Catalytic, Enantioselective Synthesis of 1,2-anti-Diols by Asymmetric Ring-Opening/Cross-Metathesis**

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General Information.

All reactions were carried out in dry glassware under an Argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres glovebox under nitrogen atmosphere. All solvents were purified by passage through solvent purification columns and further degassed with Argon.¹ NMR solvents for air-sensitive compounds were degassed by sparging with nitrogen and passed through a solvent purification column prior to use. Commercially available reagents were used as received unless otherwise noted. Substrates in the liquid state were degassed with Argon and passed through a plug of neutral alumina prior to use. Solid substrates were used after purification by silica gel column chromatography.

Standard NMR spectroscopy experiments were conducted on a Varian INOVA 500 (¹H: 500 MHz, ¹³C: 125 MHz) spectrometer. Chemical shifts are referenced to the residual solvent peak (CDCl₃) multiplicity is reported as follows: (s: singlet, d: doublet, t: triplet: q: quartet, br: broad, m: multiplet). Spectra were analyzed and processed using MestReNova.

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with an Agilent HP-5 5% phenyl methyl siloxane capillary column (J&W Scientific). GC instrument conditions: Inlet temperature-250 °C; Detector temperature- 300 °C; Hydrogen flow- 30 mL/min; Air flow- 400

mL/min; Makeup flow- 25 mL/min. GC method: 50 °C for 1 min, then temperature ramp (35 °C/min) for 7 min to 300 °C followed by an isothermal period at 300 °C for 3 min. Chiral gas chromatography was carried out on an Agilent 6850 FID gas chromatograph equipped with an Agilent GTA column. GC instrument conditions: Inlet temperature - 180 °C; Detector temperature - 250 °C; Hydrogen flow - 32 mL/min; Air flow - 400 mL/min; Makeup flow - 30 mL/min. GC method: 80 °C for 12 min, isocratic.

High-resolution mass spectra (HRMS) data were obtained on a JEOL MSRoute mass spectrometer using FAB+ or EI+ methods. Analytical SFC data was obtained on a Mettler SFC supercritical CO₂ analytical chromatography system equipped with Chiracel OD-H, OJ–H or Chirapak AD-H columns (4.6 mm x 25 cm). Column temperature was maintained at 40°C. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

**Substrates for AROCM**

Substrates for AROCM were synthesized as previously reported in the literature:

2, 2, 5a, 3 b, 3 c, 4 d were synthesized according to the provided references.

Catalyst 1 was synthesized as previously reported.6

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6 R. Gandolfi, M. Ratti, L. Toma, C. De Micheli, *Heterocycles* 1979, 12, 897.
Representative Procedure for AROCM

In a glovebox, cyclobutene 2 (26.6 mg, 0.1 mmol, 1 equiv) and allyl benzoate (6b, 113 mg, 0.7 mmol, 7 equiv) were dissolved in 0.15 mL THF. To this solution was added 50 µL of a stock solution (0.02 M in THF) of catalyst 1. The reaction vial was capped and stirred for 1.5 h and then quenched with an excess of ethyl vinyl ether. The reaction mixture was concentrated and Z/E ratios were determined by 500 MHz \(^1\)H NMR (products 7a-c, e-k) or GC (product 4). The crude was subjected to flash chromatography or preparative TLC to afford the desired AROCM product (7f, 25.9 mg, 61% isolated yield, 88:12 Z/E, 97% ee (Z), 88% ee (E)). Pure products (or E/Z mixtures in the case of 7i, and E-7j) were submitted to analytical SFC to determine enantiomer excess.

Characterization data for AROCM products

Acetate 4.

79% yield (GC), 85% Z.

Z-4:

\([\alpha]_D^{25} = 9.34^\circ\) (c = 0.52, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.24 (m, 10H), 5.88 – 5.77 (2x m, 1H), 5.71 – 5.64 (m, 1H), 5.34 (m, 1H), 5.29 (m, 1H), 4.64 (AB d, \(J = 10.5\) Hz, 1H), 4.63 (AB d, \(J = 10.5\) Hz, 1H), 4.61 (m, 1H), 4.51 – 4.46 (m, 1H), 4.45 (AB d, \(J = 10.5\) Hz, 1H), 4.43 (AB d, \(J = 10.5\) Hz, 1H), 4.21

---

(ddd, $J = 9.1, 5.0, 1.0$ Hz, 1H), 3.87 (dd, $J = 7.5, 5.0$ Hz, 1H), 2.04 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.8, 138.6, 138.4, 135.5, 131.9, 128.5, 128.4, 127.8, 127.7, 127.7, 127.5, 119.2, 82.2, 76.6, 70.7, 70.6, 60.8, 21.1. HRMS (FAB+) calculated for C$_{23}$H$_{27}$O$_4$ [M+H]: 367.1909; found 367.1904.

