Supporting Information

Platinum-Catalyzed \textit{syn}-Stereocontrolled Ring-Opening of Oxabicyclic Alkenes with Sodium Arysulfimates

Ruihua Wu, Wen Yang, Wenkun Chen, and Dingqiao Yang*

Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People’s Republic of China

Phone: +86 20 31040403; Fax: +86 20 31040403.
yangdq@scnu.edu.cn (D.Y.).

Table of Contents

1. General information.................................................................2
2. General procedures for the synthesis of substrates 1a–1e, Sodium Sulfinates 2b–2m and the products 3aa–4di.........................................................2-3
3. Analytical data of products.........................................................3-17
4. Copies of $^1$H and $^{13}$C NMR spectra of 3aa–3ea and 4ba–4dc and $^{19}$F NMR spectrum of 3ab, 3ai and 4di.........................................................18-47
5. Copy of HPLC of 3aa...................................................................48
6. References..................................................................................49
1. General information

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without further purification. DME was distilled from sodium benzophenone ketyl and CH$_3$OH, CH$_3$CH$_2$OH, i-PrOH was distilled from magnesium. Super dry solvent 1,4-dioxane were used without any pretreatment. All flasks were flame-dried under a stream of nitrogen and cooled to room temperature before use. $^1$H and $^{13}$C {$^1$H} NMR spectra were recorded at 400/500/600 MHz and 100/125/150 MHz at 25 °C in CDCl$_3$, respectively. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet); coupling constants ($J$, Hz) and number of protons. HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Enantiomeric excesses were determined with a Chiralcel OD-H column eluted with a mixture of hexane and i-propanol (hexane/i-propanol 90:10, 1.0 mL/min, λ =254 nm). Melting points were uncorrected.

2. General Procedure for the Preparation of Sodium Sulfinates (2b–2f and 2h–2m)$^1$

4-Fluorobenzenesulfinic acid sodium salt (2b) was prepared by heating 2.5 g of sodium sulfite, 2.06 g of 4-fluorobenzenesulphonyl chloride, and 1.68 g of sodium bicarbonate in 9.6 mL of water at 70–80 °C for 4 h. After cooling to room temperature, water was removed under vacuum and the residue was extracted by ethanol, recrystallization as a white solid, the yield was 67% (1.34 g). Similarly, other sodium arenesulfonates (2c–2f and 2h–2m) was prepared from their corresponding sulphonyl chlorides.

Oxabenzonorbornadienes (1a–1e) were prepared according to the literature procedures.$^2$
General Procedure for Platinum-Catalyzed syn-Stereoccontrolled Ring-Opening of Oxabenzenorbornadienes (1a–1e) with Sodium Arylsulfinate. All experiments were carried out under the N₂ atmosphere. [Pt(COD)Cl₂] (3.7 mg, 5 mol %) and PPh₃ (6.8 mg, 10 mol %) were simultaneously added to a 10.0 mL round-bottomed flask, followed by the addition of CH₃OH (3 mL). After the mixture was stirred for about 30 min, oxabenzenorbornadienes (1a–1e) (0.2 mmol), sodium arylsulfinate (3 equiv, 0.6 mmol) and AgSbF₆ (3 mol%) were put into the reaction system. The mixture was stirred at 70 °C for 15 h. After cooling to the room temperature, the mixture should be concentrated through vacuum evaporation to remove solvent, and the residue was purified by column chromatography (200–300 mesh silica gels) to obtain the desired products 3 or 4.

3. Analytical data of products.

\[
\text{(1S*,2R*)-2-Phenyl-1,2-dihydronaphthalen-1-ol (3aa)\text{[^5a]}}
\]

Prepared according to general procedure. Colorless oil (35.9 mg, 81% yield). R\(_f\) = 0.25 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.28–7.19 (m, 6H), 7.19–7.15 (m, 2H), 7.11–7.07 (m, 1H), 6.63 (dd, \(J = 9.6, 2.0\) Hz, 1H), 6.05 (dd, \(J = 9.6, 4.0\) Hz, 1H), 4.85 (t, \(J = 6.7\) Hz, 1H), 3.79 (dd, \(J = 6.0, 4.0, 2.1 \)Hz, 1H), 1.43 (d, \(J = 7.9\) Hz, 1H). \(^{13}\)C\text{[^{1}H]} NMR (125 MHz, CDCl\(_3\)) \(\delta\) 137.8, 136.1, 132.7, 129.7, 129.3, 128.7, 128.4, 128.3, 128.1, 127.5, 126.8, 126.4, 71.4, 47.4. MS (EI) \(m/z\): [M – 3H]\(^+\) calcd for C\(_{16}\)H\(_{11}\)O, 219.08; found 219.04.
(1S*,2R*)-2-(4-Fluorophenyl)-1,2-dihyronaphthalen-1-ol (3ab).\textsuperscript{[5a]} Prepared according to general procedure. A white solid (34.6 mg, 72\% yield). mp 85–86 °C. R\textsubscript{f} = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v).

