(J = 7.9\) Hz, 1H), 7.87 (d, \(J = 7.1\) Hz, 1H), 7.73 (d, \(J = 8.0\) Hz, 1H), 7.50 (p, \(J = 6.7\) Hz, 2H), 7.44 – 7.37 (m, 1H), 7.33 (d, \(J = 6.7\) Hz, 1H), 4.23 (q, \(J = 7.1\) Hz, 2H), 3.20 – 3.10 (t, 2H), 2.45 (t, \(J = 7.5\) Hz, 2H), 1.99 (p, \(J = 7.6\) Hz, 2H), 1.27 (t, \(J = 6.1\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(3\)) \(\delta\) 167.76, 137.56, 134.06, 131.86, 128.97, 126.98, 126.18, 126.02, 125.65, 125.64, 123.72, 60.93, 32.20, 28.68, 23.28, 14.66; HRMS (ESI+): Calculated for [C\(_{16}\)H\(_{16}\)N\(_2\)O\(_2\)Na]\(^+\) ([M+Na]\(^+\)]: 305.1260, Found: 305.1257.

propyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1d)

Yellow oil, 83% yield, \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 8.01 (d, \(J = 7.8\) Hz, 1H), 7.88 – 7.83 (m, 1H), 7.72 (d, \(J = 8.0\) Hz, 1H), 7.49 (p, \(J = 6.8\) Hz, 2H), 7.40 (t, \(J = 7.6\) Hz, 1H), 7.32 (d, \(J = 6.7\) Hz, 1H), 4.13 (t, \(J = 6.6\) Hz, 2H), 3.18 – 3.09 (t, \(J = 7.5\) Hz, 2H), 2.44 (t, \(J = 7.5\) Hz, 2H), 2.03 – 1.93 (m, 2H), 1.67 (dt, \(J = 14.2, 7.1\) Hz, 2H), 0.93 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(3\)) \(\delta\) 167.84, 137.55, 134.05, 131.85, 128.97, 126.98, 126.18, 126.01, 125.65, 125.64, 123.72, 66.49, 32.21, 28.71, 23.30, 22.36, 10.47; HRMS (ESI+): Calculated for [C\(_{18}\)H\(_{20}\)N\(_2\)O\(_2\)Na]\(^+\) ([M+Na]\(^+\)]: 319.1417, Found: 319.1412.

neopentyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1e)

Yellow oil, 87% yield, \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 8.04 (d, \(J = 8.0\) Hz, 1H), 7.89 (d, \(J = 7.2\) Hz, 1H), 7.75 (d, \(J = 8.1\) Hz, 1H), 7.52 (p, \(J = 6.7\) Hz, 2H), 7.43 (t, \(J = 7.5\) Hz, 1H), 7.35 (d, \(J = 6.8\) Hz, 1H), 3.91 (s, 2H), 3.17 (t, \(J = 7.7\) Hz, 2H), 2.47 (t, \(J = 7.5\) Hz, 2H), 2.03 (p, \(J = 7.3\) Hz, 2H), 0.97 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(3\)) \(\delta\) 167.70, 137.44, 134.00, 131.79, 128.91, 126.93, 126.13, 125.95, 125.57, 123.65, 74.05, 32.16, 31.56, 30.29, 29.80, 28.71, 26.45, 23.24; HRMS (ESI+): Calculated for [C\(_{20}\)H\(_{22}\)N\(_2\)O\(_2\)Na]\(^+\) ([M+Na]\(^+\)]: 347.1730, Found: 347.1720.

benzyl 2-diazo-5-(naphthalen-1-yl)pentanoate (1f)
Yellow oil, 85% yield, $^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 7.99 (d, $J = 7.4$ Hz, 1H), 7.89 – 7.83 (m, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.54 – 7.45 (m, 2H), 7.43 – 7.28 (m, 7H), 5.22 (s, 2H), 3.18 – 3.10 (t, $J = 7.5$ Hz, 2H), 2.46 (t, $J = 7.5$ Hz, 2H), 1.98 (q, $J = 7.4$ Hz, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 167.40, 137.39, 136.19, 133.97, 131.76, 128.89, 128.61, 128.23, 128.06, 126.91, 126.10, 125.95, 125.56, 123.62, 77.30, 77.09, 76.88, 66.41, 32.08, 28.56, 23.21. HRMS (ESI+): Calculated for [C$_{22}$H$_{20}$N$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 367.1417, Found: 367.1401.

**ethyl 2-diazo-5-(4-fluoronaphthalen-1-yl)pentanoate (1g)**

Yellow oil, 90% yield, $^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 8.21 – 8.12 (m, 1H), 8.01 (dt, $J = 7.3$, 2.0 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.25 (dd, $J = 7.9$, 5.5 Hz, 1H), 7.08 (dd, $J = 10.4$, 7.8 Hz, 1H), 3.15 – 3.07 (t, $J = 7.5$ Hz, 2H), 2.40 (t, $J = 7.5$ Hz, 2H), 2.02 – 1.90 (m, 2H), 1.50 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.99, 159.33, 156.01, 133.35, 133.29, 132.83, 132.77, 126.79, 125.81, 125.78, 125.58, 124.47, 124.16, 123.95, 123.73, 123.69, 121.31, 121.24, 108.97, 108.71, 81.21, 77.46, 77.03, 76.61, 31.74, 28.65, 28.38, 23.14. HRMS (ESI+): Calculated for [C$_{10}$H$_{12}$FN$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 351.1479, Found: 351.1474.

**ethyl 5-(5-bromonaphthalen-1-yl)-2-diazopentanoate (1h)**

Yellow oil, 81% yield, $^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 8.19 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.81 (dd, $J = 7.4$, 1.0 Hz, 1H), 7.53 (dd, $J = 8.6$, 7.0 Hz, 1H), 7.43 – 7.33 (m, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.20 – 3.11 (t, $J = 7.5$ Hz, 2H), 2.45 (t, $J = 7.5$ Hz, 2H), 1.98 (q, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.55, 137.95, 133.04, 132.44, 129.79, 127.02, 126.94, 126.11, 126.07, 123.84, 123.57, 60.86, 32.26, 28.65, 23.18, 14.55. Calculated for [C$_{17}$H$_{17}$BrN$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 383.0366, Found: 383.0356.

