Supporting Information

**Total Synthesis and Structural Revision of Antibiotic CJ-16,264**


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General Information:

Unless otherwise noted, all reactions were performed in flame-dried or oven-dried glassware under nitrogen atmosphere. Non-aqueous reagents were transferred using syringe techniques under nitrogen atmosphere. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), toluene, acetonitrile (MeCN), dichloromethane (CH₂Cl₂), triethylamine (Et₃N), and pyridine were obtained anhydrous by degassing with argon and then passing through activated alumina columns to remove water and oxygen.¹ Bulk grade hexanes, pentane, diethylether and ethyl acetate for chromatography were used without further treatment. Commercial reagents were obtained at the highest commercial quality and used without further purification unless otherwise stated. Yields refer to chromatographically and spectroscopically (¹H-NMR) homogeneous materials, unless otherwise stated.

Reactions were monitored by standard thin-layer chromatography (TLC) techniques using EMD silica gel 60F₂₅₄ pre-coated plates (0.25 mm thickness). Following the run, TLC plates were visualized under UV light and/or by appropriate stains (p-anisaldehyde or cerric ammonium nitrate or potassium permanganate). Flash column chromatography² was performed using Silica Gel (60, particle size 0.035 – 0.07 mm) obtained from Acros Organics. Preparative thin-layer chromatography (PTLC)
separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F254).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 600 MHz instrument equipped with a 5 mm DCH cryoprobe and calibrated using residual undeuterated solvent for $^1$H NMR [δ 7.26 (CDCl$_3$), 7.20 (C$_6$D$_6$), and 2.05 (acetone-$d_6$) ppm] and $^{13}$C deuterated solvent for $^{13}$C NMR [δ 77.0 (CDCl$_3$), 128.0 (C$_6$D$_6$), and 206.2 (acetone-$d_6$) ppm] as an internal reference at 298 K. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. NMR coupling constants and signal patterns are reported as $J$ values in Hz and δ values in parts per million (ppm). High resolution mass measurements (HRMS) were obtained on Thermo Electron Corporation MAT 95XP (EI/CI) or Agilent 1200 HPLC-6130 MSD (ESI). IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$). Optical rotations were measured on the Schmidt+Haensch Polartronic M100 polarimeter at 589.44 nm using 100 mm cells and the solvent and concentration indicated.
Experimental procedures and characterization data:

Alkyne 14: To a stirred solution of CBr₄ (21.43 g, 64.63 mmol, 2.0 equiv) in CH₂Cl₂ (110 mL) was added PPh₃ (34.0 g, 129.64 mmol, 4.0 equiv) at 0 °C and the resulting mixture was stirred for 0.5 h. A solution of (R)-citronellal (12) (5.0 g, 32.41 mmol, 1.0 equiv) in CH₂Cl₂ (32 mL) was then added dropwise at 0°C and the resulting reaction mixture was stirred for 2 h at 25 °C before it was diluted with pentane (200 mL). Insoluble solids were filtered off and the resulting crude product was quickly purified by flash column chromatography (silica, 100% hexanes) providing dibromo-olefin 12a as a yellow oil (9.85 g, 31.76 mmol, 98% yield).

To a stirred solution of dibromo-olefin 12a (9.40 g, 30.41 mmol, 1.0 equiv) in THF (150 mL) at −78 °C was added n-BuLi (36.60 mL, 2.5 M in hexanes, 91.40 mmol, 3.0 equiv) dropwise and the resulting mixture was stirred for 1 h at the same temperature. The reaction mixture was then stirred at 0 °C for 1 h before it was quenched with H₂O (20 mL) and extracted with Et₂O (3 × 50 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 5% EtOAc in hexanes) providing pure alkyne 14 as a colorless oil (4.34 g, 28.89 mmol, 95% yield). 14: [α]D₂₀ = −5.6 (c = 2.00, CHCl₃). The characterization data of 14 matched those in the literature.³,⁴

Alkyne ent-14 was synthesized through the same procedure using (S)-citronellal as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-14 matched those of 14. ent-14: [α]D₂₀ = +4.4 (c = 2.20, CHCl₃).

Note: Alkyne 14 was also synthesized from both (R)- and (S)-citronellal starting
materials through the use of the Bestmann-Ohira reagent as previously reported.\textsuperscript{5,6}

\begin{center}
\includegraphics[width=0.5\textwidth]{reaction.png}
\end{center}

**Alcohol 14a:** A stirred solution of 14 (10.0 g, 65.78 mmol, 1.0 equiv) in CH$_2$Cl$_2$:MeOH (700 mL, 2:1) was cooled to $-78^\circ$C and a stream of ozone (O$_3$) was bubbled through the solution until pale purple in color (approx. 1 h). The excess ozone was removed by passing a stream of oxygen through the solution. To the so obtained solution was then added NaBH$_4$ (2.90 g, 85.51 mmol, 1.3 equiv) in one portion at $-78^\circ$C and the resulting mixture was stirred for additional 2.5 h at $-78^\circ$C before it was quenched carefully with saturated aq. NH$_4$Cl (50 mL). The solvent was removed \textit{in vacuo} and the resulting crude product was purified by flash column chromatography (silica, gradient from 10\% EtOAc in hexanes→50\% EtOAc in hexanes) providing pure alcohol 14a as a colorless oil (7.06 g, 55.91 mmol, 85\% yield). 14a: R$_f$ = 0.61 (silica, EtOAc:hexanes, 1:1); $[\alpha]_D^{20} = +1.48$ (c = 2.50, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3370 (br), 3045, 2935, 1480, 1245, 1123, 939, 860 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 3.63 (t, $J$ = 6.6 Hz, 2H), 2.17 (ddd, $J$ = 14.4, 6.0, 3.0 Hz, 1H), 2.09 (ddd, $J$ = 14.4, 6.0, 3.0 Hz, 1H), 1.95 (t, $J$ = 3.0 Hz, 1H), 1.68 (sextet, $J$ = 6.6 Hz, 1H), 1.60 – 1.46 (m, 3H), 1.30 – 1.24 (m, 1H), 1.00 (d, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 83.3, 69.4, 63.2, 32.4, 32.1, 30.4, 25.9, 19.5; HRMS calcd for C$_8$H$_{14}$O $[M+H]^+$ 127.1117 found 127.1118.

Alcohol \textit{ent-14a} was synthesized through the same procedure using \textit{ent-14} as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data of \textit{ent-14} matched those of 14a. \textit{ent-14a}: $[\alpha]_D^{20} = -1.3$ (c = 1.35, CHCl$_3$).
Iodo-alcohol 15: To a stirred suspension of Cp$_2$ZrCl$_2$ (12.74 g, 43.58 mmol, 1.1 equiv) in 1,2-dichloroethane (170 mL) at 0 °C was added a solution of AlMe$_3$ (79 mL, 158.48 mmol, 2.0 M in hexanes, 4.0 equiv) dropwise. After stirring for 0.5 h at 25 °C, alkyne 14a (5.00 g, 39.62 mmol, 1.0 equiv) in 1,2-dichloroethane (50 mL) was added dropwise at the same temperature. The resulting yellow solution was then stirred at 25 °C for 18 h before it was cooled to –20 °C. A solution of I$_2$ in THF (50 mL) was added dropwise at –20 °C and the reaction mixture was stirred for 1 h at 0 °C. The mixture was then slowly poured into ice-cooled water (100 mL) and extracted with CH$_2$Cl$_2$ (3 × 100 mL). The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 10% EtOAc in hexanes→40% EtOAc in hexanes) providing pure alcohol 15 as a yellow oil (8.93 g, 33.30 mmol, 84% yield). 15: Rf = 0.78 (silica, EtOAc:hexanes, 1:1); [α]$_D^{20}$ = −3.8 (c = 2.50, CHCl$_3$); IR (film) ν$_{max}$ 3385 (br), 3056, 3013, 2925, 1470, 1245, 1101, 939 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ = 5.84 (d, J = 1.2 Hz, 1H), 3.63 (td, J = 6.6, 1.2 Hz, 2H), 2.21 (dd, J = 13.3, 5.9 Hz, 1H), 2.02 (dd, J = 13.5, 8.3 Hz, 1H), 1.80 (d, J = 0.9 Hz, 3H), 1.67 – 1.60 (m, 2H), 1.35 (ddt, J = 13.3, 10.8, 5.2 Hz, 2H), 1.18 – 1.10 (m, 2H), 0.84 (d, J = 6.6 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ = 147.2, 75.5, 63.4, 47.7, 32.8, 31.0, 30.4, 23.9, 19.4; HRMS calcd for C$_9$H$_{18}$I$_2$O$^+$ [M+H$^+$] 269.0397 found 269.0402.

Iodo-alcohol ent-15 was synthesized through the same procedure using ent-14a as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data matched those of 15. ent-15: [α]$_D^{20}$ = +2.4 (c = 2.80, CHCl$_3$).
**Aldehyde 15a:** To a stirred solution of hydroxy vinyl iodide 15 (10.17 g, 37.95 mmol, 1.0 equiv) in CH₂Cl₂:DMSO (3:1, 150 mL) at 0 °C were sequentially added Et₃N (21.3 mL, 151.79 mmol, 4.0 equiv), and SO₃•py (12.08 g, 75.89 mmol, 2.0 equiv). The reaction mixture was warmed to 25 °C and stirred for 1 h at the same temperature before it was quenched with saturated aq. NH₄Cl (50 mL) and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography (silica, 5% EtOAc in hexanes) providing pure aldehyde 15a as a yellow oil (9.19 g, 34.53 mmol, 91% yield). 15a: Rf = 0.72 (silica, EtOAc:hexanes, 1:4); [α]_D²⁰ = +1.5 (c = 0.65, CHCl₃); IR (film) ν_max 2956, 2923, 1722, 1458, 1378, 1272, 1143, 1094, 761 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 9.77 (d, J = 1.2 Hz, 1H), 5.87 (d, J = 1.2 Hz, 1H), 2.49 – 2.40 (m, 2H), 2.20 (dd, A of AB, J = 13.8, 6.0 Hz, 1H), 2.04 (dd, B of AB, J = 13.8, 7.8 Hz, 1H), 1.80 (s, 3H), 1.70 – 1.63 (m, 2H), 1.43 – 1.37 (m, 1H), 0.84 (d, J = 6.0 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 202.5, 146.7, 76.0, 47.5, 41.7, 30.7, 28.7, 23.9, 19.2; HRMS calcd for C₉H₁₆IO⁺ [M+H⁺] 267.0240 found 267.0232.
(2Z)-Ester 17: To a stirred solution of phosphonate ester 16 (460.0 mg, 1.38 mmol, 1.2 equiv) and 18-crown-6 (1.50 g, 5.75 mmol, 5.0 equiv) in THF (23 mL) at −78 °C was added KHMDS (1.38 mL, 1.38 mmol, 1.2 equiv) dropwise and the resulting mixture was stirred for 0.5 h at the same temperature. A solution of aldehyde 15a (300 mg, 1.15 mmol, 1.0 equiv) in THF (3 mL) was then added dropwise at −78 °C and the resulting mixture was stirred for 1 h at the same temperature before it was quenched with saturated aq. NH₄Cl (10 mL) and extracted with Et₂O (3 × 20 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 5% EtOAc in hexanes) providing pure enone 17 as a colorless oil (355.0 mg, 1.06 mmol, 92% yield, ≥ 95% Z:E dr). 17: Rf = 0.63 (silica, EtOAc:hexanes, 1:9); [α]D²⁰ = −3.2 (c = 3.10, CHCl₃); IR (film) νmax 2956, 2916, 1718, 1644, 1457, 1415, 1186, 1036, 820 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 6.18 – 6.13 (m, 1H), 5.82 (s, 1H), 5.74 (dt, J = 11.4, 1.2 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.71 – 2.66 (m, 2H), 2.22 (dd, A of AB, J = 13.2, 6.0 Hz, 1H), 1.99 (dd, B of AB, J = 13.2, 8.4 Hz, 1H), 1.76 (s, 3H), 1.66 – 1.62 (m, 1H), 1.42 – 1.37 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.24 – 1.21 (m, 1H), 0.83 (d, J = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 166.5, 150.3, 147.0, 119.9, 75.6, 59.9, 47.4, 35.8, 30.9, 26.6, 23.8, 19.3, 14.4; HRMS calcd for C₁₃H₂₂IO₂⁺ [M+H⁺] 337.0652 found 337.0654.
(2Z-Triene 19): To a stirred solution of iodide 17 (2.00 g, 5.95 mmol, 1.0 equiv) and stannyl alcohol 18 (6.44 g, 17.86 mmol, 3.0 equiv) in DMF (degassed, 20 mL) at 0 °C was added CuTC (6.81 g, 35.70 mmol, 6.0 equiv) and the resulting reaction mixture was warmed to 25 °C and stirred for 2 h at the same temperature before it was diluted with EtOAc (20 mL) and H₂O (20 mL). The insoluble solids were filtered off, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 100% hexanes → 20% EtOAc in hexanes) providing pure (2Z)-triene 19 as a yellow oil (1.42 g, 5.05 mmol, 85% yield). 19: Rf = 0.22 (silica, EtOAc:hexanes, 1:4); [α]₀²⁰ = −10.6 (c = 0.50, CHCl₃); IR (film) ν_max 3390 (br), 2922, 1719, 1644, 1459, 1415, 1183, 1035 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 6.21 – 6.17 (m, 1H), 5.75 (d, J = 11.4 Hz, 1H), 5.61 (s, 1H), 5.47 (t, J = 7.0 Hz, 1H), 4.24 (t, J = 7.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.72 – 2.64 (m, 2H), 2.07 (dd, J = 13.2, 6.6 Hz, 1H), 1.82 (dd, J = 13.2, 8.4 Hz, 1H), 1.76 (s, 3H), 1.73 (s, 3H), 1.70 – 1.61 (m, 3H), 1.37 – 1.35 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 166.7, 150.8, 136.6, 136.4, 129.7, 127.2, 119.8, 60.0, 59.8, 48.7, 36.2, 31.0, 26.9, 19.5, 18.0, 17.6, 14.5; HRMS calcd for C₁₇H₂₆O₃Na⁺ [M+Na⁺] 303.1931 found 303.1926.
(2Z)-Seco acid 11a: To a stirred solution of ethyl ester 19 (1.0 g, 3.57 mmol, 1.0 equiv) in THF (18 mL) was added LiOH (1.0 M, 18 mL) at 25 °C. After stirring for 18 h at 60 °C, the reaction mixture was cooled to 25 °C and quenched with saturated aq. NH₄Cl solution until pH is acidic, and then extracted with EtOAc (6 × 20 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 30% EtOAc in hexanes→70% EtOAc in hexanes) providing pure (2Z)-seco acid 11a as a yellow oil (890.0 mg, 3.53 mmol, 99% yield). 