Separation conditions for $Z$-$4$: OJ-H, 5% IPA, 2.5 mL/min. 95% ee

**Racemate:**

**Enantioenriched:**

**$E$-$4$:**
$[\alpha]_D^{25} - 11.8^\circ \ (c = 0.24, \text{CHCl}_3)$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 – 7.24 (m, 10H), 5.88 – 5.74 (3x m, 1H), 5.33 (m, 1H), 5.29 (m, 1H), 4.65 (AB d, $J$ = 9.3 Hz, 1H), 4.63 (AB d, 9.3 Hz, 1H), 4.61 (d, $J$ = 6.0 Hz, 2H), 4.45 (AB d, $J$ = 10.6 Hz, 1H), 4.43 (AB d, $J$ = 10.7 Hz, 1H), 3.89 (dd, $J$ = 6.4, 5.1 Hz, 1H), 3.85 (dd, $J$ = 7.2, 5.1 Hz, 1H), 2.08 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.9, 138.41, 138.33, 135.5, 131.7, 128.46, 128.45, 128.40, 127.8, 127.75, 127.6, 127.55, 119.1, 82.4, 81.3, 70.9, 70.6, 64.4, 21.1. HRMS (FAB+) calculated for C$_{23}$H$_{27}$O$_4$ [M+H]: 367.1909; found 367.1922.

Separation conditions for E-4: OJ-H, 7% IPA, 2.5 mL/min. 85% ee

Racemate:

![Racemate graph]

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Totals: 4722.50659 285.29260

Enantioenriched:

![Enantioenriched graph]
Silyl ether 7a.7

66% isolated yield, 88% Z.

Z-7a:

\[ \alpha \] D$_{25}^\text{D} + 4.72^\circ$ (c = 1.06, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.84 (ddd, $J =$ 17.3, 10.4, 6.4 Hz, 1H), 5.80 – 5.75 (m, 1H), 5.49 (ddddd, $J$ = 11.2, 8.9, 1.7, 1.1 Hz, 1H), 5.23 (ddd, $J$ = 17.3, 1.8, 1.2 Hz, 1H), 5.16 (dddd, $J$ = 10.4, 1.8, 1.0 Hz, 1H), 4.34 (ddddd, $J$ = 8.9, 7.0, 1.1 Hz, 1H), 4.15 (m, 2H), 3.90 (dddt, $J$ = 7.3, 6.4, 1.1 Hz, 1H), 2.31 (br, 1H), 0.88 (s, 9H), 0.86 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.3, 134.4, 130.3, 116.5, 77.5, 72.8, 59.3, 26.1, 25.9, 18.5, 18.3, -4.2, -4.2, -4.3, -4.5. HRMS (EI+) calculated for C$_{19}$H$_{41}$O$_3$Si$_2$ [M+H]: 375.2594; found 375.2583.

Z-7a was derivatized by benzylation and subsequent desilylation to afford a product spectroscopically identical to Z-7b prior to chiral SFC analysis, which indicated 99% ee (see directly below (p. S10) for racemic trace).

Enantioenriched:

Diol 7b.

67% isolated yield, 75% Z.

**Z-7b:**

$[\alpha]_D^{25} = -30.7^\circ$ (c = 0.60, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06 – 8.01 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 5.89 (ddd, 17.3, 10.5, 6.2 Hz, 1H), 5.93 – 5.76 (2x m, 1H), 5.38 (ddd, $J = 17.3$, 1.5, 1.4 Hz, 1H), 5.28 (ddd, $J = 10.6$, 1.5, 1.4 Hz, 1H), 5.08 (ddd, $J = 12.9$, 7.7, 0.8 Hz, 1H), 4.83 (ddd, $J = 12.6$, 5.5, 1.0 Hz, 1H), 4.63 (dd, $J = 8.0$, 4.3 Hz, 1H), 4.25 (ddt, $J = 6.8$, 4.3, 1.3 Hz, 1H), 2.85 (br, 1H), 2.34 (br, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.9, 136.0, 133.3, 132.5, 130.0, 129.8, 128.6, 127.7, 118.0, 75.5, 70.4, 61.3. HRMS (EI+) calculated for C$_{14}$H$_{17}$O$_4$ [M+H]: 249.1127; found 249.1117.

Separation conditions for **Z-7b**: OD-H, 20% IPA, 2.5 mL/min. 91% ee

**Racemate:**
Enantioenriched:

**E-7b:**

\[ \alpha \]_D^{25} = -1.57° (c = 0.06, CHCl₃); ¹H NMR (500 MHz, CDCl₃) \( \delta \) 8.08–8.01 (m, 2H), 7.60–7.54 (m, 1H), 7.48–7.41 (m, 2H), 6.02 (dt, \( J = 15.7, 5.7, 1.3 \) Hz, 1H), 5.96–5.77 (m, 2H), 5.37 (ddd, \( J = 17.3, 1.5, 1.4 \) Hz, 1H), 5.29 (ddd, \( J = 10.6, 1.5, 1.4 \) Hz, 1H), 5.07 (m, 1H), 4.87 (m, 1H), 4.68 (m, 1H), 4.25 (m, 1H), 2.89 (br, 1H), 2.00 (br, 1H). ¹³C NMR (125 MHz, CDCl₃) \( \delta \) 166.8, 135.9, 133.3, 132.5, 130.1, 129.8, 128.6, 127.9, 118.0, 75.6, 70.3, 61.2.
Separation conditions for *E*-7b: OJ-H, 20% IPA, 2.5 mL/min. 67% ee

Racemate:

![Signal 2: DAD1 B, Sig=235,8 Ref=360,100](image1)

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Totals: 1991.92078 272.37326

Enantioenriched:

![Signal 2: DAD1 B, Sig=235,8 Ref=360,100](image2)

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Totals: 4139.88293 529.21280

Benzoate 7c.

