Supporting Information for:

Total Syntheses of (–)-Majucin and (–)-Jiadifenoxolane A, Complex Majucin-Type *Illicium* Sesquiterpenes

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Table of Contents:

General Procedures:

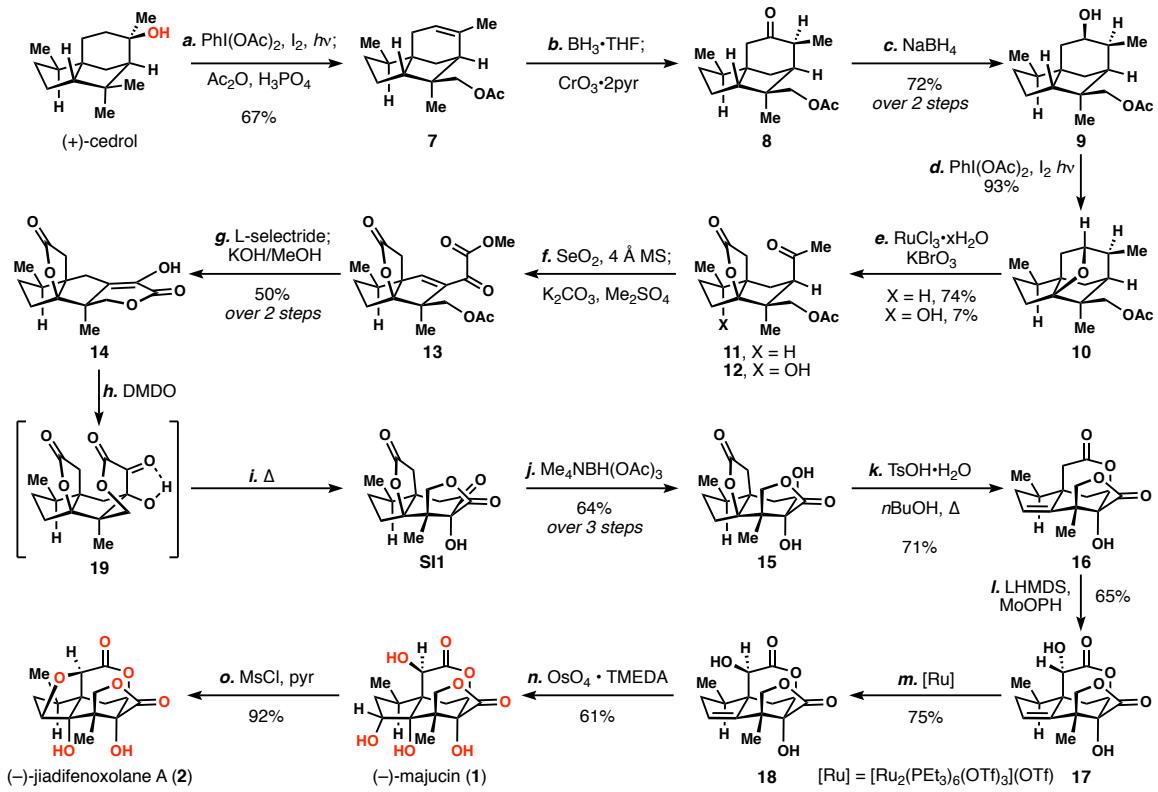
All reactions were performed in flame- or oven-dried glassware under a positive pressure of nitrogen or argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe. Volatile solvents were removed under reduced pressure rotary evaporation below 35 °C. Analytical and preparative thin-layer chromatography (TLC) were performed using glass plates pre-coated with silica gel (0.25-mm, 60-Å pore size, Silicycle SiliaPlate^{TM}) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and then were stained by submersion in an ethanolic anisaldehyde solution or a basic potassium permanganate solution, followed by brief heating on a hot plate. Flash column chromatography was performed employing silica gel purchased from Silicycle (SiliaFlash®, 60 Å, 230-400 mesh, 40-63 μm).

(+)-Cedrol was purchased from Parchem and used directly as received. The material was found to have an optical rotation of $[\alpha]_D^{23}$ = +11.9 (*c* 5, $CHCl_3$). This value compares favorably to both the Merck Index value for enantiopure cedrol ($[\alpha]_D^{23}$ = +9.9, *c* 5, $CHCl_3$), and the value reported by Sigma Aldrich ($[\alpha]_D^{23}$ = +10.5, *c* 5, $CHCl_3$).

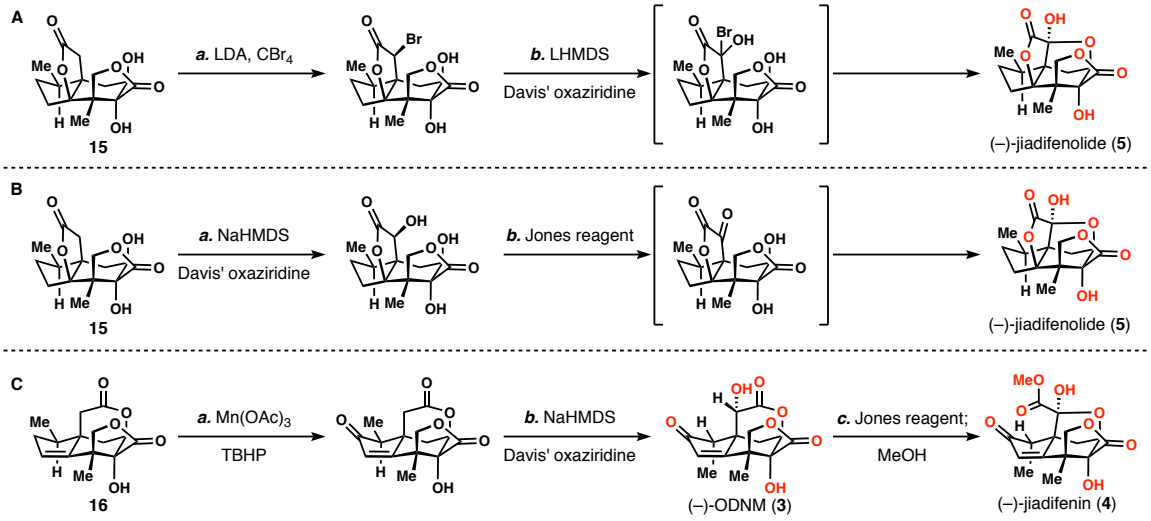
Anhydrous tetrahydrofuran (THF) and dichloromethane (DCM) were obtained by passing these previously degassed solvents through activated alumina columns. Dess-Martin periodinane (DMP) was prepared from 2-iodobenzoic acid according to the literature protocols.[1,2] Dimethyldioxirane (DMDO) and oxodiperoxymolybdenum(pyridine)-(hexamethylphosphoric triamide) (MoOPH) were prepared according to the corresponding *Organic Synthesis* procedures.[3,4] $[Ru_2(PEt_3)_6(OTf)_3](OTf)$ was generously provided by Professor John Hartwig and Christopher Hill. All other solvents and reagents were purchased at the highest commercial grade and were used as received, without further purification.

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker AV 500 (500 MHz/126 MHz), Bruker AV 600 (600 MHz/151 MHz), or Bruker AV 700 (700 MHz/176 MHz) spectrometers at 23 °C. Proton chemical shifts are expressed as parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent (C_5D_4HN: δ 8.74, $CHCl_3$: δ 7.26, CD_2HOD: δ 3.31), except where otherwise indicated. Carbon chemical shifts are

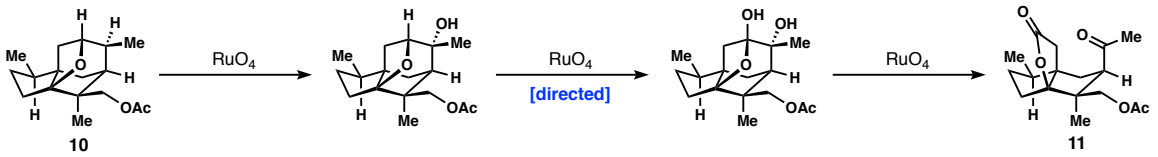
expressed as parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent (C_5D_5N: δ 150.35, $CDCl_3$: δ 77.16, CD_3OD: 49.00), except where otherwise indicated. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), and integration. Infrared (IR) spectra were recorded on a Bruker Alpha FT-IR spectrometer as thin films and are reported in frequency of absorption (cm^{-1}). Melting points were determined using a MEL-TEMP II apparatus and are uncorrected. Optical rotations were recorded on a Perkin Elmer polarimeter, model 241. High-resolution mass spectra were obtained at the QB3/Chemistry Mass Spectrometry Facility at University of California, Berkeley using a Thermo LTQ-FT mass spectrometer, and at the Lawrence Berkeley National Laboratory Catalysis Center using a Perkin Elmer AxION 2 TOF mass spectrometer. X-ray diffraction data for compounds **14**, **15**, **21**, and **1** were collected at the Small Molecule X-ray Crystallography Facility (CheXray) at University of California, Berkeley using a Bruker MicroSTAR-H APEX II QUAZAR X-ray source.



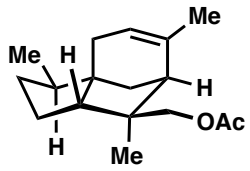
Scheme SI-1: Synthetic route to majucin (**1**) and jiadifenoxolane A (**2**).