11a: Rf = 0.24 (silica, EtOAc:hexanes, 1:1); [α]D²⁰ = −13.2 (c = 0.25, CHCl₃); IR (film) νmax 3332 (br), 2954, 2915, 1693, 1640, 1435, 1237, 1102, 989, 824 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 6.35 – 6.31 (m, 1H), 5.79 (d, J = 11.4 Hz, 1H), 5.61 (s, 1H), 5.47 (t, J = 6.6 Hz, 1H), 4.24 (d, J = 6.6 Hz, 2H), 2.68 (q, J = 7.8 Hz, 2H), 2.05 (dd, A of AB, J = 13.2, 6.6 Hz, 1H), 1.84 (dd, B of AB, J = 13.2, 7.8 Hz, 1H), 1.70 (s, 3H), 1.69 (s, 3H), 1.68 – 1.65 (m, 1H), 1.49 – 1.43 (m, 1H), 1.28 – 1.22 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 171.3, 153.5, 136.7, 136.4, 129.8, 127.1, 119.2, 59.8, 48.7, 36.1, 30.9, 27.1, 19.6, 18.1, 17.5; HRMS calcd for C₁₅H₂₄O₃Na⁺ [M+Na⁺] 275.1618 found 275.1618.
(2E)-Ester 21: To a stirred solution of vinyl iodide 15 (24.00 g, 89.51 mmol, 1.0 equiv) in CH$_2$Cl$_2$:DMSO (3:1, 350 mL) were added Et$_3$N (49.90 mL, 358.02 mmol, 4.0 equiv), and SO$_3$•py (28.51 mg, 75.86 179.02 mmol, 2.0 equiv) sequentially at 0 °C. The reaction mixture was allowed to warm to 25 °C and stirred for additional 1 h before carbethoxymethylene)triphenylphosphorane (20) (62.37 g, 75.86 179.02 mmol, 2.0 equiv) was added at the same temperature. The resulting mixture was stirred for 4 h before it was quenched with saturated aq. NH$_4$Cl (100 mL) and extracted with CH$_2$Cl$_2$ (3 × 75 mL). The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 5% EtOAc:hexanes) providing pure (2E)-ester 21 as a yellow oil (27.07 g, 80.56 mmol, 90% yield). 21: Rf = 0.50 (silica, Et$_2$O in hexanes, 1:9); [α]$^D$ = +1.9 (c = 0.15, CHCl$_3$); IR (film) $\nu_{max}$ 2924, 1719, 1654, 1459, 1367, 1271, 1188, 1047, 984 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 6.94 (dt, $J = 15.6$, 7.0 Hz, 1H), 5.86 – 5.85 (m, 1H), 5.81 (dt, $J = 15.6$, 1.6 Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 2.31 – 2.22 (m, 1H), 2.22 – 2.13 (m, 2H), 2.02 (dd, $J = 13.5$, 8.4 Hz, 1H), 1.79 (d, $J = 0.6$ Hz, 3H), 1.66 (dq, $J = 8.3$, 6.7 Hz, 1H), 1.48 – 1.41 (m, 1H), 1.29 (t, $J = 8.1$ Hz, 3H), 1.27 – 1.21 (m, 1H), 0.84 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 166.8, 149.1, 146.9, 121.6, 75.8, 60.3, 47.5, 34.9, 30.6, 29.8, 23.8, 19.2, 14.4; HRMS calcd for C$_{13}$H$_{22}$O$_2$ $^{[M+H]^+}$ 337.0659 found 337.0654.

(2E)-Ester ent-21 was synthesized through the same procedure using ent-15 as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data of ent-21 matched those of 21. ent-21: [α]$^D$ = −1.7 (c = 2.20, CHCl$_3$).
(2E)-Triene 21a: To a stirred solution of iodide 21 (8.50 g, 25.30 mmol, 1.0 equiv) and stannyl alcohol \(18^7\) (27.40 g, 75.89 mmol, 3.0 equiv) in dry DMF (degassed, 90 mL) was added CuTC \(8\) (28.94 g, 151.80 mmol, 6.0 equiv) at 0 °C. The reaction mixture was allowed to warm to 25 °C and stirred for 2 h before it was diluted with EtOAc (75 mL) and \(\text{H}_2\text{O}\) (100 mL). The insoluble solids were filtered off, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over MgSO\(_4\) and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 100% hexanes→20% EtOAc:hexanes) providing pure (2E)-triene 21a as a yellow oil (6.24 g, 22.26 mmol, 88% yield). 21a: \(R_f = 0.23\) (silica, EtOAc in hexanes, 1:4); \(\alpha_D^{20} = -2.5\) (c = 3.12, CHCl\(_3\)); IR (film) \(\nu_{\text{max}}\) 3401 (br), 2916, 1719, 1652, 1445, 1270, 1184, 1046, 986 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 7.03 - 6.94\) (m, 1H), 5.84 (d, \(J = 15.6\) Hz, 1H), 5.63 (s, 1H), 5.50 (t, \(J = 6.8\) Hz, 1H), 4.27 (t, \(J = 6.2\) Hz, 2H), 4.21 (q, \(J = 7.1\) Hz, 2H), 2.34 – 2.16 (m, 2H), 2.06 (dd, \(J = 13.1, 6.4\) Hz, 1H), 1.85 (dd, \(J = 13.1, 8.1\) Hz, 1H), 1.79 (s, 3H), 1.76 (s, 3H), 1.68 (dd, \(J = 12.9, 6.8\) Hz, 1H), 1.54 – 1.46 (m, 1H), 1.31 (t, \(J = 7.1\) Hz, 3H), 1.26 (t, \(J = 5.6\) Hz, 2H), 0.87 (d, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 166.9, 149.6, 136.5, 136.1, 129.8, 127.2, 121.4, 60.3, 59.7, 48.7, 35.1, 30.6, 29.9, 19.4, 18.0, 17.5, 14.4.); HRMS calcd for C\(_{17}\)H\(_{29}\)O\(_3\)^+ \([M+H]^+\) 281.2111 found 281.1116.

(2E)-Triene \(\text{ent-21a}\) was synthesized through the same procedure using \(\text{ent-21}\) as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data of \(\text{ent-21a}\) matched those of 21a. \(\text{ent-21a}: \alpha_D^{20} = +4.5\) (c = 2.10, CHCl\(_3\)).
(2E)-Seco acid 11b: To a stirred solution of ethyl ester 21a (6.0 g, 21.40 mmol, 1.0 equiv) in THF (130 mL) at 25 °C was added aq. LiOH (1.0 M, 130 mL). After stirring for 20 h at 60 °C, the reaction mixture was cooled to 25 °C and quenched with saturated aq. NH₄Cl solution until pH was acidic, and then extracted with EtOAc (8 × 50 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 30% EtOAc in hexanes→70% EtOAc in hexanes) providing pure (2E)-seco acid 11b as a yellow oil (1.88 g, 7.54 mmol, 99% yield). 11b: Rf = 0.32 (silica, EtOAc); [α]₀²⁰ = −4.3 (c = 0.8, CHCl₃); IR (film) νₚ₅₃ 3332 (br), 2954, 2915, 2853, 1693, 1640, 1435, 1377, 1237, 989, 824 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 7.11 – 7.03 (m, 1H), 5.83 (dt, J = 15.6, 1.5 Hz, 1H), 5.61 (s, 1H), 5.47 (t, J = 6.9 Hz, 1H), 4.25 (d, J = 6.9 Hz, 2H), 2.35 – 2.16 (m, 2H), 2.07 – 2.00 (m, 1H), 1.84 (dd, J = 13.2, 8.1 Hz, 1H), 1.76 (s, 3H), 1.74 (d, J = 1.2 Hz, 3H), 1.70 – 1.62 (m, 1H), 1.49 (ddd, J = 14.9, 5.3, 3.7 Hz, 1H), 1.30 – 1.21 (m, 1H), 0.86 (d, J = 6.6 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 170.6, 152.5, 136.5, 136.1, 129.8, 127.2, 120.4, 59.7, 48.6, 34.8, 30.6, 30.1, 19.4, 18.0, 17.5; HRMS calcd for C₁₅H₂₄O₃Na⁺ [M+Na⁺] 275.1618 found 275.1617.

(2E)-Seco acid ent-11b was synthesized through the same procedure using ent-21a as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-11b matched those of 11b. ent-11b: [α]₀²⁰ = +3.2 (c = 1.32, CHCl₃).
**Diolide 22**: To a stirred solution of seco acid 11b (2.0 g, 7.94 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (380 mL) at 25 °C were added sequentially Et$_3$N (2.21 mL, 15.88 mmol, 2.0 equiv), DMAP (100.0 mg, 0.79 mmol, 0.1 equiv), and MNBA (4.14 g, 11.91 mmol, 1.5 equiv). After stirring for 10 h at the same temperature, H$_2$O (50 mL) was added. The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography (silica, 5% EtOAc in hexanes) providing pure diolide 22 (1.49 g, 3.17 mmol, 40% yield) and and pure triolide 22a as a colorless oil (447 mg, 0.64 mmol, 8%). Diolide 22 was also prepared using 11a as the starting material in 37% yield (plus 8% yield of the corresponding triolide 22a).