\begin{align*}
^1H \text{ NMR (600 MHz, CDCl}_3\text{)} & \delta 7.29–7.15 (m, 6H), 6.94 (t, J = 8.6 Hz, 2H), 6.65 (dd, J = 9.6, 1.8 Hz, 1H), 6.04 (dd, J = 9.6, 4.1 Hz, 1H), 4.87 (d, J = 6.0 Hz, 1H), 3.80–3.78 (m, 1H), 1.18 (d, J = 6.4 Hz, 1H). \\
^{13}C\{^1H\} \text{ NMR (150 MHz, CDCl}_3\text{)} & \delta 163.3 (d, J_{C-F} = 243.8 Hz), 161.7, 136.3, 133.6(d, J_{C-F} = 3 Hz), 132.8, 131.1, 129.9, 128.7, 128.6, 128.5, 126.7(d, J_{C-F} = 15 Hz), 115.8, 115.6(d, J_{C-F} = 21.0 Hz), 71.6, 46.8. \\
^{19}F \text{ NMR (376 MHz, CDCl}_3\text{)} & \delta -115.4. MS (EI) m/z: [M - 3H]\textsuperscript{-} \text{calcd for C}_{16}H_{10}FO, 237.07; found 237.23.
\end{align*}

(1S*,2R*)-2-(4-Chlorophenyl)-1,2-dihyronaphthalen-1-ol (3ac).\textsuperscript{[5a]} Prepared according to general procedure. A white solid (44.2 mg, 87\% yield). mp 113–114 °C. R\textsubscript{f} = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). 

\begin{align*}
^1H \text{ NMR (600 MHz, CDCl}_3\text{)} & \delta 7.26–7.16 (m, 5H), 7.13–7.08 (m, 3H), 6.63 (d, J = 9.6 Hz, 1H), 6.00 (dd, J = 9.6, 4.0 Hz, 1H), 4.83 (d, J = 4.0 Hz, 1H), 3.75 (s, 1H), 1.41 (s, 1H). \\
^{13}C\{^1H\} \text{ NMR (150 MHz, CDCl}_3\text{)} & \delta 136.3, 136.0, 133.2, 132.5, 130.7, 129.3, 128.7, 128.5, 128.5, 128.2, 126.6, 126.5, 71.3, 46.7. MS (EI) m/z: [M + Na]\textsuperscript{+} \text{calcd for C}_{16}H_{13}ClONa, 279.07; found 279.13.
\end{align*}
(1S*,2R*)-2-(4-Bromophenyl)-1,2-dihydronaphthalen-1-ol (3ad).\[^{5a}\] Prepared according to general procedure. Colorless oil (37.1 mg, 62% yield). R\textsubscript{f} = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46–7.39 (m, 2H), 7.35–7.25 (m, 3H), 7.19–7.15 (m, 1H), 7.13 (d, \(J = 8.3\) Hz, 2H), 6.71 (dd, \(J = 9.6, 1.9\) Hz, 1H), 6.07 (dd, \(J = 9.6, 4.1\) Hz, 1H), 4.91 (d, \(J = 5.9\) Hz, 1H), 3.84–3.79 (m, 1H), 1.52 (s, 1H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 136.8, 135.9, 132.4, 131.6, 131.0, 129.1, 128.5, 128.4, 128.2, 126.5, 126.5, 121.3, 71.2, 46.8. MS (EI) \(m/z\): [M – 3H] \textsuperscript{−} calcd for C\(_{16}\)H\(_{10}\)BrO, 297.00; found 297.46.

\[3ad\]

(1S*,2R*)-2-(3-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (3ae).\[^{5a}\] Prepared according to general procedure. Colorless oil (46.1 mg, 90% yield). R\textsubscript{f} = 0.21 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29–7.15 (m, 6H), 6.94 (t, \(J = 8.6\) Hz, 2H), 6.65 (dd, \(J = 9.6, 1.8\) Hz, 1H), 6.04 (dd, \(J = 9.6, 4.1\) Hz, 1H), 4.87 (d, \(J = 6.0\) Hz, 1H), 3.80–3.78 (m, 1H), 1.18 (t, \(J = 6.4\) Hz, 1H). \(^{13}\)C\{\(^1\)H\} NMR (150 MHz, CDCl\(_3\)) \(\delta\) 139.9, 135.4, 133.9, 131.9, 129.3, 129.0, 128.4, 128.1, 128.1, 127.8, 127.1, 127.0, 126.3, 126.1, 70.8, 46.7. MS (EI) \(m/z\): [M – 3H] \textsuperscript{−} calcd for C\(_{16}\)H\(_{10}\)ClO, 253.04; found 253.70.
(1S*,2R*)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol (3af). Prepared according to general procedure. Colorless oil (42.5 mg, 83% yield). \( R_f = 0.19 \) on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.36 (dd, \( J = 7.4, 1.9 \) Hz, 1H), 7.34–7.25 (m, 3H), 7.25–7.14 (m, 4H), 7.13 (d, \( J = 7.4 \) Hz, 1H), 6.67 (dd, \( J = 9.6, 2.7 \) Hz, 1H), 5.97 (dd, \( J = 9.6, 2.5 \) Hz, 1H), 4.82 (d, \( J = 5.0 \) Hz, 1H), 4.42 (dt, \( J = 5.3, 2.8 \) Hz, 1H), 1.48 (s, 1H). \(^{13}\)C{\(^1\)H} NMR (125 MHz, CDCl\(_3\)) \( \delta \) 137.5, 135.8, 134.8, 132.8, 131.6, 130.2, 129.7, 129.5, 129.1, 129.0, 128.7, 128.6, 127.6, 127.4, 69.9, 44.7. MS (EI) m/z: [M – 3H]– calcld for C\textsubscript{16}H\textsubscript{10}ClO, 253.04; found 253.13.