69% isolated yield, 75% Z.

**Z-7c:**

\[ \alpha \]_D^{25} + 4.06° (c = 0.95, CHCl₃); ¹H NMR (500 MHz, CDCl₃) ð 8.09 – 8.04 (m, 2H), 8.02 – 7.97 (m, 2H), 7.61 – 7.54 (2x m, 1H), 7.49 – 7.39 (2x m, 2H), 6.09 –
5.96 (3x m, 1H), 5.83 – 5.78 (m, 1H), 5.67 (dd, J = 11.0, 9.7 Hz, 1H), 5.52 (d, J = 17.3 Hz, 1H), 5.41 (d, J = 10.5 Hz, 1H), 4.56 (ddd, J = 13.4, 7.8, 1.4 Hz, 1H), 4.20 (ddd, J = 13.4, 5.7, 1.2 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.1, 165.6, 135.4, 133.5, 133.4, 131.8, 130.0, 129.9, 129.85, 129.80, 128.6, 128.6, 125.3, 120.4, 75.6, 71.4, 58.8. HRMS (FAB+) calculated for C$_{21}$H$_{21}$O$_5$ [M+H]: 353.1389; found 353.1381.

Separation conditions for **Z-7c**: OJ-H, 5% IPA, 2.5 mL/min. 96% ee

Racemate

![Racemate chromatogram](image)

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Totals : 7153.38208 396.58324

Enantioenriched

![Enantioenriched chromatogram](image)
\[ \alpha \]D \text{25} = -1.14^\circ \ (c = 0.56, \ \text{CHCl}_3); \ ^1\text{H NMR} (500 \text{ MHz}, \ \text{CDCl}_3) \ \delta 8.10 - 7.97 \ (2x \text{ m}, 2\text{H}), 7.60 - 7.52 \ (2x \text{ m}, 1\text{H}), 7.48 - 7.39 \ (2x \text{ m}, 2\text{H}), 6.10 \ (\text{ddd}, 15.5, 4.9, 4.8 \text{ Hz}, 1\text{H}), 6.02 \ (\text{ddd}, 17.3, 10.6, 6.4 \text{ Hz}, 1\text{H}), 5.92 \ (\text{dddd}, 15.4, 6.9, 1.7, 1.6 \text{ Hz}, 1\text{H}), 5.84 \ (\text{m}, 1\text{H}), 5.80 \ (\text{m}, 1\text{H}), 5.49 \ (d, J = 17.2 \text{ Hz}, 1\text{H}), 5.39 \ (d, J = 10.5 \text{ Hz}, 1\text{H}), 4.24 - 4.18 \ (\text{m}, 2\text{H}). \ ^{13}\text{C NMR} (125 \text{ MHz}, \ \text{CDCl}_3) \ \delta 165.6, 165.5, 135.2, 133.3, 131.8, 130.1, 129.9, 128.6, 128.6, 124.4, 120.1, 75.7, 74.9, 62.8. \ \text{HRMS} \ (	ext{FAB}+) \ \text{calculated for C}_{21}\text{H}_{19}\text{O}_4 \ [\text{M-OH}]: 335.1283; \ \text{found} 335.1271. \\

\text{Separation conditions for E-7c: OJ-H, 5\% IPA, 2.5 mL/min. 82\% ee.} \\

\text{Racemate} \\

\text{Enantioenriched}
Alcohol 7e.

62% isolated yield, 89% Z.

Z-7e:

$[\alpha]_D^{25} = -2.95^\circ$ (c = 0.76, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 – 7.24 (m, 10H), 6.02 (ddd, $J = 11.1, 6.9, 6.8$ Hz, 1H), 5.83 (ddd, $J = 17.6, 10.4, 7.5$ Hz, 1H), 5.56 (dd, $J = 11.5, 8.9$ Hz, 1H), 5.39 (m, 1H), 5.37 – 5.32 (m, 1H), 4.64 (AB d, $J = 10.5$ Hz, 1H), 4.62 (AB d, $J = 11.0$ Hz, 1H), 4.42 (AB d, $J = 12.1$ Hz, 1H), 4.38 (AB d, $J = 11.7$ Hz, 1H), 4.21 (dd, $J = 8.6, 7.4, 1.0$ Hz, 1H), 4.07 – 3.93 (2x m, 1H), 3.78 (dd, $J = 7.2, 7.0$ Hz, 1H), 2.13 (br, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.2, 137.7, 135.8, 133.7, 131.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 119.5, 81.5, 76.3, 70.8, 70.7, 58.5. HRMS (FAB+) calculated for C$_{21}$H$_{25}$O$_3$ [M+H]: 325.1804; found 325.1803.