22: Rf = 0.39 (silica, EtOAc:hexanes, 1:4); [α]$_D^{20}$ = +62.7 (c = 2.0, CHCl$_3$); IR (film) $\nu_{max}$ 2951, 2915, 1717, 1654, 1441, 1375, 1258, 1155, 982, 731 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 6.93 (dt, $J$ = 15.6, 6.9 Hz, 2H), 5.80 (d, $J$ = 15.7 Hz, 2H), 5.58 (s, 2H), 5.37 (t, $J$ = 6.8 Hz, 2H), 4.72 (qd, $J$ = 12.6, 7.3 Hz, 4H), 2.28 (td, $J$ = 15.3, 6.1 Hz, 2H), 2.08 (td, $J$ = 15.0, 6.6 Hz, 2H), 1.99 (dd, $J$ = 13.0, 4.7 Hz, 2H), 1.83 (dd, $J$ = 13.2, 9.5 Hz, 2H), 1.79 (s, 6H), 1.69 (s, 6H), 1.66 – 1.63 (m, 2H), 1.52 – 1.48 (m, 2H), 1.13 – 1.05 (m, 2H), 0.88 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 166.8, 149.5, 138.4,
136.5, 129.7, 122.3, 121.5, 61.2, 49.0, 33.2, 30.1, 29.7, 20.2, 17.9, 17.6; HRMS calcd for \( \text{C}_{30}\text{H}_{45}\text{O}_{4}\text{H}^+ \) [M+H\(^+\)] 469.3312 found 469.3313.

Diolide \textit{ent-22} was synthesized through the same procedure using \textit{ent-11b} as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data matched those of 22. \textit{ent-22}: \([\alpha]_D^{20} = -51.9\) (c = 1.50, CHCl\(_3\)).

\textbf{22a}: \( Rf = 0.30 \) (silica, EtOAc:hexanes, 1:4); \([\alpha]_D^{20} = +13.5\) (c = 1.0, CHCl\(_3\)); IR (film) \( \nu_{\text{max}} \) 2960, 2913, 1720, 1655, 1372, 1260, 1155, 985 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) = 6.95 (m, 3H), 5.83 (d, \( J = 15.5 \) Hz, 3H), 5.61 (s, 3H), 5.41 (t, \( J = 7.0 \) Hz, 3H), 4.72 (d, \( J = 7.0 \) Hz, 6H), 2.28 (m, 3H), 2.16 (m, 3H), 1.94-1.88 (m, 9H), 1.79 (s, 9H), 1.72 (s, 9H), 1.66 (m, 3H), 1.50 (m, 3H), 0.86 (d, \( J = 6.5 \) Hz, 9H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta = 166.8, 149.7, 138.5, 136.6, 129.6, 122.3, 121.4, 61.3, 48.8, 34.3, 30.3, 29.9, 19.8, 18.1, 17.7; HRMS calcd for \( \text{C}_{45}\text{H}_{66}\text{O}_{6}\text{Na}^+ \) [M+Na\(^+\)] 725.4752 found 725.4753.

Triolide \textit{ent-22a} was synthesized through the same procedure using \textit{ent-11b} as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data of \textit{ent-22a} matched those of 22a. \textit{ent-22a}: \([\alpha]_D^{20} = -7.8\) (c = 4.00, CHCl\(_3\)).
IMDA adduct 25: A solution of diolide 22 (3.0 g, 6.41 mmol, 1.0 equiv) in \textit{m}-xylene (degassed, 200 mL) in a sealed tube was placed in an oil bath preheated to 220 °C and stirred for 6 h. The resulting yellow solution was concentrated \textit{in vacuo} and the so obtained crude product was purified by flash column chromatography (silica, 10% EtOAc in hexanes) to provide pure IMDA adduct 25 as a white amorphous solid (1.44 g, 3.07 mmol, 48% yield). 25: \( R_f = 0.46 \) (silica, EtOAc:hexanes, 2:8); \([\alpha]_D^{20} = -44.2 \) (c = 1.0, CHCl\(_3\)); IR (film) \( \nu_{\text{max}} \) 2949, 2919, 1736, 1449, 1378, 1223, 1149, 999 cm\(^{-1}\); mp = 119–123 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta = \) 5.22 (s, 2H), 4.59 (dd, \( J = 10.6, 4.5 \) Hz, 2H), 4.13 – 4.02 (m, 2H), 3.04 (t, \( J = 10.8 \) Hz, 2H), 2.55 (t, \( J = 9.9 \) Hz, 2H), 1.92 – 1.68 (m, 12H), 1.67 (s, 6H), 1.52 (dd, \( J = 14.1, 5.4 \) Hz, 2H), 1.24 – 1.17 (m, 2H), 1.14 (d, \( J = 4.5 \) Hz, 2H), 1.11 (s, 2H), 1.06 (s, 6H), 1.00 (d, \( J = 7.3 \) Hz, 6H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta = \) 176.16, 136.68, 126.63, 66.86, 47.61, 42.02, 41.09, 40.57, 35.02, 28.99, 27.11, 22.26, 22.24, 21.81, 21.01; HRMS calcd for \( \text{C}_{30}\text{H}_{45}\text{O}_{4}^+ [\text{M+H}^+] \) 469.3312 found 469.3313.

IMDA adduct \textit{ent-25} was synthesized through the same procedure using \textit{ent-22} as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data of \textit{ent-25} matched those of 25. \textit{ent-25}: \([\alpha]_D^{20} = +42.7 \) (c = 0.70, CHCl\(_3\)).
\(\gamma\)-Lactone 8 and hydroxy acid 26: To a stirred solution of IMDA adduct 25 (600 mg, 1.28 mmol, 1.0 equiv) in THF:MeOH (9:1, 30 mL) was added NaOMe (4.15 g, 76.80 mmol, 60 equiv) at 25 °C. The resulting solution was stirred at 65 °C for 14 h before it was cooled to 25 °C and quenched with 10% aq. HCl until pH ~ 5. The crude products were extracted with EtOAc (3 x 25 mL) and the combined organic layers were dried over MgSO\(_4\), and concentrated \textit{in vacuo}. The crude mixture of two products (8:26 ca 3:2) were separated by flash column chromatography (silica, gradient from 10% EtOAc in hexanes → 50% EtOAc in hexanes) providing pure \(\gamma\)-lactone 8 (white crystals, 305.1 mg, 1.30 mmol, 51% yield) and hydroxy acid 26 (amorphous solid, 219 mg, 0.87 mmol, 34% yield).

\(\gamma\)-Lactone 8: \(R_f = 0.81\) (silica, EtOAc:hexanes, 2:8); \([\alpha]_D^{20} = -21.7\) (c = 1.1, CHCl\(_3\)); IR (film) \(\nu_{\text{max}}\) 2949, 2924, 1771, 1445, 1375, 1212, 1172, 1034, 1017, 998 cm\(^{-1}\); mp = 103–105 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 5.21\) (d, \(J = 1.5\) Hz, 1H), 4.54 (dd, \(J = 9.8, 8.7\) Hz, 1H), 3.87 (dd, \(J = 10.6, 8.6\) Hz, 1H), 3.11 (dd, \(J = 10.2, 5.8\) Hz, 1H), 3.02 – 2.92 (m, 1H), 1.83 – 1.76 (m, 1H), 1.65 – 1.63 (m, 3H), 1.63 – 1.57 (m, 2H), 1.57 – 1.52 (m, 1H), 1.49 (dd, \(J = 12.5, 3.5\) Hz, 1H), 1.39 – 1.30 (m, 2H), 1.18 (dd, \(J = 12.8, 3.6\) Hz, 1H), 0.96 (s, 3H), 0.83 (d, \(J = 6.5\) Hz, 3H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta = 180.3, 132.1, 128.8, 72.2, 49.5, 40.6, 40.5, 37.5, 36.8, 34.9, 29.5, 29.3, 25.8, 22.6, 20.9\); HRMS calcd for \(\text{C}_{15}\text{H}_{22}\text{O}_2\text{Na}^+\) [M+Na\(^+\)] 257.1517 found 257.1515.
γ-Lactone *ent-8* was synthesized through the same procedure using *ent-25* as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data of *ent-8* matched those of 8.

*ent-8*: $[\alpha]_D^{20} = +19.0$ (c = 1.00, CHCl$_3$).

**Hydroxy acid 26:** *Rf* = 0.36 (silica, EtOAc:hexanes, 1:1); $[\alpha]_D^{20} = +30.5$; (c = 1.1, CHCl$_3$); IR (film) $\nu_{\text{max}}$ 3375 (br), 2946, 2922, 1697, 1444, 1378, 1237, 1015, 738 cm$^{-1}$; mp = 110–113 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 6.50 (br s, 1H), 5.21 (s, 1H), 3.89 (dd, $J$ = 10.8, 4.2 Hz, 1H), 3.58 (t, $J$ = 9.2 Hz, 1H), 2.86 (br s, 1H), 2.70 (t, $J$ = 3.6 Hz, 1H), 2.10 (d, $J$ = 10.8 Hz, 1H), 1.63 (s, 3H), 1.58 (d, $J$ = 11.4 Hz, 1H), 1.45 – 1.41 (m, 4H), 0.89-0.85 (m, 2H), 0.80 (s, 3H), 0.76 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 182.6, 134.0, 129.5, 64.6, 48.5, 46.1, 42.1, 40.4, 36.3, 33.9, 29.9, 29.5, 28.9, 22.5, 21.9; HRMS calcd for C$_{15}$H$_{23}$O$_3$ $[\text{M-H}]^-$ 251.1653 found 251.1654.

