**Supplementary Information**

**Construction of tetralin skeletons based on rhodium-catalysed site-selective ring opening of benzocyclobutenols**

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**Table of Contents:**

<table>
<thead>
<tr>
<th>Page</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>General Methods and Materials</td>
</tr>
<tr>
<td>S3–4</td>
<td>A typical procedure for the synthesis of benzocyclobutenols (1b, 1c)</td>
</tr>
<tr>
<td>S4–5</td>
<td>A typical procedure for the synthesis of 1-alkenylbenzocyclobutenols (5a, 5b, 5c)</td>
</tr>
<tr>
<td>S6</td>
<td>A procedure for the thermal reaction of benzocyclobutenol 1a and 2a (Scheme 1)</td>
</tr>
<tr>
<td>S7–11</td>
<td>A typical procedure for rhodium-catalyzed reactions of 1 and 2 (Scheme 2, Table 1)</td>
</tr>
<tr>
<td>S11</td>
<td>A procedure for thermal rearrangement of benzocyclobutenol 5a (Scheme 4)</td>
</tr>
<tr>
<td>S12</td>
<td>A typical procedure for rhodium-catalyzed rearrangement of 5 (Scheme 5)</td>
</tr>
<tr>
<td>S13-14</td>
<td>A typical procedure for rhodium-catalyzed asymmetric rearrangement of 5 (Scheme 6)</td>
</tr>
<tr>
<td>S15</td>
<td>References</td>
</tr>
<tr>
<td>S16–49</td>
<td>H and C NMR Spectra of 1b, 1c, 3, 4a-g, 5a-c, 7a-c</td>
</tr>
<tr>
<td>S50-55</td>
<td>HPLC chart for 7a-b</td>
</tr>
</tbody>
</table>
General Methods.

All reactions were carried out under an argon atmosphere in an oven-dried glassware with standard Schlenk techniques. Photoreactions were conducted with Rayonet RPR-100. IR measurements were performed on a FTIR SHIMADZU DR-8000. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury-vx400 ($^1$H at 400.44 MHz and $^{13}$C at 100.69 MHz) and JEOL JNM-ECA600 ($^1$H at 600.17 MHz) spectrometer. NMR data were obtained in CDCl$_3$ or C$_6$D$_6$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm (CHCl$_3$), 7.16 ppm (benzene). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm (CDCl$_3$) and 128.62 ppm (C$_6$D$_6$). High-resolution mass spectra were recorded on a Thermo Scientific Exactive (ESI, APCI, EI). Flash column chromatography was performed with silica gel 60N (Kanto). Preparative thin-layer chromatography (PTLC) was performed on silica gel plates with PF254 indicator (Merck). HPLC analysis was performed by 4.6×250 mm column. Gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC-908.

Materials.

Toluene was distilled over sodium/benzophenone ketyl. [Rh(OH)(cod)]$_2$,$^1$ [Rh(OH)(nbd)]$_2$,$^1$ 1-phenylbenzocyclobutenol $^1$$^a$,$^2$ 4-methoxy-1-phenylbenzocyclobutenol $^1$$^d$,$^3$ 6-chloro-1-phenylbenzocyclobutenol $^1$$^e$,$^3$ 4,6-diisopropyl-2,2-dimethyl-1-phenylbenzocyclobutenol $^1$$^f$,$^4$ and (E)-1-iodo-1-octene$^5$ were prepared according to the literature procedures. All other chemicals were available from commercial sources and were used as received without further purification.
A procedure for the synthesis of benzocyclobutenols (1b, 1c)

