Supporting Information for

Organocatalytic Asymmetric Chlorinative Dearomatization of Naphthols

Qin Yin, Shou-Guo Wang, Xiao-Wei Liang, De-Wei Gao, Jun Zheng and Shu-Li You*

State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032, China
Fax: (+86) 21-54925087
E-mail: slyou@sioc.ac.cn

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1. General considerations

Unless stated otherwise, all solvents were purified and dried according to standard methods prior to use. $^1$H and $^{19}$F NMR spectra were recorded on Varian or Agilent instrument (400 MHz and 376 MHz, 300 MHz and 282 MHz, respectively) and referenced relative to tetramethylsilane signal or residual protio solvent signals and CFCl$_3$ respectively. $^{13}$C NMR spectra were recorded on Varian or Agilent instrument (100 MHz or 75 MHz) and referenced relative to residual solvent signals. Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet or unresolved, $br$ = broad singlet, coupling constant(s) in Hz, integration). Data for $^{13}$C NMR and $^{19}$F NMR are reported in terms of chemical shift ($\delta$, ppm).

Methyl 2-hydroxy-1-naphthoate (1a) and Methyl 1-hydroxy-2-naphthoate (1t) were purchased from Alfa Aesar and used without further purification. Substituted 2-hydroxy-1-naphthoates (1b, 1d, 1e) and compounds (1r, 1s) are known compounds and prepared according to the literature.$^1$

2. Experimental procedures, analytical and spectroscopic data

2.1 Procedure for preparation of 1c

![Chemical Structure](image)

To a solution of 2-hydroxy-1-naphthoic acid (944 mg, 5 mmol) in DMF (10 mL), potassium hydrogen carbonate (600 mg, 6 mmol) was added. The mixture was stirred at rt for 10 min, followed by addition of allyl bromide (908 mg, 7.5 mmol). Then the mixture was stirred at 40 °C until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of water (5 mL). The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.
Allyl 2-hydroxy-1-naphthoate (1c)

Colorless liquid. Analytical data for 1c: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.86 (d, $J = 5.7$ Hz, 2H), 5.24 (dd, $J = 1.2$, 10.5 Hz, 1H), 5.36 (dd, $J = 1.2$, 17.1 Hz, 1H), 5.94-6.05 (m, 1H), 7.02 (d, $J = 9.0$ Hz, 1H), 7.22 (t, $J = 6.9$ Hz, 1H), 7.42 (td, $J = 8.4$, 1.2 Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.72 (d, $J = 8.7$ Hz, 1H), 8.65 (d, $J = 9.0$ Hz, 1H), 12.16 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 66.3, 104.5, 119.2, 119.3, 123.5, 125.2, 128.4, 128.5, 129.0, 131.5, 131.7, 136.8, 164.4, 172.0; IR (film) 2986, 1641, 1201, 825 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{14}$H$_{13}$O$_3$$^+$ (M+H) requires $m/z$ 229.0859. Found $m/z$ 229.0865.

2.2 General procedure for preparation of 1f-1h, 1k

To a 25 mL two-neck round-bottomed flask equipped with a condenser, methyl 6-bromo-2-hydroxy-1-naphthoate (562 mg, 2.0 mmol), boronic acid (3.0 mmol), (i-Pr)$_2$NH (202 mg, 2.0 mmol), Pd(OAc)$_2$ (9.0 mg, 0.04 mmol) and H$_2$O (4.0 mL) were added successively. The mixture was reacted at 100 °C until the reaction was complete (monitored by TLC). The mixture was filtered through a pad of celite and washed with ethyl acetate. The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/50, v/v) to afford the product.
Methyl 2-hydroxy-6-phenyl-1-naphthoate (1f)

White solid. Analytical data for 1f: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.04 (s, 3H), 7.12 (d, \(J = 8.8\) Hz, 1H), 7.34-7.46 (m, 3H), 7.64-7.85 (m, 5H), 8.72 (d, \(J = 8.8\) Hz, 1H), 12.31 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.3, 104.4, 119.5, 125.8, 126.6, 126.9, 127.0, 127.3, 127.6, 128.8, 130.7, 136.0, 137.0, 140.1, 164.3, 172.7; IR (film) 2958, 1648, 1220 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{18}\)H\(_{15}\)O\(_3\)\(^+\) (M+H) requires \(m/z\) 279.1016. Found \(m/z\) 279.1008.

Methyl 6-(3,5-dimethylphenyl)-2-hydroxy-1-naphthoate (1g)

White solid. Analytical data for 1g: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.41 (s, 6H), 4.11 (s, 3H), 7.02 (br, 1H), 7.17-7.32 (m, 3H), 7.79-7.92 (m, 3H), 8.77 (d, \(J = 7.2\) Hz, 1H), 12.30 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.5, 52.5, 104.6, 119.6, 125.0, 125.7, 126.8, 127.9, 129.0, 130.8, 135.7, 136.4, 137.1, 138.4, 140.3, 164.3, 172.8; IR (film) 2955, 1646, 1217 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{20}\)H\(_{19}\)O\(_3\)\(^+\) (M+H) requires \(m/z\) 307.1329. Found \(m/z\) 307.1320.

Methyl 6-(4-fluorophenyl)-2-hydroxy-1-naphthoate (1h)

White solid. Analytical data for 1h: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.00 (s, 3H), 7.03-7.09 (m, 3H), 7.52 (br, 2H), 7.63 (d, \(J = 8.7\) Hz, 1H), 7.74-7.80 (m, 2H), 8.66 (d, \(J = 8.7\) Hz, 1H), 12.26 (s, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 52.8, 104.8, 116.0 (d, \(J = 21.2\) Hz), 120.1, 126.2, 126.8, 127.8, 128.8 (d, \(J = 8.0\) Hz), 129.1, 131.0, 135.4, 136.6, 137.3, 162.7 (d, \(J = 244.7\) Hz), 164.7, 173.0; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -114.2; IR (film) 2957, 1647, 1216 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{18}\)H\(_{14}\)FO\(_3\)\(^+\) (M+H) requires \(m/z\) 297.0921. Found \(m/z\) 297.0918.
\( (E) \)-Methyl 2-hydroxy-6-styryl-1-naphthoate (1k)

Yellow solid. Analytical data for 1k: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.09 (s, 3H), 7.15-7.19 (m, 3H), 7.31-7.42 (m, 3H), 7.55-7.57 (m, 2H), 7.71 (s, 1H), 7.76 (d, \( J = 8.4 \text{ Hz}, \) 1H), 7.84 (d, \( J = 8.4 \text{ Hz}, \) 1H), 8.69 (d, \( J = 8.8 \text{ Hz}, \) 1H), 12.32 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 52.5, 104.9, 119.7, 125.7, 126.2, 126.5, 127.4, 127.7, 127.9, 128.7, 128.8, 128.9, 131.2, 132.6, 136.9, 137.3, 164.4, 172.7; IR (film) 1645, 1335, 1225 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{20}\)H\(_{17}\)O\(_3^+\) (M+H) requires \( m/z \) 305.1172. Found \( m/z \) 305.1167.