Hydroxy acid *ent-26* was synthesized through the same procedure using *ent-25* as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data of *ent-26* matched those of 26. *ent-26*: $[\alpha]_D^{20} = -24.4$ (c = 2.00, CHCl$_3$).
**Hydroxy acid 26 and γ-Lactone 8**: To a stirred solution of IMDA adduct 25 (760 mg, 1.62 mmol, 1.0 equiv) in THF:MeOH:H₂O (4:2:1, 49 mL) at 25 °C was added solid LiOH·H₂O (5.38 g, 129.60 mmol, 80 equiv). The resulting solution was stirred at 80 °C for 24 h before it was cooled to 25 °C and quenched with 10% aq. HCl until pH ~ 5. The crude products were extracted with EtOAc (3 × 30 mL) and the combined organic layers were dried over MgSO₄, and concentrated in vacuo. The crude mixture of two products (26:8 ca 2:1) were separated by flash column chromatography (silica, gradient from 10% EtOAc in hexanes → 50% EtOAc in hexanes) providing pure hydroxy acid 26 (amorphous solid, 507 mg, 2.01 mmol, 62% yield) and γ-lactone 8 (white crystals, 235 mg, 1.00 mmol, 31% yield).
**Diol 8a:** To a stirred solution of γ-lactone 8 (220 mg, 0.94 mmol, 1.0 equiv) in THF (9.0 mL) at −78 °C was added LAH (3.8 mL, 1.0 M in THF, 3.78 mmol, 4.0 equiv) dropwise and the resulting mixture was stirred for 0.5 h at the same temperature. The reaction mixture was then transferred to 0 °C water bath and stirred at the same temperature for 1.5 h before it was quenched with 10% aq. NaOH (5 mL), and saturated aq. sodium potassium tartrate solution (5 mL). After vigorous stirring and separation of the layers, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 25% EtOAc in hexanes) providing pure diol 8a (219 mg, 0.92 mmol, 98% yield) as a colorless gum. 8a: Rf = 0.27 (silica, EtOAc:hexanes, 3:7); [α]D²⁰ = +90.8 (c = 0.78, CHCl₃); IR (film) νmax 3318 (br), 2945, 1454, 1375, 1080, 1012 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.09 (s, 1H), 4.08 (t, J = 11.2 Hz, 1H), 3.97 (dd, J = 10.4, 8.4 Hz, 1H), 3.78 (d, J = 10.8 Hz, 1H), 3.62 (dd, J = 11.2, 4.4 Hz, 1H), 2.93 (br s, 1H), 2.72 – 2.53 (m, 1H), 2.36 (t, J = 7.4 Hz, 1H), 1.77 (s, 3H), 1.59 – 1.53 (m, 1H), 1.47 (d, J = 13.3 Hz, 1H), 1.42 – 1.35 (m, 1H), 1.32 – 1.26 (m, 2H), 1.24 – 1.18 (m, 1H), 1.11 (qd, J = 12.8, 3.3 Hz, 1H), 0.96 (s, 3H), 0.89 (t, J = 12.8 Hz, 3H), 0.79, (d, J = 6.5 Hz, 1H), 0.72 (ddd, J = 25.1, 12.8, 2.9 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ = 133.7, 131.5, 65.0, 62.3, 50.3, 43.7, 42.6, 38.7, 37.5, 35.5, 31.3, 29.7, 25.3, 22.8, 22.7; HRMS calcd for C₁₅H₂₇O₂⁺ [M+H⁺] 239.2005 found 239.2014.
**Sulfonate 8b:** To a stirred solution of diol 8a (175.0 mg, 0.74 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (20 mL) at 25 °C was sequentially added Ag$_2$O (310.0 mg, 1.33 mmol, 1.8 equiv), KI (24.6 mg, 0.15 mmol, 0.2 equiv), and 2,4,6-tri-iso-propylbenzenesulfonyl chloride (359.0 mg, 1.18 mmol, 1.6 equiv) and the resulting mixture was stirred for 24 h at the same temperature. The reaction mixture was then diluted with CH$_2$Cl$_2$ (15 mL) and passed through a plug of Celite®. The organic layer was concentrated in vacuo and the resulting crude product was purified by flash column chromatography (silica, 10% EtOAc:hexanes) providing pure sulfonate 8b as a yellow oil (235.0 mg, 0.47 mmol, 63% yield, 79% brsm) and starting material diol 8a (35.5 mg, 0.15 mmol, 20% recovered). Small quantities (~5-10%) of the corresponding furan side-product was also isolated (formed through intramolecular displacement of sulfonate). 8b: R$_f$ = 0.60 (silica, EtOAc:hexanes, 1:4); [$\alpha$]$_D^{20}$ = + 76.9 (c = 0.13, CHCl$_3$); IR (film) $\nu_{max}$ 2957, 2930, 1457, 1347, 1178, 1042, 945, 791 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.19 (s, 2H), 5.10 (d, J = 1.1 Hz, 1H), 4.39 (dd, J = 10.6, 4.9 Hz, 1H), 4.13 (dt, J = 13.5, 6.8 Hz, 2H), 4.06 (dd, J = 10.6, 3.8 Hz, 1H), 3.94 (dd, J = 11.2, 9.1 Hz, 1H), 3.63 (dd, J = 11.3, 6.1 Hz, 1H), 2.91 (dq, J = 20.8, 6.9 Hz, 1H), 2.59 – 2.53 (m, 1H), 2.49 – 2.44 (m, 1H), 1.68 (s, 3H), 1.52 (d, J = 12.5 Hz, 1H), 1.48 (d, J = 13.3 Hz, 1H), 1.39 – 1.32 (m, 2H), 1.29 – 1.24 (m, 18H), 1.22 – 1.12 (m, 1H), 0.96 (s, 3H), 0.92 – 0.81 (m, 2H), 0.78 (d, J = 6.5 Hz, 3H), 0.76 – 0.67 (m, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ = 154.1, 151.1, 134.3, 131.3, 129.6, 124.0, 69.0, 63.5, 50.2, 40.9, 40.2, 39.4,
TBS-protected Sulfonate 8c: To a stirred solution of sulfonate 8b (115.0 mg, 0.22 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) at 25 °C was added imidazole (45.0 mg, 0.66 mmol, 3.0 equiv) and TBSCI (66.4 mg, 0.44 mmol, 2.0 equiv) and the resulting mixture was stirred for 12 h at the same temperature. The solution was then concentrated in vacuo and the resulting crude product was purified by flash column chromatography (silica, 5% Et₂O in hexanes) providing pure TBS-protected sulfonate 8c as a colorless oil (123.0 mg, 0.20 mmol, 90% yield). 8c: Rf = 0.18 (silica, hexanes); [α]_D^{20} = +28.2 (c = 1.0, CHCl₃); IR (film) ν_max 2954, 2927, 2860, 1600, 1562, 1426, 1374, 1332, 1254, 1092, 940, 836 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 7.17 (s, 2H), 5.09 (d, J = 1.3 Hz, 1H), 4.21 (dd, J = 10.1, 4.1 Hz, 1H), 4.18 – 4.11 (m, 3H), 3.71 (dd, J = 10.1, 6.8 Hz, 1H), 3.61 (dd, J = 10.1, 8.4 Hz, 1H), 2.91 (hept, J = 6.9 Hz, 1H), 2.46 (tt, J = 7.7, 3.9 Hz, 1H), 2.33 (ddd, J = 7.5, 4.0, 0.8 Hz, 1H), 1.67 (s, 3H), 1.53 – 1.47 (m, 2H), 1.45 (dd, J = 9.0, 6.5 Hz, 2H), 1.36 (dd, J = 12.9, 3.6 Hz, 2H), 1.28 – 1.23 (m, 18H), 1.18 (ddd, J = 9.2, 5.7, 2.5 Hz, 1H), 0.93 (s, 3H), 0.85 (s, 9H), 0.79 (d, J = 6.5 Hz, 3H), 0.74 – 0.65 (m, 1H), 0.01 (s, 3H), -0.01 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 153.8, 150.9, 134.3, 131.7, 130.0, 123.9, 68.6, 62.8, 50.4, 40.2, 39.6, 39.4, 37.3, 35.2, 34.5, 31.1, 29.8, 26.1, 25.1, 25.0, 24.7, 23.8, 22.8, 22.6, 18.4, -5.1, -5.2; HRMS calcd for C₃₆H₆₂O₄SSiNa⁺ [M+Na⁺] 641.4036 found 641.4037.
TBS ether 27: To a stirred solution of TBS-protected sulfonate 8c (100.0 mg, 0.16 mmol, 1.0 equiv) in THF (5 mL) at 25 °C was added LiBEt₃H (97 µL, 1.0 M in THF, 0.97 mmol, 6.0 equiv). The reaction mixture was then heated under microwave irradiation at 80 °C for 10 minutes before it was allowed to cool to 0 °C and quenched with H₂O (2 mL). The reaction mixture was then extracted with Et₂O (3 × 5 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 5% Et₂O in hexanes) providing pure TBS ether 27 as a yellow oil (44.2 mg, 0.13 mmol, 82% yield).

27: Rf = 0.28 (silica, hexanes); [α]D²⁰ = +30.1 (c = 0.3, CHCl₃); IR (film) νmax 2949, 2858, 1614, 1459, 1095, 836, 773 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.02 (s, 1H), 3.75 (dd, J = 9.6, 8.4 Hz, 1H), 3.60 (dd, J = 9.8, 7.0 Hz, 1H), 2.34 (qd, J = 7.7, 2.5 Hz, 1H), 2.16 (pent, J = 7.3 Hz, 1H), 1.69 (s, 3H), 1.56 (s, 1H), 1.48 (dt, J = 13.2, 2.8 Hz, 1H), 1.39 (dd, J = 7.0, 3.5 Hz, 1H), 1.38 (m, 1H), 1.31 – 1.26 (m, 2H), 0.98 (d, J = 7.6 Hz, 3H), 0.95 (s, 3H), 0.90 (s, 9H), 0.84 – 0.77 (m, 1H), 0.80 (d, J = 6.5 Hz, 3H), 0.73 – 0.64 (m, 1H), 0.06 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ = 136.0, 131.0, 64.1, 50.6, 41.6, 38.8, 37.2, 35.6, 33.9, 31.5, 29.7, 26.1, 25.1, 22.9, 22.5, 18.4, 14.1, -5.1, -5.2; HRMS calcd for C₂₁H₄₁O₄Si⁺ [M+H⁺] 337.2927 found 337.2925.
Alcohol 27a: To a stirred solution of TBS-ether 27 (45.0 mg, 0.13 mmol, 1.0 equiv) in THF (2 mL) at 25 °C was added TBAF (200 µL, 1.0 M in THF, 0.20 mmol, 1.5 equiv) and the resulting reaction mixture was stirred for 1.5 h at the same temperature before it was quenched with saturated aq. NaHCO₃ (1 mL). The reaction mixture was then extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 10% EtOAc in hexanes) providing pure alcohol 27a as a colorless oil (27.0 mg, 0.12 mmol, 91% yield). 27a: Rf = 0.17 (silica, Et₂O:hexanes, 1:9); [α]_D²⁰ = +132.5 (c = 0.16, CHCl₃); IR (film) νₘₚ₁₃ 3336 (br), 2946, 2922, 1455, 1375, 1047, 1023, 843 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.04 (s, 1H), 3.83 (dd, J = 10.3, 8.2 Hz, 1H), 3.70 (dd, J = 10.1, 7.2 Hz, 1H), 2.39 (dd, J = 13.8, 6.5 Hz, 1H), 2.20 (dt, J = 14.9, 7.4 Hz J, 1H), 1.70 (s, 3H), 1.58 (d, J = 12.7 Hz, 1H), 1.50 (d, J = 13.1 Hz, 1H), 1.43 – 1.36 (m, 2H), 1.33 – 1.24 (m, 2H), 1.02 (d, J = 7.6 Hz, 3H), 0.97 (s, 3H), 0.92 – 0.85 (m, 1H), 0.81 (d, J = 6.4 Hz, 3H), 0.76 – 0.68 (m, 1H); ¹³C NMR (151 MHz, CDCl₃) δ = 135.6, 131.0, 64.2, 50.5, 41.6, 39.0, 37.2, 35.5, 33.8, 31.5, 29.7, 25.1, 22.8, 22.4, 14.2; HRMS calcd for C₁₅H₂₇O⁺ [M+H⁺] 223.2056 found 223.2061.
**Aldehyde 7**: To a stirred solution of alcohol **27a** (30.0 mg, 0.14 mmol, 1.0 equiv) in CH₂Cl₂ (3 mL) at 0 °C was added DMP (143.0 mg, 0.34 mmol, 2.5 equiv). The resulting mixture was stirred at 25 °C for 2 h before it was quenched with saturated aq. NaHCO₃:saturated aq. Na₂S₂O₃ (1:1, 2 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography (silica, 5% Et₂O in hexanes) providing pure aldehyde 7 as a colorless oil (25.0 mg, 0.11 mmol, 81% yield). 7: Rf = 0.66 (silica, Et₂O:hexanes, 1:9); [α]D²⁰ = +62.0 (c = 0.10, CHCl₃); IR (film) νmax 2921, 1723, 1455 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 9.91 (s, 1H), 5.08 (d, J = 1.2 Hz, 1H), 2.96 (dd, J = 7.2, 3.1 Hz, 1H), 2.66 – 2.58 (m, 1H), 1.89 (d, J = 12.7 Hz, 1H), 1.73 (s, 3H), 1.64 – 1.60 (m, 2H), 1.56 – 1.52 (m, 1H), 1.42 – 1.35 (m, 1H), 1.35 – 1.29 (m, 2H), 1.18 (d, J = 7.4 Hz, 3H), 0.96 (s, 3H), 0.84 (d, J = 6.5 Hz, 3H), 0.80 (m, J = 12.4, 3.2 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ = 206.0, 134.7, 131.3, 51.1, 50.0, 40.2, 37.0, 35.3, 32.5, 31.3, 29.8, 26.4, 22.8, 22.0, 16.5; HRMS calcd for C₁₅H₂₅O⁺ [M+H⁺] 221.1905 found 221.1906.
Diastereoisomeric alcohols 30 and 31: To a stirred solution of enantiopure aldehyde 7 (25.0 mg, 0.12 mmol, 1.0 equiv) and racemic iodide 6° (178.0 mg, 0.42 mmol, 3.5 equiv) in toluene (3 mL) at −78 °C was added BEt₃ (0.42 mL, 1.0 M in hexanes, 0.42 mmol, 3.5 equiv). The resulting mixture was stirred for 2 h at the same temperature before it was quenched with H₂O (1 mL). The reaction mixture was extracted with Et₂O (3 × 10 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The crude mixture of diastereoisomers 30 and 31 (30:31 ca 3.5:1 dr) was purified by flash column chromatography (silica, gradient from 100% hexanes→5% EtOAc in hexanes) providing pure diastereoisomers 30 (yellow amorphous solid, 42 mg, 0.078 mmol, 68% yield) and 31 (colorless oil, 12 mg, 0.022 mmol, 19% yield).