(1S*,2R*)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol (3ag). Prepared according to general procedure. Colorless oil (39.1 mg, 83% yield). \( R_f = 0.20 \) on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.25 (d, \( J = 7.3 \) Hz, 1H), 7.20 (t, \( J = 7.3 \) Hz, 1H), 7.16–7.13 (m, 1H), 7.08–7.01 (m, 5H), 6.60 (d, \( J = 9.6 \) Hz, 1H), 6.02 (dd, \( J = 9.6, 4.1 \) Hz, 1H), 4.83 (d, \( J = 5.6 \) Hz, 1H), 3.74 (s, 1H), 2.23 (s, 3H), 1.40 (s, 1H). \(^{13}\)C{\(^1\)H} NMR (150 MHz, CDCl\(_3\)) \( \delta \) 136.7, 135.8, 134.0, 132.3, 129.5, 129.0, 128.8, 127.9, 127.7, 127.60, 126.3, 126.0, 71.0, 46.5, 20.7. MS (EI) m/z: [M – 3H]– calcld for C\textsubscript{17}H\textsubscript{13}O, 233.10; found 233.16.

(1S*,2R*)-2-(4-Nitrophenyl)-1,2-dihydronaphthalen-1-ol (3ah). Prepared according to general procedure. A pale yellow solid (21.3 mg, 40% yield). mp 122.3–123.6°C. \( R_f = 0.3 \) on silica gel (ethyl acetate/petroleum ether 1:5,
v/v). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 8.7$ Hz, 2H), 7.41 (d, $J = 8.7$ Hz, 2H), 7.28 (dt, $J = 24.6$, 6.2 Hz, 3H), 7.17 (d, $J = 6.9$ Hz, 1H), 6.73 (dd, $J = 9.6$, 2.0 Hz, 1H), 6.04 (dd, $J = 9.6$, 3.8 Hz, 1H), 4.90 (d, $J = 5.2$ Hz, 1H), 3.92 (dd, $J = 6.8$, 4.7 Hz, 1H), 1.54 (s, 1H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 147.3, 146.5, 135.6, 132.1, 130.2, 129.0, 128.8, 128.5, 128.1, 126.8, 126.7, 123.6, 71.2, 58.5, 47.3. MS (EI) $m/z$: [M – 3H]$^-$ calcd for C$_{16}$H$_{10}$NO$_3$, 264.08; found 264.05.

![3ai](image)

(1$^S$,2$^R$*)-2-(4-Trifluoromethylphenyl)-1,2-dihydronaphthalen-1-ol (3ai). Prepared according to general procedure. A white solid (38.9 mg, 67% yield). mp 112–114 °C. R$_f$ = 0.11 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.27–7.17 (m, 3H), 7.12 (d, $J = 7.2$ Hz, 1H), 6.67 (dd, $J$ = 9.6, 1.5 Hz, 1H), 6.02 (dd, $J$ = 9.6, 3.8 Hz, 1H), 4.85 (d, $J$ = 5.7 Hz, 1H), 3.84 (s, 1H), 1.46 (s, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 143.1, 136.4, 133.0, 130.3, 130.2, 129.5 (q, $^{2}$J$_{C\cdot F}$ = 30.0 Hz), 129.4, 129.3, 129.0, 127.4, 127.3 (q, $^{1}$J$_{C\cdot F}$ = 271.3 Hz), 126.1, 126.0 (q, $^{3}$J$_{C\cdot F}$ = 3.7 Hz), 72.0, 47.9. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.51. MS (EI) $m/z$: [M – 3H]$^-$ calcd for C$_{17}$H$_{10}$F$_3$O, 287.06; found 287.08.