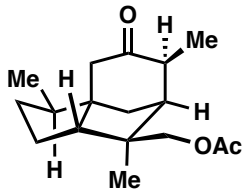
Scheme SI-2: Reported conversions of intermediate **15** to **5**, and **16** to **3** and **4**. **A** See ref. 5. **B** See ref. 6. **C** See ref. 6.



Scheme SI-3: Proposed mechanism for the conversion of **10** to **11**. First, RuO_4 oxidizes the tertiary C-6 position of **10**. That hydroxyl then directs a second equivalent of RuO_4 to oxidize the tertiary C-11 position. Finally, C-C bond cleavage of the resulting diol gives rise to keto lactone **11**.

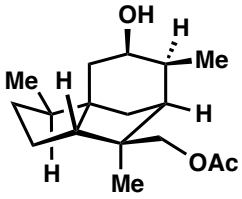


Alkene 7. Cyclohexane (1.8 L) was added to a 3 L flask containing diacetoxyiodobenzene (42.5 g, 132 mmol, 1.1 equiv) and iodine (12.2 g, 48 mmol, 0.4 equiv). The suspension was stirred at room temperature until the iodine had completely dissolved. At this point, (+)-cedrol (26.7 g, 120 mmol, 1.0 equiv) was added in a single portion. The deep purple mixture was irradiated with a 90 W halogen lamp for 1.5 h. Upon consumption of the starting material, the lamp was turned off and acetic anhydride (113 mL, 1.2 mol, 10.0 equiv) and phosphoric acid (85%, 14.7 mL, 240 mmol, 2.0 equiv) were added sequentially. The resulting solution was stirred for 30 min before being carefully quenched with saturated *aq.* $NaHCO_3$ (750 mL) and saturated *aq.* $Na_2S_2O_3$ (250 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 750 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (1% → 5% Et_2O in hexanes) to afford alkene **7** (21.1 g, 80 mmol, 67% yield) as a pale yellow oil. $[\alpha]_D^{23}$ = –99.7 (*c* 2.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (dt, *J* = 4.1, 2.0 Hz, 1H), 4.00 (d, *J* = 10.4 Hz, 1H), 3.90 (d, *J* = 10.4 Hz, 1H), 2.18 (dt, *J* = 17.0, 2.5 Hz, 1H), 2.04 (s, 3H), 1.96 (d, *J* = 3.8 Hz, 1H), 1.90 – 1.83 (m, 1H), 1.82 – 1.73 (m, 2H), 1.73 – 1.65 (m, 2H), 1.64 (d, *J* = 2.0 Hz, 3H), 1.62 – 1.55 (m, 1H), 1.45 (d, *J* = 11.1 Hz, 1H), 1.43 – 1.35 (m, 2H), 1.01 (s, 3H), 0.85 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 139.1, 120.71, 72.4, 55.9, 53.4, 52.4, 51.6, 41.3, 40.3, 38.8, 36.3, 25.4, 24.1, 21.2, 20.6, 15.5; IR (thin film) ν_{max}: 2939, 2873, 1740, 1470, 1372, 1235, 1031 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{26}O_2$: 262.1933, found: 262.1935;



Ketone 8. Alkene **7** (2.0 g, 7.6 mmol, 1.0 equiv) was dissolved in degassed THF (30 mL) and cooled to 0 ºC. Borane-THF complex (1 M in THF, 9.9 mL, 9.9 mmol, 1.3 equiv) was added dropwise over 15 min. At the conclusion of the addition, the resulting solution was allowed to warm to room temperature and stirred for 1.5h. In a separate flask, pyridine (30.7 mL, 382 mmol, 50 equiv) was dissolved in DCM (160 mL) and was cooled to 0 ºC. CrO_3 was added portion-wise over 20 min (4 x 4.8 g portions, 19.1 g, 191 mmol, 25 equiv) and the suspension was warmed to room temperature and stirred for 30 min. Upon

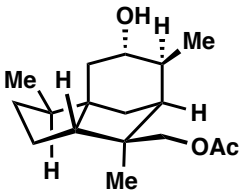
completion of the hydroboration reaction (as judged by TLC), the so-prepared CrO_3•2py solution was added to the reaction mixture in two portions over 30 min, with the first portion being added carefully to quench unreacted borane. The suspension was further diluted with DCM (150 mL), filtered through celite, washed with 1 M HCl (100 mL) and concentrated *in vacuo*. The crude ketone was afforded as a red oil (*ca*. 1.85 g) and was used directly in the next step without further purification. An analytical sample was isolated by preparative TLC (20% Et_2O in hexanes). $[\alpha]_D^{23}$ = –26.1 (*c* 1.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (d, *J* = 11.3 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 1H), 2.54 (qd, *J* = 7.1, 3.2 Hz, 1H), 2.33 (br s, 2H), 2.16 (br t, *J* = 4.0 Hz, 1H), 2.05 (br dd, *J* = 12.3, 4.8 Hz, 1H), 1.93 – 1.84 (m, 2H), 1.80 (br d, *J* = 12.1 Hz, 1H), 1.74 (br t, *J* = 8.3 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.46 – 1.38 (m, 1H), 1.38 – 1.29 (m, 1H), 1.10 (d, *J* = 7.1 Hz, 3H), 0.99 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.2, 171.0, 71.0, 56.0, 55.8, 54.8, 51.7, 51.5, 48.0, 46.1, 41.6, 37.1, 26.4, 23.0, 21.0, 15.6, 14.2; IR (thin film) ν_{max}: 2951, 2875, 1735, 1700, 1362, 1234, 1035 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{26}O_3$: 278.1882, found: 278.1880.



Alcohol 9. Ketone **8** (*ca.* 1.85 g, 6.6 mmol, 1.0 equiv) was dissolved in MeOH (66 mL) and cooled to 0 ºC. $NaBH_4$ (375 mg, 9.9 mmol, 1.5 equiv) was added in 3 portions over 30 min. At the end of the addition, the reaction mixture was quenched with *aq.* HCl (1 M, 50 mL) and diluted with Et_2O/hexanes (1:1, 100 mL). The layers were separated and the aqueous phase was further extracted with Et_2O/hexanes (1:1, 2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by column chromatography (10% → 15% EtOAc in hexanes) to afford alcohol **9** (1.56 g, 5.6 mmol, 72% yield over two steps) as a white solid (mp = 69 – 70 ºC). $[\alpha]_D^{23}$ = –29.3 (*c* 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.41 (d, *J* = 10.3 Hz, 1H), 4.39 (d, *J* = 10.3 Hz, 1H), 4.01 (q, *J* = 3.8 Hz, 1H), 2.54 (dd, *J* = 9.3, 6.3 Hz, 1H), 2.03 (s, 3H), 1.92 (ddq, *J* = 11.4, 7.6, 3.9, 3.2 Hz, 1H), 1.86 (dd, *J* = 11.5, 4.8 Hz, 1H), 1.83 – 1.76 (m, 4H), 1.69 (h, *J* = 6.8 Hz, 1H), 1.63 (br s, 1H), 1.59 – 1.49 (m, 1H), 1.41 (dq, *J* = 12.7, 6.3 Hz, 1H), 1.32 (dq, *J* = 12.2, 6.1 Hz, 1H), 1.15 (d, *J* = 11.4 Hz, 1H), 1.08 (d, *J* = 7.6 Hz, 3H), 1.01 (s, 3H), 0.84 (d, *J* = 7.2

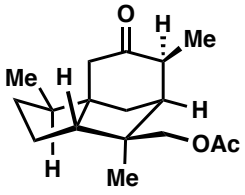
Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 72.8, 69.8, 53.1, 52.9, 50.7, 47.4, 47.0, 43.1, 43.0, 41.8, 36.0, 26.0, 23.3, 21.2, 17.3, 15.7; IR (thin film) ν_{max}: 3502, 2932, 2872, 1715, 1324, 1244, 1028 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{28}O_3Na$ $[M+Na]^+$: 303.1936, found: 303.1937.