Separation conditions for Z-7e: OJ-H, 10% IPA, 2.5 mL/min. 93% ee

Racemate:
Enantioenriched:

$\alpha_D^{25} = -2.93^\circ$ (c = 0.30, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 – 7.23 (m, 10H), 5.93 – 5.79 (2x m, 1H), 5.71 (ddd, $J_1 = 15.7$, 7.5, 7.3 Hz, 1H), 5.33 (m, 1H), 5.29 (m, 1H), 4.65 (AB d, $J_1 = 12.2$ Hz, 1H), 4.62 (AB d, $J_1 = 12.2$ Hz, 1H), 4.47 (AB d, $J_1 = 12.2$ Hz, 1H), 4.43 (AB d, $J_1 = 12.1$ Hz, 1H), 4.18 (m, 2H), 3.90 (dd, $J_1 = 7.9$, 5.6 Hz, 1H), 3.86 (dd, $J_1 = 7.4$, 4.8, 0.9 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.7, 138.6, 135.6, 133.7, 128.8, 128.4, 127.9, 127.8, 127.6, 127.5, 119.0,
82.5, 81.6, 70.8, 70.7, 63.2. HRMS (FAB+) calculated for C_{21}H_{25}O_3 [M+H]:
325.1804; found 325.1812.

Separation conditions for \textit{E-7e}: OJ-H, 10\% IPA, 2.5 mL/min. 86\% ee

Racemate:

\begin{table}[h]
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1 & 6.977 & 0.1991 & 1499.56213 & 109.99121 & 50.4390 \\
2 & 7.720 & 0.2202 & 1473.65618 & 97.57201 & 49.5610 \\
\hline
Totals: & 2973.01831 & 207.56322 \\
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\end{tabular}
\caption{HPLC separation for \textit{E-7e}.}
\end{table}

Enantioenriched:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Peak & RetTime & Width & Area & Height & Area \\
\hline
1 & 7.071 & 0.2045 & 342.74240 & 24.91814 & 6.8119 \\
2 & 7.788 & 0.2910 & 4015.99163 & 288.76002 & 93.0981 \\
\hline
Totals: & 4958.73703 & 313.67815 \\
\hline
\end{tabular}
\caption{HPLC separation for \textit{Z-7f}.}
\end{table}

Benzoate \textit{7f}.

61\% isolated yield, 88\% \textit{Z}.

\textit{Z-7f}:
$[\alpha]_D^{25} = -50.9^\circ$ (c = 0.74, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.08 – 8.02 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.22 (m, 10H), 5.97 (dddd, $J = 11.3$, 7.8, 5.8, 1.1 Hz, 2H), 5.85 (dddd, $J = 17.1$, 10.5, 7.5 Hz, 1H), 5.73 (ddd, $J = 10.7$, 9.2, 1.5 Hz, 1H), 5.35 – 5.33 (m, 1H), 5.31 (m, 1H), 4.87 (ddd, $J = 13.2$, 7.8, 1.4 Hz, 1H), 4.73 (ddd, $J = 13.2$, 5.8, 1.6 Hz, 2H), 4.68 (AB d, $J = 12.2$ Hz 1H), 4.64 (AB d, $J = 12.1$ Hz, 1H), 4.49 (AB d, $J = 12.1$ Hz, 1H), 4.44 (AB d, $J = 12.2$ Hz, 1H), 4.30 (ddd, $J = 9.1$, 5.0, 1.1 Hz, 2H), 3.90 (dd, $J = 7.5$, 5.0 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.4, 138.6, 138.4, 135.5, 133.1, 132.1, 130.2, 129.7, 128.55, 128.50, 128.45, 128.40, 127.8, 127.75, 127.70, 127.5, 119.2, 82.3, 76.7, 70.7, 70.7, 61.2. HRMS (FAB+) calculated for C$_{28}$H$_{29}$O$_4$ [M+H]: 429.2066; found 429.2056.

Separation conditions for Z-7f: OJ-H, 20% IPA, 2.5 mL/min. 97% ee

Racemate:

Enantioenriched:
$^1$H NMR (500 MHz, CDCl$_3$) δ 8.08 – 8.04 (m, 2H), 7.61 – 7.54 (m, 1H), 7.45 (m, 2H), 7.36 – 7.21 (m, 10H), 5.98 – 5.79 (3x m, 1H), 5.34 (m, 1H), 5.29 (m, 1H), 4.87 (2x m, 1H), 4.64 (AB d, $J = 12.0$ Hz, 2H), 4.47 (AB d, $J = 12.1$ Hz, 1H), 4.43 (AB d, $J = 12.1$ Hz, 1H), 3.92 (dd, $J = 6.8$, 5.3 Hz, 1H), 3.87 (dd, $J = 6.8$, 5.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.4, 138.50, 138.42, 135.6, 133.1, 131.8, 130.1, 129.82, 129.80, 128.55, 128.52, 128.44, 128.36, 127.8, 127.60, 127.56, 119.1, 82.4, 81.3, 70.9, 70.6, 64.8.

Separation conditions for $E$-$7f$: OD-H, 20% IPA, 2.5 mL/min. 88% ee

Racemate:
Silyl ether 7g.

68% yield, 87% Z. Initial product mixture derivatized by treatment with TBAF (3 equiv) to aid in purification; isolated product is spectroscopically identical to alcohol 7e (see above, p. S14).