![3aj](image)

(1$^S$,2$^R$*)-2-(2,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol (3aj). Prepared according to general procedure. Colorless oil (39.0 mg, 78%
yield). \( R_f = 0.27 \) on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.24 (dd, \( J = 9.8, 7.3 \) Hz, 2H), 7.17 (d, \( J = 7.2 \) Hz, 1H), 7.10 (d, \( J = 7.3 \) Hz, 1H), 7.03 (d, \( J = 6.9 \) Hz, 2H), 6.92 (d, \( J = 7.3 \) Hz, 1H), 6.63 (dd, \( J = 9.6, 2.5 \) Hz, 1H), 5.98 (dd, \( J = 9.6, 2.7 \) Hz, 1H), 4.66 (d, \( J = 5.0 \) Hz, 1H), 4.07 (dt, \( J = 5.3, 2.8 \) Hz, 1H), 2.28 (s, 3H), 2.19 (s, 3H), 1.48 (s, 1H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 136.1, 135.2, 134.7, 132.8, 131.9, 130.0, 129.9, 129.4, 128.1, 127.4, 127.3, 127.2, 127.1, 126.0, 68.8, 42.8, 20.3, 18.7. MS (El) \( m/z \): [M – 3H]– calcd for C\(_{18}\)H\(_{15}\)O, 247.11; found 247.21.

\((1S^*,2R^*)\)-1',2'-Dihydro-[1,2']binaphthalenyl-1'-ol (3a\(^l\)).\(^{[10c]}\) Prepared according to general procedure. Colorless oil (29.9 mg, 55% yield). \( R_f = 0.22 \) on silica gel (ethyl acetate/petroleum ether 1:20, v/v). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.05 (d, \( J = 8.4 \) Hz, 1H), 7.82–7.79 (m, 1H), 7.70 (t, \( J = 7.8 \) Hz, 1H), 7.47–7.35 (m, 4H), 7.25 (dd, \( J = 7.2, 6.4, 2.4 \) Hz, 2H), 7.19–7.16 (m, 1H), 7.14–7.12 (m, 1H), 6.70 (dt, \( J = 7.8, 3.9 \) Hz, 1H), 6.10 (dd, \( J = 9.6, 2.5 \) Hz, 1H), 4.82 (d, \( J = 4.9 \) Hz, 1H), 4.70 (s, 1H), 1.42 (s, 1H). \(^{13}\)C\{\(^1\)H\} NMR (150 MHz, CDCl\(_3\)) \( \delta \) 135.5, 135.1, 134.4, 132.9, 132.2, 130.6, 129.5, 129.1, 128.6, 128.4, 128.3, 128.2, 127.3, 127.1, 126.7, 126.0, 125.9, 123.4, 70.6, 43.1. MS (El) \( m/z \): [M + CH\(_3\)]+ calcd for C\(_{21}\)H\(_{19}\)O, 287.15; found 287.06.
(15*,2R*)-1,2-Dihydro-[2,2'-binaphthalen]-1-ol (3am). Prepared according to general procedure. Colorless oil (26.1 mg, 48% yield). R$_f$ = 0.22 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82–7.76 (m, 4H), 7.48–7.43 (m, 2H), 7.36–7.30 (m, 3H), 7.24 (ddd, $J = 22.5$, 14.4, 6.8 Hz, 2H), 6.77 (dd, $J = 9.6$, 2.0 Hz, 1H), 6.22 (dd, $J = 9.6$, 4.0 Hz, 1H), 5.01 (d, $J = 5.9$ Hz, 1H), 4.04 (ddd, $J = 6.0$, 4.0, 2.1 Hz, 1H), 1.53 (s, 1H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 136.1, 135.3, 133.4, 132.8, 132.7, 129.5, 128.4, 128.3, 128.1, 127.8, 127.6, 127.3, 126.7, 126.5, 126.1, 125.8, 71.3, 47.5. MS (EI) m/z: [M – 3H$^-$] calcd for C$_{20}$H$_{13}$O, 269.10; found 268.88.

\[
\begin{array}{c}
\text{OMe} \\
\text{OMe} \\
\text{Me}
\end{array}
\]

1,4-Dimethoxy-6-phenynaphthalene (4ba). Prepared according to general procedure. White solid (50.2 mg, 95% yield). mp 87.2–87.8 °C. R$_f$ = 0.2 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.40 (d, $J = 1.8$ Hz, 1H), 8.23 (d, $J = 8.7$ Hz, 1H), 7.72 (ddd, $J = 8.3$, 7.5, 1.4 Hz, 3H), 7.45–7.42 (m, 2H), 7.34–7.31 (m, 1H), 6.69–6.65 (m, 2H), 3.94 (d, $J = 1.8$ Hz, 6H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 150.3, 150.1, 141.9, 139.1, 129.3, 128.1, 127.8, 127.2, 126.0, 125.9, 123.0, 120.4, 104.2, 103.9, 56.4, 56.3. MS (EI) m/z: [M – CH$_3$]$^-$ calcd for C$_{17}$H$_{13}$O$_2$, 249.08; found 248.52.