2.3 General procedure for preparation of 1i, 1n, 1o-1q (1q as an example, substituted 2-naphthols are commercially available)

\[
\begin{align*}
\text{R} & \quad \text{OH} & \quad \text{AlCl}_3, \text{ClCO}_2\text{Me} & \quad \text{DCE, reflux} & \quad \text{R} & \quad \text{OH} & \quad \text{CO}_2\text{Me}
\end{align*}
\]

To a 25 mL two-neck round-bottomed flask equipped with a condenser, AlCl\(_3\) (1.29 g, 10 mmol) and DCE (20 mL) were added successively. Then methyl chloroformate (945 mg, 10 mmol) was added and the mixture was stirred for 10 min at rt. 3-Bromo-2-naphthol (1.12 g, 5 mmol) was added and the mixture was stirred under reflux for 10 h. Then H\(_2\)O (10 mL) was added at 0 \( ^\circ \text{C} \). The aqueous layer was extracted with DCM. The organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/50, v/v) to afford the product.

Methyl 2-hydroxy-6-methyl-1-naphthoate (1i)

Yellow solid. Analytical data for 1i: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 2.37 (s, 3H), 3.99
(s, 3H), 7.04 (d, $J = 8.8$ Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 1H), 7.42 (s, 1H), 7.71 (d, $J =$ 8.8 Hz, 1H), 8.52 (d, $J = 8.8$ Hz, 1H), 12.10 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.9, 52.3, 104.6, 119.2, 125.2, 128.3, 128.9, 129.7, 130.5, 133.1, 136.4, 163.8, 172.9; IR (film) 2956, 1639, 1215 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{13}$H$_{13}$O$_3^+$ (M+H) requires m/z 217.0859. Found m/z 217.0859.

![Methyl 4-bromo-2-hydroxy-1-naphthoate (1n)](image)

**Methyl 4-bromo-2-hydroxy-1-naphthoate (1n)**

Yellow solid. Analytical data for 1n: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.99 (s, 3H), 7.33-7.35 (m, 1H), 7.42 (s, 1H), 7.42-7.46 (m, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 8.61 (d, $J = 8.8$ Hz, 1H), 12.10 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 52.7, 104.7, 123.6, 124.8, 125.5, 127.1, 128.2, 129.1, 132.0, 132.3, 163.1, 172.3; IR (film) 1647, 1216 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{12}$H$_{10}$O$_3$Br$^+$ (M+H) requires m/z 280.9808. Found m/z 280.9806.

![Methyl 7-bromo-2-hydroxy-1-naphthoate (1o)](image)

**Methyl 7-bromo-2-hydroxy-1-naphthoate (1o)**

Yellow solid. Analytical data for 1o: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.03 (s, 3H), 7.07 (d, $J = 9.2$ Hz, 1H), 7.37 (dd, $J = 8.8$, 1.6 Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.74 (d, $J =$ 8.8 Hz, 1H), 8.82 (s, 1H), 12.30 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 52.7, 103.9, 119.8, 123.5, 127.0, 127.8, 130.3, 130.4, 132.8, 136.6, 165.0, 172.4; IR (film) 2955, 1648, 1217 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{12}$H$_9$O$_3$Br$^+$ requires m/z 279.9730. Found m/z 279.9728.

![Methyl 2-hydroxy-7-methoxy-1-naphthoate (1p)](image)

**Methyl 2-hydroxy-7-methoxy-1-naphthoate (1p)**

White solid. Analytical data for 1p: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.92 (s, 3H), 4.08
(s, 3H), 6.98-7.02 (m, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 8.16 (s, 1H), 12.30 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.3, 55.2, 103.9, 106.2, 114.5, 116.6, 123.8, 130.5, 133.4, 136.7, 159.9, 165.1, 172.8; IR (film) 1643, 1617, 1194 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{13}\)H\(_{13}\)O\(_4\)\(^+\) requires \(m/z\) 233.0808. Found \(m/z\) 233.0810.

Methyl 3-bromo-2-hydroxy-1-naphthoate (1q)

Yellow solid. Analytical data for 1q: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.99 (s, 3H), 7.24 (td, \(J = 8.0, 2.7\) Hz, 1H), 7.42 (td, \(J = 8.4, 1.2\) Hz, 1H), 7.50 (d, \(J = 8.0\) Hz, 1H), 8.03 (s, 1H), 8.51 (d, \(J = 8.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 52.9, 105.8, 112.9, 124.4, 125.3, 128.2, 128.7, 130.7, 139.2, 160.3, 172.6; IR (film) 2956, 1646, 1215 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{12}\)H\(_{10}\)BrO\(_3\)\(^+\) (M+H) requires \(m/z\) 280.9808. Found \(m/z\) 280.9813.

2.4 Procedure for preparation of 1j

To a solution of 1k (304 mg, 1 mmol) in ethyl acetate (3 mL), 10% Pd/C (20 mg) was added under Ar atmosphere. Then the reaction was charged with 1 atm of hydrogen and stirred at room temperature for 17 h. The reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/30, v/v) to afford the product.

Methyl 2-hydroxy-6-phenethyl-1-naphthoate (1j)
White solid. Analytical data for 1j: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.89-2.92 (m, 4H), 3.97 (s, 3H), 7.02-7.20 (m, 6H), 7.29 (d, $J = 9.2$ Hz, 1H), 7.39 (s, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 8.54 (d, $J = 9.2$ Hz, 1H), 12.13 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 37.2, 37.6, 52.3, 104.5, 119.2, 125.3, 125.9, 127.8, 128.3, 128.4, 128.8, 129.7, 130.0, 136.5, 136.8, 141.5, 163.9, 172.8; IR (film) 1641, 1335, 1236 cm$^{-1}$; HRMS (ESI) exact mass calcld for C$_{20}$H$_{19}$O$_3$ (M+H) requires m/z 307.1329. Found m/z 307.1329.

2.5 General procedure for preparation of 1l-1m (1l as an example)

To a solution of 1d (843 mg, 3 mmol) in Et$_3$N (10 mL), phenylacetylene (460 mg, 4.5 mmol), bis(triphenylphosphine)palladium(II) chloride (84 mg, 0.12 mmol) and cuprous iodide (12 mg, 0.06 mmol) were added successively under Ar atmosphere. The reaction mixture was stirred at 70 °C until the reaction was complete (monitored by TLC). The mixture was filtered through a pad of celite, washed with ethyl acetate, and followed by concentration. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.