An alternative route to decagram scale quantities of alcohol **9** was developed to mitigate concerns about the large amount of chromium waste produced in the above sequence:

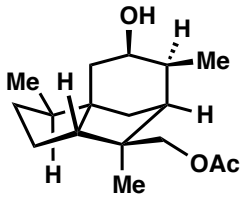


Alcohol SI-2. Alkene **7** (19.0 g, 72.5 mmol, 1.0 equiv) was dissolved in degassed THF (300 mL) and cooled to 0 ºC. Borane-THF complex (1 M in THF, 94.2 mL, 94.2 mmol, 1.3 equiv) was added dropwise over 15 min. At the conclusion of the addition, the resulting solution was allowed to warm to room temperature and stirred for 1.5 h. Upon consumption of the starting material, an internal thermometer was added and the solution was cooled until the solution temperature reached 5 ºC. pH 7.5 phosphate buffer (100 mL) was then carefully added (significant hydrogen gas evolution occurs) followed by H_2O_2 (35% in H_2O, 31 mL, 362 mmol, 5 equiv) dropwise. Additions were monitored such that the internal temperature of the reaction mixture never exceeded 10 ºC. At the end of the addition, the solution was allowed to warm to room temperature and stirred for 30 min. Et_2O was added (300 mL) and the layers were separated. The aqueous layer was further extracted with Et_2O (2 x 300 mL). The combined organic layers were then washed with water (750 mL) and brine (500 mL), dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by column chromatography (20% → 35% EtOAc in hexanes) to afford alcohol **SI-2** (14.2 g, 50.6 mmol, 70% yield) as a white solid (mp = 88 – 91ºC). $[\alpha]_D^{23}$ = –4.3 (*c* 1.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 (d, *J* = 10.6 Hz, 1H), 3.97 (d, *J* = 10.7 Hz, 1H), 3.73 (td, *J* = 10.0, 6.5 Hz, 1H), 2.04 (s, 3H), 2.01 – 1.94 (m, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.70 (m, 3H), 1.68 – 1.58 (m, 2H), 1.51 (dq, *J* = 14.1, 6.6 Hz, 1H), 1.41 (dq, *J* = 13.6, 7.2 Hz, 1H), 1.34 – 1.28 (m, 1H), 1.29 – 1.21 (m, 2H), 1.08 (d, *J* = 7.2 Hz, 3H), 1.02 (s, 3H), 0.86 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 73.0, 71.3, 54.8, 54.7, 53.7, 47.8, 46.6, 45.7, 43.7, 41.7, 36.8, 26.4, 23.5,

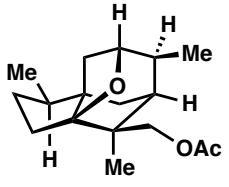
21.1, 17.9, 15.6; IR (thin film) ν_{max}: 3282, 2935, 2873, 1736, 1475, 1373, 1028 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{28}O_3Na$ $[M+Na]^+$: 303.1936, found: 303.1916.



Ketone 8. Alcohol **SI-2** (14.0 g, 50 mmol, 1.0 equiv) was dissolved in DCM (200 mL) at room temperature and *t*-BuOH (14.2 mL, 150 mmol, 3.0 equiv) was added. Freshly prepared DMP (31.8 g, 75 mmol, 1.5 equiv), was added in a single portion. The resulting cloudy white solution was stirred for 30 min before being diluted with Et_2O (200 mL) and quenched with saturated *aq.* $NaHCO_3$ (300 mL) and saturated *aq.* $Na_2S_2O_3$ (200 mL). The biphasic mixture was stirred vigorously until becoming clear. The layers were separated and the organic layer was washed with saturated *aq.* $NaHCO_3$ (250 mL) and brine (250 mL), dried over $MgSO_4$, filtered, and concentrated. The crude residue (*ca.* 14 g) was used directly in the next step without further purification. Analytical data were in agreement with those from the previously described preparation of this ketone.

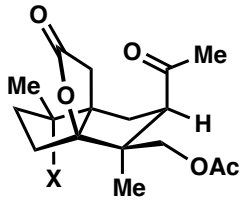


Alcohol 9. Ketone **8** (*ca.* 14 g, 50 mmol, 1.0 equiv) was dissolved in MeOH (200 mL) and cooled to 0 ºC. $NaBH_4$ (2.8 g, 75 mmol, 1.5 equiv) was added in 3 portions over 30 min. At the end of the addition, the reaction mixture was quenched with *aq.* HCl (1 M, 100 mL) and diluted with Et_2O/hexanes (1:1, 500 mL). The layers were separated and the aqueous phase was further extracted with Et_2O/hexanes (1:1, 2 x 250 mL). The combined organic layers were washed with brine (500 mL), dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by column chromatography (10% → 15% EtOAc in hexanes) to afford alcohol **9** (12.5 g, 44.6 mmol, 89% yield over two steps) as a white solid. Analytical data were in agreement with those from the previously described preparation of this alcohol.



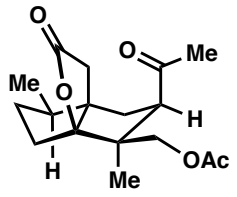
Ether 10. Alcohol **9** (6.0 g, 21.4 mmol, 1.0 equiv) was dissolved in degassed DCM (710 mL) and cooled to 0 ºC. Diacetoxyiodobenzene (20.7 g, 64.2 mmol, 3.0 equiv) was added followed by iodine (5.4 g, 21.4 mmol 1.0 equiv). The deep purple mixture was brought into a

cold room (*ca.* 5 ºC) and irradiated with a 90W halogen lamp for 1.5 h. Upon consumption of the starting material, the reaction mixture was removed from the cold room and quickly quenched with saturated *aq.* $NaHCO_3$ (250 mL) and saturated *aq.* $Na_2S_2O_3$ (50 mL). The layers were separated and the aqueous layer was extracted with DCM (300 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (5% → 10% EtOAc in hexanes) to afford ether **10** (5.5 g, 19.7 mmol, 92% yield) as a clear, colorless oil. $[\alpha]_D^{23} = -1.0$ (*c* 4.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.53 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 4.7 Hz, 1H), 2.12 (s, 1H), 2.04 (d, *J* = 1.2 Hz, 3H), 1.95 – 1.79 (m, 3H), 1.76 (qd, *J* = 7.7, 1.9 Hz, 1H), 1.73 – 1.58 (m, 4H), 1.54 (d, *J* = 11.9 Hz, 1H), 1.41 (h, *J* = 8.0 Hz, 1H), 1.13 (d, *J* = 7.5 Hz, 3H), 0.96 (s, 3H), 0.92 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 101.7, 82.9, 70.1, 62.9, 54.7, 48.3, 43.5, 42.8, 42.0, 40.6, 36.2, 28.7, 22.8, 21.2, 19.8, 14.9; IR (thin film) ν_{max}: 2951, 2872, 1736, 1372, 1241, 1031 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{26}O_3Na$ $[M+Na]^+$: 301.1780, found: 303.1782.

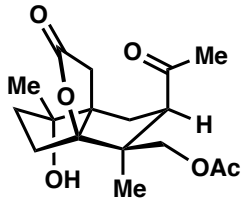


Keto lactone 11 (X = H) and alcohol 12 (X = OH). Ether **10** (8.9 g, 32.0 mmol, 1.0 equiv) was dissolved in MeCN:CCl_4:H_2O (2:2:3, 320 mL) and $KBrO_3$ (26.7 g, 160 mmol, 5.0 equiv) was added. The biphasic mixture was stirred vigorously at room temperature for 10 min before $RuCl_3$•xH_2O (199 mg, 0. 96 mmol, 0.03 equiv) was added. The organge/brown solution was heated at 75 ºC for 24 h. At that point, the suspension was cooled to room temperature and another portion of $KBrO_3$ (26.7 g, 160 mmol, 5.0 equiv) and $RuCl_3$•xH_2O (199 mg, 0.96 mmol, 0.03 equiv) was added. The suspension was reheated at 75 ºC for another 24 h. The suspension was then cooled to room temperature again and a final portion of $RuCl_3$•xH_2O (199 mg, 0.96 mmol, 0.03 equiv) was added (no additional $KBrO_3$ was added with it). The suspension was once again heated at 75 ºC for another 24 h. At the conclusion of the 72 h reaction, the resulting mixture was cooled to room temperature and diluted with EtOAc (500 mL) and water (500 mL). The layers were separated and the aqueous layer was extracted with EtOAc (250 mL). The combined organic layers were washed with saturated *aq.* $Na_2S_2O_3$ (250 mL), water (500 mL), and brine (500 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was pu-

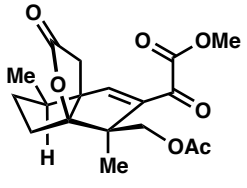
rified by column chromatography (30% → 50% EtOAc in hexanes) to afford keto lactone **11** as a white solid (7.1 g, 23 mmol, 72% yield). A C1 hydroxylated derivative, alcohol **12**, (750 mg, 2.3 mmol, 7% yield) could also be isolated from this mixture (eluting the column with 100% EtOAc) as a white solid.



Keto lactone 11: mp = 73 – 76 ºC; $[\alpha]_D^{23}$ = –16.0 (*c* 1.7, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 4.04 (d, *J* = 11.7 Hz, 1H), 3.96 (d, *J* = 11.7 Hz, 1H), 2.75 (dd, *J* = 12.7, 6.8 Hz, 1H), 2.71 (d, *J* = 19.1 Hz, 1H), 2.40 (d, *J* = 19.1 Hz, 1H), 2.21 (dd, *J* = 13.2, 12.7 Hz, 1H), 2.18 (s, 3H), 1.99 (s, 3H), 1.95 (dd, *J* = 13.2, 5.7 Hz, 1H), 1.89 (dd, *J* = 13.2, 6.8 Hz, 1H), 1.80 – 1.72 (m, 2H), 1.69 – 1.61 (m, 1H), 1.31 (s, 3H), 1.23 – 1.13 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.9, 177.4, 169.8, 106.0, 65.6, 58.8, 55.2, 49.5, 46.4, 39.8, 37.3, 35.3, 31.4, 31.2, 20.7, 20.1, 14.2; IR (thin film) ν_{max}: 2954, 2876, 1768, 1740, 1703, 1362, 1235, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{24}O_5Na$ $[M+Na]^+$: 331.1521, found: 331.1520.