Diastereoisomer 30: Rf = 0.65 (silica, EtOAc:hexanes, 1:4); [α]D²⁰ = +10.0 (c = 0.25, CHCl₃); IR (film) νmax 2952, 2930, 1794, 1703, 1374, 1138, 839 cm⁻¹; m.p. = 175–178 °C; ¹H NMR (600 MHz, CDCl₃) δ = 5.03 (s, 1H), 4.76 (d, J = 4.0 Hz, 1H), 4.31 (br s, 1H), 3.91 – 3.85 (m, 1H), 3.60 (d, J = 3.1 Hz, 1H), 3.36 – 3.26 (m, 2H), 3.10 (dd, J = 8.6, 2.4 Hz, 1H), 2.64 – 2.51 (m, 2H), 2.46 (br s, 1H), 2.13 (dt, J = 14.4, 7.2 Hz, 1H), 2.00 (dd, J = 13.2, 3.2 Hz, 1H), 1.70 (s, 3H), 1.63 (d, J = 11.7 Hz, 1H), 1.59 (d, J = 12.6 Hz, 1H), 1.52 (d, J = 13.2 Hz, 1H), 1.45 – 1.36 (m, 1H), 1.34 – 1.27 (m, 1H), 1.20 (d, J = 7.5 Hz, 3H), 0.99 (s, 3H), 0.90 (s, 9H), 0.87 – 0.82 (m, 1H), 0.81 (d, J = 6.5 J, 3H), 0.73 (ddd, J = 15.5, 13.4, 3.4 Hz, 1H), 0.18 (s, 3H), 0.16 (s, 3H); ¹³C NMR (151
MHz, CDCl₃) δ = 176.3, 174.8, 136.1, 131.0, 100.9, 82.9, 70.4, 50.9, 49.7, 49.4, 42.5, 41.0, 38.9, 38.0, 37.0, 35.9, 31.7, 29.8, 29.1, 25.8, 25.6, 22.9, 22.4, 18.0, 15.8, -3.1, -3.4; HRMS calcd for C₂₉H₄₈NO₅Si Na⁺ [M+Na⁺] 540.3116 found 540.3117.

**Diastereoisomer 31:** Rf = 0.60 (silica, EtOAc:hexanes, 1:4); [α]D²⁰ = +26.7 (c = 0.15, CHCl₃); IR (film) νmax 2951, 2925, 1795, 1705, 1303, 1141, 1057, 1033, 839 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.02 (s, 1H), 4.86 (d, J = 3.7 Hz, 1H), 4.33 (dd, J = 9.4, 6.5 Hz, 1H), 3.81 (dt, J = 11.7, 8.2 Hz, 1H), 3.34 – 3.28 (m, 1H), 3.22 (dd, J = 6.1, 3.9 Hz, 1H), 3.10 (dd, J = 7.3, 3.0 Hz, 1H), 2.62 – 2.53 (m, 3H), 2.38 (dt, J = 14.2, 7.1 Hz, 1H), 1.71 (s, 3H), 1.62 (d, J = 12.6 Hz, 1H), 1.56 – 1.50 (m, 2H), 1.49 – 1.41 (m, 1H), 1.35 – 1.26 (m, 2H), 1.18 (d, J = 7.4 Hz, 3H), 0.99 (s, 3H), 0.90 (s, 9H), 0.89 – 0.83 (m, 1H), 0.81 (d, J = 6.5 J, 3H), 0.65 (ddd, J = 25.2, 12.7, 2.9 Hz, 1H), 0.17 (s, 3H), 0.15 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 176.1, 174.6, 136.5, 129.9, 100.5, 84.1, 68.8, 50.8, 49.7, 49.6, 42.4, 40.8, 37.8, 36.7, 35.9, 34.0, 31.9, 29.8, 28.9, 25.8, 25.6, 22.9, 22.6, 18.0, 14.7, -3.1, -3.5; HRMS calcd for C₂₉H₄₇NO₅SiNa⁺ [M+Na⁺] 540.3116 found 540.3117.
**Diol 32**: To a stirred solution of TBS ether 30 (10.0 mg, 0.019 mmol, 1.0 equiv) in THF (1 mL) at 0°C was added TASF (9.6 mg, 0.035 mmol, 1.8 equiv) and the resulting mixture was stirred for three (3) minutes at the same temperature before it was quenched with H₂O (2 mL). The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 10% EtOAc in hexanes→50% EtOAc in hexanes) providing pure diol 32 as a colorless oil (6.2 mg, 0.015 mmol, 81% yield). 32: Rf = 0.25 (silica, EtOAc:hexanes, 1:1); [α]D²⁰ = +6.8 (c = 0.19, acetone-d₆); IR (film) ν_max 3402 (br), 2925, 1790, 1696, 1376, 1064 cm⁻¹; ¹H NMR (600 MHz, acetone-d₆) δ = 5.05 (s, 1H), 4.98 (d, J = 4.1 Hz, 1H), 4.24 (dd, J = 12.0, 6.8 Hz, 1H), 4.00 (d, J = 3.5 Hz, 1H), 3.78 (ddd, J = 11.4, 9.5, 6.0 Hz, 1H), 3.51 (dd, J = 6.7, 4.3 Hz, 1H), 3.33 – 3.27 (m, 2H), 2.81 (br s, 1H), 2.73 – 2.65 (m, 1H), 2.50 (br m, 1H), 2.40 (dddd, J = 13.9, 9.3, 4.9, 1.9 Hz, 1H), 2.16 (dt, J = 13.9, 6.9 Hz, 1H), 2.10 – 2.07 (m, 1H), 1.78 (d, J = 12.4 Hz, 1H), 1.71 (s, 3H), 1.60 – 1.50 (m, 2H), 1.41 (ddd, J = 26.2, 13.2, 3.4 Hz, 1H), 1.33 – 1.27 (m, 1H), 1.22 (d, J = 7.5 Hz, 3H), 0.99 (s, 3H), 0.94 (t, J = 12.7 Hz, 1H), 0.81 (d, J = 6.5 J, 3H), 0.74 (ddd, J = 15.2, 12.8, 3.0 Hz, 1H); ¹³C NMR (151 MHz, acetone-d₆) δ = 176.7, 176.0, 137.0, 131.5, 100.4, 83.0, 70.9, 70.8, 51.4, 49.9, 49.2, 42.3, 41.2, 39.7, 39.6, 38.4, 37.5, 36.4, 31.9, 26.6, 23.1, 22.3, 16.1; HRMS calcd for C₂₃H₃₃NO₅SiNa⁺ [M+Na⁺] 426.2251 found 426.2252
**CJ-16,264 diastereoisomer corrected-ent-1**: To a stirred solution of diol 32 (5.0 mg, 0.012 mmol, 1.0 equiv) in degassed CH$_2$Cl$_2$ (1 mL) at 0 °C was added DMP (86.0 µL, 0.1M solution in CH$_2$Cl$_2$, 0.0086 mmol, 1.4 equiv) and the resulting mixture was stirred for 30 minutes at the same temperature before it was diluted with Et$_2$O (5 mL) and passed through a plug of Celite®. The resulting crude product was purified by passing through a short plug of silica (gradient from 10% EtOAc in hexanes → 50% EtOAc in hexanes) furnishing pure CJ-16,264 isomer corrected-ent-1 as a colorless oil (3.9 mg, 0.010 mmol, 80% yield). corrected-ent-1: R$_f$ = 0.30 (silica, EtOAc:hexanes, 1:1). R$_f$ = 0.42 (silica, EtOAc:hexanes, 1:1); [α]$_D^{20} = -10.9$ (c = 0.11, methanol); IR (film) $\nu_{\text{max}}$ 3448 (br), 2926, 1796, 1696, 1379, 1299, 1114, 1032 cm$^{-1}$; $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta$ = 4.96 (s, 1H), 4.66 (br s, 1H), 4.18 (s, 1H), 4.08 (s, 1H), 3.51 (ddd, $J = 11.9$, 9.4, 5.9 Hz, 1H), 3.26 (dd, $J = 6.4$, 2.7 Hz, 1H), 2.76 (ddd, $J = 11.9$, 9.9, 4.9 Hz, 1H), 2.68 (dd, $J = 9.2$, 1.8 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.11 – 2.03 (m, 1H), 1.97 – 1.89 (m, 1H), 1.87 (d, $J = 13.0$ Hz, 1H), 1.76 – 1.68 (m, 1H), 1.63 (s, 3H), 1.54 – 1.48 (m, 1H), 1.46 – 1.31 (m, 4H), 1.20 (d, $J = 7.3$ Hz, 3H), 0.99 (s, 3H), 0.86 (d, $J = 6.5$ Hz, 3H), 0.75 – 0.65 (m, 1H); $^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$ = 209.9, 173.9, 167.3, 135.3, 130.5, 100.9, 80.5, 63.6, 52.9, 50.1, 47.6, 41.9, 41.7, 37.6, 35.3, 32.7, 31.3, 29.9, 29.8, 26.4, 22.7, 21.8, 17.2; HRMS calcd for C$_{23}$H$_{31}$NO$_5$Na [M+Na$^+$] 424.2094 found 424.2092.
**Diol 33:** To a stirred solution of TBS ether 31 (8.0 mg, 0.015 mmol, 1.0 equiv) in THF (1 mL) at 0°C was added TASF (9.6 mg, 0.035 mmol, 1.8 equiv) and the resulting mixture was stirred for three (3) minutes at the same temperature before it was quenched with H₂O (2 mL). The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 10% EtOAc in hexanes→ 50% EtOAc in hexanes) furnishing pure diol 33 as a colorless oil (4.5 mg, 0.011 mmol, 73% yield). 33: Rf = 0.26 (silica, EtOAc:hexanes, 1:1); [α]D²⁰ = +61.1 (c = 0.18, acetone-d₆); IR (film) νmax 3399 (br), 2949, 2922, 1789, 1379, 1332, 1057, 1013 cm⁻¹; ¹H NMR (600 MHz, acetone-d₆) δ = 6.20 (br s, 1H), 5.13 (d, J = 3.9 Hz, 1H), 5.03 (s, 1H), 4.52 (d, J = 2.9 Hz, 1H), 4.29 – 4.24 (m, 1H), 3.75 (ddd, J = 11.6, 9.4, 6.3 Hz, 1H), 3.42 (dd, J = 6.7, 4.0 Hz, 1H), 3.34 – 3.26 (m, 2H), 2.74 – 2.65 (m, 1H), 2.59 – 2.55 (m, 1H), 2.45 – 2.35 (m, 2H), 1.72 – 1.71 (m, 1H), 1.71 (s, 3H), 1.60 – 1.49 (m, 2H), 1.49 – 1.41 (m, 2H), 1.33 – 1.27 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H), 0.99 (s, 3H), 0.93 – 0.88 (m, 1H), 0.80 (d, J = 6.5 J, 3H), 0.74 (ddd, J = 15.4, 12.6, 3.2 Hz, 1H); ¹³C NMR (151 MHz, acetone-d₆) δ = 176.4, 175.9, 137.3, 130.8, 100.2, 84.0, 69.9, 69.7, 55.5, 51.3, 49.9, 49.1, 43.7, 42.4, 42.1, 38.3, 36.3, 34.7, 32.0, 26.2, 23.0, 22.6, 15.1; HRMS calcd for C₂₃H₃₃NO₅SiNa⁺ [M+Na⁺] 426.2243 found 426.2252.
CJ-16,264 diastereoisomer 34: To a stirred solution of diol 33 (5.0 mg, 0.012 mmol, 1.0 equiv) in degassed CH₂Cl₂ (1 mL) at 0°C was added DMP (86.0 µL, 0.1M solution in CH₂Cl₂, 0.0086 mmol, 1.4 equiv) and the resulting mixture was stirred for 30 minutes at the same temperature before it was diluted with Et₂O (5 mL) and passed through a short plug of Celite®. The resulting crude product was purified by passing through a short plug of silica (gradient from 10% EtOAc in hexanes→50% EtOAc in hexanes) furnishing pure CJ-16,264 isomer 34 as a colorless oil (4.0 mg, 0.010 mmol, 83% yield). Rf = 0.40 (silica, EtOAc:hexanes, 1:1); [α]_D^{20} = +50.0 (c = 0.12, methanol); IR (film) ν_{max} 3442 (br), 2924, 1793, 1692, 1456, 1377, 1299, 1162, 1030 cm⁻¹; ^1H NMR (600 MHz, C₆D₆) δ = 5.01 (s, 1H), 4.78 (s, 1H), 4.30 (s, 1H), 4.14 (s, 1H), 3.71 (dd, J = 7.2, 2.5 Hz, 1H), 3.47 (ddd, J = 12.0, 9.4, 5.7 Hz, 1H), 2.75 – 2.67 (m, 2H), 2.41 (dt, J = 14.4, 7.3 Hz, 1H), 2.14 – 2.10 (m, 1H), 2.09 – 2.02 (m, 1H), 1.93 (ddd, J = 13.6, 9.5, 4.8 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.65 – 1.59 (m, 1H), 1.59 (s, 3H), 1.48 – 1.24 (m, 4H), 0.91 (s, 3H), 0.84 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 7.4 Hz, 3H); ^13C NMR (151 MHz, C₆D₆) δ = 209.5, 174.1, 167.1, 134.1, 131.8, 101.1, 80.1, 63.8, 51.1, 50.1, 47.6, 41.7, 40.6, 37.3, 35.5, 34.1, 30.6, 29.92, 29.91, 25.9, 22.7, 21.6, 16.8; HRMS calcd for C_{23}H_{31}NO_5Na^+ [M+Na^+] 402.2094 found 424.2100.
Hydroxy methyl ester 26a: To a stirred solution of hydroxy acid 26 (190 mg, 0.76 mmol, 1.0 equiv) in DMF (3 mL) at 0 °C was added K₂CO₃ (137.0 mg, 0.99 mmol, 1.3 equiv) and MeI (85 µL, 1.37 mmol, 1.8 equiv) and the resulting mixture was stirred at the same temperature for 2 h before it was quenched with H₂O. The reaction mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash column chromatography (silica, 30% EtOAc in hexanes) to give pure hydroxy methyl ester 26a (172.0 mg, 0.65 mmol, 85% yield) as a colorless oil. 26a: Rf = 0.50 (silica, EtOAc:hexanes, 1:1); [α]D₂₀ = +35.3 (c =0.17, CHCl₃); IR (film) νmax 3472 (br), 2947, 1732, 1196 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.21 (s, 1H), 3.83 (dd, J = 10.8, 4.0 Hz, 1H), 3.70 (s, 3H), 3.61 (dd, J = 10.8, 7.6 Hz, 1H), 2.90 (br s, 1H), 2.70 (t, J = 4.0 Hz, 1H), 2.04 (m, 1H), 1.74 (s, 3H), 1.64 (m, 1H), 1.56 – 1.40 (m, 4H), 0.99 – 0.92 (m, 2H), 0.86 (d, J = 6.8 Hz, 3H), 0.85 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 177.7, 134.2, 129.6, 64.7, 52.1, 48.2, 46.1, 42.2, 41.0, 36.2, 33.6, 29.6, 29.4, 28.8, 22.5, 21.9; HRMS calcd for C₁₈H₂₆O₃Na⁺ [M+Na]⁺ 289.1774 found 289.1776.