**tert-butyl 5-(6-benzyloxy)naphthalen-1-yl)-2-diazopentanoate (1i)**

Yellow oil, 88% yield, $^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 7.85 (dt, $J = 8.6$, 1.0 Hz, 1H), 7.52 (d, $J = 8.2$ Hz, 1H), 7.45 – 7.38 (m, 2H), 7.36 – 7.23 (m, 4H), 7.20 – 7.15 (m, 2H), 7.09 (dd, $J = 7.1$, 1.2 Hz, 1H), 5.10 (s, 2H), 3.05 – 2.97 (t, $J = 7.5$ Hz, 2H), 2.30 (t, $J = 7.5$ Hz, 2H), 1.91 – 1.81 (m, 2H), 1.39 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.05, 156.47, 137.66, 136.96, 135.23, 128.68, 128.08, 127.64, 127.35, 126.28, 125.84, 125.39, 124.13, 118.88, 108.16, 81.19, 70.05, 32.25, 28.76, 28.46, 23.26. HRMS (ESI+): Calculated for [C$_{25}$H$_{24}$N$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 439.1992, Found: 439.1982.

**tert-butyl 5-(6-(allyloxy)naphthalen-1-yl)-2-diazopentanoate (1j)**

Yellow oil, 89% yield, $^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 7.94 (d, $J = 9.1$ Hz, 1H), 7.62 (d, $J = 8.2$ Hz, 1H), 7.37 (dd, $J = 8.2$, 7.0 Hz, 1H), 7.25 – 7.16 (m, 3H), 6.16 (ddt, $J = 17.2$, 10.6, 5.3 Hz, 1H), 5.57 – 5.33 (m, 2H), 4.69 (dt, $J = 5.3$, 1.6
tert-butyl 2-diazo-5-(6-(3-phenylprop-2-yn-1-yl)oxy)naphthalen-1-yl)pentanoate (1k)  
Yellow oil, 85% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.88 (d, $J = 9.2$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.38 (dd, $J = 7.3$, 2.4 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.30 – 7.14 (m, 5H), 7.13 (d, $J = 7.0$ Hz, 1H), 4.97 (s, 2H), 3.08 – 2.97 (t, $J = 7.8$ Hz, 2H), 2.31 (t, $J = 7.5$ Hz, 2H), 1.88 (p, $J = 7.5$ Hz, 2H), 1.40 (s, 9H).  
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.92, 158.73, 143.06, 133.43, 129.36, 120.97, 117.49, 114.99, 112.07, 81.06, 68.67, 35.00, 29.18, 28.39, 22.74. Calculated for [C$_{22}$H$_{26}$N$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 389.1836, Found: 389.1827

tert-butyl 2-diazo-5-(6-morpholinonaphthalen-1-yl)pentanoate (1l)  
Yellow oil, 82% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.92 (d, $J = 9.2$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 1H), 7.38 – 7.28 (m, 2H), 7.15 (dd, $J = 6.7$, 1.7 Hz, 2H), 3.99 – 3.87 (m, 4H), 3.33 – 3.22 (m, 4H), 3.14 – 3.03 (t, $J = 4.8$ Hz 2H), 2.38 (t, $J = 7.5$ Hz, 2H), 2.00 – 1.87 (m, 2H), 1.48 (s, 9H).  
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.03, 148.71, 137.40, 135.12, 126.84, 126.16, 125.75, 124.73, 123.87, 118.62, 108.48, 87.36, 83.80, 81.18, 56.72, 32.22, 28.71, 28.40, 23.22. Calculated for [C$_{28}$H$_{29}$N$_2$O$_3$Na]$^+$ ([M+Na]$^+$): 463.1992, Found: 463.1984

tert-butyl 2-diazo-5-(6-(((trifluoromethyl)sulfonyl)oxy)naphthalen-1-yl)pentanoate (1m)  
Yellow oil, 87% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 8.12 (d, $J = 9.3$ Hz, 1H), 7.83 – 7.72 (t, $J = 7.5$ Hz 2H), 7.60 – 7.49 (m, 1H), 7.49 – 7.37 (m, 2H), 3.20 – 3.10 (t, $J = 4.8$ Hz 2H), 2.42 (t, $J = 7.5$ Hz, 2H), 2.00 – 1.87 (m, 2H), 1.48 (s, 9H).  
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.88, 146.92, 138.06, 134.12, 130.82, 127.49, 127.35, 126.94, 126.58, 119.95, 119.40, 81.28, 32.14, 28.63, 28.37, 23.24. HRMS (ESI+): Calculated for [C$_{20}$H$_{21}$F$_3$N$_2$OSNa]$^+$ ([M+Na]$^+$): 418.2101, Found: 418.2093

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tert-butyl 5-(6-allylnaphthalen-1-yl)-2-diazopentanoate (1o)

Yellow oil, 87% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$
7.94 (d, $J = 8.7$ Hz, 1H), 7.69 – 7.61 (m, 2H), 7.36 (ddd, $J = 8.1$, 4.2, 2.3 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.05 (ddt, $J = 16.8$, 10.1, 6.6 Hz, 1H), 5.21 – 5.06 (m, 2H), 3.55 (d, $J = 6.9$ Hz, 2H), 3.18 – 3.01 (t, $J = 7.5$ Hz, 2H), 2.38 (t, $J = 7.5$ Hz, 2H), 2.01 – 1.89 (m, 2H), 1.47 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.06, 137.41, 137.28, 137.18, 134.17, 130.39, 127.61, 127.38, 126.43, 125.68, 125.54, 123.76, 116.09, 81.16, 40.18, 32.16, 28.64, 28.40, 23.19. HRMS (ESI+): Calculated for [C$_{22}$H$_{26}$N$_2$O$_2$Na]$^+$ ([M+Na]$^+$): 373.1886, Found: 373.1870

methyl 4-(5-(5-(tert-butoxy)-4-diazo-5-oxopentyl)naphthalen-2-yl)benzoate (1p)

Yellow oil, 81% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$
8.20 – 8.07 (m, 4H), 7.84 – 7.80 (m, 4H), 7.47 (dd, $J = 8.1$, 7.0 Hz, 1H), 7.38 (d, $J = 6.4$ Hz, 1H), 3.98 (s, 3H), 3.28 – 3.08 (t, $J = 7.5$ Hz, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 2.12 – 1.93 (m, 2H), 1.50 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.99, 145.32, 137.57, 136.83, 134.11, 131.32, 130.20, 128.94, 127.29, 127.22, 127.19, 126.63, 126.28, 125.16, 124.53, 81.19, 52.16, 32.11, 28.66, 28.41, 23.22. HRMS (ESI+): Calculated for [C$_{27}$H$_{28}$N$_2$O$_4$Na]$^+$ ([M+Na]$^+$): 467.1941, Found: 467.1926

tert-butyl 5-((2,2'-binaphthalen)-5-yl)-2-diazopentanoate (1q)