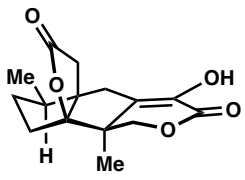


Alcohol 12: mp = 70 – 72 ºC; $[\alpha]_D^{23}$ = –118.0 (*c* 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 4.06 (d, *J* = 11.6 Hz, 1H), 3.97 (d, *J* = 11.6 Hz, 1H), 3.04 (dd, *J* = 12.3, 7.0 Hz, 1H), 2.68 (d, *J* = 19.2 Hz, 1H), 2.64 (d, *J* = 19.2 Hz, 1H), 2.32 (dd, *J* = 13.2, 7.0 Hz, 1H), 2.23 (td, *J* = 13.6, 6.1 Hz, 1H), 2.18 (s, 3H), 2.03 (dd, *J* = 13.2, 12.3 Hz, 1H), 2.00 (s, 3H), 1.88 (dd, *J* = 13.6, 5.9 Hz, 1H), 1.75 (dd, *J* = 13.6, 6.1 Hz, 1H), 1.67 (td, *J* = 13.6, 5.9 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.9, 177.0, 169.9, 107.2, 82.1, 66.1, 61.3, 59.4, 49.1, 42.0, 38.67, 35.4, 33.0, 31.3, 24.5, 20.8, 20.4; IR (thin film) ν_{max}: 3742, 2957, 1742, 1701, 1234, 1198, 1092 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{24}O_6Na$ $[M+Na]^+$: 319.1158, found: 319.1151.



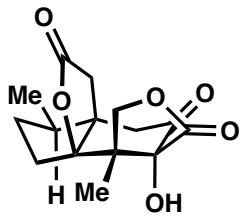
Enone ester 13. Keto lactone **11** (500 mg, 1.62 mmol, 1.0 equiv), SeO_2 (630 mg, 5.68 mmol, 3.5 equiv), and 4Å molecular sieves (500 g) were dissolved in diglyme (5 mL) and heated at 130 ºC for 4 h. The suspension was cooled to room temperature and diluted with

acetone (5 mL). K_2CO_3 (670 g, 4.86 mmol, 3.0 equiv) was added followed by Me_2SO_4 (230 µL, 2.43 mmol, 1.5 equiv). After stirring for 1 h, the suspension was diluted with acetone (5 mL) and filtered through a pad of celite. The residue was concentrated directly and used without further purification in the next step (quantitative yield assumed). An analytical sample of enone ester **11**, a colorless oil, was isolated by preparative TLC (50% EtOAc in hexanes). $[\alpha]_D^{23}$ = –96.7 (*c* 0.6 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (s, 1H), 4.42 (d, *J* = 11.0 Hz, 1H), 4.14 (d, *J* = 11.0 Hz, 1H), 3.89 (s, 3H), 2.79 (d, *J* = 18.8 Hz, 1H), 2.48 (d, *J* = 18.8 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.97 – 1.93 (m, 1H), 1.94 (s, 3H), 1.92 – 1.84 (m, 2H), 1.40 (ddd, *J* = 13.1, 12.2, 4.6 Hz, 1H), 1.36 (s, 3H), 1.12 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 183.2, 176.4, 169.9, 162.6, 153.3, 139.9, 104.6, 66.2, 63.8, 53.1, 53.1, 43.3, 34.1, 33.7, 32.5, 20.7, 18.6, 15.1; IR (thin film) ν_{max}: 2958, 2873, 1774, 1740, 1673, 1605, 1285 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}O_7Na$ $[M+Na]^+$: 373.1263, found: 373.1256.

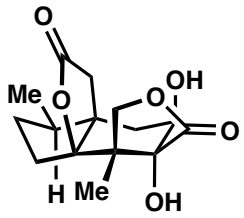


Enol lactone 14. Crude enone ester **13** (*ca*. 560 mg, 1.6 mmol, 1.0 equiv) was dissolved in THF (16 mL) and cooled to –78 ºC. L-Selectride (1 M in THF, 1.9 mL, 1.9 mmol, 1.2 equiv) was added and the solution was stirred for 30 min. KOH (1 M in MeOH, 16 mL, 16 mmol, 10.0 equiv) was added, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. DCM (25 mL) and HCl (1 M, 25 mL) were added and the layers were separated. The aqueous layer was extracted with DCM (2 x 25 mL). The combined organic layers were washed with half-saturated brine (25 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (35% → 45% EtOAc in hexanes) to afford enol lactone **14** (228 mg, 0.82 mmol, 50% over two steps) as a white solid (mp = 217 – 219 ºC). $[\alpha]_D^{23}$ = –167.1 (*c* 1.4 $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.58 (s, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 4.16 (d, *J* = 11.1 Hz, 1H), 2.81 (d, *J* = 17.4 Hz, 1H), 2.81 (d, *J* = 18.9 Hz, 1H), 2.51 (d, *J* = 17.4 Hz, 1H), 2.35 (d, *J* = 18.9 Hz, 1H), 2.12 (ddd, *J* = 12.7, 11.4, 6.7 Hz, 1H), 2.05–1.99 (m, 2H), 1.82 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.59 (dq, *J* = 12.0, 6.4 Hz, 1H), 1.38 (s, 3H), 1.05 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 163.2, 135.7, 132.8, 106.9, 74.8, 62.7,

46.7, 45.6, 38.6, 36.7, 35.1, 31.7, 22.5, 14.8; IR (thin film) ν_{max}: 3315, 2975, 2891, 1763, 1708 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1052, found: 301.1042.

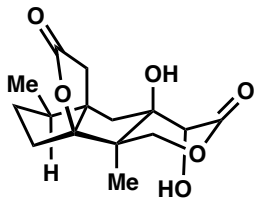


Ring shift ketone SI-1. Enol lactone **14** (280 mg, 1.01 mmol, 1.0 equiv) was dissolved in DMDO solution (*ca.* 0.06 M in acetone, 25 mL, 1.5 equiv) at room temperature. The solution was stirred for 12 h before being concentrated directly. The intermediate α-ketol was extremely sensitive and thus was not subjected to additional work-up or purification. The crude residue was transferred to a microwave vial and suspended in α,α,α-trifluorotoluene (20 mL). The vial was sealed and heated in the microwave reactor at 170 ºC for 2 h. The solution was concentrated and the crude ketone was typically of sufficient purity to be used in the subsequent step without further purification (quantitative yield assumed). An analytical sample of ring shift ketone **SI-1** was isolated by preparative TLC (50% EtOAc in hexanes). Characterization data were in agreement with previously reported values.[5] $[\alpha]_D^{23}$ = –137 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (d, *J* = 10.5 Hz, 1H), 4.33 (d, *J* = 10.5 Hz, 1H), 4.30 (s, 1H), 2.99 (d, *J* = 19.5 Hz, 1H), 2.79 (d, *J* = 13.6 Hz, 1H), 2.70 (d, *J* = 13.6 Hz, 1H), 2.54 (d, *J* = 19.5 Hz, 1H), 2.08 (dd, *J* = 14.3, 5.4 Hz, 1H), 1.76 (ddd, *J* = 13.0, 6.0, 5.4 Hz, 1H), 1.67 (dqd, *J* = 13.0, 6.7, 6.0 Hz, 1H), 1.51 (ddd, *J* = 14.3, 13.0, 6.0 Hz, 1H), 1.44 (s, 1H), 1.18 (qd, *J* = 13.0, 5.4 Hz, 1H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.0, 174.1, 171.1, 96.8, 82.2, 75.1, 52.4, 51.9, 45.6, 43.7, 37.4, 35.7, 29.5, 18.5, 13.7; IR (thin film) ν_{max}: 3435, 2963, 1767, 1723, 1175 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ $[M+Na]^+$: 317.1001, found: 317.1005.



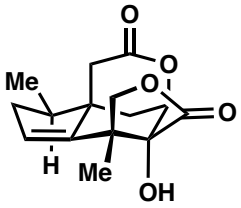
Diol 15. The following procedure is modified from conditions reported in the literature for this transformation.[5] Crude ring shift ketone **14** (*ca*. 290 mg, 1.0 mmol, 1.0 equiv) was dissolved in MeCN/AcOH (3:1, 10 mL) and cooled to –40 ºC. $Me_4NBH(OAc)_3$ (1.8 g, 7.0 mmol, 7.0 equiv) was added and the solution was stirred at that temperature for 16 h. The reaction mixture was diluted with EtOAc (25 mL) and quenched by the addition of *sat. aq.* $NaHCO_3$ (10 mL). The layers were separated and the organic layer was

further washed with *sat. aq.* $NaHCO_3$ (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (50% → 75% EtOAc in hexanes) to afford diol **15** (190 mg, 0.64 mmol, 64% yield over three steps), a white solid (mp: 183 – 185 ºC, bp: 212 – 215 ºC), as a single diastereomer. Characterization data were in agreement with the previously reported values.[5] $[\alpha]_D^{23}$ = –118.0 (*c* 0.5, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.31 (d, *J* = 9.9 Hz, 1H), 3.96 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.91 (d, *J* = 9.9 Hz, 1H), 2.84 (d, *J* = 19.7 Hz, 1H), 2.81 (d, *J* = 19.7 Hz, 1H), 2.13 (dp, *J* = 13.2, 6.8 Hz, 1H), 2.02 (dd, *J* = 13.7, 5.6 Hz, 1H), 1.95 (dd, *J* = 14.4, 4.1 Hz, 1H), 1.88 – 1.72 (m, 3H), 1.27 (s, 3H), 1.15 (qd, *J* = 12.5, 5.4 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 177.7, 100.1, 81.1, 75.1, 73.6, 50.4, 50.2, 45.0, 39.0, 38.5, 37.0, 31.4, 19.2, 15.2; IR (thin film) ν_{max}: 3431, 2958, 1762 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_6Na$ $[M+Na]^+$: 319.1158, found: 319.1151.