To a solution of benzocyclobutenone A (354 mg, 3.0 mmol) in THF (10 mL), a solution of i-PrMgBr in THF (3.0 M, 2.5 mL, 0.84 mmol) was added dropwise at 0 °C. Then, the reaction mixture was warmed to room temperature. The resulting mixture was quenched by addition of a saturated NH₄Cl solution and the aqueous solution was extracted with ethyl acetate. The combined organic layer was washed with H₂O and brine, and then was dried over Na₂SO₄. The solvent was removed by reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5/1) and GPC to give benzocyclobutenol 1b (203 mg, 1.3 mmol, 42%) as colorless oil; IR (ATR): 3383, 2961, 1456, 1364, 752, 716 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (d, J = 6.8 Hz, 3H), 1.09 (d, J = 7.2 Hz, 3H), 1.82-2.08 (m, 2H), 3.06 (d, J = 14.4 Hz, 1H), 3.39 (d, J = 14.0 Hz, 1H), 7.15-7.30 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 17.2, 17.3, 35.3, 44.9, 83.9, 121.5, 123.8, 126.9, 129.1, 141.9, 149.8; HRMS (APCI): Calcd for C₁₁H₁₅O, [M+H]⁺ 163.1117. Found m/z 163.1115.

Benzocyclobutenol 1c

According to the procedure analogous to that described for 1b, 1c (81 mg, 0.5 mmol, 24%) was prepared from benzocyclobutenone (244 mg, 2.1 mmol). Purified by GPC after column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1) as white solid; IR (ATR): 3207,
3007, 1456, 1352 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = -0.02\) to -0.04 (m, 1H), 0.43 to 0.61 (m, 3H), 1.41 to 1.48 (m, 1H), 2.06 (s, 1H), 3.19 (d, J = 14.0 Hz, 1H), 3.39 (d, J = 14.0 Hz, 1H), 7.08 to 7.29 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 9.1, 31.8, 46.4, 81.4, 121.1, 123.9, 127.1, 129.2, 141.5, 150.2\); HRMS (APCI): Calcd for C\(_{11}\)H\(_{13}\)O, [M+H]\(^+\) 161.0961. Found m/z 161.0959.

A procedure for the synthesis of 1-alkenylbenzocyclobutenols (5a, 5b, 5c)

![Chemical structure](image)

To a solution of (E)-1-iodo-1-octene (7.14 g, 30 mmol) in Et\(_2\)O (40 mL), t-BuLi (1.67 M, 37.5 mL, 60 mmol) was added dropwise at -78 °C. After 0.5 h, the reaction mixture was warmed to room temperature for 1 h. The reaction mixture was cooled to -78 °C. Then, benzocyclobutenone (3.54 g, 30 mmol) was added dropwise. After 1 h, the resulting mixture was quenched by addition of HCl (2.0 M) at -78 °C and the aqueous solution was extracted with Et\(_2\)O. The combined organic layer was washed with a saturated Na\(_2\)S\(_2\)O\(_3\) solution and brine, and then was dried over Na\(_2\)SO\(_4\). The solvent was removed by reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10/1) and GPC to give benzocyclobutenol 5a (3.7 g, 16 mmol, 54%) as colorless oil; IR (ATR): 3321, 2922, 2853, 1456 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.87\) (t, J = 6.8 Hz, 3H), 1.21 to 1.39 (m, 8H), 2.00 to 2.13 (m, 2H), 2.30 (s, 1H), 3.31 (d, J = 14.4 Hz, 1H), 3.45 (d, J = 14.0 Hz, 1H), 5.78 (dt, J = 15.2, 6.4 Hz, 1H), 5.87 (d, J = 15.6 Hz, 1H), 7.17 to 7.32 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 14.1, 22.6, 28.9, 29.1, 31.7, 32.1, 48.1, 80.1, 121.3, 124.1, 127.3, 129.4, 130.7, 131.6, 141.7, 149.1\); HRMS (EI): Calcd for C\(_{16}\)H\(_{25}\)O, [M+H]\(^+\) 231.1743. Found m/z 231.1740.
Benzocyclobutenol 5b

According to the procedure analogous to that described for 5a, 5b (0.59 g, 2.6 mmol, 26%) was prepared from benzocyclobutenone (1.18 g, 10 mmol). Purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) and GPC to give benzocyclobutenol 5b as white solid; IR (ATR): 3314, 1668, 1599, 1495 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.45\) (s, 1H), 3.42 (d, \(J = 14.0\) Hz, 1H), 3.58 (d, \(J = 14.4\) Hz, 1H), 6.57 (d, \(J = 16.0\) Hz, 1H), 6.74 (d, \(J = 16.0\) Hz, 1H), 7.22-7.40 (m, 9H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 48.5, 80.2, 121.5, 124.2, 126.6, 127.56, 127.56, 128.5, 128.7, 129.7, 131.5, 136.6, 141.6, 148.8\); HRMS (ESI): Calcd for C\(_{16}\)H\(_{15}\)O, [M+H]\(^+\) 223.1117. Found m/z 223.1114.