Optical rotations and enantiopurity of derivatized products:

Derivative of Z-7g: $[\alpha]_D^{25} = -2.2^\circ$ (c = 0.61, CHCl$_3$)

89% ee

Enantioenriched:
Derivative of $E$-7g: $[\alpha]_D^{25} - 3.4^\circ$ (c = 0.31, CHCl$_3$)

77% ee

Benzyl ether 7h.

64% isolated yield, 86% Z.

Z-7h:

$[\alpha]_D^{25} - 29.7^\circ$ (c = 0.66, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 – 7.23 (m, 10H), 5.91 (dddd, $J$ = 11.4, 7.3, 5.4, 1.1 Hz, 1H), 5.83 (ddd, $J$ = 17.2, 10.4, 7.6 Hz, 1H), 5.61 (dddd, $J$ = 11.0, 9.2, 1.7, 1.6 Hz, 1H), 5.34 – 5.30 (m, 1H), 5.28 (m, 1H), 4.64 (AB d, $J$ = 12.2 Hz, 1H), 4.61 (AB d, $J$ = 12.1 Hz, 1H), 4.43 (AB d, $J$ =
12.2 Hz, 1H), 4.43 – 4.41 (2x AB d, 1H), 4.40 (AB d, J = 12.1 Hz, 1H), 4.16 (ddd,
J = 9.2, 4.9, 1.1 Hz, 1H), 4.04 (ddd, J = 12.6, 7.3, 1.6 Hz, 1H), 3.93 (ddd, J =
12.6, 5.4, 1.8 Hz, 1H), 3.82 (ddddd, J = 7.6, 5.0, 1.2, 0.9 Hz, 1H). $^{13}$C NMR (125
MHz, CDCl$_3$) δ 138.6, 138.5, 138.3, 135.5, 131.6, 130.3, 128.52, 128.39, 128.36,
127.84, 127.81, 127.77, 127.76, 127.56, 127.53, 119.1, 82.5, 76.4, 72.5, 70.6,
70.4, 66.4. HRMS (FAB+) calculated for C$_{28}$H$_{31}$O$_3$ [M+H]: 415.2273; found
415.2260.

Separation conditions for Z-7h: OD-H, 15% IPA, 2.5 mL/min. 91% ee

Racemate:

Enantioenriched:
Isolated as an inseparable 9:1 Z/E mixture, 76% yield.

Z-7i: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 – 7.25 (m, 10H), 7.06 – 7.00 (m, 2H), 6.79 – 6.75 (m, 2H), 5.95 – 5.82 (2x m, 1H), 5.54 (ddd, $J = 11.0, 9.4, 1.7, 1.5$ Hz, 1H), 5.37 (m, 1H), 5.29 (m, 1H), 4.67 (2x AB d, $J = 12.2$ Hz, 2H), 4.49 (AB d, $J = 12.2$ Hz, 1H), 4.47 (AB d, $J = 12.1$ Hz, 1H), 4.36 (ddd, $J = 9.3, 4.8, 1.1$ Hz, 1H), 3.89 (dd, $J = 7.7, 4.9$ Hz, 1H), 3.78 (s, 3H), 3.34 – 3.20 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.0, 138.77, 138.76, 135.7, 133.9, 132.4, 129.63, 129.45, 128.4, 128.0, 127.84, 127.78, 127.53, 127.49, 119.0, 114.0, 82.7, 76.3, 70.6, 70.3, 55.4, 33.4. HRMS (FAB+) calculated for C$_{28}$H$_{31}$O$_3$ [M+H]: 415.2273; found 415.2287.

Separation conditions for Z/E product mixture: AD-H, 10% IPA, 2.5 mL/min. Z: 93% ee; E: 79% ee.

Racemate:
Enantioenriched:

Ketone 7j.

65% isolated yield, 90% Z.

Z-7j:

\[ \alpha \]_D^{25} = -7.98^\circ (c = 1.35, CHCl_3); \ ^1H NMR (500 MHz, CDCl_3) \delta 7.39 – 7.22 (m, 10H), 5.86 (ddd, J = 17.2, 10.4, 7.6 Hz, 1H), 5.65 (dtd, J = 11.1, 7.5, 1.0 Hz, 1H), 5.46 (ddt, J = 10.9, 9.3, 1.6 Hz, 1H), 5.35 (m, 1H), 5.27 (m, 1H), 4.66 (AB d, J = 12.1 Hz, 1H), 4.61 (AB d, J = 12.2 Hz, 1H), 4.45 (AB d, J = 12.1 Hz, 1H), 4.43 (AB d, J = 12.2 Hz, 1H), 4.23 (ddd, J = 9.3, 5.0, 1.0 Hz, 1H), 3.84 (dd, J = 7.6, 5.0, 1H), 2.38 (m, 2H), 2.24 (m, 2H), 2.04 (s, 3H). \ ^13C NMR (125 MHz, CDCl_3) \delta 208.0, 138.753, 138.746, 135.7, 133.2, 128.6, 128.36, 128.34, 127.81, 127.75,
127.51, 127.49, 118.9, 82.6, 76.3, 70.6, 70.3, 43.3, 30.0, 22.3. HRMS (FAB+) calculated for C$_{24}$H$_{29}$O$_3$ [M+H]: 365.2117; found 365.2113.