\[
\begin{array}{c}
\text{OMe} \\
\text{OMe} \\
\text{Me}
\end{array}
\]
1,4-Dimethoxy-6-(p-tolyl)naphthalene (4bg). Prepared according to general procedure. A white solid (56.8 mg, 90% yield). mp 113.2–114.4 °C. R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.44 (d, \( J = 1.6 \) Hz, 1H), 8.27 (d, \( J = 8.7 \) Hz, 1H), 7.78 (dd, \( J = 8.7, 1.9 \) Hz, 1H), 7.68 (d, \( J = 8.1 \) Hz, 2H), 7.30 (d, \( J = 7.9 \) Hz, 2H), 6.71 (q, \( J = 8.3 \) Hz, 2H), 3.98 (t, \( J = 3.4 \) Hz, 6H), 2.43 (s, 3H). \( ^{13} \)C\{\( ^1 \)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 150.1, 149.9, 138.8, 138.7, 137.4, 129.9, 127.7, 127.0, 125.6, 122.8, 119.8, 104.0, 103.5, 56.13, 21.5. HRMS (ESI-ion trap) \( m/z \): [M + H]\(^+\) calcd for C\(_{19}\)H\(_{19}\)O\(_2\), 279.1386; found 279.1375.

(1S*,2R*)-2-(4-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3bc)\[^{5a}\]. Prepared according to general procedure. A white solid (50.8 mg, 80% yield). mp 115.6–117.2 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.28 (d, \( J = 9.2 \) Hz, 4H), 7.01 (dd, \( J = 9.8, 3.2 \) Hz, 1H), 6.74 (q, \( J = 9.0 \) Hz, 2H), 6.00–5.97 (m, 1H), 4.98 (d, \( J = 4.2 \) Hz, 1H), 3.75 (d, \( J = 8.3 \) Hz, 6H), 3.69–3.66 (m, 1H), 1.15 (p, \( J = 9.0 \) Hz, 1H). \( ^{13} \)C\{\( ^1 \)H\} NMR (150 MHz, CDCl\(_3\)) \( \delta \) 149.6, 148.7, 138.1, 131.7, 129.5, 127.5, 127.4, 123.2, 121.3, 121.2, 110.5, 110.0, 63.3, 55.2, 55.1, 45.6. MS (EI) \( m/z \): [M - 3H]\(^+\) calcd for C\(_{18}\)H\(_{14}\)ClO\(_3\), 313.06; found 313.14.
(1S*,2R*)-2-(4-Bromophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3bd). Prepared according to general procedure. A white solid (28.8 mg, 40% yield). mp 91.6–93.8 °C. R_f = 0.29 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^1H NMR (600 MHz, CDCl_3) δ 7.45–7.41 (m, 2H), 7.24–7.21 (m, 2H), 7.03–6.99 (m, 1H), 6.77–6.72 (m, 2H), 5.98 (ddd, J = 9.8, 2.2, 1.6 Hz, 1H), 4.99 (d, J = 4.1 Hz, 1H), 3.75 (d, J = 8.1 Hz, 6H), 3.67–3.65 (m, 1H), 1.53 (s, 1H). ^13C[^1H] NMR (150 MHz, CDCl_3) δ 150.6, 149.7, 139.6, 131.5, 130.9, 128.3, 124.2, 122.3, 122.2, 120.8, 111.5, 111.0, 64.2, 56.2, 56.1, 46.7. MS (EI) m/z: [M – H]^- calcd for C_{18}H_{16}BrO_3, 359.02; found 359.01.

(1S*,2R*)-2-(3-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (3be). Prepared according to general procedure. Colorless oil (57.9 mg, 92% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^1H NMR (600 MHz, CDCl_3) δ 7.36 (s, 1H), 7.24 (d, J = 5.2 Hz, 2H), 7.22–7.19 (m, 1H), 7.02 (dd, J = 9.8, 3.2 Hz, 1H), 6.75 (q, J = 8.9 Hz, 2H), 6.02–5.99 (m, 1H), 5.02–5.00 (m, 1H), 3.75 (d, J = 5.9 Hz, 6H), 3.69–3.67 (m, 1H), 1.53 (s, 1H). ^13C[^1H] NMR (150 MHz, CDCl_3) δ 150.9, 150.0, 143.0, 134.6, 130.0, 129.6, 128.3, 127.6, 127.4, 124.6, 122.7, 122.5, 111.8, 111.4, 64.5, 56.5, 56.4, 47.3. MS (EI) m/z: [M + Na]^+ calcd for C_{18}H_{17}ClO_3Na, 339.08; found 338.84.
(1S*,2R*)-2-(2-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol \((3bf)\) Prepared according to general procedure. A white solid (55.4 mg, 92% yield). mp 98–99 °C. \(R_f = 0.3\) on silica gel (ethyl acetate/petroleum ether 1:5, v/v). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.50 (dd, \(J = 7.6, 1.5\) Hz, 1H), 7.42 (dd, \(J = 7.9, 1.0\) Hz, 1H), 7.30 (td, \(J = 7.5, 1.0\) Hz, 1H), 7.25 – 7.22 (m, 1H), 7.11 (dd, \(J = 9.8, 3.2\) Hz, 1H), 6.82 (q, \(J = 9.0\) Hz, 2H), 6.07 – 6.04 (m, 1H), 5.23 (d, \(J = 4.2\) Hz, 1H), 4.35 – 4.33 (m, 1H), 3.83 (d, \(J = 4.8\) Hz, 6H), 1.59 (d, \(J = 33.7\) Hz, 1H). \(^{13}\)C\{^1\}H NMR (150 MHz, CDCl\(_3\)) \(\delta\) 150.8, 149.6, 137.9, 134.0, 131.4, 129.4, 128.6, 128.2, 126.8, 124.1, 122.2, 122.1, 111.5, 111.0, 61.6, 56.2, 56.1, 43.8. MS (EI) \(m/z\): [M – 3H]\(^−\) calcd for C\(_{18}\)H\(_{14}\)ClO\(_3\), 313.06; found 313.14.