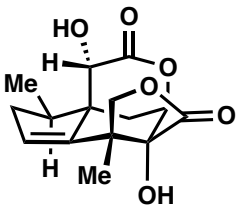


Diol 21. Enol lactone **14** (20 mg, 0.072 mmol, 1.0 equiv) was dissolved in pyridine (360 μL) and SeO_2 (16 mg, 0.144 mmol, 2.0 equiv) was added. The solution was heated at 110 ºC for 16 h. The suspension was filtered through celite and concentrated. The intermediate epimeric α-ketol was sensitive and thus not subjected to additional work-up or purification. Instead, the crude residue was directly dissolved in MeCN/AcOH (3:1, 800 μL) and cooled to –40 ºC. $Me_4NBH(OAc)_3$ (130 mg, 0.50 mmol, 7.0 equiv) was added and the resulting solution was stirred at that temperature for 16 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched by the addition of *sat. aq.* $NaHCO_3$ (5 mL). The layers were separated and the organic layer was further washed with *sat. aq.* $NaHCO_3$ (5 mL) and brine (5 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by preparative TLC (50% EtOAc in hexanes) to afford diol **21** (11 mg, 0.037 mmol, 51%), a white solid (mp > 250 ºC), as a single diastereomer. $[\alpha]_D^{23}$ = –90.8 (*c* 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 4.97 (d, *J* = 10.0 Hz, 1H), 4.07 (d, *J* = 10.0 Hz, 1H), 3.97 (s, 1H), 2.81 (d, *J* = 18.4 Hz, 1H), 2.44 (d, *J* = 18.4 Hz, 1H), 2.26 (d, *J* = 13.7 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.02 – 1.90 (m, 2H), 1.83 (d, *J* = 13.7 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.25 (s, 3H), 1.03 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.8, 175.0, 108.4, 87.6, 75.6, 75.0, 62.2, 47.6, 47.2, 44.9, 40.0, 35.7, 32.7,

20.1, 14.2; IR (thin film) ν_{max}: 3400, 2957, 1736, 1717, 1004 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}O_6Na$ $[M+Na]^+$: 319.1158, found: 319.1153.

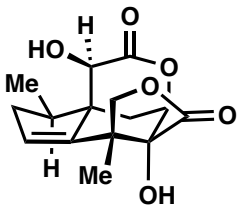


Lactone 16. Diol **15** (82 mg, 0.27 mmol, 1.0 equiv) was dissolved in *n*-BuOH (8 mL) and TsOH•H_2O (113 mg, 0.594 mmol, 2.2 equiv) was added. The solution was heated at 150 ºC for 26 h. The reaction mixture was cooled to room temperature and directly concentrated. The crude residue was purified by column chromatography (30% → 45% EtOAc in hexanes) to afford lactone **16** (55 mg, 0.20 mmol, 71%) as a white foam. Characterization data were in agreement with the previously reported values.[6] $[\alpha]_D^{23}$ = –70.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 5.97 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.73 (dd, *J* = 4.6, 1.5 Hz, 1H), 4.01 (d, *J* = 9.8 Hz, 1H), 3.74 (br d, *J* = 9.8 Hz, 1H), 2.70 (d, *J* = 18.4 Hz, 1H), 2.42 (ddd, *J* = 15.3, 6.7, 3.4 Hz, 1H), 2.42 (dd, *J* = 18.4, 2.8 Hz, 1H), 2.19 (dd, *J* = 13.8, 4.6 Hz, 1H), 2.09 (dp, *J* = 10.8, 6.7 Hz, 1H), 2.04 (ddd, *J* = 15.3, 10.8, 1.7 Hz, 1H), 1.89 (ddd, *J* = 13.8, 2.8, 1.5 Hz, 1H), 1.32 (br s, 3H), 1.06 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 178.9, 172.6, 148.0, 130.6, 81.3, 78.1, 76.7, 46.3, 46.1, 43.4, 38.5, 38.4, 30.9, 22.6, 13.8; IR (thin film) ν_{max}: 3412, 2958, 1772, 1739, 1366 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}O_5Na$ $[M+Na]^+$: 301.1052, found: 301.1055.

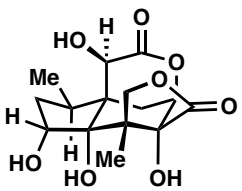


Alcohol 17. Lactone **16** (37 mg, 0.131 mmol, 1.0 equiv) was dissolved in THF (1.3 mL) and cooled to –78 ºC. LHMDS (1.0 M in THF, 0.4 mL, 0.40 mmol, 3.0 equiv) was added and the solution was stirred for 30 min. MoOPH (280 mg, 0.665 mmol, 5.0 equiv) was added in a single portion and the solution was allowed to slowly warm to 0 ºC. The reaction mixture was stirred for 2 h and then was quenched with HCl (1 M, 5 mL). EtOAc (5 mL) was added and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with saturated *aq*. $Na_2S_2O_3$ (5 mL) and brine (5 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (50% → 75% Et_2O in hexanes) to afford alcohol **17** (25 mg, 0.085 mmol, 65%) as a white foam. Characterization data were in agreement with the previously reported values.[6] $[\alpha]_D^{23}$ = –64.7 (*c* 0.3, MeOH); ^{1}H NMR

(700 MHz, CD_3OD) δ 6.14 (dd, *J* = 3.8, 1.7 Hz, 1H), 4.72 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.05 (d, *J* = 1.6 Hz, 1H), 3.98 (d, *J* = 9.8 Hz, 1H), 3.73 (br d, *J* = 9.8 Hz, 1H), 2.79 (dd, *J* = 13.8, 5.0 Hz, 1H), 2.37 (ddd, *J* = 16.1, 7.0, 3.8 Hz, 1H), 2.19 (ddd, *J* = 16.1, 11.0, 1.7 Hz, 1H), 2.10 (dqd, *J* = 11.0, 7.3, 7.0 Hz, 1H), 1.75 (ddd, *J* = 13.8, 1.6, 1.2 Hz, 1H), 1.30 (br s, 3H), 1.22 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (176 MHz, CD_3OD) δ 179.3, 172.5, 146.2, 134.3, 81.5, 77.18, 77.16, 70.8, 50.8, 49.5, 43.0, 38.5, 24.5, 24.3, 16.5; IR (thin film) ν_{max}: 3434, 2959, 1766, 1728, 1369 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ $[M+Na]^+$: 317.1001, found: 317.1011.

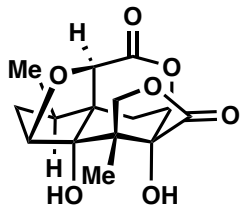


Alcohol 18. Operations for this reaction were carried out in a nitrogen-filled glove box. Alcohol **17** (6 mg, 0.02 mmol, 1.0 equiv), $[Ru_2(PEt_3)_6(OTf)_3](OTf)$ (3.1 mg, 0.002 mmol, 0.1 equiv), and *N*-methylmorpholine (0.5 μL, 0.004 mmol, 0.2 equiv) were combined and dissolved in TFE:dioxane (1:1, 0.3 mL). The solution was heated at 120 ºC for 18 h. At this point, the solution was cooled to room temperature. Degassed, anhydrous *i*PrOH (10 μL) was added. The solution was heated at 120 ºC for an additional 5 h. The reaction mixture was cooled to room temperature and concentrated directly. The crude residue was purified by preparative TLC (100% Et_2O) to afford epimeric alcohol **18** (4.5 mg, 0.015 mmol, 75%), a white solid (mp > 250 ºC), as a single diastereomer. $[\alpha]_D^{23}$ = –23.0 (*c* 0.1, MeOH); ^1H NMR (600 MHz, CD_3OD) δ 6.08 (dd, *J* = 3.3, 1.7 Hz, 1H), 4.60 (d, *J* = 4.0 Hz, 1H), 4.21 (s, 1H), 3.93 (d, *J* = 10.3 Hz, 1H), 3.89 (d, *J* = 10.3 Hz, 1H), 2.33 (ddd, *J* = 15.1, 7.9, 3.3 Hz, 1H), 2.29 (dd, *J* = 14.1, 4.0 Hz, 1H), 2.17 (ddd, *J* = 15.1, 10.4, 1.7 Hz, 1H), 2.10 (ddq, *J* = 10.4, 7.9, 6.8 Hz, 1H), 1.94 (d, *J* = 14.1 Hz, 1H), 1.35 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 178.9, 176.1, 141.8, 133.7, 80.8, 78.5, 76.0, 72.3, 50.9, 46.7, 43.3, 40.3, 32.1, 22.8, 13.5. IR (thin film) ν_{max}: 3443, 2958, 1770, 1729, 1634, 1368; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ $[M+Na]^+$: 317.1001, found: 317.1004.