Hydroxy methyl ester ent-26a was synthesized through the same procedure using ent-26 as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-26a matched those of 26a. ent-26a: [α]D₂₀ = -45.4 (c = 1.80, CHCl₃).
Mesylate 26b: To a stirred solution of alcohol 26a (120.0 mg, 0.45 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) at 0 °C was added Et₃N (190 μL, 1.35 mmol, 3.0 equiv) and MsCl (70 μL, 0.90 mmol, 2.0 equiv) and the resulting mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with H₂O (10 mL), extracted with CH₂Cl₂ (3 × 10 mL) and the combined organic layers were dried over MgSO₄, and concentrated in vacuo. The crude product was purified by flash column chromatography (silica, 20% EtOAc in hexanes) to give pure mesylate 26b (139.0 mg, 0.41 mmol, 90%) as a colorless oil. 26b: Rf = 0.36 (silica, EtOAc:hexanes, 1:4); [α]D²⁰ = +66.4 (c =0.67, CHCl₃); IR (film) νmax 2948, 1728, 1448, 1356, 1203, 1175, 953 cm⁻¹; ¹H NMR (600 MHz, CDCl₃); δ = 5.26 (s, 1H), 4.33 (dd, J = 9.6, 3.6 Hz, 1H), 4.27 (dd, J = 9.6, 6.6 Hz, 1H), 3.71 (s, 3H), 3.18 (br s, 1H), 3.01 (s, 3H), 2.55 (t, J = 3.0 Hz, 1H), 2.08 (dt, J = 11.4, 3.0 Hz, 1H), 1.77 (s, 3H), 1.63 – 1.61 (m, 1H), 1.53 – 1.49 (m, 1H), 1.46 – 1.43 (m, 1H), 1.41 – 1.35 (m, 2H), 0.96 – 0.92 (m, 2H), 0.85 (d, J = 6.4 Hz, 3H), 0.82 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ: 176.5, 134.8, 128.0, 71.2, 52.3, 48.9, 46.4, 42.2, 37.7, 37.4, 36.3, 34.3, 30.3, 29.2, 29.0, 22.5, 21.7; HRMS calcd for C₁₇H₂₆O₃SNa⁺ [M+Na]⁺ 367.1550 found 367.1552.

Mesylate ent-26b was synthesized through the same procedure using ent-26a as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-26b matched those of 26b. ent-26b: [α]D²⁰ = −56.7 (c = 1.30, CHCl₃).
Methyl ester 28: To a stirred solution of 26b (100.0 mg, 0.30 mmol, 1.0 equiv) in DME (4 mL) at 25 °C was added NaI (438.0 mg, 2.92 mmol, 10.0 equiv) and activated Zn dust (382.0 mg, 5.84 mmol, 20.0 equiv) and the resulting mixture was stirred at 95 °C for 16 h. The reaction mixture was then cooled to 25 °C, passed through a short plug of Celite® and then concentrated in vacuo. The crude product was purified by flash column chromatography (silica, 10% Et₂O in hexanes) to give pure methyl ester 28 (62.3 mg, 0.25 mmol, 83%) as a colorless oil. 28: Rf = 0.65 (silica, Et₂O:hexanes, 1:19); [α]_D^{20} = +37.6 (c = 0.13, CHCl₃); IR (film) ν_max 2947, 1735, 1434, 1195 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 5.07 (s, 1H), 3.68 (s, 3H), 2.75 – 2.74 (m, 1H), 2.27 (t, J = 4.8 Hz, 1H), 1.98 – 1.95 (m, 1H), 1.69 (s, 3H), 1.66 – 1.35 (m, 5H), 1.07 (d, J = 7.2 Hz, 3H), 0.99 – 0.94 (m, 2H), 0.88 (d, J = 6.8 Hz, 3H), 0.86 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ = 177.4, 133.2, 131.5, 51.9, 51.7, 47.7, 42.7, 36.1, 32.9, 32.8, 29.7, 28.8, 28.6, 22.4, 21.9, 20.5; HRMS calcd for C₁₆H₂₇O₂⁺ [M+H]⁺ 251.2011 found 251.2006.

Methyl ester ent-28 was synthesized through the same procedure using ent-26b as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-28 matched those of 28. ent-28: [α]_D^{20} = −52.1 (c = 1.50, CHCl₃).
Alcohol 28a: To a stirred solution of methyl ester 28 (100.0 mg, 0.40 mmol) in hexane (10 mL) at –78 °C was added DIBAL-H (1.4 mL, 1.0 M in hexanes, 1.37 mmol) dropwise and the resulting mixture was stirred for 1 h at the same temperature before it was quenched with 10% aq. NaOH (5 mL). The reaction mixture was extracted with Et₂O (3 × 10 mL) and the combined organic layers were dried over MgSO₄, and concentrated in vacuo. The crude product was purified by flash column chromatography (silica, 20% Et₂O in hexanes) to give pure alcohol 28a (82.6 mg, 0.37 mmol, 93% yield) as a colorless oil. 28a: Rf = 0.12 (silica, Et₂O:hexanes, 1:9); [α]₀²⁰ = +40.0 (c =0.10, CHCl₃); IR (film) νmax 3345 (br), 2920, 1472, 1033 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ: 5.11 (s, 1H), 3.71 – 3.60 (m, 2H), 1.82 (m, 1H), 1.72 (m, 1H), 1.68 (s, 3H), 1.54 (m, 1H), 1.44 – 1.34 (m, 6H), 1.13 (d, J = 7.2 Hz, 3H), 0.90 (s, 3H), 0.87 (m, 1H), 0.82 (d, J = 6.8 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ: 134.3, 131.1, 68.8, 51.7, 50.4, 41.9, 36.3, 35.1, 34.2, 32.9, 31.1, 28.9, 22.6, 22.1, 21.7; HRMS calcd for C₁₅H₂₇O⁺ [M+H]⁺ 223.2056 found 223.2063.

Alcohol ent-28a was synthesized through the same procedure using ent-28 as the starting material. The ¹H NMR and ¹³C NMR spectral data of ent-28a matched those of 28a. ent-28a: [α]₀²⁰ = −57.1 (c = 2.50, CHCl₃).
Aldehyde 29: To a stirred solution of alcohol 28a (40.0 mg, 0.18 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (4 mL) at 0 °C was added DMP (176.0 mg, 0.42, 2.3 equiv) and the resulting mixture was stirred for 1 h at the same temperature before it was quenched with saturated aq. NaHCO$_3$:saturated aq. Na$_2$S$_2$O$_3$ (1:1, 2 mL) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, 10% Et$_2$O in hexanes) providing pure aldehyde 29 as a colorless oil (34.5 mg, 0.16 mmol, 87% yield). 29: R$_f$ = 0.85 (silica, Et$_2$O:hexanes, 1:9); [α]$^D_{20}$ = +14.4 (c =0.16, CHCl$_3$); IR (film) $\nu$$_{max}$ 3345 (br), 2920, 1472, 1033 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ = 9.75 (s, 1H), 5.04 (s, 1H), 2.81 (m, 1H), 2.00 – 1.97 (m, 2H), 1.71 (s, 3H), 1.65 – 1.55 (m, 2H), 1.51 – 1.41 (m, 2H), 1.40 – 1.33 (m, 1H), 1.13 (d, J = 7.6 Hz, 3H), 0.94 – 0.88 (m, 2H), 0.85 (d, J = 6.4 Hz, 3H), 0.72 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 205.1, 132.8, 130.2, 60.9, 49.7, 41.7, 36.5, 35.3, 31.9, 31.4, 29.3, 28.8, 22.6, 22.1, 21.6; HRMS calcd for C$_{15}$H$_{25}$O$^+$ [M+H$^+$] 221.1905 found 221.1907.

Aldehyde ent-29 was synthesized through the same procedure using ent-28a as the starting material. The $^1$H NMR and $^{13}$C NMR spectral data of ent-29 matched those of 29. ent-29: [α]$^D_{20}$ = –17.1 (c = 2.00, CHCl$_3$).
Diastereoisomeric alcohols 35 and 36: To a stirred solution of enantiopure aldehyde 29 (43.0 mg, 0.20 mmol, 1.0 equiv) and racemic iodide 6 (290.0 mg, 0.68 mmol, 3.5 equiv) in toluene (4 mL) at -78°C was added BEt$_3$ (0.68 mL, 1.0 M in hexanes, 0.68 mmol, 3.5 equiv) and the resulting mixture was stirred for 2 h at the same temperature before it was quenched with H$_2$O (5 mL). The reaction mixture was extracted with Et$_2$O (3 x 15 mL) and the combined organic layers were dried over MgSO$_4$, and concentrated in vacuo. The crude mixture of diastereoisomers 35 and 36 (35:36 ca 2.5:1 dr) was purified by flash column chromatography (silica, gradient from 100% hexanes→5% EtOAc in hexanes) providing pure diastereoisomers 35 (white crystals, 61 mg, 0.11 mmol, 59% yield) and 36 (white crystals, 24 mg, 0.05 mmol, 24% yield).