Yellow oil, 85% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$
8.22 (t, $J = 2.2$ Hz, 2H), 8.02 – 7.90 (m, 6H), 7.58 – 7.44 (m, 4H), 7.40 – 7.35 (m, 1H), 3.21 (t, $J = 7.7$ Hz, 2H), 2.46 (t, $J = 7.5$ Hz, 2H), 2.04 (dd, $J = 10.2$, 5.1 Hz, 2H), 1.53 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.09, 138.26, 138.03, 137.57, 134.33, 133.80, 132.73, 131.02, 128.59, 128.30, 127.73, 127.23, 127.01, 126.40, 126.27, 126.15, 126.09, 126.06, 125.71, 124.41, 81.23, 77.55, 77.12, 76.70, 32.19, 28.71, 28.46, 23.26. HRMS (ESI+): Calculated for [C$_{29}$H$_{28}$N$_2$O$_2$Na]$^+$ ([M+Na]$^+$): 459.2043, Found: 459.2063

tert-butyl 2-diazo-5-(6-phenynaphthalen-1-yl)pentanoate (1r)

Yellow oil, 86% yield, $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$
8.16 – 8.10 (m, 2H), 7.81 (ddd, $J = 12.9$, 8.2, 2.0 Hz, 4H), 7.57 – 7.43 (m, 4H), 7.38 (d, $J = 7.0$ Hz, 1H), 3.24 – 3.18 (t, $J = 7.5$ Hz, 2H), 2.47 (t, $J = 7.5$ Hz, 2H), 2.05 (p, $J = 7.6$ Hz, 2H), 1.54 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.03, 140.97, 138.18, 137.52, 134.25, 130.95, 128.91, 127.41, 127.18, 126.70, 126.19, 126.07, 125.56, 124.30, 81.20, 77.53, 77.10, 76.68, 32.19, 28.70, 28.44, 23.26. HRMS (ESI+): Calculated for [C$_{25}$H$_{26}$N$_2$O$_2$Na]$^+$ ([M+Na]$^+$): 409.1886, Found: 409.1877.

tert-butyl 2-diazo-5-(6-(thiophen-2-yl)naphthalen-1-yl)pentanoate (1s)
2.2 Characterization data of products 2

**methyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]napthalene-3a(3bH)-carboxylate (2a)**

Light yellow oil, 84% yield, 85% ee; $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.61 (d, $J$ = 7.3 Hz, 1H), 7.49 (dd, $J$ = 8.4, 6.8 Hz, 1H), 7.36 – 7.18 (m, 3H), 3.51 – 3.32 (m, 4H), 3.20 – 3.03 (t, $J$ = 7.5 Hz, 2H), 2.51 – 2.31 (t, $J$ = 7.8 Hz, 2H), 2.06 – 1.89 (m, 2H), 1.51 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.08, 146.56, 144.31, 139.60, 133.30, 130.28, 127.61, 127.46, 119.12, 119.08, 119.01, 81.12, 30.57, 29.87, 28.70, 28.41, 23.09. HRMS (ESI+): Calculated for [C$_{21}$H$_{25}$NO$_3$Na]$^+$ ([M+Na]$^+$): 359.1730, Found: 359.1738.
2.84 (td, J = 12.0, 8.8 Hz, 1H), 2.46 (dd, J = 10.9, 4.3 Hz, 2H), 2.38 (d, J = 8.4 Hz, 1H), 2.04 (dd, J = 12.6, 7.7 Hz, 1H), 1.85 (dd, J = 13.5, 8.0 Hz, 1H), 1.39 (d, J = 11.5 Hz, 1H); 13C NMR (75 MHz, CDCl3) δ 169.11, 133.08, 132.27, 128.63, 127.53, 127.25, 126.39, 125.84, 122.69, 51.35, 41.55, 31.24, 31.07, 30.86, 26.56, 18.84; HRMS (ESI+): Calculated for [C16H27O4+ \([\text{M}+\text{H}]^+\)]: 241.1222, Found: 241.1230. HPLC conditions (Agilent 1260): Chiralpak IC (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.5 mL/min; Retention time: 9.136 min(major), 9.977 min(minor).

tert-butyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2b)

Light yellow oil, 80% yield, 99% ee; 1H NMR (300 MHz, Chloroform-d) δ 7.57 (d, J = 7.7 Hz, 1H), 7.24 – 7.06 (m, 3H), 6.45 (d, J = 9.6 Hz, 1H), 6.15 (dd, J = 9.6, 5.2 Hz, 1H), 2.79 (td, J = 12.1, 8.6 Hz, 1H), 2.43 – 2.25 (m, 3H), 1.97 (dd, J = 12.6, 7.7 Hz, 1H), 1.79 (dt, J = 15.8, 8.1 Hz, 1H), 1.28 (m, 1H), 1.06 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 169.62, 143.02, 141.86, 138.24, 131.42, 127.97, 122.62, 121.96, 112.02, 79.46, 39.95, 31.69, 30.32, 29.86, 27.90, 27.57, 19.32. HRMS (ESI+): Calculated for [C19H28O2Na+ ([M+Na]+)): 305.1512, Found: 305.1517. HPLC conditions (Agilent 1260): Chiralpak OJ-H (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.1 mL/min; Retention time: 44.811 min(major), 47.513 min(minor).

ethyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2c)

Light yellow oil, 86% yield, 91% ee; 1H NMR (300 MHz, Chloroform-d) δ 7.59 (d, J = 7.4 Hz, 1H), 7.28 – 7.18 (m, 2H), 7.15 (t, J = 6.9 Hz, 1H), 6.54 (d, J = 9.6 Hz, 1H), 6.12 (dd, J = 9.6, 5.3 Hz, 1H), 3.84 (qq, J = 10.8, 7.1 Hz, 2H), 2.82 (td, J = 12.0, 8.6 Hz, 1H), 2.46 – 2.29 (m, 3H), 2.01 (dd, J = 12.6, 7.7 Hz, 1H), 1.81 (dt, J = 15.9, 8.1 Hz, 1H), 1.40 – 1.28 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 169.18, 133.01, 132.56, 128.37, 127.51, 127.20, 126.28, 125.87, 123.10, 60.00, 41.22, 31.27, 31.06, 30.64, 27.09, 18.95, 14.00; HRMS (ESI+): Calculated for [C19H28O2Na+ ([M+Na]+)): 305.1380, Found: 305.1390. HPLC conditions (Agilent 1260): Chiralpak OJ-H (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=8/92; flow=0.3 mL/min; Retention time: 15.220 min(major), 16.155 min(minor).

propyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2d)

Colorless oil, 92% yield, 88% ee; 1H NMR (300 MHz, Chloroform-d) δ 7.58 (d, J = 7.3 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.17 – 7.11 (m, 1H), 6.53 (d, J = 9.6 Hz, 1H), 6.11 (dd, J = 9.5, 5.3 Hz, 1H), 3.83 – 3.65 (m, 2H), 2.81 (td, J = 11.8, 8.5 Hz, 1H), 2.38 (qd, J = 12.6, 12.1, 6.9 Hz, 3H), 2.01 (dt, J = 12.4, 5.5 Hz, 1H), 1.80 (dt, J = 15.1, 8.1 Hz, 1H), 1.32 – 1.28 (m, 2H), 0.89 (d, J = 7.3 Hz, 1H), 0.69 (t, J = 7.4 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 169.36, 133.00, 132.58, 128.40,
127.57, 127.24, 126.33, 125.90, 123.13, 65.82, 41.25, 31.35, 31.17, 30.67, 29.85, 21.87, 18.93, 10.41; HRMS (ESI+): Calculated for [C₁₈H₂₁O₂⁺] ([M+H⁺]): 269.1536, Found: 269.1546.