Benzocyclobutenol 5c

According to the procedure analogous to that described for 5a, 5c (587 mg, 2.3 mmol, 46%) was prepared from 2-methoxybenzocyclobutenone (740 mg, 5.0 mmol). Purified by column chromatography (hexane/ethyl acetate = 7/1) and GPC to give (1-octenyl)-6-methoxybenzocyclobutenol 5c as colorless oil; IR (ATR): 3418, 2924, 1603, 1580 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.88\) (t, \(J = 6.8\) Hz, 3H), 1.24-1.39 (m, 8H), 2.03-2.09 (m, 2H), 2.54 (s, 1H), 3.25 (d, \(J = 14.0\) Hz, 1H), 3.39 (d, \(J = 14.0\) Hz, 1H), 3.88 (s, 3H), 5.79 (dt, \(J = 15.6, 6.0\) Hz, 1H), 5.86 (d, \(J = 15.6\) Hz, 1H), 6.71 (d, \(J = 8.4\) Hz, 1H), 6.76 (d, \(J = 7.2\) Hz, 1H), 7.22 (dd, \(J = 8.4, 7.2\) Hz, 1H).
Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.1, 22.6, 28.9, 29.1, 31.7, 32.1, 48.4, 57.3, 79.6, 113.7, 116.1, 130.0, 131.1, 132.8, 132.9, 143.2, 154.0; HRMS (ESI): Calcd for C$_{17}$H$_{25}$O$_2$, [M+H]$^+$ 261.1849. Found m/z 261.1844.

**A procedure for thermal reaction of benzocyclobutenol 1a and 2a (Scheme 1)**

A solution of benzocyclobutenol 1a (39.2 mg, 0.20 mmol) and methyl vinyl ketone 2a (32.6 µL, 0.40 mmol, 2 equiv) in toluene (1 mL) was stirred at 130 °C for 12 h. After the reaction mixture was cooled to room temperature, concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 10/1) to give tetralin 3a (31.9 mg, 0.12 mmol, 60%). IR (ATR): 3437, 1697, 1447, 1198 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.95-2.07 (m, 4H), 2.31-2.42 (m, 1H), 3.00-3.04 (m, 2H), 3.36 (dd, $J$ = 11.2, 2.8 Hz, 1H), 4.83 (s, 1H), 6.90 (d, $J$ = 8.0 Hz, 1H), 7.07 (t, $J$ = 7.2 Hz, 1H), 7.13-7.36 (m, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 22.4, 28.9, 31.0, 58.3, 75.8, 126.51, 126.53, 126.9, 127.5, 127.9, 128.5, 129.4, 135.4, 140.9, 146.8, 214.3; HRMS (ESI): Calcd for C$_{18}$H$_{18}$O$_2$Na, [M+Na]$^+$ 289.1199. Found m/z 289.1189.
A typical procedure for rhodium-catalyzed reactions (Scheme 2, Table1)