**Diastereoisomer 35:** R$_f$ = 0.17 (silica, Et$_2$O:hexanes, 1:9); [α]$_D^{20}$ = -8.1 (c = 0.16, C$_6$D$_6$); IR (film) $\nu_{\text{max}}$ 3385 (br), 2924, 2855, 1788, 1698, 1378, 1054 cm$^{-1}$; m.p. = 142–145 °C; $^1$H NMR (600 MHz, C$_6$D$_6$) δ = 5.24 (s, 1H), 4.80 (br s, 1H), 4.48 (d, $J$ = 3.9 Hz, 1H), 4.42 – 4.39 (m, 1H), 3.48 – 3.40 (m, 1H), 3.26 (dd, $J$ = 8.6, 3.8 Hz, 1H), 2.87 – 2.81 (m, 1H), 2.73 – 2.66 (m, 1H), 2.41 (dd, $J$ = 8.8, 1.2 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.82 (s, 3H), 1.80 – 1.74 (m, 1H), 1.72 (br s, 1H), 1.70 – 1.51 (m, 4H), 1.50 – 1.43 (m, 1H), 1.35 (s, 3H), 1.29 (d, $J$ = 7.5 Hz, 3H), 1.01 – 0.89 (m, 2H), 1.07 – 1.00 (m, 1H), 0.93 (d, $J$ = 6.6 Hz, 3H), 0.83 (s, 9H), -0.07 (s, 3H), -0.17 (s, 3H); $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ = 177.0, 173.7, 134.6, 131.4, 100.4, 82.6, 73.0, 51.6, 51.2, 50.9, 49.2, 45.9, 42.5,
36.2, 35.3, 33.6, 30.6, 30.0, 29.3, 28.7, 25.4, 23.1, 22.8, 22.5, 17.7, -3.7, -4.1; HRMS calcd for C\(_{29}\)H\(_{48}\)NO\(_5\)Si\(^+\) [M+H\(^+\)] 518.3296 found 518.3300.

Diastereoisomer *ent-35* was synthesized through the same procedure using *ent-29* as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data of *ent-35* matched those of *35*. *ent-35*: \(\alpha\)_D\(^{20}\) = +8.7 (c = 3.50, C\(_6\)D\(_6\)).

**Diastereoisomer 36**: Rf = 0.26 (silica, Et\(_2\)O:hexanes, 1:9); \(\alpha\)_D\(^{20}\) = +52.9 (c = 0.17, C\(_6\)D\(_6\)); IR (film) \(\nu_{\text{max}}\) 3385 (br), 2930, 2854, 1790, 1700, 1255, 1456, 1332, 1163 cm\(^{-1}\); m.p. = 130–134 \(^\circ\)C; \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) \(\delta\) = 5.44 (s, 1H), 4.89 (br s, 1H), 4.43 (d, \(J = 3.9\) Hz, 1H), 4.35 (d, \(J = 3.7\) Hz, 1H), 3.50 – 3.32 (m, 1H), 3.30 (dd, \(J = 9.9, 3.7\) Hz, 1H), 2.73 – 2.66 (m, 1H), 2.65 – 2.56 (m, 1H), 2.38 (d, \(J = 7.8\) Hz, 1H), 2.12 – 2.05 (m, 1H), 1.91 (dd, \(J = 12.5, 4.3\) Hz, 1H), 1.84 – 1.74 (m, 1H), 1.81 (s, 3H), 1.72 – 1.65 (m, 2H), 1.57 – 1.48 (m, 2H), 1.40 (s, 3H), 1.37 – 1.31 (m, 1H), 1.19 (d, \(J = 7.0\) Hz, 3H), 1.16 – 1.12 (m, 1H), 1.07 – 1.00 (m, 1H), 0.97 (d, \(J = 6.5\) Hz, 3H), 0.83 (s, 9H), -0.07 (s, 3H), -0.17 (s, 3H); \(^{13}\)C NMR (151 MHz, C\(_6\)D\(_6\)) \(\delta\) = 177.7, 173.6, 136.3, 132.6, 100.4, 82.1, 68.9, 53.3, 51.4, 49.7, 49.1, 42.2, 40.4, 38.9, 38.0, 37.1, 36.9, 36.0, 32.3, 30.4, 29.2, 28.6, 25.3, 22.9, 21.7, 19.2, 17.7, -3.7, -4.1; HRMS calcd for C\(_{29}\)H\(_{48}\)NO\(_5\)Si\(^+\) [M+H\(^+\)] 518.3296 found 518.3297.

Diastereoisomer *ent-36* was synthesized through the same procedure using *ent-29* as the starting material. The \(^1\)H NMR and \(^{13}\)C NMR spectral data of *ent-36* matched those of *36*. *ent-36*: \(\alpha\)_D\(^{20}\) = -58.2 (c = 1.80, C\(_6\)D\(_6\)).
Diol 37: To a stirred solution of TBS ether 35 (10.0 mg, 0.019 mmol, 1.0 equiv) in THF (1 mL) at 0°C was added TASF (9.6 mg, 0.035 mmol, 1.8 equiv) and the resulting mixture was stirred for three (3) minutes at the same temperature before it was quenched with H₂O (2 mL). The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried over MgSO₄, and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 10% EtOAc in hexanes→ 50% EtOAc in hexanes) providing pure diol 37 as a colorless oil (6.0 mg, 0.015 mmol, 78% yield). 37: R<sub>f</sub> = 0.19 (silica, EtOAc:hexanes, 2:3); [α]<sub>D</sub><sup>20</sup> = +13.8 (c = 0.28, acetone-<i>d</i><sub>6</sub>); IR (film) ν<sub>max</sub> 3352 (br), 2918, 1792, 1700, 1684, 1374, 1055 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, acetone-<i>d</i><sub>6</sub>) δ = 6.29 (br s, 1H), 5.07 (d, J = 3.5 Hz, 1H), 5.05 (s, 1H), 4.54 (d, J = 2.5 Hz, 1H), 4.07 – 4.01 (m, 1H), 3.77 (ddd, J = 11.4, 9.6, 6.3 Hz, 1H), 3.36 (dd, J = 8.0, 4.0 Hz, 1H), 3.33 – 3.28 (m, 2H), 2.79 (br s, 1H), 2.70 (dtd, J = 15.6, 9.5, 6.2 Hz, 1H), 2.55 (dd, J = 14.5, 7.2 Hz, 1H), 2.43 (dddd, J = 13.8, 9.2, 4.7, 1.7 Hz, 1H), 1.69 (s, 3H), 1.65 (br s, 1H), 1.58 – 1.53 (m, 1H), 1.48 – 1.40 (m, 3H), 1.35 – 1.28 (m, 1H), 1.18 (d, J = 7.5 Hz, 3H), 1.08 (s, 3H), 0.94 – 0.87 (m, 1H), 0.86 – 0.76 (m, 1H), 0.82 (d, J = 6.5 Hz, 3H); <sup>13</sup>C NMR (151 MHz, acetone-<i>d</i><sub>6</sub>) δ = 176.7, 175.9, 135.6, 131.1, 100.2, 83.1, 73.4, 52.2, 51.6, 51.5, 49.1, 46.0, 42.2, 36.7, 36.1, 33.9, 30.6, 29.9, 29.6, 29.4, 23.3, 22.9, 22.6; HRMS calcd for C<sub>23</sub>H₃₅NO₅Na<sup>+</sup> [M+Na<sup>+</sup>] 426.2251 found 426.2254.

Diol ent-37 was synthesized through the same procedure using ent-35 as the starting
material. The $^1$H NMR and $^{13}$C NMR spectral data of ent-37 matched those of 37. ent-37: $[\alpha]_D^{20} = -18.5$ (c = 0.65, acetone-$d_6$).

**Enantioisomeric CJ-16,264 [(-)-38]:** To a stirred solution of diol 37 (6.0 mg, 0.015 mmol, 1.0 equiv) in degassed CH$_2$Cl$_2$ (1 mL) at 0°C was added DMP (180.0 µL, 0.1M solution in CH$_2$Cl$_2$, 0.018 mmol, 1.2 equiv) and the resulting mixture was stirred for 40 min at the same temperature before it was diluted with Et$_2$O (5 mL) and passed through a plug of Celite®. The resulting crude product was purified by passing it through a short plug of silica (gradient from 10% EtOAc in hexanes→ 50% EtOAc in hexanes) furnishing pure diastereoisomer (-)-38 as a colorless oil (5.0 mg, 0.012 mmol, 83% yield). No efforts were made to obtain crystalline solid for (-)-38 although its enantiomer (+)-38 (see page SI-41) was obtained as a white crystalline solid. (-)-38:

$\text{Rf} = 0.30$ (silica, EtOAc:hexanes, 1:1); $[\alpha]_D^{20} = -9.8$ (c = 0.50, methanol); IR (film) $\nu_{\text{max}}$ 3442 (br), 2923, 2960, 1794, 1720, 1688, 1456, 1335, 1281, 1163, 1022, 764 cm$^{-1}$; $^1$H NMR (600 MHz, C$_6$D$_6$) $\delta = 5.09$ (s, 1H), 5.01 (s, 1H), 4.16 (s, 1H), 4.03 (s, 1H), 3.53 (ddd, $J = 11.9$, 9.4, 6.1 Hz, 1H), 2.98 (br s, 1H), 2.78 (ddd, $J = 11.9$, 9.9, 4.8 Hz, 1H), 2.73 – 2.69 (m, 1H), 2.55 (br d, $J = 11.0$ Hz, 1H), 2.14 (dd, $J = 3.9$, 3.0 Hz, 1H), 2.12 – 2.04 (m, 1H), 1.97 – 1.88 (m, 1H), 1.68 (s, 3H), 1.62 – 1.56 (m, 1H), 1.46 – 1.32 (m, 4H), 1.09 – 1.00 (m, 2H), 0.95 (d, $J = 7.4$ Hz, 3H), 0.93 (s, 3H), 0.89 (d, $J = 6.5$ Hz, 3H);

$^{13}$C NMR (151 MHz, C$_6$D$_6$) $\delta$: 209.8, 173.9, 167.6, 133.1, 131.4, 100.9, 81.1, 63.7, 63.6,
48.8, 47.5, 41.8, 38.9, 37.0, 34.2, 31.9, 29.7, 29.7, 29.1, 28.8, 22.3, 21.6, 21.0; HRMS calcd for C_{23}H_{31}NO_5Na^+ [M+Na^+] 424.2094 found 424.2099.