**HPLC conditions (Agilent 1260):** Chiralpak IC (Particle Size: 5 µm, Dimensions: 4.6 mm Φ x 250 mmL); detected at 254 nm; temperature 25°C; i-propanol/hexane=5/95; flow=0.3 mL/min; Retention time: 16.880 min(major), 17.975 min(minor).

**neopentyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2e)**

Light yellow oil, 61% yield, 92% ee; ¹H NMR (600 MHz, Chloroform-d) δ 7.58 (d, J = 7.7 Hz, 1H), 7.23 (td, J = 7.5, 1.6 Hz, 1H), 7.18 (td, J = 7.4, 1.3 Hz, 1H), 7.13 (dd, J = 7.5, 1.5 Hz, 1H), 6.53 (d, J = 9.6 Hz, 1H), 6.12 (dd, J = 9.7, 5.2 Hz, 1H), 3.54 – 3.46 (m, 2H), 2.82 (td, J = 12.0, 8.2 Hz, 1H), 2.46 – 2.40 (m, 2H), 2.36 (dd, J = 12.8, 8.2 Hz, 1H), 2.01 (dd, J = 12.5, 7.7 Hz, 1H), 1.81 (dt, J = 13.5, 8.2 Hz, 1H), 1.35 – 1.28 (m, 1H), 0.72 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 169.01, 132.72, 132.36, 128.24, 127.61, 127.18, 126.23, 125.78, 123.04, 73.55, 41.08, 31.25, 31.21, 31.01, 30.39, 27.21, 26.28, 18.80.

**HRMS (ESI+):** Calculated for [C₂₀H₂₄O₂Na⁺] ([M+Na⁺]): 319.1669, Found: 319.1665.

**benzyl (3aR,3bR,9bR)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2g)**

Colorless oil, 95% yield, 91% ee; ¹H NMR (300 MHz, Chloroform-d) δ 7.62 (d, J = 7.5 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.22 (dd, J = 7.4, 1.4 Hz, 1H), 7.12 (dd, J = 7.3, 1.6 Hz, 1H), 7.03 (dd, J = 6.5, 3.0 Hz, 2H), 6.52 (d, J = 9.7 Hz, 1H), 6.14 (dd, J = 9.7, 5.3 Hz, 1H), 4.99 – 4.75 (m, 2H), 2.85 (td, J = 12.1, 8.3 Hz, 1H), 2.56 – 2.33 (m, 3H), 2.04 (dd, J = 12.7, 7.8 Hz, 1H), 1.84 (dt, J = 13.9, 8.2 Hz, 1H), 1.44 – 1.26 (m, 1H), ¹³C NMR (151 MHz, CDCl₃) δ 168.82, 136.05, 132.23, 128.39, 128.25, 127.84, 127.74, 127.60, 127.15, 126.30, 125.85, 122.88, 77.23, 77.02, 76.81, 65.77, 41.42, 31.20, 31.01, 30.66, 26.89, 18.79.

HRMS (ESI+): Calculated for [C₂₂H₂₃O₂⁺] ([M+H⁺]): 317.1536, Found: 317.1550.

**HPLC conditions (Agilent 1260):** Chiralpak IC (Particle Size: 5 µm, Dimensions: 4.6 mm Φ x 250 mmL); detected at 254 nm; temperature 25°C; i-propanol/hexane=1/99; flow=0.5 mL/min; Retention time: 10.082 min(major), 10.956 min(minor).

**tert-butyl (3aR,3bR,9bR)-5-fluoro-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2g)**

Colorless oil, 68% yield, 96% ee; ¹H NMR (300 MHz, Chloroform-d) δ 7.61 (dt, J = 7.5, 1.8 Hz, 1H), 7.50 (dd, J = 7.5, 1.7 Hz, 1H), 7.37 – 7.25 (m, 2H), 5.70 (dd, J = 13.6, 5.7 Hz, 1H), 2.78 (td, J = 12.0, 8.4 Hz, 1H), 2.47 – 2.27 (m, 3H), 1.99 (dd, J = 12.6, 7.7 Hz, 1H), 1.81 (dt, J = 13.3, 8.2 Hz, 1H), 1.48 – 1.38 (m, 1H), 1.11 (s, 9H), ¹³C NMR (75 MHz, CDCl₃) δ 169.21, 154.96, 134.89, 128.13, 126.17, 126.12, 125.99, 120.87, 120.79, 100.55, 100.25, 80.33, 39.35, 31.43,
ethyl (3aR,3bR,9bR)-6-bromo-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2h)

Colorless oil, 51% yield, 99% ee. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.56 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.35 (m, 1H), 7.13 – 6.98 (m, 2H), 6.52 (dd, $J = 9.8$, 5.4 Hz, 1H), 3.96 – 3.77 (m, 2H), 2.89 – 2.72 (m, 1H), 2.48 – 2.34 (m, 3H), 2.07 – 1.94 (m, 2H), 1.83 (dd, $J = 14.3$, 6.9 Hz, 1H), 1.48 – 1.35 (m, 1H), 0.92 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.12, 148.84, 130.55, 130.10, 127.68, 126.31, 125.55, 125.14, 122.87, 60.10, 41.14, 31.44, 30.94, 30.63, 30.20, 18.77, 13.78. HRMS (ESI+): Calculated for [C$_{16}$H$_{12}$O$_2$Na]$^+$ ([M+Na]$^+$): 355.0304, Found: 355.0298.