\[3ca\]

Prepared according to general procedure. Colorless oil (68.2 mg, 90% yield). \(R_f = 0.29\) on silica gel (ethyl acetate/petroleum ether 1:10, v/v). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.51 (s, 1H), 7.33 (d, \(J = 3.8\) Hz, 1H), 7.23 (tt, \(J = 4.7, 3.6\) Hz, 3H), 7.12 – 7.09 (m, 2H), 6.53 (dd, \(J = 9.6, 1.5\) Hz, 1H), 6.14 (dd, \(J = 9.6, 4.8\) Hz, 1H), 4.90 (t, \(J = 7.0\) Hz, 1H), 3.76 (ddd, \(J = 6.5, 4.8, 1.6\) Hz, 1H), 1.44 (d, \(J = 8.6\) Hz, 1H). \(^{13}\)C\{^1\}H NMR (150 MHz, CDCl\(_3\)) \(\delta\) 137.1, 135.6, 133.5, 131.8, 131.4, 130.8, 129.3, 128.9, 127.9, 126.4, 124.0, 123.6, 70.3, 46.7. MS (EI) \(m/z\): [M – H]\(^−\) calcd for C\(_{16}\)H\(_{11}\)Br\(_2\)O, 376.93; found 376.94.
(1S*,2R*)-6,7-Dibromo-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol (3cg)\(^{[13]}\).

Prepared according to general procedure. A white solid (62.9 mg, 80% yield). mp 108–109 °C. R\(_f\) = 0.24 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 4.5\) Hz, 1H), 7.45–7.39 (m, 1H), 7.16 (dd, \(J = 7.7, 1.8\) Hz, 4H), 6.60–6.51 (m, 1H), 6.09 (td, \(J = 9.4, 3.3\) Hz, 1H), 4.79–4.73 (m, 1H), 3.75–3.68 (m, 1H), 2.37 (s, 3H), 2.06 (t, \(J = 9.3\) Hz, 1H). \(^1\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)) \(\delta\) 137.3, 137.1, 136.6, 133.4, 132.4, 131.2, 130.8, 129.7, 128.3, 125.9, 124.0, 123.5, 73.6, 49.5, 21.1. MS (EI) \(m/z\): [M – CH\(_3\)]\(^-\) calcd for C\(_{16}\)H\(_{11}\)Br\(_2\)O, 376.91; found 376.87.

(1S*,2R*)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol (3cc)\(^{[5a]}\) Prepared according to general procedure. Colorless oil (69.87 mg, 85% yield). R\(_f\) = 0.3 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 9.5\) Hz, 1H), 7.32 (d, \(J = 3.4\) Hz, 1H), 7.02 (t, \(J = 6.0\) Hz, 2H), 6.97 (d, \(J = 8.1\) Hz, 2H), 6.50 (dd, \(J = 9.7, 1.1\) Hz, 1H), 6.11 (dd, \(J = 9.7, 4.9\) Hz, 1H), 4.87 (d, \(J = 6.7\) Hz, 1H), 3.73–3.69 (m, 1H), 1.54–1.47 (m, 1H). \(^1\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.7, 137.3, 133.6, 132.2, 132.0, 131.4, 130.7, 129.6, 129.2, 126.2, 123.9, 123.5, 70.2, 46.2. MS (EI) \(m/z\): [M – H]\(^-\) calcd for C\(_{16}\)H\(_{10}\)Br\(_2\)ClO, 410.88; found 410.81.

(1S*,2R*)-6,7-Dibromo-2-(3-chlorophenyl)-1,2-dihydronaphthalen-1-ol (3ce). Prepared according to general procedure. Colorless oil
(71.9 mg, 87% yield). R<sub>f</sub> = 0.32 on silica gel (ethyl acetate/petroleum ether 1:10, v/v).