(–)-majucin (1). TMEDA (5.6 μL, 0.037 mmol, 1.0 equiv) and OsO_4 (9.5 mg, 0.037 mmol, 1.0 equiv) were combined in DCM (3.7 mL) at –78 ºC, creating a bright orange-red solution. The so-

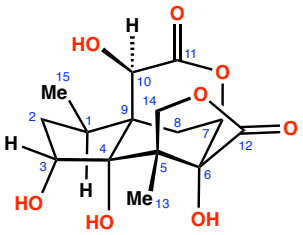
prepared OsO_4•TMEDA solution was quickly added via syringe into neat alcohol **18** (11 mg, 0.037 mmol, 1.0 equiv) at –78 ºC and the reaction mixture was slowly warmed up to 0 ºC over 2 h, upon which the solution had turned completely golden-brown. Water (3.7 mL) was added directly to the reaction mixture, followed by sodium bisulfite (40 mg, 0.37 mmol, 10.0 equiv). The resulting biphasic mixture was vigorously stirred at room temperature for 16 h. During this time, the organic layer gradually turned colorless, while the aqueous phase turned a deep purple. HCl (2 M, 5 mL) and EtOAc (5 mL) were added and the layers were separated. The aqueous layer was further extracted with EtOAc (5 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by preparative TLC (100% EtOAc) to afford (–)-majucin (7.5 mg, 0.023 mmol, 61%), a white solid (mp = 248 – 250 ºC), as a single diastereomer. $[\alpha]_D^{23}$ = –60.7 (*c* 0.15, dioxane); ^{1}H NMR (700 MHz, C_5D_5N, referenced to Me_4Si at δ = 0.00 ppm) δ 8.96 (br d, *J* = 4.7 Hz, 1H), 8.41 (br s, 1H), 6.94 (br s, 1H), 5.25 (br s, 1H), 5.21 (br dd, *J* = 9.1, 4.3 Hz, 1H), 5.15 (dd, *J* = 3.4, 2.4 Hz, 1H), 5.12 (br d, *J* = 10.9 Hz, 1H), 4.66 (d, *J* = 4.7 Hz, 1H), 4.31 (d, *J* = 10.9 Hz, 1H), 3.12 (dd, *J* = 14.2, 2.4 Hz, 1H), 3.03 (ddq, *J* = 10.3, 9.1, 7.0 Hz, 1H), 2.48 (dt, *J* = 12.8, 9.1 Hz, 1H), 2.22 (ddd, *J* = 12.8, 10.3, 4.3 Hz, 1H), 2.05 (dd, *J* = 14.2, 3.4 Hz, 1H), 1.95 (br s, 3H), 1.11 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, C_5D_5N, referenced to Me_4Si at δ = 0.00 ppm) δ 177.9, 174.9, 82.9, 80.7, 80.0, 72.7, 72.5, 70.4, 51.6, 47.6, 43.0, 38.2, 27.1, 20.9, 14.2. IR (thin film) ν_{max}: 3390, 2936, 1719, 1077; HRMS (ESI) calcd for $C_{15}H_{19}O_8$ $[M–H]^-$: 327.1085, found: 327.1082.



(–)-jiadifenoxolane A (2). (–)-majucin (3.0 mg, 0.009 mmol, 1.0 equiv) and pyridine (7.4 µL, 0.09 mmol, 10.0 equiv) were dissolved in 1,2-dichloroethane (0.3 mL). MsCl (3.6 µL, 0.045 mmol, 5.0 equiv) was added and the solution was stirred for 2h at room temperature. At this point, the reaction mixture was heated to 80 ºC and stirred at that temperature for 15 h. The solution was cooled to room temperature and HCl (1 M, 1 mL) and EtOAc (2 mL) were added. The aqueous layer was further extracted with EtOAc (5 x 2 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by preparative TLC (100%

EtOAc) to afford (–)-jiadifenoxolane A (2.6 mg, 0.008 mmol, 92%) as an amorphous white solid. $[\alpha]_D^{23}$ = –62.0 (*c* 0.1, MeOH); ^{1}H NMR (600 MHz,CD_3OD) δ 4.71 (br d, *J* = 11.2 Hz, 1H), 4.67 (br d, *J* = 3.8 Hz, 1H), 4.37 (s, 1H), 4.09 (br s, 1H), 4.01 (d, *J* = 11.2 Hz, 1H), 2.60 (dqd, *J* = 10.3, 7.1, 5.5 Hz, 1H), 2.30 (br dd, *J* = 13.2, 10.3 Hz, 1H), 2.23 (br d, *J* = 14.6 Hz, 1H), 2.15 (dd, *J* = 14.5, 3.5 Hz, 1H), 1.34 (br s, 3H), 1.23 (dd, *J* = 13.2, 5.5 Hz, 1H), 1.07 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, MeOD) δ 178.8, 171.2, 82.0, 81.4, 81.1, 77.5, 74.9, 73.5, 51.5, 46.2, 39.9, 34.5, 22.6, 20.1, 13.4; IR (thin film) ν_{max}: 3434, 2959, 1766, 1738, 1012 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{17}O_7$ $[M–H]^-$: 309.0980, found: 309.0979.

(–)-Majucin ^{1}H NMR spectra comparison:

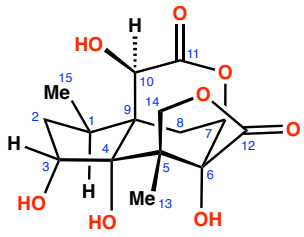


(–)-majucin

Position	^{1}H NMR (δ) Natural Sample (400 MHz, C_5D_5N)[7]	^{1}H NMR (δ) Synthetic Sample (700 MHz, C_5D_5N)
1	3.02 (ddq, *J* = 10.2, 9.5, 7.0 Hz, 1H)	3.03 (ddq, *J* = 10.3, 9.1, 7.0 Hz, 1H)
2β	2.48 (dt, *J* = 12.6, 9.5 Hz, 1H)	2.48 (dt, *J* = 12.8, 9.1 Hz, 1H)
2α	2.21 (ddd, *J* = 12.6, 10.2, 4.4 Hz, 1H)	2.22 (ddd, *J* = 12.8, 10.3, 4.3 Hz, 1H)
3	5.21 (dd, *J* = 9.5, 4.4 Hz, 1H)	5.22 (dd, *J* = 9.1, 4.3 Hz, 1H)
3-OH	-	5.25 (br s, 1H)
4-OH	-	6.94 (br s, 1H)*
5	-	-
6-OH	-	8.41 (br s, 1H)*
7	5.14 (dd, *J* = 3.3, 2.2 Hz, 1H)	5.15 (dd, *J* = 3.4, 2.4 Hz, 1H)
8β	2.05 (dd, *J* = 14.3, 3.3 Hz, 1H)	2.05 (dd, *J* = 14.2, 3.4 Hz, 1H)
8α	3.11 (dd, *J* = 14.3, 2.2 Hz, 1H)	3.12 (dd, *J* = 14.2, 2.4 Hz, 1H)
9	-	-
10	4.65 (br d, *J* = 4.5 Hz, 1H)	4.66 (d, *J* = 4.7 Hz, 1H)
10-OH	8.95 (br d, *J* = 4.5 Hz, 1H)	8.96 (br d, *J* = 4.7 Hz, 1H)
11	-	-
12	-	-
13	1.95 (br s, 3H)	1.95 (br s, 3H)
14	4.30 (d, *J* = 10.8 Hz, 1H) 5.11 (br d, *J* = 10.8 Hz, 1H)	4.31 (d, *J* = 10.9 Hz, 1H) 5.12 (br d, *J* = 10.9 Hz, 1H)
15	1.10 (d, *J* = 7.0 Hz, 3H)	1.11 (d, *J* = 7.0 Hz, 3H)

*Indicates tentative assignment.

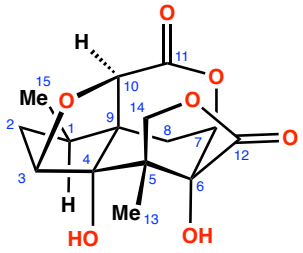
(–)-Majucin ^{13}C NMR spectra comparison:



(–)-majucin

Position	^{13}C NMR (δ) Natural Sample (101 MHz, C_5D_5N)[7]	^{13}C NMR (δ) Synthetic Sample (151 MHz, C_5D_5N)
1	38.0	38.2
2	42.9	43.0
3	72.7	72.7
4	82.8	82.9
5	47.5	47.6
6	79.9	80.0
7	80.6	80.7
8	27.1	27.1
9	51.5	51.6
10	70.3	70.4
11	174.7	174.9
12	177.6	177.9
13	20.9	20.9
14	72.4	72.5
15	14.1	14.2

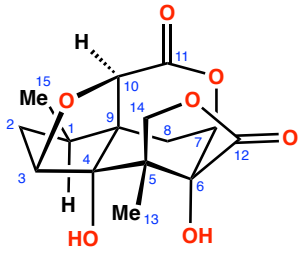
(–)-Jiadifenoxolane A ^{1}H NMR Spectra Comparison:



(–)-jiadifenoxolane A

Position	^{1}H NMR (δ) Natural Sample (600 MHz, CD_3OD)[8]	^{1}H NMR (δ) Synthetic Sample (600 MHz, CD_3OD)
1	2.59 (dqd, *J* = 10.3, 7.1, 5.4 Hz, 1H)	2.60 (dqd, *J* = 10.3, 7.1, 5.5 Hz, 1H)
2β	2.30 (ddd, *J* = 13.0, 10.3, 2.6 Hz, 1H)	2.30 (br dd, *J* = 13.2, 10.3 Hz, 1H)
2α	1.22 (dd, *J* = 13.0, 5.4 Hz, 1H)	1.23 (dd, *J* = 13.2, 5.5 Hz, 1H)
3	4.08 (d, *J* = 2.6 Hz, 1H)	4.09 (br s, 1H)
4	-	-
5	-	-
6	-	-
7	4.66 (dd, *J* = 4.0, 1.9 Hz, 1H)	4.67 (br d, *J* = 3.8 Hz, 1H)
8β	2.15 (dd, *J* = 14.7, 4.0 Hz, 1H)	2.15 (dd, *J* = 14.6, 3.5 Hz, 1H)
8α	2.23 (dd, *J* = 14.7, 1.9 Hz, 1H)	2.23 (br d, *J* = 14.6 Hz, 1H)
9	-	-
10	4.36 (s,1H)	4.37 (s, 1H)
11	-	-
12	-	-
13	1.33 (d, *J* = 1.1 Hz, 3H)	1.34 (br s, 3H)
14β	4.70 (dd, *J* = 11.1, 1.1 Hz, 1H)	4.71 (br d, *J* = 11.2 Hz, 1H)
14α	4.00 (d, *J* = 11.1 Hz, 1H)	4.01 (d, *J* = 11.2 Hz, 1H)
15	1.06 (d, *J* = 7.1 Hz, 3H)	1.07 (d, *J* = 7.1 Hz, 3H)

(–)-Jiadifenoxolane A ^{13}C NMR Spectra Comparison:



(–)-jiadifenoxolane A

Position	^{13}C NMR (δ) Natural Sample (150 MHz, CD_3OD)[8]	^{13}C NMR (δ) Synthetic Sample (151 MHz, CD_3OD)
1	34.5	34.5
2	39.9	39.9
3	82.0	82.0
4	81.4	81.4
5	46.1	46.2
6	77.5	77.5
7	81.1	81.1
8	20.1	20.1
9	51.5	51.5
10	73.5	73.5
11	171.2	171.2
12	178.9	178.8
13	22.6	22.6
14	74.9	74.9
15	13.4	13.4

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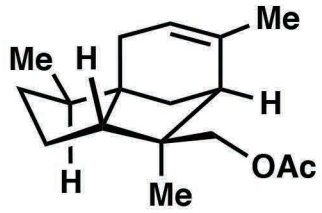
8. Kubo, M.; Okada, C.; Huang, J.-M.; Harada, K.; Hioki, H.; Fukuyama, Y. *Org. Lett.* **2009**, *11*, 5190.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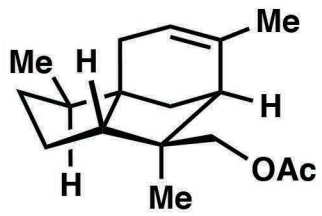
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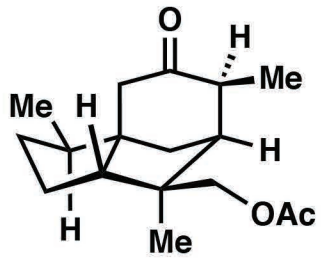
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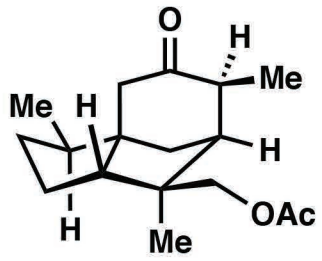
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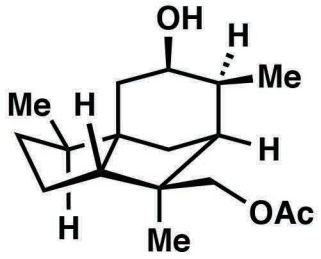
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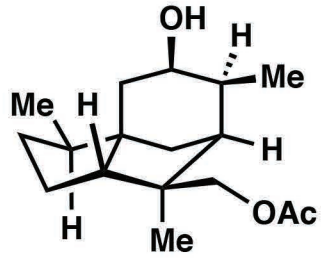
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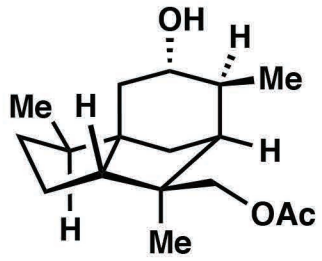
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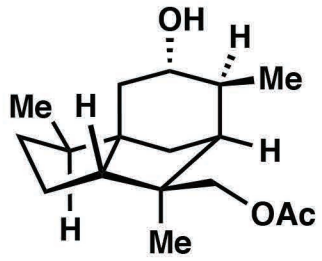
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Me

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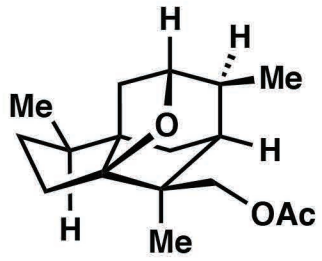
f1 (ppm)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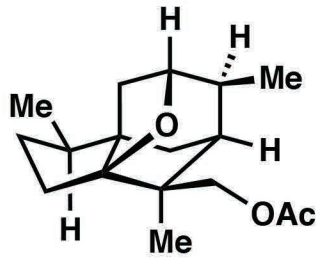
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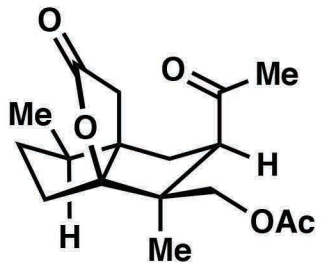
f1 (ppm)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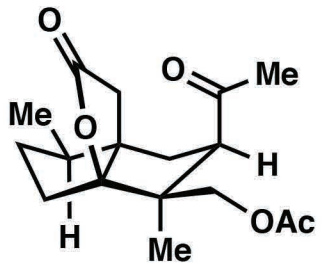
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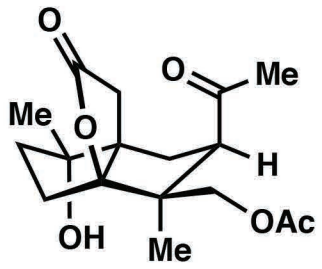
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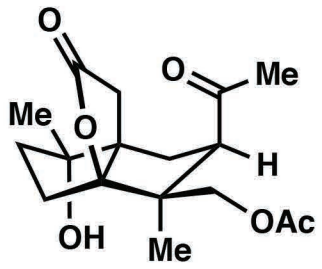
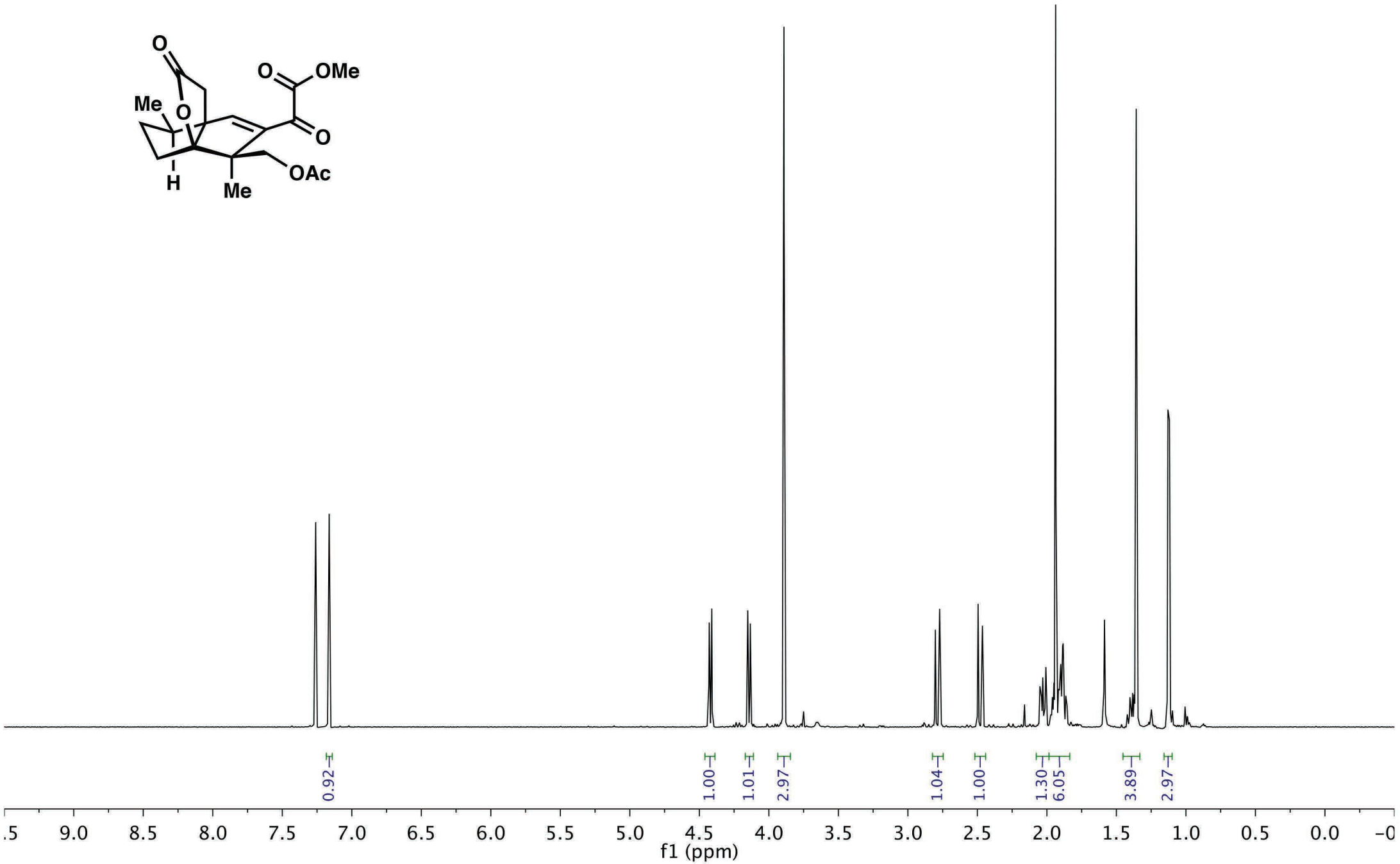
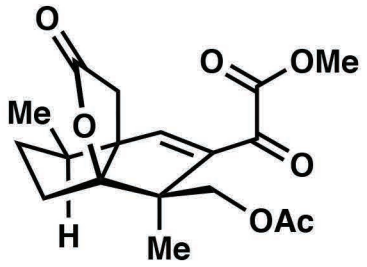
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