To an oven-dried flask equipped with a stirrer bar were added \([\text{Rh(OH)(nbd)}]_2\) (5.0 µmol, 2.5 mol %) and benzocyclobutenol 1a (39.3 mg, 0.20 mmol, 1.0 equiv). The flask was capped with a rubber septum, evacuated and refilled with argon three times. Then, a solution of methyl vinyl ketone (2a, 32.6 µL, 0.40 mmol, 2.0 equiv) in dry toluene (1 mL) was added by syringe. After being stirred at 100 °C for 30 min, the reaction mixture was cooled to room temperature. The resulting mixture was passed through a pad of Florisil® and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) to give tetralin 4a as yellow solid (43.5 mg, 0.16 mmol, 82%); IR (ATR): 3474, 1695, 1167, 1067 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.04\) (s, 3H), 3.00-3.05 (m, 2H), 3.17 (d, \(J = 17.4\) Hz, 1H), 3.27 (dd, \(J = 16.2, 12.6\) Hz, 1H), 3.65 (dd, \(J = 12.6, 4.8\) Hz, 1H), 4.21 (d, \(J = 2.4\) Hz, 1H), 7.07-7.08 (m, 1H), 7.16-7.17 (m, 3H), 7.27 (t, \(J = 7.8\) Hz, 1H), 7.36-7.39 (m, 2H), 7.50-7.52 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 30.0, 31.8, 44.2, 53.3, 73.7, 124.7, 126.0, 126.4, 127.1, 128.2, 128.5, 129.2, 133.3, 134.0, 146.8, 214.7\); HRMS (APCI): Calcd for C\(_{18}\)H\(_{19}\)O\(_2\), [M+H]\(^+\) 267.1380. Found m/z 267.1373.
Tetraline 4b

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) as white solid; IR (ATR): 3501, 2961, 1692, 1169 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 0.90 (d, $J$ = 7.2 Hz, 3H), 1.07 (d, $J$ = 6.6 Hz, 3H), 1.94-1.99 (m, 1H), 2.38 (s, 3H), 2.70 (d, $J$ = 17.4 Hz, 1H), 2.77 (d, $J$ = 17.4 Hz, 1H), 2.92 (dd, $J$ = 15.6, 4.2 Hz, 1H), 3.06-3.11 (m, 1H), 3.18 (dd, $J$ = 12.6, 6.6 Hz, 1H), 3.58 (d, $J$ = 1.8 Hz, 1H), 7.11-7.18 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 16.4, 18.3, 30.4, 31.1, 33.4, 35.9, 51.2, 74.6, 125.6, 126.3, 127.9, 129.7, 133.7, 134.1, 215.3; HRMS (APCI): Calcd for C$_{15}$H$_{21}$O$_2$, [M+H]$^+$ 233.1536. Found m/z 233.1529.

Tetralin 4c

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) as white solid; IR (ATR): 3503, 1693, 1364, 752 cm$^{-1}$; $^1$H NMR (600 MHz, C$_6$D$_6$): $\delta$ = 0.13-0.20 (m, 2H), 0.36-0.39 (m, 1H), 0.42-0.45 (m, 1H), 0.58-0.60 (m, 1H), 1.81 (s, 3H), 2.34-2.42 (m, 2H), 2.55 (d, $J$ = 16.8 Hz, 1H), 2.83 (d, $J$ = 16.8 Hz, 1H), 3.09 (dd, $J$ = 15.6, 12.0 Hz, 1H), 3.26 (d, $J$ = 1.8 Hz, 1H), 6.91-6.93 (m, 1H), 6.96-6.97 (m, 1H), 7.04-7.09 (m, 2H); $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ = -0.1, 2.1, 21.1, 30.6, 32.7, 42.4, 54.3, 69.8, 126.5, 127.0, 129.1, 130.1, 134.9, 135.3, 214.9; HRMS
(APCI): Calcd for C_{15}H_{19}O_{2}, [M+H]^+ 231.1380. Found m/z 231.1375.