**Methyl 2-hydroxy-6-(phenylethynyl)-1-naphthoate (1l)**

Yellow solid. Analytical data for 1l: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.07 (s, 3H), 7.14 (d, $J = 8.8$ Hz, 1H), 7.34-7.35 (m, 3H), 7.55-7.57 (m, 2H), 7.62 (dd, $J = 9.2$, 1.6 Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 0.8$ Hz, 1H), 8.66 (d, $J = 8.8$ Hz, 1H), 12.35 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 52.6, 89.2, 89.7, 104.8, 118.4, 120.1, 123.2, 125.5, 128.3, 128.4, 131.0, 131.3, 131.6, 132.3, 136.6, 164.9, 172.6; IR (film)
1657, 1323, 1211 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{20}$H$_{14}$O$_3^+$ requires m/z 302.0937. Found m/z 302.0936.

Methyl 2-hydroxy-6-(3-hydroxyprop-1-yn-1-yl)-1-naphthoate (1m)

Yellow solid. Analytical data for 1m: $^1$H NMR (400 MHz, CDCl$_3$) δ 2.34 (br, 1H), 3.98 (s, 3H), 4.47 (s, 2H), 7.03 (d, $J = 9.2$ Hz, 1H), 7.39 (dd, $J = 9.2$, 1.2 Hz, 1H), 7.63 (d, $J = 9.2$ Hz, 1H), 7.66 (s, 1H), 8.48 (d, $J = 8.8$ Hz, 1H), 12.26 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 51.6, 52.6, 85.4, 87.5, 104.7, 117.6, 120.0, 125.4, 128.1, 130.9, 131.3, 132.4, 136.5, 164.8, 172.5; IR (film) 1639, 1230, 1028 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{15}$H$_{13}$O$_4^+$ (M+H) requires m/z 257.0808. Found m/z 257.0807.

2.6 General procedure for asymmetric chlorination of naphthols

![Chemical Reaction Image]

To a Schlenk tube, DCDMH (70.9 mg, 0.36 mmol), (DHQD)$_2$PHAL (23.4 mg, 0.03 mmol) and toluene (2.0 mL) were added. After stirred for 10 min at -78 °C, 1 (0.3 mmol) was added in one portion. After the reaction was complete (monitored by TLC), the reaction was quenched by the addition of saturated Na$_2$SO$_3$ aqueous solution (3.0 mL). The organic layer was extracted with ethyl acetate, washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.
(R)-Methyl 1-chloro-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2a)
Pale yellow solid (1.38 g, 97% yield, 6.0 mmol scale). Analytical data for 2a: $[\alpha]_D^{20} = -58.5$ (c = 1.0 CHCl$_3$, 92% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.77 (s, 3H), 6.28 (d, $J$ = 10.0 Hz, 1H), 7.37-7.54 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.1, 67.3, 123.1, 128.3, 128.8, 129.9, 130.0, 131.0, 137.3, 145.7, 166.7, 189.8; IR (film) 1760, 1671, 1207, 1011 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_{13}$NO$_3$Cl$^+$ (M+NH$_4^+$) requires m/z 254.0578. Found m/z 254.0577. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda$ = 254 nm, t (major) = 11.81 min, t (minor) = 14.26 min.

![Chemical Structure](image)

(R)-Ethyl 1-chloro-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2b)
Pale yellow solid (92.8 mg, 93% yield, 0.4 mmol scale). Analytical data for 2b: $[\alpha]_D^{20} = -43.4$ (c = 1.0 CHCl$_3$, 88% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.17 (t, $J$ = 7.2 Hz, 3H), 4.18-4.29 (m, 2H), 5.73-5.80 (m, 1H), 6.27 (d, $J$ = 10.4 Hz, 1H), 7.39-7.54 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.7, 63.5, 67.3, 123.1, 128.2, 128.7, 129.9, 129.9, 130.9, 137.4, 145.6, 166.1, 189.9; IR (film) 1756, 1675, 1202, 1022 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{13}$H$_{15}$NO$_3$Cl$^+$ (M+NH$_4^+$) requires m/z 268.0735. Found m/z 268.0729. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda$ = 254 nm, t (major) = 10.14 min, t (minor) = 11.84 min.

![Chemical Structure](image)

(R)-Allyl 1-chloro-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2c)
Pale yellow solid (110.2 mg, 91% yield, 0.46 mmol scale). Analytical data for 2c: $[\alpha]_D^{20} = -52.2$ (c = 1.0 CHCl$_3$, 86% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.65-4.67 (m, 2H), 5.14-5.18 (m, 2H), 5.73-5.80 (m, 1H), 6.28 (d, $J$ = 10.0 Hz, 1H), 7.39-7.49 (m, 3H), 7.52-7.55 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 67.3, 67.5, 118.9, 123.1, 128.2, 128.8, 129.9, 130.0, 130.4, 130.9, 137.2, 145.7, 165.8, 189.7; IR (film) 1757, 112.
1672, 1197 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₄H₁₅NO₃Cl⁺ (M+NH₄) requires m/z 280.0735. Found m/z 280.0731. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 0.6 mL/min, λ = 254 nm, t (major) = 17.96 min, t (minor) = 21.31 min.

(R)-Methyl 6-bromo-1-chloro-2-oxo-1,2-dihydonaphthalene-1-carboxylate (2d)
Pale yellow solid (82.9 mg, 88% yield, 0.3 mmol scale). Analytical data for 2d: [α]D²⁰ = -15.9 (c = 1.0 CHCl₃, 95% ee); ¹H NMR (400 MHz, CDCl₃) δ 3.77 (s, 3H), 6.32 (d, J = 10.4 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 10.0 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.59 (dd, J = 8.4, 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 54.4, 66.9, 124.1, 124.4, 130.1, 130.5, 132.5, 133.8, 136.1, 144.0, 166.3, 189.2; IR (film) 1759, 1675, 1202 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₂H₁₁NO₃ClBr⁺ (M+NH₄) requires m/z 331.9684. Found m/z 331.9676. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 22.32 min, t (minor) = 24.32 min.

(R)-Methyl 1-chloro-6-cyano-2-oxo-1,2-dihydonaphthalene-1-carboxylate (2e)
Pale yellow solid (22.3 mg, 85% yield, 0.1 mmol scale). Analytical data for 2e: [α]D²⁰ = 3.13 (c = 1.0 CHCl₃, 94% ee); ¹H NMR (400 MHz, CDCl₃) δ 3.77 (s, 3H), 6.40 (d, J = 10.0 Hz, 1H), 7.50 (d, J = 10.0 Hz, 1H), 7.65-7.75 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 54.7, 66.7, 114.3, 117.2, 125.3, 129.5, 129.9, 132.9, 133.8, 141.6, 143.1, 165.8, 188.3; IR (film) 1733, 1675, 1251 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₃H₁₂N₂O₃Cl⁺ (M+NH₄) requires m/z 279.0531. Found m/z 279.0524. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 37.72 min, t (minor) = 43.26 min.
(R)-Methyl 1-chloro-2-oxo-6-phenyl-1,2-dihyronaphthalene-1-carboxylate (2f)

Pale yellow solid (76.8 mg, 82% yield, 0.3 mmol scale). Analytical data for 2f: [α]$_D^{20}$ = -32.3 (c = 1.0 CHCl$_3$, 96% ee); $^1$H NMR (400 MHz, CDCl$_3$) δ 3.78 (s, 3H), 6.31 (d, J = 10.0 Hz, 1H), 7.39-7.49 (m, 3H), 7.55-7.60 (m, 5H), 7.65 (dd, J = 8.4, 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 54.3, 67.3, 123.6, 127.1, 128.4, 128.6, 128.8, 129.1, 129.4, 129.6, 135.9, 139.1, 143.2, 145.7, 166.8, 189.9; IR (film) 1754, 1677, 1016 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{18}$H$_{17}$NO$_3$Cl$^+$ (M+NH$_4^+$) requires m/z 330.0891. Found m/z 330.0880. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 36.20 min, t (minor) = 41.73 min.