Separation conditions for Z-7j: OJ-H, 5% IPA, 2.5 mL/min. 92% ee

Racemate

![Racemate chromatogram]

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Totals: 9011.13965 343.95483

Enantioenriched

![Enantioenriched chromatogram]

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Totals: 7608.44189 423.55034

E/Z-7j mixture:
Enantioenriched: \( E \ 85\% \ \text{ee} \).

**Boronic ester** 7k.

50% isolated yield of \( Z \) product.

\[ [\alpha]_D^{25} = -7.98^\circ \ (c = 0.64, \ \text{CHCl}_3); \ \] \( ^1\text{H} \ \text{NMR} \ (500 \ \text{MHz}, \ \text{CDCl}_3) \ \delta \ 7.37 - 7.28 \ (m, \ 10\text{H}), 5.94 - 5.78 \ (2x \ m, \ 1\text{H}), 5.43 \ (dddd, \ J = 11.0, 9.3, 1.7, 1.5 \ \text{Hz}, \ 1\text{H}), 5.28 \ (m, \ 1\text{H}), 5.25 \ (m, \ 1\text{H}), 4.67 \ (AB \ d, \ J = 12.2 \ \text{Hz}, \ 1\text{H}), 4.64 \ (AB \ d, \ J = 12.3 \ \text{Hz}, \ 1\text{H}), 4.47 \ (AB \ d, \ J = 12.4 \ \text{Hz}, \ 1\text{H}), 4.44 \ (AB \ d, \ J = 12.2 \ \text{Hz}, \ 1\text{H}), 4.30 \ (ddd, \ J = 9.4, 4.0, 1.1 \ \text{Hz}, \ 1\text{H}), 3.88 \ (dd, \ J = 7.7, 4.0 \ \text{Hz}, \ 1\text{H}), 1.69 \ (m, \ 2\text{H}), 1.23 \ (s, \ 6\text{H}), 1.22 \]
(s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 139.1, 139.0, 135.7, 130.0, 128.31, 128.30, 127.7, 127.6, 127.34, 127.33, 126.9, 118.8, 83.5, 82.8, 76.2, 70.5, 70.1, 24.94, 24.93. HRMS (FAB+) calculated for C$_{20}$H$_{28}$O$_3$B [M-OBn]: 327.2132; found 327.2138.

Separation conditions for Z-7k: OJ-H, 5% IPA, 2.5 mL/min. 91% ee

**Racemate**

![Racemate HPLC graph]

**Enantioenriched**

![Enantioenriched HPLC graph]
Synthesis of (+)-endo-brevicomin, 11

Alcohol 9.

Alcohol 9 was synthesized following the general AROCM procedure in 85% isolated yield, 91% Z, and 1:1 dr.

Z-9:

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 – 7.24 (m, 10H), 5.89 – 5.78 (2x m, 1H), 5.54 – 5.43 (dddd, $J$ = 11.1, 9.8, 1.3, 1.0 Hz, 1H), 5.38 (m, 1H), 5.32 (m, 1H), 4.66 (AB d, $J$ = 12.3 Hz, 2H), 4.59 (AB d, $J$ = 12.2 Hz, 2H), 4.41 (AB d, $J$ = 12.4 Hz, 2H), 4.38 (AB d, $J$ = 12.1 Hz, 2H), 4.20 (ddd, $J$ = 9.8, 6.9, 0.9 Hz, 2H), 3.78 (dd, $J$ = 7.7, 6.9 Hz, 1H), 3.74 (m, 1H), 2.81 (br, 1H), 2.18 – 2.10 (m, 2H), 1.16 (d, $J$ = 6.2 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.5, 137.9, 135.9, 131.8, 131.1, 128.40, 128.37, 128.2, 127.82, 127.75, 127.6, 119.7, 81.2, 75.6, 70.23, 70.18, 66.9, 38.1, 23.2. HRMS (FAB+) calculated for C$_{23}$H$_{29}$O$_3$ [M+H]: 353.2117; found 353.2108.

Ketone 10:

Dess-Martin periodinane (302 mg, 0.713 mmol, 2 equiv) was added in one portion to a cold (0°C) solution of alcohols Z-9 (126 mg, 0.356 mmol) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Aqueous 1:1 NaHCO$_3$/ Na$_2$S$_2$O$_3$ solution was added and the biphasic mixture stirred vigorously for 1 h. The layers were separated, and the aqueous layer extracted with CH$_2$Cl$_2$. The combined organic layers were dried over
MgSO₄, filtered and concentrated. The crude residue was purified by flash chromatography to afford 110.4 mg, 88% yield of ketone 10.

$[\alpha]_D^{25} = -14.4^\circ$ (c = 0.83, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ 7.36 – 7.24 (m, 10H), 5.93 (ddddd, J = 11.1, 10.8, 7.2, 1.1 Hz, 1H), 5.85 (dd, J = 17.2, 10.4, 7.6 Hz, 1H), 5.63 (ddddd, J = 11.0, 9.1, 1.7, 1.4 Hz, 1H), 5.36 – 5.33 (m, 1H), 5.33 – 5.27 (m, 1H), 4.63 (2x ABd, J = 12.0 Hz, 2H), 4.43 (AB d, J = 10.8 Hz, 1H), 4.39 (AB d, J = Hz, 1H), 4.09 (ddd, J = 9.1, 5.2, 1.1 Hz, 1H), 3.84 (dd, J = 7.6, 5.3 Hz, 1H), 3.08 (dd, J = 7.2, 1.7 Hz, 2H), 2.03 (s, 3H). $^{13}$C NMR (125 MHz, CDCl₃) δ 206.1, 138.6, 138.4, 135.6, 130.7, 128.40, 128.37, 127.87, 127.86, 127.62, 127.58, 126.4, 119.1, 82.4, 76.3, 70.7, 70.3, 42.7, 29.8. HRMS (FAB+) calculated for C₂₃H₂₇O₃ [M+H]: 351.1960; found 351.1954.