HPLC conditions (Agilent 1260): Chiralpak IB (Particle Size: 5 µm, Dimensions: 4.6 mm Φ × 250 mM); detected at 210 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.5 mL/min; Retention time: 9.471 min(major), 11.014 min(minor).

tert-butyl (3aR,3bR,9bR)-7-(benzoxyl)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2i)

Colorless oil, 78% yield, 95% ee. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.52 – 7.29 (m, 6H), 6.89 (dd, $J = 8.6$, 2.8 Hz, 1H), 6.77 (d, $J = 2.8$ Hz, 1H), 6.42 (d, $J = 9.6$ Hz, 1H), 6.19 (dd, $J = 9.7$, 5.2 Hz, 1H), 5.09 (s, 2H), 2.82 – 2.67 (m, 1H), 2.48 – 2.23 (m, 3H), 1.97 (d, $J = 12.5$, 7.7 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.33 (d, $J = 12.7$ Hz, 1H), 1.10 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.19, 156.93, 137.22, 133.77, 128.54, 127.85, 127.52, 127.39, 126.81, 125.65, 124.90, 113.65, 113.47, 79.94, 69.98, 40.18, 31.40, 31.34, 29.22, 28.51, 27.71, 18.96. HRMS (ESI+): Calculated for [C$_{28}$H$_{23}$O$_3$Na]$^+$ ([M+Na]$^+$): 411.1931, Found: 411.1921. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 µm, Dimensions: 4.6 mm Φ × 250 mM); detected at 254 nm; temperature 25 °C; i-propanol/hexane=8/92; flow=0.5 mL/min; Retention time: 11.436 min(minor), 12.554 min(major).

tert-butyl (3aR,3bR,9bR)-7-(allyloxy)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2j)

Colorless oil, 72% yield, 97% ee. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.48 (d, $J = 8.5$ Hz, 1H), 6.83 (dd, $J = 8.5$, 2.8 Hz, 1H), 6.70 (d, $J = 2.7$ Hz, 1H), 6.42 (d, $J = 9.7$ Hz, 1H), 6.19 (dd, $J = 9.7$, 5.3 Hz, 1H), 6.07 (ddt, $J = 15.8$, 10.5, 5.3 Hz, 1H), 5.47 – 5.37 (m, 1H), 5.29 (dd, $J = 10.4$, 1.6 Hz, 1H), 4.55 (dt, $J = 5.4$, 1.5 Hz, 2H), 2.75 (td, $J = 12.0$, 8.4 Hz, 1H), 2.51 – 2.24 (m, 3H), 1.97 (dd, $J = 12.6$, 7.7 Hz, 1H), 1.79 (dt, $J = 13.5$, 8.1 Hz, 1H), 1.38 – 1.28 (m, 1H), 1.11 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.20, 156.77, 133.74, 133.46, 127.52, 126.78,
 tert-butyl (3aR,3bR,9bR)-7-((3-phenylprop-2-yn-1-yl)oxy)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (2k)

Colorless oil, 67% yield, 99% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.52 (d, J = 8.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 6.94 (dd, J = 8.5, 2.8 Hz, 1H), 6.82 (d, J = 2.8 Hz, 1H), 6.45 (d, J = 9.6 Hz, 1H), 6.21 (dd, J = 9.7, 5.3 Hz, 1H), 4.93 (s, 2H), 2.76 (td, J = 12.0, 8.3 Hz, 1H), 2.47 – 2.24 (m, 3H), 1.98 (dd, J = 12.6, 7.7 Hz, 1H), 1.80 (dt, J = 13.3, 8.1 Hz, 1H), 1.30 (d, J = 12.5 Hz, 1H), 1.08 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 169.21, 152.49, 149.56, 142.92, 133.36, 127.88, 126.52, 124.56, 115.01, 79.83, 66.93, 49.89, 40.24, 31.41, 31.24, 29.28, 28.66, 27.73, 18.98. HRMS (ESI+): Calculated for [C23H18O2Na]+ ([M+Na]+): 435.1931. Found: 435.1922. HPLC conditions (Agilent 1260): Chiralpak IB (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.5 mL/min; Retention time: 11.026 min(minor), 13.471 min(major).

tert-butyl (3aR,3bR,9bR)-7-morpholino-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (2l)

Yellow oil, 63% yield, 85% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.48 (d, J = 8.5 Hz, 1H), 6.85 (dd, J = 8.5, 2.7 Hz, 1H), 6.70 (d, J = 2.7 Hz, 1H), 6.42 (d, J = 9.6 Hz, 1H), 6.17 (dd, J = 9.7, 5.3 Hz, 1H), 3.97 – 3.82 (m, 4H), 3.15 (dd, J = 5.8, 3.8 Hz, 4H), 2.75 (td, J = 12.0, 8.3 Hz, 1H), 2.47 – 2.22 (m, 3H), 1.96 (dd, J = 12.5, 7.7 Hz, 1H), 1.80 (dd, J = 13.5, 8.0 Hz, 1H), 1.40 – 1.25 (m, 1H), 1.12 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 169.22, 152.49, 149.56, 142.92, 133.36, 127.88, 126.52, 124.56, 115.01, 79.83, 66.93, 49.89, 40.24, 31.41, 31.24, 29.28, 28.66, 27.73, 18.98. HRMS (ESI+): Calculated for [C23H30NO3]+ ([M+Na]+): 368.2220. Found: 368.2227. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.5 mL/min; Retention time: 12.448 min(major), 13.147 min(minor).

tert-butyl (3aR,3bR,9bR)-7-((trifluoromethyl)sulfonyl)oxy)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (2m)

Yellow oil, 68% yield, 99% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.64 (d, J = 8.6 Hz, 1H), 7.14 (dd, J = 8.6, 2.7 Hz, 1H), 7.03 (d, J = 2.7 Hz, 1H), 6.44 (d, J = 9.7 Hz, 1H), 6.38 – 6.27 (m, 1H), 2.77 (td, J = 12.0, 8.3 Hz, 1H), 2.47 – 2.30 (m, 3H), 2.01 (dd, J = 12.5, 7.7 Hz, 1H), 1.93 – 1.77 (m, 1H), 1.43 – 1.31 (m, 1H), 1.09 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 168.50, 147.65, 134.71, 133.58, 127.51, 127.01, 126.01, 119.35, 119.12, 80.55, 39.97, 31.33, 29.71,
tert-butyl (3aR,3bR,9bR)-7-vinyl-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2n)

Colorless oil, 75% yield, 98% ee; 1H NMR (300 MHz, Chloroform-d) δ 7.55 (d, J = 8.0 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.17 (d, J = 1.9 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 6.48 (d, J = 9.6 Hz, 1H), 6.19 (dd, J = 9.6, 5.3 Hz, 1H), 5.73 (dd, J = 17.6, 1.0 Hz, 1H), 5.22 (dd, J = 10.9, 1.0 Hz, 1H), 2.80 (td, J = 12.0, 8.2 Hz, 1H), 2.47 – 2.28 (m, 3H), 1.98 (dd, J = 12.6, 7.7 Hz, 1H), 1.80 (dd, J = 14.5, 6.9 Hz, 1H), 1.36 – 1.28 (m, 1H), 1.10 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 169.11, 137.66, 137.49, 132.66, 130.83, 127.60, 127.56, 127.25, 125.85, 124.03, 115.51, 79.94, 40.28, 39.79, 31.43, 31.25, 29.43, 28.71, 27.65, 19.00. HRMS (ESI+): Calculated for [C21H20O2Na]+ ([M+Na]+): 331.1669, Found: 331.1672 HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.5 mL/min; Retention time: 28.077 min(minor), 34.785 min(major).