(R)-Methyl 1-chloro-6-(3,5-dimethylphenyl)-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2g)

Pale yellow solid (81.6 mg, 80% yield, 0.3 mmol scale). Analytical data for 2g: [α]$_D^{20}$ = -25.5 (c = 1.0 CHCl$_3$, 95% ee); $^1$H NMR (400 MHz, CDCl$_3$) δ 2.39 (s, 6H), 3.79 (s, 3H), 6.31 (d, J = 10.0 Hz, 1H), 7.06 (s, 1H), 7.20 (s, 2H), 7.55-7.58 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.4, 54.3, 67.3, 123.5, 125.0, 125.0, 128.6, 128.7, 129.3, 129.6, 130.0, 135.7, 138.7, 139.1, 143.5, 145.7, 166.9, 189.9; IR (film) 1738, 1676, 1215 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{20}$H$_{21}$NO$_3$Cl$^+$ (M+NH$_4^+$) requires m/z 358.1204. Found m/z 358.1203. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t
(major) = 31.31 min, t (minor) = 37.60 min.

(R)-Methyl
1-chloro-6-(4-fluorophenyl)-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2h)
Pale yellow foam (90.7 mg, 85% yield, 0.32 mmol scale). Analytical data for 2h: \([\alpha]_D^{20} = -28.3 (c = 1.0 \text{ CHCl}_3, 96\% \text{ ee})\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.76 (s, 3H), 6.30 (d, \(J = 10.0 \text{ Hz}, 1\)H), 7.12-7.16 (m, 2H), 7.51-7.60 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 54.2, 67.2, 115.9 (d, \(J = 21.3 \text{ Hz}\)), 123.6, 128.3, 128.6, 128.7, 128.8, 129.3 (d, \(J = 13.7 \text{ Hz}\)), 135.1 (d, \(J = 3.0 \text{ Hz}\)), 135.8, 142.1, 145.5, 162.9 (d, \(J = 246.7 \text{ Hz}\)), 166.7, 189.7; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -112.5; IR (film) 1757, 1676, 1224 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{18}\)H\(_{16}\)ClFNO\(_3\)\(^+\) (M+NH\(_4\)) requires \(m/z\) 348.0797. Found \(m/z\) 348.0787. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 0.6 mL/min, \(\lambda = 254\) nm, t (major) = 31.73 min, t (minor) = 29.59 min.

(R)-Methyl 1-chloro-6-methyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2i)
Pale yellow foam (65.3 mg, 87% yield, 0.3 mmol scale). Analytical data for 2i: \([\alpha]_D^{20} = -56.9 (c = 1.0 \text{ CHCl}_3, 93\% \text{ ee})\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.39 (s, 3H), 3.76 (s, 3H), 6.25 (d, \(J = 10.0 \text{ Hz}, 1\)H), 7.18 (s,1H), 7.27-7.25 (m, 1H), 7.41 (d, \(J = 8.0 \text{ Hz}, 1\)H), 7.45 (d, \(J = 10.0 \text{ Hz}, 1\)H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 21.1, 54.1, 67.3, 123.2, 128.2, 128.9, 130.5, 131.7, 134.4, 140.3, 145.7, 166.9, 190.0; IR (film) 1756, 1674, 1232 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{13}\)H\(_{12}\)ClO\(_3\)\(^+\) (M+H) requires \(m/z\) 251.0469. Found \(m/z\) 251.0471. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, \(\lambda = 254\) nm, t (major) = 37.18 min, t (minor) = 45.75 min.
(R)-Methyl 1-chloro-2-oxo-6-phenethyl-1,2-dihyronaphthalene-1-carboxylate (2j)

Pale yellow solid (91.8 mg, 90% yield, 0.3 mmol scale). Analytical data for 2j: [α]D20 = -46.2 (c = 1.0 CHCl3, 94% ee); 1H NMR (400 MHz, CDCl3) δ 2.93-2.96 (m, 4H), 3.75 (s, 3H), 6.25 (d, J = 9.6 Hz, 1H), 7.17-7.31 (m, 7H), 7.42-7.46 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 37.2, 37.2, 54.1, 67.3, 123.1, 126.1, 128.2, 128.3, 128.4, 128.9, 130.0, 131.1, 134.8, 140.8, 144.0, 145.8, 166.8, 190.0; IR (film) 1762, 1675, 1213 cm⁻¹; HRMS (ESI) exact mass calcd for C20H21ClN3O3+ (M+NH4) requires m/z 358.1204. Found m/z 358.1206. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 39.45 min, t (minor) = 47.75 min.

(R,E)-Methyl 1-chloro-2-oxo-6-styryl-1,2-dihyronaphthalene-1-carboxylate (2k)

Yellow solid (89.7 mg, 88% yield, 0.3 mmol scale). Analytical data for 2k: [α]D20 = -30.3 (c = 1.0 CHCl3, 94% ee); 1H NMR (400 MHz, CDCl3) δ 3.77 (s, 3H), 6.30 (d, J = 9.6 Hz, 1H), 7.08 (d, J = 16.0 Hz, 1H), 7.18 (d, J = 16.0 Hz, 1H), 7.31-7.33 (m, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.48-7.57 (m, 6H); 13C NMR (100 MHz, CDCl3) δ 54.2, 67.3, 123.6, 126.4, 126.7, 127.7, 128.4, 128.6, 128.7, 128.8, 129.3, 131.2, 135.7, 136.4, 139.3, 145.5, 166.7, 189.8; IR (film) 1761, 1674, 1211 cm⁻¹; HRMS (ESI) exact mass calcd for C20H19ClNO3+ (M+NH4) requires m/z 356.1048. Found m/z 356.1047. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 24.14 min, t (minor) = 20.81 min.
(R)-Methyl

1-chloro-2-oxo-6-(phenylethynyl)-1,2-dihydronaphthalene-1-carboxylate (2l)

Yellow solid (92.2 mg, 91% yield, 0.3 mmol scale). Analytical data for 2l: $[\alpha]_{D}^{20} = -17.4$ (c = 1.0 CHCl₃, 93% ee); $^1$H NMR (400 MHz, CDCl₃) δ 3.77 (s, 3H), 6.31 (d, $J = 10.0$ Hz, 1H), 7.37-7.38 (m, 3H), 7.47-7.60 (m, 6H); $^{13}$C NMR (100 MHz, CDCl₃) δ 54.3, 67.1, 87.5, 91.9, 122.3, 123.9, 125.4, 128.4, 128.5, 128.9, 128.9, 131.7, 132.6, 133.6, 136.5, 144.9, 166.4, 189.4; IR (film) 1769, 1680, 1221 cm⁻¹; HRMS (ESI) exact mass calcd for C₂₀H₁₇ClN₃O₃⁺ (M+NH₄⁺) requires m/z 354.0891. Found m/z 354.0892. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 25.08 min, t (minor) = 27.97 min.