Tetralin 4d

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) as white solid; IR (ATR): 3485, 1699, 1611, 1504 cm\(^{-1}\); \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)): \(\delta = 1.50\) (s, 3H), 2.46 (dd, \(J = 16.2, 5.4\) Hz, 1H), 2.80 (d, \(J = 17.4\) Hz, 1H), 2.89-2.93 (m, 2H), 3.10 (dd, \(J = 15.6, 12.0\) Hz, 1H), 3.37 (s, 3H), 4.44 (d, \(J = 3.0\) Hz, 1H), 6.52 (d, \(J = 1.8\) Hz, 1H), 6.81 (dd, \(J = 8.4, 2.4\) Hz, 1H), 6.91 (d, \(J = 8.4\) Hz, 1H), 7.07 (t, \(J = 7.2\) Hz, 1H), 7.16-7.19 (m, 2H), 7.36-7.38 (m, 2H); \(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)): \(\delta = 30.2, 31.9, 45.6, 53.9, 55.4, 74.5, 113.4, 114.4, 125.8, 126.7, 127.6, 129.1, 130.0, 136.8, 148.6, 159.3, 214.6\); HRMS (APCI): Calcd for C\(_{19}\)H\(_{21}\)O\(_3\), [M+H]^+ 297.1485. Found m/z 297.1479.

Tetralin 4e

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1)
as white solid; IR (ATR): 3429, 1651, 1595, 1213 cm$^{-1}$; $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 2.91 (d, $J$ = 17.6 Hz, 1H), 3.03 (d, $J$ = 17.2 Hz, 1H), 3.28-3.37 (m, 2H), 4.06 (dd, $J$ = 10.4, 8.0 Hz, 1H), 5.02 (d, $J$ = 2.8 Hz, 1H), 6.72 (d, $J$ = 7.6 Hz, 1H), 6.81 (t, $J$ = 8.0 Hz, 1H), 6.89-6.95 (m, 3H), 7.01-7.06 (m, 3H), 7.14-7.16 (m, 1H), 7.44-7.46 (m, 2H), 7.55-7.57 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 29.7, 45.1, 46.8, 73.8, 124.6, 126.8, 127.0, 127.2, 127.7, 128.2, 128.4, 128.9, 131.8, 133.7, 134.0, 136.1, 136.6, 146.6, 205.6; HRMS (APCI): Calcd for C$_{23}$H$_{20}$O$_2$Cl, [M+H]$^+$ 363.1146. Found m/z 363.1136.

**Tetralin 4f**

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) as white solid; IR (ATR): 3422, 2961, 1657, 1447 cm$^{-1}$; $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ = 1.05 (d, $J$ = 6.8 Hz, 3H), 1.18 (d, $J$ = 6.8 Hz, 3H), 1.25 (s, 3H), 1.28 (d, $J$ = 2.0 Hz, 3H), 1.29 (d, $J$ = 2.0 Hz, 3H), 1.61 (s, 3H), 2.82-2.92 (m, 2H), 3.22 (dd, $J$ = 16.0, 5.2 Hz, 1H), 3.44 (dd, $J$ = 16.4, 12.4 Hz, 1H), 4.89 (dd, $J$ = 12.4, 5.2 Hz, 1H), 4.98 (s, 1H), 6.75 (t, $J$ = 7.6 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 7.00-7.04 (m, 3H), 7.09-7.16 (m, 2H), 7.21 (t, $J$ = 8.0 Hz, 1H), 7.31 (d, $J$ = 1.6 Hz, 1H), 7.84-7.86 (m, 2H), 8.14 (d, $J$ = 7.6 Hz, 1H); $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ = 23.6, 24.28, 24.34, 25.10, 25.14, 29.4, 30.2, 32.7, 35.4, 44.3, 45.0, 79.7, 120.9, 124.3, 127.4, 127.5, 127.6, 129.0, 129.7, 130.1, 134.3, 137.8, 145.97, 146.04, 146.2, 147.5, 207.1; HRMS (APCI): Calcd for C$_{31}$H$_{37}$O$_2$, [M+H]$^+$ 441.2788. Found m/z 441.2778.
**Tetralin 4g**

![Diagram of Tetralin 4g](image)