tert-butyl (3aR,3bR,9bR)-7-allyl-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2o)

Colorless oil, 73% yield, 97% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.40 (t, J = 8.1 Hz, 1H), 7.02 (dd, J = 8.1, 1.9 Hz, 1H), 6.94 (d, J = 1.9 Hz, 1H), 6.44 (d, J = 9.6 Hz, 1H), 6.14 (dd, J = 9.6, 5.2 Hz, 1H), 5.94 (dtt, J = 17.6, 10.0, 6.7 Hz, 1H), 5.12 – 5.00 (m, 2H), 3.30 – 3.33 (m, 2H), 2.83 – 2.69 (m, 1H), 2.45 – 2.23 (m, 3H), 1.95 (dd, J = 12.6, 7.7 Hz, 1H), 1.78 (dt, J = 13.2, 8.1 Hz, 1H), 1.38 – 1.27 (m, 1H), 1.07 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 169.11, 137.66, 137.49, 132.66, 130.83, 127.60, 127.56, 127.25, 125.85, 124.03, 115.51, 79.94, 40.28, 39.79, 31.43, 31.25, 29.43, 28.71, 27.65, 19.00. HRMS (ESI+): Calculated for [C22H22O2Na]+ ([M+Na]+): 345.1825, Found: 345.1820. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.2 mL/min; Retention time: 22.464 min(minor), 25.104 min(major).

tert-butyl (3aR,3bR,9bR)-7-(4-(methoxycarbonyl)phenyl)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2p)

White solid, 61% yield, 99% ee. 1H NMR (300 MHz, Chloroform-d) δ 8.11 (d, J = 8.4 Hz, 2H), 7.74 – 7.66 (m, 3H), 7.53 (dd, J = 8.1, 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 6.56 (d, J = 9.7 Hz, 1H), 6.25 (dd, J = 9.6, 5.3 Hz, 1H), 3.96 (s, 3H), 2.94 – 2.76 (m, 1H), 2.49 – 2.34 (m, 3H), 2.03 (dd, J = 13.2, 8.4 Hz, 1H), 1.93 – 1.79 (m, 1H), 1.39 – 1.28 (m, 1H), 1.11 (s, 9H). 13C NMR (75 MHz,
CDCl$_3$ $\delta$ 168.80, 167.04, 145.47, 137.40, 133.43, 133.18, 130.07, 128.63, 127.34, 126.78, 126.45, 126.03, 125.67, 124.82, 80.13, 52.12, 40.23, 31.42, 31.25, 29.67, 29.50, 27.67, 19.02. HRMS (ESI$^+$): Calculated for [C$_2$H$_3$O$_2$Na]$^+$ ([M+Na]$^+$): 439.1880. Found: 439.1864. HPLC conditions (Agilent 1260): Chiralpak IC (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=8/92; flow=0.5 mL/min. Retention time: 12.421 min(major), 14.568 min(minor).

**tert-butyl (3aR,3bR,9bR)-7-(naphthalen-2-yl)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2q)**

White solid, 63% yield, 99% ee. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 8.06 (s, 1H), 7.95 – 7.86 (m, 3H), 7.81 – 7.69 (m, 2H), 7.63 (dd, $J$ = 8.1, 2.0 Hz, 1H), 7.57 – 7.46 (m, 3H), 6.59 (d, $J$ = 9.7 Hz, 1H), 6.25 (dd, $J$ = 9.6, 5.3 Hz, 1H), 2.96 – 2.78 (m, 1H), 2.53 – 2.30 (m, 3H), 2.05 (dd, $J$ = 12.6, 7.6 Hz, 1H), 1.85 (dt, $J$ = 15.4, 7.9 Hz, 1H), 1.37 – 1.31 (m, 1H), 1.12 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.03, 138.55, 138.35, 134.23, 133.69, 133.10, 132.50, 128.34, 128.13, 127.63, 127.57, 126.37, 126.24, 125.86, 125.80, 125.50, 125.39, 124.58, 116.58, 80.14, 40.30, 31.45, 31.27, 29.62, 29.39, 27.67, 19.06. HRMS (ESI$^+$): Calculated for [C$_4$H$_3$O$_2$Na]$^+$ ([M+Na]$^+$): 431.1982. Found: 431.1979. HPLC conditions (Agilent 1260): Chiralpak AY-3 (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.5 mL/min. Retention time: 10.468 min(major), 13.691 min(minor).

**tert-butyl 7-phenyl-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2r)**

White solid, 71% yield, 92% ee; $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.69 – 7.60 (m, 3H), 7.52 – 7.42 (m, 3H), 7.39 – 7.34 (m, 2H), 6.55 (d, $J$ = 9.6 Hz, 1H), 6.24 (dd, $J$ = 9.7, 5.2 Hz, 1H), 2.92 – 2.76 (m, 1H), 2.50 – 2.33 (m, 3H), 2.03 (dd, $J$ = 12.6, 7.7 Hz, 1H), 1.84 (dt, $J$ = 15.2, 8.0 Hz, 1H), 1.42 – 1.31 (m, 1H), 1.10 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.06, 141.08, 138.71, 132.98, 132.36, 128.71, 127.54, 127.05, 126.96, 126.26, 126.03, 125.63, 124.53, 80.11, 77.45, 77.03, 76.60, 40.29, 31.45, 31.25, 29.57, 29.35, 27.64, 19.07. HRMS (ESI$^+$): Calculated for [C$_{29}$H$_{26}$O$_2$Na]$^+$ ([M+Na]$^+$): 381.1825. Found: 381.1830. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.5 mL/min. Retention time: 8.333 min(major), 9.150 min(minor).

**tert-butyl (3aR,3bR,9bR)-7-(thiophen-2-yl)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalene-3a(3bH)-carboxylate (2s)**

Colorless oil, 68% yield, 95% ee. $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.60 (d, $J$ = 8.1 Hz, 1H), 7.51 (dd, $J$ = 8.1, 2.0 Hz, 1H), 7.38 (d, $J$ = 2.0 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.10 (dd, $J$ = 5.1, 3.6 Hz, 1H), 6.52 (d, $J$ = 9.7 Hz, 1H), 6.23 (dd, $J$ = 9.7, 5.2 Hz, 1H), 2.81 (td, $J$ = 12.0, 8.4 Hz, 1H), 2.52 – 2.30 (m, 3H), 2.01 (dd, $J$ = 12.5, 7.7 Hz, 1H), 1.83 (dt, $J$ = 15.5, 7.8 Hz, 1H), 1.40 – 1.29 (m, 1H), 1.12 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.92, 144.48,
tort-butyln (3aR,3bR,9bR)-7-cyano-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (2t)