(R)-Methyl

1-chloro-6-(3-hydroxyprop-1-yn-1-yl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2m)

Yellow foam (69.4 mg, 80% yield, 0.3 mmol scale). Analytical data for 2m: $[\alpha]_{D}^{20} = -20.6$ (c = 1.0 CHCl₃, 78% ee); $^1$H NMR (400 MHz, CDCl₃) δ 2.18 (br, 1H), 3.77 (s, 3H), 4.52 (s, 2H), 6.30 (d, $J = 10.4$ Hz, 1H), 7.43-7.49 (m, 4H); $^{13}$C NMR (100 MHz, CDCl₃) δ 51.4, 54.4, 67.1, 83.7, 89.9, 124.0, 124.8, 128.5, 129.0, 132.7, 133.7, 136.9, 144.8, 166.5, 189.5; IR (film) 1761, 1675, 1214 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₅H₁₅ClNO₃⁺ (M+NH₄⁺) requires m/z 308.0684. Found m/z 308.0685. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 32.70 min, t (minor) = 30.07 min.
(R)-Methyl 4-bromo-1-chloro-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2n)

Yellow foam (55.9 mg, 90% yield, 0.2 mmol scale). Analytical data for 2n: $[\alpha]_D^{20} = -38.4$ (c = 1.0 CHCl$_3$, 92% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.77 (s, 3H), 6.85 (s, 1H), 7.53-7.54 (m, 3H), 7.96-7.98 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 54.4, 67.5, 127.2, 127.7, 128.7, 130.3, 130.4, 132.0, 145.6, 166.3, 186.7; IR (film) 1758, 1670, 1237 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_{12}$BrClNO$_3$ (M+NH$_4$) requires m/z 331.9684. Found m/z 331.9686. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda$ = 254 nm, t (major) = 12.17 min, t (minor) = 19.71 min.

(2o)

(2o)

(R)-Methyl 1-chloro-7-methoxy-2-oxo-1,2-dihyronaphthalene-1-carboxylate

Yellow foam (53.6 mg, 85% yield, 0.2 mmol scale). Analytical data for 2o: $[\alpha]_D^{20} = -11.8$ (c = 1.0 CHCl$_3$, 91% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.78 (s, 3H), 6.29 (d, $J$ = 10.0 Hz, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.44 (d, $J$ = 10.0 Hz, 1H), 7.57 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.67 (d, $J$ = 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.5, 66.7, 123.6, 125.6, 127.3, 131.0, 132.1, 133.3, 139.1, 144.5, 166.3, 188.9; IR (film) 1763, 1673, 1218 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_{12}$BrClNO$_3$ (M+NH$_4$) requires m/z 331.9684. Found m/z 331.9686. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda$ = 254 nm, t (major) = 20.79 min, t (minor) = 27.06 min.
(2p)

Yellow solid (78.0 mg, 95% yield, 0.3 mmol scale). Analytical data for 2p: $[^\alpha]_D^{20} = -55.5$ (c = 1.0 CHCl$_3$, 90% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.76 (s, 3H), 3.85 (s, 3H), 6.13 (d, $J = 10.0$ Hz, 1H), 6.94 (dd, $J = 8.4, 2.8$ Hz, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 10.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.2, 55.7, 67.2, 115.1, 115.1, 120.5, 121.4, 131.7, 139.4, 145.9, 161.9, 166.8, 189.9; IR (film) 1752, 1662, 1602, 1225 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{13}$H$_{12}$ClO$_4$+ (M+H) requires m/z 267.0419. Found m/z 267.0421. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 41.17 min, t (minor) = 59.60 min.

(R)-Methyl 3-bromo-1-chloro-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2q)

Yellow foam (83.2 mg, 88% yield, 0.3 mmol scale). Analytical data for 2q: $[^\alpha]_D^{20} = -37.0$ (c = 1.0 CHCl$_3$, 73% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.74 (s, 3H), 7.32 (d, $J = 6.8$ Hz, 1H), 7.42-7.49 (m, 3H), 7.91 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 54.5, 68.0, 119.0, 128.7, 129.0, 129.5, 130.3, 131.3, 136.8, 146.9, 166.1, 183.6; IR (film) 1759, 1679, 1246, 1222 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_{12}$BrClNO$_3$+ (M+NH$_4$) requires m/z 331.9684. Found m/z 331.9673. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 21.28 min, t (minor) = 27.04 min.

(R)-Methyl 1-chloro-3-methyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2r)

Yellow liquid (19.3 mg, 94% yield, 0.1 mmol scale, 10 mol% of (DHQ)$_2$PHAL was utilized). Analytical data for 2r: $[^\alpha]_D^{20} = 52.4$ (c = 1.0 CHCl$_3$, 86% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.01 (s, 3H), 2.07 (s, 3H), 7.23-7.26 (m, 2H), 7.32-7.41 (m, 2H), 7.71 (d, $J = 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 16.1, 28.2, 65.4, 127.7, 128.7,
128.8, 129.0, 129.5, 131.5, 140.9, 141.6, 194.7; IR (film) 1669, 1261, 756 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₂H₁₂OCl⁺ (M+H) requires m/z 207.0571. Found m/z 207.0575. The enantiomeric ratio was determined by Daicel Chiralpak IC (25 cm), Hexane / IPA = 49 / 1, 0.5 mL/min, λ = 254 nm, t (major) = 25.53 min, t (minor) = 23.29 min.

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\text{(S)-1-Chloro-1-methyl-3-phenynaphthalen-2(1H)-one (2s)}
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Yellow liquid (23.8 mg, 89% yield, 0.1 mmol scale, 10 mol% of (DHQ)₂PHAL was utilized). Analytical data for 2s: [α]D²⁰ = 212.9 (c = 1.0 CHCl₃, 82% ee); ¹H NMR (400 MHz, CDCl₃) δ 2.13 (s, 3H), 7.37-7.47 (m, 7H), 7.54-7.56 (m, 2H), 7.77 (d, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 66.2, 127.5, 128.4, 128.4, 128.5, 129.2, 129.4, 129.9, 130.1, 134.7, 135.1, 140.3, 141.2, 193.0; IR (film) 1663, 1361, 761 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₇H₁₄OCl⁺ (M+H) requires m/z 269.0728. Found m/z 269.0721. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 60 / 1, 0.61 mL/min, λ = 254 nm, t (major) = 23.18 min, t (minor) = 21.43 min.