Separation conditions for 10: AD-H, 5% IPA, 2.5 mL/min. 95% ee

Racemate:

![DAD1 A, Sig=210,8 Ref=360,100 (C:\CHEMS2\10DAT\NTKQ\DEF LC 2013-08-30 13-19-192-JH-065-RAC-4.D)](image)

Enantioenriched:
(+)-endo-brevicomin (11).

Ketone 10 (35 mg, 0.10 mmol) was dissolved in 5:1 MeOH/1 N HCl (aq.) and the reaction flask purged with Argon. Palladium on carbon (10%, 35 mg) was added, and the flask was purged by a balloon filled with H₂. The reaction mixture was stirred under 1 atm of H₂ for 2 h. The reaction flask was then purged with Argon and Celite was added. The suspension was filtered through Celite and the organic layer was extracted with pentane. The combined pentane layers were washed with water, brine, and dried over MgSO₄. The pentane layers were filtered and carefully concentrated to afford the crude reaction mixture (9.9 mg, 67% yield), containing 90% purity (+)-endo-brevicomin. Analytical samples were afforded by flash chromatography.

\[ \alpha \]_D^{25} + 49.6° (c = 0.11, CHCl₃), lit.\(^8\) \[ \alpha \]_D^{20} + 49° (c = 1.0, ether, 96.5% ee, 90% purity), lit.\(^9\) \[ \alpha \]_D^{20} + 77.9° (c = 1.2, ether, 99.3% ee); \(^1\)H NMR (500 MHz, CDCl₃) \( \delta \)
4.21 (dt, \( J = 4.6, 2.3 \text{ Hz}, 1\text{H} \)), 3.99 (tdd, \( J = 7.2, 4.1, 1.0 \text{ Hz}, 1\text{H} \)), 1.99 – 1.72 (m,

---

4H), 1.68 – 1.51 (m, 4H), 1.43 (s, 3H), 0.99 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 107.0, 81.6, 76.6, 34.4, 25.0, 23.6, 21.9, 17.6, 10.9. HRMS (FAB+) calculated for C$_9$H$_{17}$O$_2$ [M+H]: 157.1229; found 157.1206.

Separation conditions (GC, GTA column): 80°C, isocratic. 96% ee

Racemate:

![GC chromatogram of racemate with retention times and areas](chart1)

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Enantioenriched:

![GC chromatogram of enantioenriched with retention times and areas](chart2)

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Synthesis of ribose derivative 13

Diol 12.

To a biphasic mixture of 1:1 tBuOH/water containing diene Z-7g (38.5 mg, 0.089 mmol) was sequentially added potassium carbonate (37 mg, 0.27 mmol), potassium ferricyanide (89 mg, 0.27 mmol, 3 equiv), and potassium osmate dihydrate (1.7 mg, 4.6 μmol, 5 mol%) at 0°C. The reaction was stirred vigorously at 23°C for 24 h. Upon completion, solid Na₂SO₃ was added stirred continued at 23°C for 2 h. EtOAc was added and the layers separated. The aqueous layer was extracted with EtOAc and the combined organic layers washed with water, brine, and dried over MgSO₄. After filtration and concentration, the crude residue was subject to flash chromatography to afford 27.5 mg, 66% yield of diol 12.

Major diastereomer:

[α]D₂⁵ − 62.1° (c = 1.35, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.05 – 8.01 (m, 2H), 7.60 – 7.55 (m, 1H), 7.44 (dd, J = 8.5, 7.2 Hz, 2H), 7.37 – 7.22 (m, 26H), 6.05 – 5.97 (m, 1H), 5.86 – 5.78 (m, 1H), 4.89 – 4.83 (m, 2H), 4.77 (d, J = 11.1 Hz, 1H), 4.67 (d, J = 11.8 Hz, 1H), 4.65 – 4.62 (m, 1H), 4.60 (dd, J = 9.6, 4.6 Hz, 1H), 4.45 (d, J = 11.7 Hz, 1H), 3.72 (dt, J = 13.1, 5.0 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 166.6, 138.1, 137.8, 133.3, 131.3, 129.87, 128.78, 128.65, 128.62, 128.58, 128.3, 128.02, 128.01, 128.0, 80.9, 76.1, 74.6, 72.1, 70.8, 66.3, 63.7, 61.2. HRMS (FAB+) calculated for C₃₈H₆₁O₆ [M+H]: 463.2121; found 463.2125.
Methyl glycoside 13.