Colorless oil, 18% yield, 84% ee. ^1H NMR (300 MHz, Chloroform-d) δ 7.68 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.41 (s, 1H), 6.46 (d, J = 9.7 Hz, 1H), 6.32 (d, J = 5.2 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.39 (dd, J = 8.9, 4.8 Hz, 3H), 2.10 – 1.75 (m, 2H), 1.44 – 1.32 (m, 2H), 1.11 (s, 8H). ^13C NMR (75 MHz, CDCl3) δ 174.32, 143.06, 139.31, 135.87, 134.71, 130.30, 129.40, 127.05, 122.54, 81.05, 40.67, 38.25, 33.37, 31.12, 29.70, 27.66, 15.94. HRMS (ESI+): Calculated for [C22H22O2Na]^+ ([M+Na]+): 387.1389, Found: 387.1384. HPLC conditions (Agilent 1260): Chiralpak MX (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=1/99; flow=1 mL/min; Retention time: 4.897 min(major), 5.413 min(minor).

tort-butyln (3aR,3bR,9bR)-9-(methoxy methyl)-2,3-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (2u)

Colorless oil, 53% yield, 91% ee. ^1H NMR (400 MHz, Chloroform-d) δ 7.24 (dd, J = 7.7, 1.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.99 (dd, J = 7.4, 1.5 Hz, 1H), 6.41 (d, J = 9.5 Hz, 1H), 6.08 (dd, J = 9.5, 5.2 Hz, 1H), 4.59 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 3.37 (s, 3H), 2.64 (ddd, J = 13.0, 10.8, 9.0 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.19 (ddd, J = 13.1, 8.5, 1.6 Hz, 1H), 2.06 (d, J = 5.2 Hz, 1H), 1.94 (ddd, J = 13.2, 9.0, 1.8 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.40 – 1.32 (m, 1H), 1.01 (s, 9H). ^13C NMR (151 MHz, CDCl3) δ 169.94, 137.54, 134.31, 130.65, 129.29, 128.98, 127.41, 126.42, 123.61, 80.00, 77.23, 77.02, 76.81, 73.56, 58.29, 39.28, 34.13, 31.72, 30.97, 27.59, 26.63, 20.22. HRMS (ESI+): Calculated for [C22H26O3Na]^+ ([M+Na]+): 349.1774, Found: 349.1764. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.5 mL/min; Retention time: 7.304 min(major), 8.154 min(minor).

tort-butyln (3aR,3bR,9bR)-2,3,5,6-tetrahydro-1H-cyclopenta[2,3]cyclopropa[1,2]-eacenaphthylene-3a(3bH)-carboxylate (2v)

Colorless oil, 74% yield, 93% ee. ^1H NMR (300 MHz, Chloroform-d) δ 7.34 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.16 – 7.08 (m, 1H), 5.85 – 5.78 (m, 1H), 3.06 (t, J = 6.9 Hz, 2H), 2.93 – 2.69 (m, 3H), 2.44 – 2.29 (m, 3H), 1.97 (dd, J = 12.6, 7.7 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.35 (s, 1H), 1.06 (s, 9H). ^13C NMR (75 MHz, CDCl3) δ 171.39, 143.03, 141.86, 138.24, 131.41, 127.98, 122.62, 121.96, 112.01, 79.49, 39.95, 31.67, 31.25, 30.70, 30.31, 29.85, 27.90, 27.56, 19.31. HRMS (ESI+): Calculated for [C21H24O2Na]^+ ([M+Na]+): 331.1669, Found: 331.1661.
HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=5/95; flow=0.5 mL/min; Retention time: 6.915 min(minor), 7.718 min(major).

tert-butyl (3aR,3bR,9bR)-2,3,4,5-tetrahydro-1H-cyclopenta[1,3]cyclopropa[1,2]-anaphthalene-3a(3bH)-carboxylate (4)

Colorless oil, 88% yield, 94% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.33 (d, J = 7.6 Hz, 1H), 7.15 (dt, J = 7.9, 4.3 Hz, 1H), 7.06 (d, J = 4.4 Hz, 2H), 2.78 (ddd, J = 16.3, 11.3, 5.9 Hz, 1H), 2.53 – 2.28 (m, 3H), 2.28 – 2.06 (m, 2H), 1.98 (ddd, J = 15.1, 12.9, 8.1 Hz, 2H), 1.83 – 1.70 (m, 2H), 1.47 – 1.33 (m, 1H), 1.09 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 171.90, 138.82, 135.81, 127.78, 127.72, 125.99, 125.63, 79.84, 43.54, 37.42, 33.59, 31.64, 28.84, 27.79, 25.04, 20.11, 19.63. HRMS (ESI+): Calculated for [C10H13O2Na+] ([M+Na]+): 307.1669, Found: 307.1664. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.1 mL/min; Retention time: 34.789 min(minor), 36.256 min(major).

tert-butyl (1S,2S)-3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalene]-2-carboxylate (5)

Colorless oil, 85% yield, 95% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.33 (d, J = 7.4 Hz, 1H), 7.20 – 7.07 (m, 3H), 3.26 (dd, J = 12.6, 6.2 Hz, 1H), 2.97 – 2.47 (m, 4H), 2.30 – 2.18 (m, 1H), 2.03 – 1.67 (m, 4H), 1.63 – 1.43 (m, 3H), 1.16 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 175.23, 142.77, 140.09, 128.81, 126.92, 125.84, 125.32, 79.79, 53.96, 52.22, 41.97, 41.06, 36.28, 30.43, 27.71, 25.01, 23.43. HRMS (ESI+): Calculated for [C10H26O2Na+] ([M+Na]+): 309.1825, Found: 309.1819. HPLC conditions (Agilent 1260): Chiralpak OJ (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.1 mL/min; Retention time: 35.097 min(minor), 36.643 min(major).

(3aR,4R,5R,9bR)-4-bromo-2,3,3b,4-tetrahydro-1H,5H-5,3a-(epoxymethano)cyclopenta[1,3]cyclopropa[1,2-a]naphthalen-11-one (6)

White solid, 93% yield, 95% ee. 1H NMR (300 MHz, Chloroform-d) δ 7.55 – 7.44 (m, 2H), 7.40 – 7.33 (m, 2H), 5.30 (dd, J = 4.2, 2.0 Hz, 1H), 4.83 (ddd, J = 3.9, 2.6, 1.0 Hz, 1H), 2.69 – 2.41 (m, 3H), 2.25 (dd, J = 12.8, 7.6 Hz, 1H), 2.11 (dd, J = 13.5, 7.7 Hz, 1H), 1.94 (dt, J = 13.6, 8.1 Hz, 1H), 1.49 (dt, J = 13.7, 12.1, 7.6 Hz, 1H). 13C NMR (75 MHz, CDCl3) δ 168.21, 134.13, 130.21, 129.07, 128.85, 126.88, 125.38, 76.92, 45.76, 41.89, 39.33, 28.67, 28.57, 28.49, 19.03. HRMS (ESI+): Calculated for [C10H12BrO2Na+] ([M+Na]+): 326.9991, Found: 326.9998. HPLC conditions (Agilent 1260): Chiralpak AD (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25 °C; i-propanol/hexane=10/90; flow=0.5 mL/min; Retention time: 10.841 min(minor), 12.022 min(major).