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\text{(R)-Methyl 2-chloro-1-oxo-1,2-dihyronaphthalene-2-carboxylate (2t)}
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The reaction was carried out at -70 °C in CHCl₃/CCl₄ (1.0 mL : 1.0 mL) with 10 mol% of (DHQD)₂PYR. Yellow solid (66.5 mg, 94% yield, 0.3 mmol scale). Analytical data for 2t: [α]D²⁰ = -116.6 (c = 1.0 CHCl₃, 90% ee); ¹H NMR (400 MHz, CDCl₃) δ 3.79 (s, 3H), 6.22 (d, J = 9.6 Hz, 1H), 6.72 (d, J = 9.6 Hz, 1H), 7.29 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 54.2, 65.4, 127.4, 128.2, 128.3, 128.4, 128.9, 129.6, 135.7, 136.1, 166.5, 189.2; IR (film) 1756, 1683, 1216 cm⁻¹; HRMS (ESI) exact mass calcd for C₁₂H₁₀Clo₃⁺ (M+H) requires m/z 237.0313. Found m/z 237.0312. The enantiomeric
ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.23 min, t (minor) = 10.27 min.

Methyl 1-bromo-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2u)

The reaction was carried out with 1.2 equiv. of 1,3-dibromo-5,5-dimethylhydantoin. Pale yellow solid (80.9 mg, 96% yield, 9% ee, 0.3 mmol scale). 2u is sensitive to proton solvent. Analytical data for 2u: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.78 (s, 3H), 6.28 (d, $J$ = 9.6 Hz, 1H), 7.36-7.49 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.4, 60.2, 123.1, 127.9, 129.1, 130.0, 130.1, 137.9, 145.1, 166.6, 189.9; IR (film) 2951, 1750, 1671, 1237 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_9$BrO$_3$ (M+NH$_4^+$) requires m/z 298.0073. Found m/z 298.0075. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 14.07 min, t (minor) = 19.85 min.

1,1-Dichloronaphthalen-2(1H)-one (2v)

The reaction was carried out at rt with 10 mol% of DMAP. White solid (63.5 mg, 100% yield, 0.3 mmol scale). Analytical data for 2v: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.33 (d, $J$ = 10.0 Hz, 1H), 7.32 (dd, $J_1$ = 7.6, $J_2$ = 1.2 Hz, 1H), 7.41-7.46 (m, 2H), 7.52 (m, td, $J_1$ = 7.6, $J_2$ = 1.2 Hz., 1H), 8.06 (dd, $J_1$ = 8.0, $J_2$ = 0.8 Hz., 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 80.5, 122.6, 127.0, 129.6, 129.6, 130.7, 131.3, 140.7, 144.9, 185.9; IR (film) 3359, 3085, 1683, 1231 cm$^{-1}$; HRMS (EI) exact mass calcd for C$_{10}$H$_6$Cl$_2$O$_2^+$ requires m/z 211.9790. Found m/z 211.9800.

2.7 Transformations of 2a and 2t.
To a solution of 2a (70.8 mg, 0.3 mmol) in DCM (2.0 mL), Dibal-H (0.4 mL, 1.5 M in toluene) was added dropwise at -60 °C under Ar atmosphere. After the reaction was complete (monitored by TLC), saturated NH₄Cl aqueous solution or 1 M NaOH aqueous solution (2.0 mL) was added. The aqueous layer was extracted with DCM. The organic layer was washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether/Et₃N = 2/4/0, v/v/v) to afford the product.

(1R,2R)-Methyl 1-chloro-2-hydroxy-1,2-dihydronaphthalene-1-carboxylate (3a)

Yellow solid (36.2 mg, 51% yield, 0.3 mmol scale). Analytical data for 3a: [α]D²⁰ = -60.0 (c = 1.0 CHCl₃, 92% ee); ¹H NMR (400 MHz, CDCl₃) δ 3.53 (d, J = 9.6 Hz, 1H), 3.67 (s, 3H), 4.79 (d, J = 8.8 Hz, 1H), 6.03 (dd, J = 9.6, 2.8 Hz, 1H), 6.38 (dd, J = 9.6, 2.0 Hz, 1H), 7.02-7.04 (m, 1H), 7.22-7.28 (m, 2H), 7.11 (dd, J = 6.4, 3.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 53.6, 72.4, 74.8, 127.1, 127.9, 128.3, 128.8, 129.6, 130.6, 132.1, 132.3, 169.7; IR (film) 3444, 1721, 1267, 1208 cm⁻¹; HRMS (DART) exact mass calcd for C₁₂H₁₅O₃NCl⁺ (M+NH₄) requires m/z 256.0735. Found m/z 256.0732. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 9.25 min, t (minor) = 10.15 min.
(1aR,7bS)-Methyl 1a,7b-dihydronaphtho[1,2-b]oxirene-7b-carboxylate (3b)

Yellow solid (30.3 mg, 50% yield, 0.3 mmol scale). Analytical data for 3b: $[\alpha]_D^{20} = 124.9$ (c = 1.0 CHCl$_3$, 92% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.83 (s, 3H), 4.13-4.14 (m, 1H), 6.30 (dd, $J = 9.6, 3.6$ Hz, 1H), 6.76 (dd, $J = 9.6, 1.2$ Hz, 1H), 7.25-7.35 (m, 3H), 7.68 (dd, $J = 7.2, 1.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 52.8, 58.9, 59.9, 122.5, 128.2, 129.0, 129.2, 129.8, 131.8, 133.2, 168.6; IR (film) 1727, 1211, 1020 cm$^{-1}$; HRMS (DART) exact mass calcd for C$_{12}$H$_{11}$O$_3$+ (M+H) requires m/z 203.0703. Found m/z 203.0701. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 13.07 min, t (minor) = 11.61 min.

To a stirred mixture of 2a (23.6 mg, 0.1 mmol) and KBr (30.0 mg, 0.25 mmol) in CH$_3$CN (1.0 mL) and water (40 $\mu$L), Selectfluor (70.8 mg, 0.2 mmol) was added. Then the reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of saturated Na$_2$SO$_3$ aqueous solution (3.0 mL). The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford 2q (23.2 mg, 74% yield, 89% ee).