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 7/1) as white solid; IR (ATR): 3464, 3024, 2363, 1651, 1661 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 3.11-3.18\) (m, 2H), 3.25 (d, \(J = 17.4\) Hz, 1H), 3.45 (dd, \(J = 15.6, 12.6\) Hz, 1H), 4.58 (dd, \(J = 13.2, 5.4\) Hz, 1H), 4.80 (d, \(J = 2.4\) Hz, 1H), 7.13-7.22 (m, 5H); 7.26-7.29 (m, 2H), 7.47 (t, \(J = 7.8\) Hz, 2H), 7.55 (d, \(J = 7.8\) Hz, 2H), 7.60 (t, \(J = 7.8\) Hz, 1H), 7.92 (d, \(J = 7.2\) Hz, 2H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 31.6, 45.0, 47.2, 74.2, 124.6, 125.9, 126.4, 126.8, 128.16, 128.18, 128.3, 128.8, 129.2, 133.6, 133.9, 134.3, 136.1, 147.2, 205.7\); HRMS (APCI): Calcd for C\(_{23}\)H\(_{21}\)O\(_2\), [M+H]\(^+\) 329.1536. Found m/z 329.1527.

**A procedure for thermal rearrangement of benzocyclobutenol 5a (Scheme 4)**

![Diagram of thermal rearrangement](image)

A solution of benzocyclobutenol 5a (33.2 mg, 0.14 mmol) in C\(_6\)D\(_6\) (1 mL) was heated at 80 °C for 4.5 h. After the reaction mixture was cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 10/1) to give 1-tetralone 6a (30.3 mg, 0.127 mmol, 91%). IR (ATR): 2924, 2855, 1682, 1601 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.89\)
(t, J = 6.8 Hz, 3H), 1.29-1.47 (m, 10H), 2.14-2.24 (m, 1H), 2.31 (dd, J = 16.0, 12.0 Hz, 1H), 2.69 (dd, J = 16.4, 10.8 Hz, 1H), 2.77 (dd, J = 16.4, 3.2, 2.0 Hz, 1H), 3.00 (ddd, J = 16.0, 3.6, 1.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.30 (pseudo t, J = 7.2 Hz, 1H), 7.47 (pseudo td, J = 7.6, 1.6 Hz, 1H), 8.01 (dd, J = 8.0, 1.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 14.1, 22.6, 26.5, 29.3, 31.8, 35.4, 35.8, 36.2, 45.5, 126.6, 127.0, 128.9, 132.5, 133.5, 143.8, 198.6; HRMS (ESI): Calcd for C$_{16}$H$_{23}$O, [M+H]$^+$ 231.1743. Found m/z 231.1741.

A typical procedure for rhodium-catalyzed rearrangement (Scheme 5)

To an oven-dried vial equipped with a stirrer bar was added [Rh(OH)(cod)]$_2$ (2.2 mg, 5.0 µmol, 2.5 mol %). The vial was purged with nitrogen gas. Then, a solution of 5a (46.0 mg, 0.20 mmol) in dry toluene (0.8 mL) was added and heated at 40 °C for 2 h. The reaction mixture was then cooled to room temperature. The resulting mixture was passed through a pad of Florisil® and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 11/1) to give 2-tetralone 7a as yellow oil (38.4 mg, 0.17 mmol, 83%); IR (ATR): 2924, 2855, 1717, 1456 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ = 0.87 (t, J = 6.8 Hz, 3H), 1.26-1.65 (m, 10H), 2.54 (dd, J = 16.4, 4.4 Hz, 1H), 2.69 (dd, J = 16.4, 5.6 Hz, 1H), 3.05-3.12 (m, 1H), 3.60 (s, 2H), 7.11-7.13 (m, 1H), 7.19-7.23 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 14.0, 22.6, 27.3, 29.2, 31.7, 35.0, 39.6, 43.8, 44.2, 126.6, 126.7, 127.7, 128.7, 132.7, 140.2, 210.6; HRMS (EI): Calcd for C$_{16}$H$_{22}$O, [M]$^+$ 230.1671. Found m/z 230.1670.
A typical procedure for rhodium-catalyzed asymmetric rearrangement (Scheme 6)