**Synthetic CJ-16,264 [(+)-38]:** Synthetic CJ-16,264 was prepared from ent-37 according to the same procedure used to prepare its enantioisomer (−)-38 from diol 37. The $^1$H NMR and $^{13}$C NMR spectral data of (+)-38 matched very well with those of (−)-38 as well as those reported for natural CJ-16,264.\(^\text{10}\) (+)-38:

Rf = 0.30 (silica, EtOAc:hexanes, 1:1); [α]$_D^{20}$ = +7.7 (c = 0.30, MeOH); IR (film) $\nu_{\text{max}}$ 3445 (br), 2920, 1794, 1719, 1688, 1335, 1281, 1155, 1020, 763 cm$^{-1}$; $^1$H NMR (600 MHz, C$_6$D$_6$) δ = 5.09 (s, 1H), 5.01 (s, 1H), 4.16 (s, 1H), 4.04 (s, 1H), 3.53 (ddd, $J$ = 11.9, 9.4, 6.1 Hz, 1H), 2.98 (br s, 1H), 2.77 (ddd, $J$ = 11.9, 9.9, 4.8 Hz, 1H), 2.72 (dd, $J$ = 9.2, 1.7 Hz, 1H), 2.55 (br d, $J$ = 11.0 Hz, 1H), 2.15 (dd, $J$ = 3.9, 3.0 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.98 – 1.89 (m, 1H), 1.68 (s, 3H), 1.64 – 1.58 (m, 1H), 1.46 – 1.32 (m, 4H), 1.09 – 1.00 (m, 2H), 0.95 (d, $J$ = 7.4 Hz, 3H), 0.93 (s, 3H), 0.89 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (151 MHz, C$_6$D$_6$) δ: 209.8, 173.9, 167.6, 133.1, 131.4, 100.9, 81.1, 63.7, 63.6, 48.8, 47.5, 41.8, 38.9, 37.0, 34.2, 31.9, 29.7, 29.7, 29.1, 28.8, 22.3, 21.6, 21.0; HRMS calcd for C_{23}H_{31}NO_5Na^+ [M+Na^+] 424.2094 found 424.2081.
**Diol 39**: To a stirred solution of TBS ether 36 (10.0 mg, 0.019 mmol, 1.0 equiv) in THF (1 mL) at 0°C was added TASF (9.6 mg, 0.035 mmol, 1.8 equiv) and the resulting mixture was stirred for three (3) minutes at the same temperature before it was quenched with H₂O (2 mL). The reaction mixture was extracted with EtOAc (3 × 5 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (silica, gradient from 10% EtOAc in hexanes→ 50% EtOAc in hexanes) providing pure diol 39 as a colorless oil (7.0 mg, 0.017 mmol, 91% yield). 39: Rf = 0.19 (silica, EtOAc:hexanes, 2:3); [α]D²⁰ = +42.4 (c = 0.32, acetone-d₆); IR (film) νmax 3375 (br), 2930, 1795, 1702, 1472, 1370, 916 cm⁻¹; ¹H NMR (600 MHz, acetone-d₆) δ = 6.34 (br s, 1H), 5.26 (s, 1H), 4.96 – 4.60 (m, 1H), 4.07 (dd, J = 9.1, 4.0 Hz, 1H), 3.77 (ddd, J = 11.3, 9.5, 6.4 Hz, 1H), 3.39 (dd, J = 9.5, 3.8 Hz, 1H), 3.35 – 3.22 (m, 2H), 2.74 – 2.65 (m, 1H), 2.48 – 2.38 (m, 1H), 2.34 – 2.24 (m, 1H), 1.82 – 1.73 (m, 1H), 1.73 (s, 3H), 1.59 – 1.50 (m, 2H), 1.43 – 1.27 (m, 3H), 1.17 (d, J = 7.2 Hz, 1H), 1.10 (d, J = 7.1 Hz, 3H), 0.99 (s, 3H), 0.89 – 0.85 (m, 1H), 0.84 (d, J = 6.5 Hz, 3H); ¹³C NMR (151 MHz, acetone-d₆) δ = 177.7, 175.9, 136.3, 132.7, 100.3, 82.7, 69.9, 69.8, 53.6, 53.5, 51.9, 50.1, 49.0, 42.1, 40.3, 37.1, 36.6, 36.4, 32.8, 30.6, 23.0, 21.9, 19.8; HRMS calcd for C₂₃H₃₃NO₅Na [M+Na⁺] 426.2251 found 426.2249.

Diol **ent-39** was synthesized through the same procedure using **ent-36** as the starting material. The ¹H NMR and ¹³C NMR spectral data of **ent-39** matched those of 39. **ent-39**:
[α]_D^20 = −60.3 (c = 1.50, acetone-d₆).

CJ-16,264 diastereoisomer 40: To a stirred solution of diol 39 (5.0 mg, 0.012 mmol, 1.0 equiv) in degassed CH₂Cl₂ (1 mL) at 0°C was added DMP (86.0 µL, 0.1M solution in CH₂Cl₂, 0.0086 mmol, 1.4 equiv) and the resulting mixture was stirred for 20 min at the same temperature before it was diluted with Et₂O (5 mL) and passed through a plug of Celite®. The resulting crude product was purified by passing it through a short plug of silica (gradient from 10% EtOAc in hexanes→ 50% EtOAc in hexanes) furnishing pure CJ-16,264 diastereoisomer 40 as a colorless oil (4.1 mg, 0.010 mmol, 82% yield). Rf = 0.30 (silica, EtOAc:hexanes, 1:1). [α]_D^20 = +70.9 (c = 0.11, methanol); IR (film) ν_max 3449 (br), 2923, 1795, 1715, 1690, 1456, 1374, 1335, 1282, 1162, 1032 cm⁻¹; ¹H NMR (600 MHz, C₆D₆) δ = 4.99 (s, 1H), 4.77 (br s, 1H), 4.37 (s, 1H), 4.35 (s, 1H), 3.51 – 3.44 (m, 1H), 3.02 (dd, J = 14.3, 7.4 Hz, 1H), 2.78 – 2.66 (m, 3H), 2.12 – 2.01 (m, 1H), 1.96 – 1.87 (m, 1H), 1.78 – 1.68 (m, 1H), 1.64 (s, 3H), 1.52 – 1.36 (m, 5H), 1.33-1.22 (m, 2H), 0.93 (d, J = 7.6 Hz, 3H), 0.85 (d, J = 6.5 Hz, 3H), 0.71 (d, 3H); ¹³C NMR (151 MHz, C₆D₆) δ: 210.2, 174.1, 167.2, 134.2, 125.8, 101.1, 80.5, 63.1, 61.0, 49.8, 47.6, 43.4, 41.8, 36.9, 35.0, 29.93, 29.7, 29.91, 29.3, 28.9, 22.5, 21.8, 20.6; HRMS calcd for C₂₃H₃₂NO₅⁺ [M+H⁺] 402.2275 found 402.2291.

CJ-16,264 diastereoisomer ent-40 was synthesized from diol ent-39 by the same procedure. The ¹H NMR and ¹³C NMR spectral data matched those of 40. ent-40: [α]_D^20 = −56.7 (c = 0.15, MeOH).
Table 1. Comparison of $^1$H NMR spectral data for synthetic [(-)-38 and (+)-38] and natural CJ-16264.

<table>
<thead>
<tr>
<th>H</th>
<th>(-)-38 (600 MHz, CD$_6$D)</th>
<th>(+)-38 (600 MHz, CD$_6$D)</th>
<th>Natural$^{10}$ (600 MHz, CD$_6$D)</th>
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<tr>
<td>1</td>
<td>2.14 (dd, J = 3.9, 3.0 Hz)</td>
<td>2.15 (dd, J = 3.9, 3.0 Hz)</td>
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<td>2</td>
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<td>2.98 (br s)</td>
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<td>3</td>
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<tr>
<td>4</td>
<td>5.01 (s)</td>
<td>5.01 (s)</td>
<td>5.08 (s)</td>
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<tr>
<td>4a</td>
<td>--</td>
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</tr>
<tr>
<td>5</td>
<td>1.46 – 1.32 (m), 1.09 – 1.00 (m)</td>
<td>1.46 – 1.32 (m), 1.09 – 1.00 (m)</td>
<td>1.42 (m), 1.06 (m)</td>
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<td>1.46 – 1.32 (m)</td>
<td>1.46 – 1.32 (m)</td>
<td>1.42 (m)</td>
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<td>7</td>
<td>1.62 – 1.56 (m), 1.09 – 1.00 (m)</td>
<td>1.64 – 1.58 (m), 1.09 – 1.00 (m)</td>
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<td>1.46 – 1.32 (m)</td>
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<td>8a</td>
<td>2.55 (br d, J = 11.0 Hz)</td>
<td>2.55 (br d, J = 11.0 Hz)</td>
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<td>2-CH$_3$</td>
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<td>0.95 (d, J = 7.4 Hz)</td>
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<td>0.93 (s)</td>
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<td>6-CH$_3$</td>
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<td>0.89 (d, J = 6.5 Hz)</td>
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<td>2'a</td>
<td>2.73 – 2.69 (m)</td>
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<td>2.12 – 2.04 (m), 1.97 – 1.88 (m)</td>
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<td>4.04 (s)</td>
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Table 2. Comparison of $^{13}$C NMR spectral data for synthetic [(-)-38 and (+)-38] and natural CJ-16264.

![Molecular Structure of (+)-38](image)

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<th>(+)-38 (151 MHz, C$_6$D$_6$)</th>
<th>Natural$^{20}$ (151 MHz, C$_6$D$_6$)</th>
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References:


$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 12a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 12a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 14

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 14
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 14a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 14a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 15

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 15
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 15a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 15a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 17

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 17
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 19

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 19
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound 11a

\[^{13}\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound 11a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 21

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 21
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 21a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 21a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 11b

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 11b
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 22

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 22
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 22a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 22a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 25

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 25
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 8

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 8
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$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 26
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 8a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 8a
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound 8b

\(^{13}\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound 8b
\(^1\text{H NMR spectrum (CDCl}_3, 600 \text{ MHz)} \) of compound 8c

\(^{13}\text{C NMR spectrum (CDCl}_3, 151 \text{ MHz)} \) of compound 8c
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$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 27
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 27a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 27a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 7

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$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 30

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$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 31

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 31
$^1$H NMR spectrum (acetone-$d_6$, 600 MHz) of compound 32

$^{13}$C NMR spectrum (acetone-$d_6$, 151 MHz) of compound 32
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of CJ-16,264 diastereoisomer corrected-ent-1

$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of CJ-16,264 diastereoisomer corrected-ent-1

$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^1$H NMR spectrum (acetone-$d_6$, 600 MHz) of compound 33

$^{13}$C NMR spectrum (acetone-$d_6$, 151 MHz) of compound 33
$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of CJ-16,264 diastereoisomer 34

$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of CJ-16,264 diastereoisomer 34

$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 26a

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 26a
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 26b

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 26b
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$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 29

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 29
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 35

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 35
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 36

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 36
$^1$H NMR spectrum (acetone-$d_6$, 600 MHz) of compound 37

$^{13}$C NMR spectrum (acetone-$d_6$, 151 MHz) of compound 37
$^1$H NMR spectrum ($C_6D_6$, 600 MHz) of CJ-16,264 enantioisomer (−)-38

$^{13}$C NMR spectrum ($C_6D_6$, 151 MHz) of CJ-16,264 enantioisomer (−)-38
\[^{1}\text{H NMR spectrum (C}_6\text{D}_6, 600 MHz) of synthetic CJ-16,264 [(+)-38]}\]

\[
\begin{align*}
&\text{HO} \\
&\text{H} \\
&\text{O} \\
&\text{O} \\
&\text{H} \\
&\text{Me} \\
&\text{Me} \\
&\text{Me} \\
&\text{Me}
\end{align*}
\]

\[^{1}\text{H NMR spectrum (C}_6\text{D}_6, 600 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)}\]
$^{13}$C NMR spectrum ($C_6D_6$, 151 MHz) of synthetic CJ-16,264 [(+)-38]

$^{13}$C NMR spectrum ($C_6D_6$, 151 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^1$H NMR spectrum (acetone-$d_6$, 600 MHz) of compound 39

$^{13}$C NMR spectrum (acetone-$d_6$, 151 MHz) of compound 39
$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of CJ-16,264 diastereoisomer 40

$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of CJ-16,264 diastereoisomer 40

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of natural CJ-16,264 (provided by Dr. Y Sugie)
Deuterium incorporation experiment: Time lapsed $^1$H NMR spectra (C$_6$D$_6$, 600 MHz) of synthetic CJ-16,264 [(+)-38]

- Before D$_2$O addition
- D$_2$O addition-5 min
- D$_2$O addition-72 h
Deuterium incorporation experiment: Time lapsed $^{13}$C NMR spectra (C$_6$D$_6$, 151 MHz) of synthetic CJ-16,264 [(+)-38]
Deuterium incorporation experiment: Time lapsed $^{13}$C NMR spectra (zoomed in image) 
($C_6D_6$, 151 MHz) of synthetic CJ-16,264 [(+)-38]

- Decrease in signal of C7’
- Signal of C7’ at 63.7 ppm
- $D_2O$ addition - 72 h
- Before $D_2O$ addition
X-ray derived ORTEP of *ent-25* (provided by Dr. J. D. Korp, University of Houston, Houston, Texas)

The sample crystal was a two-domain twin with significant overlap between domains (see Crystallographic data for crystal structures *ent-25*, which is available free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif) under deposition number 1400327).