1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, J = 4.5 Hz, 1H), 7.35 (s, 1H), 7.21–7.12 (m, 4H), 7.02–6.98 (m, 1H), 6.55 (dd, J = 9.7, 1.5 Hz, 1H), 6.09 (dd, J = 9.7, 4.5 Hz, 1H), 4.86 (d, J = 6.3 Hz, 1H), 3.99 (t, J = 6.7 Hz, 1H), 3.73 (dd, J = 7.8, 3.1 Hz, 1H), 1.54 (t, J = 4.6 Hz, 1H). 13C{1H} NMR (100 MHz, CDCl<sub>3</sub>) δ 138.3, 136.7, 134.6, 133.1, 131.5, 131.0, 130.9, 130.0, 129.5, 128.0, 127.3, 127.0, 124.3, 123.8, 70.1, 46.5. HRMS (ESI-ion trap) m/z: [M – 3H]<sup>−</sup> calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>ClO, 408.8628; found 408.8627.

\[
\begin{align*}
\text{(1S*,2R*)-6,7-Dibromo-2-(2-chlorophenyl)-1,2-} \\
\text{dihydronaphthalen-1-ol (3cf)}
\end{align*}
\]

Prepared according to general procedure. Colorless oil (64.4 mg, 78% yield). R<sub>f</sub> = 0.32 on silica gel (ethyl acetate/petroleum ether 1:10, v/v).

1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (s, 1H), 7.37 (s, 1H), 7.21–7.14 (m, 4H), 6.57 (dd, J = 9.7, 2.3 Hz, 1H), 6.06 (dd, J = 9.7, 3.5 Hz, 1H), 4.85 (d, J = 5.3 Hz, 1H), 4.38 (dt, J = 5.7, 2.9 Hz, 1H), 1.53 (dd, J = 14.8, 6.3 Hz, 1H). 13C{1H} NMR (100 MHz, CDCl<sub>3</sub>) δ 135.8, 135.3, 134.3, 132.8, 132.6, 131.2, 131.0, 130.7, 129.7, 128.8, 127.2, 126.6, 124.6, 123.5, 68.4, 43.3. HRMS (ESI-ion trap) m/z: [M – 3H]<sup>−</sup> calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>ClO, 408.8628; found 408.8632.

\[
\begin{align*}
\text{4da}
\end{align*}
\]
6,7-Dimethoxy-2-phenyl-naphthalene (4da).\textsuperscript{[13a]} Prepared according to general procedure. A white solid (49.6 mg, 88% yield). mp 121–122 °C. R$_f$ = 0.35 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 1.5 Hz, 1H), 7.66 (d, $J$ = 8.4 Hz, 1H), 7.63–7.60 (m, 2H), 7.52 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.38 (dd, $J$ = 10.6, 4.8 Hz, 2H), 7.29–7.24 (m, 1H), 7.07 (d, $J$ = 19.6 Hz, 2H), 3.93 (d, $J$ = 1.2 Hz, 6H). $^{13}$C\{$^1$H} NMR (125 MHz, CDCl$_3$) $\delta$ 149.9, 149.6, 141.4, 137.0, 129.5, 128.8, 128.4, 127.3, 127.1, 126.8, 124.4, 123.9, 106.6, 106.1, 55.9. MS (EI) m/z: [M – H]$^-$ calcd for C$_{18}$H$_{15}$O$_2$, 263.11; found 263.00.

6,7-Dimethoxy-2-(4-methylphenyl)-naphthalene (4dg).

Prepared according to general procedure. A white solid (47.8 mg, 86% yield). mp 136.2–137.3 °C. R$_f$ = 0.36 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J$ = 1.4 Hz, 1H), 7.65 (d, $J$ = 8.4 Hz, 1H), 7.51 (ddd, $J$ = 7.1, 4.2, 1.8 Hz, 3H), 7.20 (d, $J$ = 7.9 Hz, 2H), 7.09 (s, 1H), 7.05 (s, 1H), 3.93 (d, $J$ = 2.2 Hz, 6H), 2.33 (s, 3H). $^{13}$C\{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 150.4, 150.1, 139.1, 137.5, 137.4, 130.1, 130.1, 128.8, 127.7, 127.3, 124.6, 124.4, 107.1, 106.7, 56.5, 21.7. HRMS (ESI-ion trap) m/z: [M + H]$^+$ calcd for C$_{19}$H$_{19}$O$_2$ 279.1386; found, 279.1375.
6,7-Dimethoxy-2-(4-chlorophenyl)-naphthalene (4dc). Prepared according to general procedure. A white solid (47.1 mg, 79% yield). mp 139–140 °C. $R_f = 0.15$ on silica gel (ethyl acetate/petroleum ether 1:10, v/v). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.34 (d, $J = 1.7$ Hz, 1H), 8.17 (d, $J = 8.7$ Hz, 1H), 7.68 (dd, $J = 8.7, 1.8$ Hz, 1H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 6.65–6.60 (m, 2H), 3.90 (d, $J = 2.7$ Hz, 6H). $^{13}$C{$^1$H} NMR (150 MHz, CDCl$_3$) $\delta$ 150.6, 150.4, 140.5, 136.4, 133.8, 130.1, 129.6, 129.2, 129.1, 127.6, 125.0, 124.2, 107.2, 106.7, 56.6, 56.5. HRMS (ESI-ion trap) $m/z$: [M + 3H]$^+$ calcd for C$_{18}$H$_{18}$ClO$_2$, 301.0998; found 301.1002.