(3aR,4R,5R,9bR)-4-hydroxy-2,3,3b,4-tetrahydro-1H,5H-5,3a-(epoxymethano)cyclopenta[1,3]cyclopropa[1,2-a]naphthalen-11-one (7)
White solid, 94% yield, 96% ee. $^1$H NMR (300 MHz, Chloroform-\(d\)) $\delta$ 7.57 – 7.43 (m, 2H), 7.40 – 7.30 (m, 2H), 5.14 (dd, $J = 4.6$, 2.0 Hz, 1H), 4.57 (dd, $J = 4.3$, 2.9, 0.9 Hz, 1H), 2.64 – 2.34 (m, 3H), 2.22 (dd, $J = 12.7$, 7.5 Hz, 1H), 2.07 (dd, $J = 13.5$, 7.5 Hz, 1H), 1.92 (dt, $J = 13.5$, 8.0 Hz, 1H), 1.48 (ddt, $J = 13.4$, 12.1, 7.6 Hz, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.47, 136.60, 130.08, 128.39, 126.95, 125.32, 76.57, 61.38, 44.08, 40.43, 38.49, 28.48, 27.90, 19.06. HRMS (ESI+): Calculated for $[\text{C}_{15}\text{H}_{15}\text{O}_3]^+$ ($[\text{M}+\text{H}]^+$): 243.1016, Found: 243.1022.

HPLC conditions (Agilent 1260): Chiralpak AD (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25°C; i-propanol/hexane=10/90; flow=0.5 mL/min; Retention time: 14.000 min(major), 15.419 min(minor).

$((3aR,3bR,9bR)-2,3$-dihydro-1H-cyclopenta[1,3]cyclopropa[1,2-a]naphthalen-3a(3bH)-yl) methanol (8)

White solid, 90% yield, 91% ee. $^1$H NMR (300 MHz, Chloroform-\(d\)) $\delta$ 7.58 – 7.50 (m, 1H), 7.26 – 7.10 (m, 3H), 6.48 (d, $J = 9.6$ Hz, 1H), 6.16 (dd, $J = 9.6$, 5.3 Hz, 1H), 3.35 – 3.04 (m, 2H), 2.71 (dd, $J = 11.9$, 8.3 Hz, 1H), 2.29 – 2.19 (m, 2H), 2.11 (d, $J = 5.3$ Hz, 1H), 1.95 (dd, $J = 12.5$, 7.7 Hz, 1H), 1.80 (ddt, $J = 17.2$, 8.7, 4.0 Hz, 1H), 1.37 – 1.20 (m, 1H), 0.97 (s, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 133.23, 132.07, 127.78, 127.30, 127.04, 125.75, 125.54, 124.37, 60.40, 39.40, 31.19, 31.15, 29.06, 24.80, 19.21. HRMS (ESI+): Calculated for $[\text{C}_{15}\text{H}_{16}\text{ONa}]^+$ ($[\text{M}+\text{Na}]^+$): 235.1075, Found: 235.1093. HPLC conditions (Agilent 1260): Chiralpak AD (Particle Size: 5 μm, Dimensions: 4.6 mm Φ × 250 mmL); detected at 254 nm; temperature 25°C; i-propanol/hexane=10/90; flow=0.5 mL/min; Retention time: 18.648 min(minor), 20.193 min(major).

3. X-ray crystal structure of 6 and 7

Fig. S1 X-ray crystal structure of 6 (CCDC 2191640 for 6 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures)
Fig. S2 X-ray crystal structure of 7 (CCDC 2191583 for 7 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structutres).

Reference:

[1] J. Li, S. Qu, W. Zhao, Angew. Chem. Int. Ed. 2020, 59, 2360–2364.
[2] D. F. Taber, K. You, Y. Song, J. Org. Chem. 1995, 60, 1093-1094.
4. NMR Spectra of Compounds

NMR Spectrum for substrates 1

![NMR Spectrum Image]
NMR Spectrum for product

[Image of NMR spectra with chemical structures and peaks labeled]
2o

[Chemical structure image]

2o

[Chemical structure image]
6. HPLC spectra of products 2

Chiral HPLC spectrum of racemic 2a

Chiral HPLC spectrum of 2a

Chiral HPLC spectrum of racemic 2b

Chiral HPLC spectrum of 2b
Chiral HPLC spectrum of racemic \(2c\)

Chiral HPLC spectrum of \(2c\)

Chiral HPLC spectrum of racemic \(2d\)

Chiral HPLC spectrum of \(2d\)
### Chiral HPLC spectrum of racemic 2k

| Ret. Time | Area | Height | Area% |
|-----------|------|--------|-------|
| 11.000    | 457.02 | 34.36  | 48.63 |
| 11.504    | 344.82  | 34.95  | 38.27 |

### Chiral HPLC spectrum of 2k

| Ret. Time | Area | Height | Area% |
|-----------|------|--------|-------|
| 11.598    | 707.68  | 44.49  | 4.86  |
| 12.471    | 13874.55 | 805.35 | 90.15 |

### Chiral HPLC spectrum of racemic 2l

### Chiral HPLC spectrum of 2l
Chiral HPLC spectrum of racemic 2m

Chiral HPLC spectrum of 2m

Chiral HPLC spectrum of racemic 2n

Chiral HPLC spectrum of 2n
Chiral HPLC spectrum of racemic 2q

Chiral HPLC spectrum of 2q

Chiral HPLC spectrum of racemic 2r

Chiral HPLC spectrum of 2r
Chiral HPLC spectrum of racemic \(2s\)

Chiral HPLC spectrum of \(2s\)

Chiral HPLC spectrum of racemic \(2t\)

Chiral HPLC spectrum of \(2t\)
Chiral HPLC spectrum of racemic 8

![Chiral HPLC spectrum of racemic 8](image)

| Peak | Retention Time (min) | Area | Height | % Area |
|------|----------------------|------|--------|--------|
| 1    | 16.196               | 0.642 | 23.4 | 94.5982 | 50.5660 |
| 2    | 19.262               | 0.632 | 22.2 | 53.3363 | 49.4240 |

Chiral HPLC spectrum of 8

![Chiral HPLC spectrum of 8](image)

| Peak | Retention Time (min) | Area | Height | % Area |
|------|----------------------|------|--------|--------|
| 1    | 18.488               | 0.401 | 41.2 | 41.3293 | 16.1731 | 6.2257 |
| 2    | 20.183               | 0.412 | 41.4 | 33.8564 | 52.6763 |