Diol 12 (34.6 mg, 0.075 mmol) was dissolved in 1:1 CH₂Cl₂/MeOH and cooled to -78°C. Ozone was bubbled through the solution until a blue color persisted for 10 min. At this point, oxygen was bubbled through the solution until the reaction appeared colorless. Excess dimethyl sulfide (0.1 mL) was added and the reaction was allowed to come to room temperature and stir for 16 h. The reaction mixture was concentrated and the crude residue used in the following step. The crude aldehyde was then dissolved in MeOH (5 mL) and cooled to 0°C. HCl in MeOH (0.4 M, 0.5 mL) was added and the reaction was warmed to room temperature. The reaction was stirred for 14 h, at which time Amberlyst IRA-400 (OH⁻) was added. The mixture was filtered and concentrated; preparative TLC afforded 10.6 mg (0.031 mmol, 47% yield over two steps) of methyl glycoside 13. 

\([\alpha]_D^{25} = -36.4^\circ \text{ (c = 0.27, CHCl}_3\text{)}, \text{ lit.}^{10} \text{ ent-13} \ \ [\alpha]_D^{25} = +31.7 \ (\text{c = 1.94, CHCl}_3); \)

\(^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta \ 7.40 - 7.27 \text{ (m, 10H), 4.89 (s, 1H), 4.66 (AB d, } J = 12.0 \text{ Hz, 1H), 4.63 (AB d, } J = 12.0 \text{ Hz, 1H), 4.58 (AB d, } J = 11.7 \text{ Hz, 1H), 4.49 (AB d, } J = 11.7 \text{ Hz, 1H), 4.28 (m, 1H), 4.13 (dd, } J = 7.1, 4.7 \text{ Hz, 1H), 3.87 (d, } J = 4.7 \text{ Hz, 1H), 3.83 - 3.77 \text{ (m, 1H), 3.58 (m, 1H), 3.37 (s, 3H), 1.95 (br, 1H).} \)

\(^{13}\text{C NMR (125 MHz, CDCl}_3\text{)} \delta 137.81, 137.79, 128.6, 128.1 \ (4C), 128.04 \ (3C), 128.00 \ (3C), 107.0, 82.4, 80.3, 77.4, 72.8, 72.6, 62.8, 55.7. \text{ HRMS (FAB+) calculated for C}_{20}\text{H}_{23}\text{O}_5 [M+H-H}_2\text{: 343.1545; found 343.1553.} \)

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Figure S3. $^1$H NMR (500 MHz, CDCl$_3$) of E-4.
Figure S4. $^{13}$C NMR (125 MHz, CDCl$_3$) of E-4.
Figure S19. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7f.
Figure S20. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7f.
Figure S21. $^1$H NMR (500 MHz, CDCl$_3$) of E-7f.
Figure S22. $^{13}$C NMR (125 MHz, CDCl$_3$) of E-7f.
Figure S15. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7e.
Figure S16. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7e.
Figure S17. $^1$H NMR (500 MHz, CDCl$_3$) of E-7e.
Figure S18. $^{13}$C NMR (125 MHz, CDCl$_3$) of $E$-$7e$. 
Figure S23. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7g.
Figure S24. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7h.
Figure S25. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7h.
Figure S26. $^1$H NMR (500 MHz, CDCl$_3$) of 7i.
Figure S27. $^{13}$C NMR (125 MHz, CDCl$_3$) of 7i.
Figure S11. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7c.
Figure S12. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7c.
Figure S7. $^{1}$H NMR (500 MHz, CDCl$_3$) of Z-7b.
CARBON01
1-JH-275
Major product (Z)

Figure S8. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7b.
Figure S9. $^1$H NMR (500 MHz, CDCl$_3$) of $E$-7b.
Figure S5. $^1$H NMR (500 MHz, CDCl₃) of Z-7a.
Figure S6. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7a.
Figure S32. $^1$H NMR (500 MHz, CDCl$_3$) of Z-9.
Figure S33. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-9.
Figure S34. $^1$H NMR (500 MHz, CDCl$_3$) of 10.
Figure S35. $^{13}$C NMR (125 MHz, CDCl$_3$) of 10.
Figure S36. $^1$H NMR (500 MHz, CDCl$_3$) of 11.
Figure S38. $^1$H NMR (500 MHz, CDCl$_3$) of 12.
Figure S39. $^{13}$C NMR (125 MHz, CDCl$_3$) of 12.
Figure S40. $^1$H NMR (500 MHz, CDCl$_3$) of 13.
Figure S41. $^{13}$C NMR (125 MHz, CDCl$_3$) of 13.
Figure S13. $^1$H NMR (500 MHz, CDCl$_3$) of E-7c.
Figure S14. $^{13}$C NMR (125 MHz, CDCl$_3$) of $E$-7c.
Figure S28. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7j.
Figure S29. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7j.
Figure S30. $^1$H NMR (500 MHz, CDCl$_3$) of Z-7k.
Figure S31. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-7k.
Figure S10. $^{13}$C NMR (125 MHz, CDCl$_3$) of $E$-7b.
Figure S37. $^{13}$C NMR (125 MHz, CDCl$_3$) of 11.
Figure S2. $^{13}$C NMR (125 MHz, CDCl$_3$) of Z-4.
Figure S1. $^1$H NMR (500 MHz, CDCl$_3$) of Z-4.