To a solution of 2t (47.3 mg, 0.2 mmol) in DCM (1.0 mL) and water (1.0 mL), KBr (71.4 mg, 0.6 mmol) and PhI(OAc)$_2$ (88.2 mg, 0.2 mmol) were added successively.
Then the reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of saturated NaHCO₃ aqueous solution (3.0 mL). The aqueous layer was extracted with DCM. The organic layer was washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/40, v/v) to afford the product.

\[(2R,3S,4S)-\text{Methyl} \] 3,4-dibromo-2-chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3c)

White solid (67.1 mg, 85% yield, 0.2 mmol scale). Analytical data for 3c: \([\alpha]_D^{20} = 26.1 (c = 1.0 \ \text{CHCl}_3, 88\% \ \text{ee}); \) \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 3.95 (s, 3H), 5.33 (d, \(J = 9.2 \ \text{Hz}, 1\)H), 5.69 (d, \(J = 9.2 \ \text{Hz}, 1\)H), 7.52 (t, \(J = 7.6 \ \text{Hz}, 1\)H), 7.72 (t, \(J = 7.2 \ \text{Hz}, 1\)H), 7.87 (d, \(J = 8.0 \ \text{Hz}, 1\)H), 8.06 (d, \(J = 7.6 \ \text{Hz}, 1\)H); \(^1^3\)C NMR (100 MHz, CDCl₃) \(\delta\) 50.6, 54.5, 56.5, 75.2, 127.2, 128.6, 129.6, 132.0, 135.7, 139.2, 164.6, 184.3; IR (film) 1737, 1698, 1274 cm\(^{-1}\); HRMS (ESI) exact mass calcd for C\(_{12}\)H\(_{13}\)Br\(_2\)ClNO\(_3\) (M+NH\(_4^+\)) requires \(m/z\) 411.8945. Found \(m/z\) 411.8943. The enantiomeric ratio was determined by Daicel Chiralpak OD-H (25 cm), Hexane / IPA = 90 / 10, 1.0 mL/min, \(\lambda = 254 \ \text{nm}, t \text{ (major)} = 8.88 \ \text{min}, t \text{ (minor)} = 10.72 \ \text{min}.

\[
\begin{align*}
\text{2t} & \quad \text{TCCA} \\
\text{acetone/H}_2\text{O} & \quad \text{rt} \\
\rightarrow & \quad \text{3d}
\end{align*}
\]

To a solution of 2t (46.4 mg, 0.2 mmol) in acetone (1.0 mL) and water (0.2 mL), TCCA (46.4 mg, 0.2 mmol) was added. Then the reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of saturated Na\(_2\)SO\(_3\) aqueous solution (3 mL). The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried
over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/6, v/v) to afford the product.

(2R,3R,4S)-Methyl 2,3-dichloro-4-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3d)

White foam (39.8 mg, dr = 11:1, 70% yield, 0.2 mmol scale). Analytical data for 3d: $[\alpha]_D^{20} = 18.1$ (c = 1.0 CHCl$_3$, 86% ee); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.17 (d, $J = 4.8$ Hz, 1H), 3.95 (s, 3H), 4.94 (d, $J = 9.2$ Hz, 1H), 5.17 (dd, $J = 9.2$, 4.8 Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.76 (td, $J = 7.2$, 1.2 Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 8.10 (dd, $J = 8.0$, 1.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.5, 65.8, 70.2, 74.7, 127.1, 128.9, 129.1, 135.8, 136.0, 141.0, 164.9, 185.0; IR (film) 3498, 1749, 1694, 1243 cm$^{-1}$; HRMS (ESI) exact mass calcd for C$_{12}$H$_{14}$Cl$_2$NO$_4$ (M+NH$_4$) requires m/z 306.0294. Found m/z 306.0294. The enantiomeric ratio was determined by Daicel Chiralpak AD-H (25 cm), Hexane / IPA = 80 / 3, 0.83 mL/min, $\lambda$ = 254 nm, t (major) = 48.66 min, t (minor) = 63.02 min.

3.1 Mechanistic Investigations

To a Schlenk tube, DCDMH (47.3 mg, 0.24 mmol), (DHQD)$_2$PHAL (15.6 mg, 0.02 mmol) and toluene (1.0 mL) were added. Then 1u (43.2 mg, 0.2 mmol) was added in one portion. Very low conversion of 1u was observed and no product 2a was detected after the reaction mixture was stirred for 20 h at rt.
To a Schlenk tube, DCDMH (78.8 mg, 0.4 mmol), (DHQD)$_2$PHAL (15.6 mg, 0.02 mmol) and toluene (1.0 mL) were added. Then 1v (54.8 mg, 0.2 mmol) was added in one portion. After stirred for 48 h at rt, the reaction was quenched by the addition of saturated Na$_2$SO$_3$ aqueous solution (3.0 mL). The organic layer was extracted with ethyl acetate, washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product 2a (21.5 mg, 45% yield, 20% ee).

To a flame-dried Schlenk tube, 1a (60.6 mg, 0.3 mmol), 18-crown-6 (82.2 mg, 0.32 mmol) and toluene (2.0 mL) were added. Then potassium methoxide (22.2 mg, 0.32 mmol) was added. After stirred for 0.5 h at rt, a homogeneous solution was formed. To another Schlenk tube, DCDMH (71.0 mg, 0.36 mmol), (DHQD)$_2$PHAL (23.4 mg, 0.03 mmol) and toluene (1.0 mL) were added. After stirred for 10 min at -78 °C, the previously prepared homogeneous solution of 1a was added. The reaction was quenched by the addition of saturated Na$_2$SO$_3$ aqueous solution (3.0 mL) after stirred for 30 min at -78 °C. The organic layer was extracted with ethyl acetate, washed with brine, dried over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product 2a (66.3 mg, 94% yield, 7% ee).

To a Schlenk tube, DCDMH (23.5 mg, 0.12 mmol), (DHQD)$_2$PHAL (7.8 mg, 0.01
mmol), methanol (4.0 μL, 3.5 mg), 18-crown-6 (26.3 mg, 0.1 mmol) and toluene (1.0 mL) were added successively. After stirred for 10 min at -78 °C, 1α (20.2 mg, 0.1 mmol) was added. Then the reaction mixture was stirred at -78 °C until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of saturated Na₂SO₃ aqueous solution (3.0 mL) after stirred for 30 min at -78 °C. The organic layer was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product 2a (21.5 mg, 90% yield, 91% ee).

To a Schlenk tube, DCDMH (70.9 mg, 0.36 mmol), (DHQD)₂PHAL (23.4 mg, 0.03 mmol), benzoic acid (7.3 mg, 0.06 mmol) and toluene (2.0 mL) were added successively. After stirred for 10 min at -78 °C, 1α (60.6 mg, 0.3 mmol) was added. Then the reaction mixture was stirred at -78 °C until the reaction was complete (monitored by TLC). The reaction was quenched by the addition of saturated Na₂SO₃ aqueous solution (3.0 mL). The organic layer was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product 2α (65.8 mg, 93% yield, 64% ee).