To an oven-dried vial equipped with a stirrer bar were added [Rh(OH)(cod)]₂ (2.2 mg, 5.0 µmol, 2.5 mol %) and (R)-MeO-F₁₂-BIPHEP (9.6 mg, 12.0 µmol, 6.0 mol %). The vial was purged with nitrogen gas. Then, toluene (0.5 mL) was added and the reaction mixture was stirred at room temperature for 12 h. A solution of 5a (46.0 mg, 0.20 mmol) in dry toluene (0.5 mL) was added and the reaction mixture was stirred at 50 °C for 10 h. The reaction mixture was then cooled to room temperature. The resulting mixture was passed through a pad of Florisil® and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 14/1) to give (−)-2-tetralone 7a as yellow oil (37.6 mg, 0.16 mmol, 82%, er = 91:9 (Daicel CHIRALPAK IB column, hexane:i-PrOH = 99.5:0.5, 0.67 mL/min, retention times: t₁ = 7.95 min, t₂ = 8.71 min), [α]²³_D = −45.6 (c = 2.6×10⁻² M in CHCl₃)). The absolute stereochemistry was assigned by analogy of 7b.

Tetralone 7b

Purified by preparative thin-layer chromatography (hexane/ethyl acetate = 15/1) as yellow oil (19.5 mg, 0.09 mmol, 44%, er = 16:84 (Daicel CHIRALPAK IB column, hexane:i-PrOH = 99.5:0.5, 0.67 mL/min, retention times: t₁ = 19.53 min, t₂ = 26.26 min), [α]²⁵_D = +5.17 (c = 1.8×10⁻² M in CHCl₃)); IR(ATR): 3026, 1713, 1601, 1495 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.90 (dd, J =
16.8, 6.0 Hz, 1H), 2.95 (dd, \(J = 16.4, 7.2\) Hz, 1H), 3.60 (d, \(J = 20.0\) Hz, 1H), 3.68 (d, \(J = 20.0\) Hz, 1H), 4.47 (pseudo t, \(J = 6.4\) Hz, 1H), 7.01 (d, \(J = 7.6\) Hz, 1H), 7.14 (d, \(J = 7.6\) Hz, 2H), 7.18-7.22 (m, 2H), 7.24-7.28 (m, 2H), 7.32-7.36 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 44.6, 44.9, 45.7, 126.97, 126.98, 127.3, 127.9, 128.1, 128.5, 128.8, 133.3, 139.3, 141.4, 209.4\); HRMS (EI): Calcd for \(C_{16}H_{14}O\), \([M]^+\) 222.1045. Found m/z 222.1048. The absolute stereochemistry was assigned by comparison of the optical rotation with the reported data.\(^6\)

**Tetralone 7c**

![Tetralone 7c structure](image)

Purified by preparative thin-layer chromatography on silica gel (eluent: hexane/ethyl acetate = 13/1) as yellow oil (31.5 mg, 0.12 mmol, 61\%, er = 99:1 ((Daicel CHIRALPAK IB column, hexane:i-PrOH = 99.5:0.5, 0.67 mL/min, retention times: \(t_1 = 8.65\) min, \(t_2 = 11.38\) min), \([\alpha]^{23}_D = -113.1\) (\(c = 1.7\times10^{-2}\) M in CHCl\(_3\))); IR (ATR): 2926, 2855, 1717, 1585 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)); \(\delta = 0.87\) (t, \(J = 6.8\) Hz, 3H), 1.18-1.51 (m, 10H), 2.54 (dd, \(J = 16.0, 6.8\) Hz, 1H), 2.67 (dd, \(J = 16.0, 2.4\) Hz, 1H), 3.57 (s, 2H), 3.59-3.65 (m, 1H), 3.84 (s, 3H), 6.71 (d, \(J = 7.6\) Hz, 1H), 6.77 (d, \(J = 8.4\) Hz, 1H), 7.17 (pseudo t, \(J = 7.6\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)); \(\delta = 14.1, 22.6, 27.1, 29.1, 31.7, 32.4, 34.5, 43.1, 43.5, 55.3, 108.4, 120.8, 127.4, 129.2, 134.2, 156.5, 211.1\); HRMS (EI): Calcd for \(C_{17}H_{24}O_2\), \([M]^+\) 260.1776. Found m/z 260.1772. The absolute stereochemistry was assigned by analogy of 7b.
References


1b

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7c
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