![Image of 6,7-Dimethoxy-2-(4-trifluoromethylphenyl)-naphthalene (4di)](image)

6,7-Dimethoxy-2-(4-trifluoromethylphenyl)-naphthalene (4di) Prepared according to general procedure. A white solid (36.5 mg, 55% yield). mp 113–114 °C. $R_f = 0.3$ on silica gel (ethyl acetate/petroleum ether 1:10, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (s, 1H), 7.72–7.60 (m, 6H), 7.49 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.08 (d, $J = 15.6$ Hz, 2H), 3.93 (s, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 149.7 (q, $^2$J$_{C,F} = 30$Hz ), 144.6, 135.1, 129.3, 129.1 (q, $^3$J$_{C,F} = 15$Hz ), 128.6, 127.1 (q, $^3$J$_{C,F} = 18$Hz ), 126.8, 125.5, 125.4 (q, $^4$J$_{C,F} = 4$Hz ), 124.5, 123.4, 123.2, 106.3, 105.7, 55.6. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.30. HRMS (ESI-ion trap) $m/z$: [M + H]$^+$ calcd for C$_{19}$H$_{16}$F$_3$O$_2$, 333.1103; found 333.1094.

![Image of (1S*,2R*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (3ea)](image)

(1S*,2R*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (3ea).[5a]
Prepared according to general procedure. A white solid (26.4 mg, 41% yield). mp 156–158 °C. Rf = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ¹H NMR (500 MHz, CDCl₃): δ 8.70–8.64 (m, 2H), 8.27–8.22 (m, 1H), 8.21–8.14 (m, 1H), 7.64–7.50 (m, 5H), 7.48–7.45 (m, 2H), 7.42–7.37 (m, 2H), 7.34–7.28 (m, 1H), 6.41 (ddd, J = 9.8, 2.3, 1.5 Hz, 1H), 5.36 (t, J = 4.7 Hz, 1H), 3.98–3.89 (m, 1H), 1.60 (d, J = 5.7 Hz, 1H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 140.3, 131.1, 131.0, 130.8, 130.1, 129.4, 129.0, 128.9, 128.8, 127.6, 127.5, 127.2, 127.1, 126.8, 126.6, 124.3, 124.2, 124.0, 123.3, 123.2, 67.8, 48.2. MS (EI) m/z: [M – 3H]⁻ calcd for C₂₄H₁₅O, 319.11; found 319.86.

4. Copies of ¹H, ¹³C and ¹⁹F NMR spectra
**3ab**
376 MHz, CDCl₃

**3ac**
600 MHz, CDCl₃
3ad
100 MHz, CDCl₃

3ae
500 MHz, CDCl₃
3ae
125 MHz, CDCl₃

3af
500 MHz, CDCl₃
**3af**

125 MHz, CDCl₃

**3ag**

600 MHz, CDCl₃
3ag
150 MHZ, CDCl₃

3ah
600MHZ, CDCl₃
3ah
150 MHz, CDCl₃

3ai
400 MHz, CDCl₃
3ai
100 MHz, CDCl₃

3ai
376 MHz, CDCl₃
3aj
400 MHz, CDCl₃

3aj
100 MHz, CDCl₃
3al
600 MHz, CDCl₃

3al
150 MHz, CDCl₃
4bg
400 MHz, CDCl₃

4bg
100 MHz, CDCl₃
$3\text{be}$

$600 \text{ MHz, CDCl}_3$

$3\text{be}$

$150 \text{ MHz, CDCl}_3$
3bf
600 MHz, CDCl₃

3bf
150 MHz, CDCl₃
3cc
400 MHz, CDCl₃

3cc
100 MHz, CDCl₃
$3cf$
$400 \text{ MHz, CDCl}_3$
4dg
600 MHz, CDCl₃

4dg
150 MHz, CDCl₃
4dc
600 MHz, CDCl$_3$

4dc
150 MHz, CDCl$_3$
3ea
125 MHz, CDCl$_3$
5. Copy of HPLC of 3aa

HPLC trace for racemic-3aa

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Time (min)</th>
<th>Area (mV*s)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.564</td>
<td>12964386</td>
<td>49.15</td>
</tr>
<tr>
<td>2</td>
<td>11.326</td>
<td>13410796</td>
<td>50.85</td>
</tr>
</tbody>
</table>

HPLC trace for enantioenriched-3aa \((ee = 75\%)\)

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Time (min)</th>
<th>Area (mV*s)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.578</td>
<td>7443</td>
<td>87.2</td>
</tr>
<tr>
<td>2</td>
<td>11.274</td>
<td>1092</td>
<td>12.8</td>
</tr>
</tbody>
</table>
6. References