4. Crystal data

In order to determine the absolute configuration of the products, the crystal of enantiopure 2d was obtained by slow evaporation in hexane and EA and a single crystal X-ray analysis determined its configuration as R (Fig. 1) (CCDC 1048302).
Table 1. Crystal data and structure refinement for (R)-2d.

| Property                        | Value                        |
|---------------------------------|------------------------------|
| Identification code             | cd21437                      |
| Empirical formula               | C12 H8 Br Cl O3              |
| Formula weight                  | 315.54                       |
| Temperature                     | 293(2) K                     |
| Wavelength                      | 0.71073 Å                    |
| Crystal system, space group     | Orthorhombic, P2(1)2(1)2(1) |
| Unit cell dimensions            | a = 7.4500(9) Å, alpha = 90 deg. |
|                                  | b = 7.7960(9) Å, beta = 90 deg. |
|                                  | c = 21.193(3) Å, gamma = 90 deg. |
| Volume                          | 1230.9(3) Å³                |
| Z, Calculated density           | 4, 1.703 Mg/m³               |
| Absorption coefficient          | 3.548 mm⁻¹                   |
| F(000)                          | 624                          |
| Crystal size                    | 0.211 x 0.165 x 0.123 mm     |
| Theta range for data collection | 2.78 to 26.00 deg.           |
| Limiting indices                | -9<=h<=9, -9<=k<=8, -26<=l<=25 |
| Reflections collected / unique  | 7410 / 2418 [R(int) = 0.0475] |
| Completeness to theta = 26.00   | 99.9 %                       |
| Absorption correction           | Empirical                    |
| Max. and min. transmission      | 1.00000 and 0.45967          |
| Refinement method               | Full-matrix least-squares on F^2 |
| Data / restraints / parameters  | 2418 / 0 / 156               |
| Goodness-of-fit on F^2          | 1.026                        |
Final R indices [I>2sigma(I)]  \( R_1 = 0.0386, \ wR_2 = 0.0941 \)

R indices (all data)  \( R_1 = 0.0494, \ wR_2 = 0.0988 \)

Absolute structure parameter  0.007(12)

Extinction coefficient  0.0013(14)

Largest diff. peak and hole  0.530 and -0.519 e.A\(^{-3}\)

In order to determine the absolute configuration of 2t, the crystal of enantiopure 2t was obtained by slow evaporation in hexane and Et\(_2\)O and a single crystal X-ray analysis determined its configuration as \( R \) (Fig. 2) (CCDC 1048128).

![Fig. 2](image_url)

**Table 2.** Crystal data and structure refinement for \((R)-2t\).

| Property                          | Value                        |
|----------------------------------|------------------------------|
| Identification code              | dm14320                      |
| Empirical formula                | C12 H9 Cl O3                 |
| Formula weight                   | 236.64                       |
| Temperature                      | 133(2) K                     |
| Wavelength                       | 0.71073 Å                    |
| Crystal system                   | Orthorhombic                 |
| Space group                      | P 2 1 2 1 2 1                |
| Unit cell dimensions             | \( a = 9.632(2) \) Å \hspace{1cm} \( a = 90^\circ \) \hspace{1cm} \( b = 9.726(2) \) Å \hspace{1cm} \( b = 90^\circ \) \hspace{1cm} \( c = 11.729(3) \) Å \hspace{1cm} \( g = 90^\circ \) |
| Volume                           | 1098.7(4) Å\(^3\)           |
| \( Z \)                          | 4                            |
| Density (calculated)             | 1.431 Mg/m\(^3\)            |
| Absorption coefficient           | 0.335 mm\(^{-1}\)           |
| \( F(000) \)                     | 488                          |
Crystal size 0.211 x 0.176 x 0.123 mm$^3$

Theta range for data collection 2.721 to 25.494°.

Index ranges -11<=h<=11, -11<=k<=11, -11<=l<=14

Reflections collected 7270

Independent reflections 2040 [R(int) = 0.0550]

Completeness to theta = 25.242° 99.4 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7457 and 0.4633

Refinement method Full-matrix least-squares on F$^2$

Data / restraints / parameters 2040 / 0 / 147

Goodness-of-fit on F$^2$ 1.073

Final R indices [I>2sigma(I)] R1 = 0.0437, wR2 = 0.1154

R indices (all data) R1 = 0.0471, wR2 = 0.1182

Absolute structure parameter 0.11(5)

Largest diff. peak and hole 0.432 and -0.233 e.Å$^{-3}$

5. References

1. (a) Bobrov, S.; Cai, C.; Katritzky, A. R.; Singh, S. K. J. Org. Chem. 2006, 71, 3364.
   (b) Aoyama, T.; Okutome, T.; Nakayama, T.; Yaegashi, T.; Matsui, R.; Nunomura, S.; Kurumi, Y.; Fujii, S. Chem. Pharm. Bull. 1985, 33, 1458. (c) Oguma, T.; Katsuki, T. J. Am. Chem. Soc. 2012, 134, 20017.
6. Copies of NMR spectra

Compound 1c’s NMR Spectra
Compound 1f's NMR Spectra
Compound 1g’s NMR Spectra
Compound 1h’s NMR Spectra
Compound 1i’s NMR Spectra
Compound 1k's NMR Spectra
Compound 11's NMR Spectra
Compound 1m’s NMR Spectra
Compound 1o's NMR Spectra
Compound 1p's NMR Spectra
Compound 1q’s NMR Spectra
Compound 2a's NMR Spectra
Compound 2b’s NMR Spectra
Compound 2c's NMR Spectra
Compound 2d’s NMR Spectra
Compound 2e's NMR Spectra
Compound 2f's NMR Spectra
Compound 2g’s NMR Spectra
Compound 2i's NMR Spectra
Compound 2j's NMR Spectra
Compound 2k's NMR Spectra
Compound 2l’s NMR Spectra
Compound 2m's NMR Spectra
Compound 2n’s NMR Spectra
Compound 2o's NMR Spectra
Compound 2p’s NMR Spectra
Compound 2q’s NMR Spectra
Compound 2s’s NMR Spectra
Compound 2t's NMR Spectra
Compound 2u's NMR Spectra
Compound 2v's NMR Spectra
Compound 3a’s NMR Spectra
Compound 3b’s NMR Spectra
Compound 3c's NMR Spectra
5. Copies of HPLC spectra

![HPLC spectra image with peaks and data tables]

| RT (min) | Area (µV·sec) | % Area | Height (µV) | % Height |
|---------|---------------|--------|-------------|----------|
| 1       | 12.016        | 49.00  | 585461      | 57.39    |
| 2       | 14.047        | 51.00  | 411247      | 42.11    |

![HPLC spectra image with peaks and data tables]

| RT (min) | Area (µV·sec) | % Area | Height (µV) | % Height |
|---------|---------------|--------|-------------|----------|
| 1       | 11.608        | 85.86  | 1043399     | 85.68    |
| 2       | 14.256        | 4.04   | 44814       | 4.12     |
| RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---------|---------------|--------|-------------|----------|
| 1       | 19850034      | 50.15  | 408669      | 52.06    |
| 2       | 19734986      | 48.85  | 376259      | 47.94    |

| RT (min) | Area (µV*sec) | % Area | Height (µV) | % Height |
|---------|---------------|--------|-------------|----------|
| 1       | 62941958      | 11.14  | 186885      | 13.02    |
| 2       | 66192567      | 83.86  | 1291612     | 66.69    |