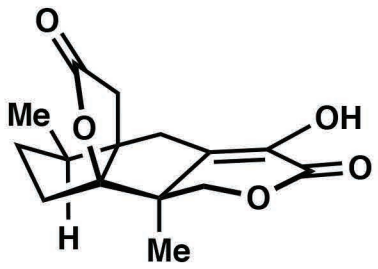

O
O
Me
Me
O
H
OAc
OH
Me

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

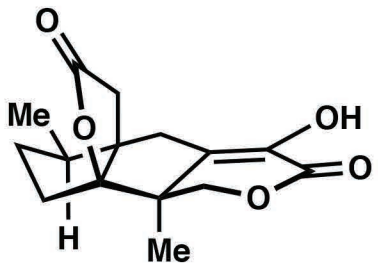

O
O
OMe
Me
O
O
OAc
H
Me
0.92
1.00
1.01
2.97
1.04
1.00
1.30
6.05
3.89
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
OMe
Me
O
O
OAc
H
Me

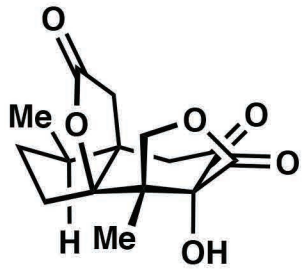
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
Me
O
OH
O
O
H
Me

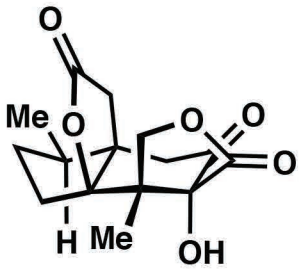
1.03
1.00
1.03
2.03
1.00
1.01
1.06
2.08
1.05
1.31
3.03
3.28
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


O
Me
O
OH
O
O
H
Me

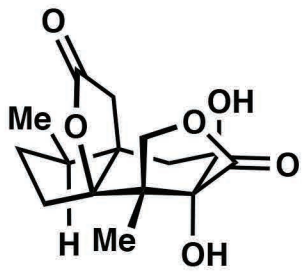
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
Me
O
O
O
O
H
Me
OH

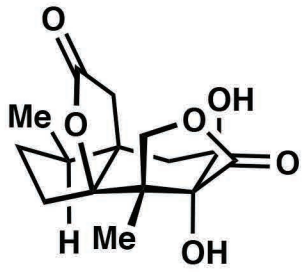
1.00
1.02
0.90
1.00
1.02
1.03
1.00
1.04
1.06
1.16
1.12
3.04
1.06
3.10
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


O
Me
O
O
O
O
H
Me
OH

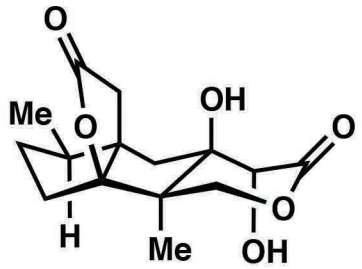
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
Me
O
O
OH
O
H
Me
OH

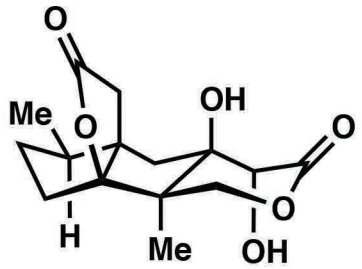
1.00
1.05
1.00
2.10
1.13
1.14
1.09
3.12
3.29
1.34
3.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
Me
O
O
OH
O
H
Me
OH

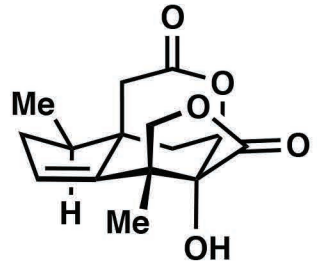
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Me
O
OH
O
O
H
Me
OH

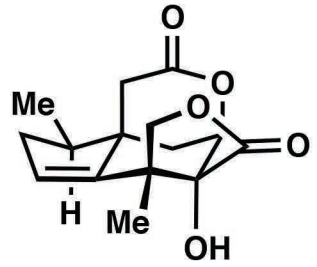
1.00
0.99
0.91
1.01
1.00
2.04
2.01
1.04
2.06
3.10
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
Me
O
OH
O
O
H
Me
OH

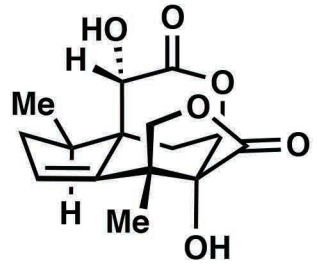
f1 (ppm)


O
O
O
O
Me
H
Me
OH

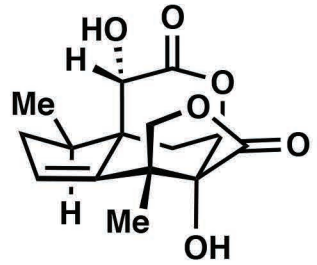
1.00
1.01
1.07
1.10
1.06
2.14
1.21
2.27
1.14
3.23
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
Me
O
O
H
Me
OH

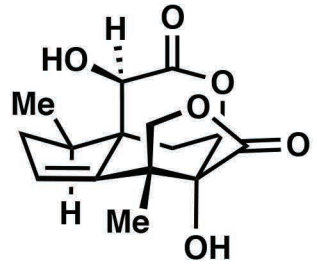
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
H
O
Me
O
O
H
Me
OH

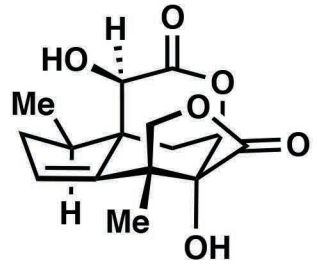
1.00
0.96
0.97
1.04
1.03
1.00
1.04
1.15
1.08
1.09
3.65
3.25
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


HO
O
H
O
Me
O
O
H
Me
OH

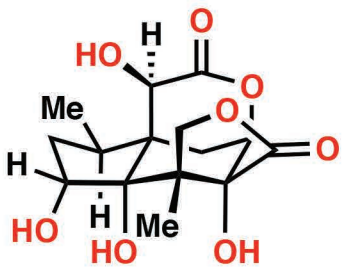
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


H
O
HO
O
Me
O
O
H
Me
OH

1.00
0.97
0.99
1.03
1.03
2.07
1.07
1.07
1.06
3.12
3.10
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

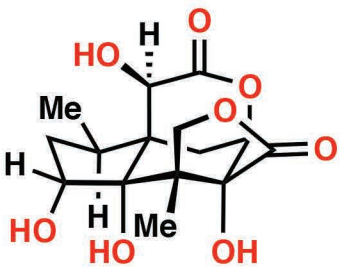

H
O
HO
O
Me
O
O
H
Me
OH

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


HO
H
O
O
O
Me
O
H
HO
H
Me
HO
OH

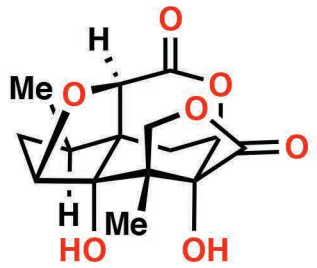
(–)-majucin (**1**)

1.00
0.97
0.94
0.84
0.91
0.87
0.92
1.00
1.03
1.00
1.08
1.05
1.07
1.04
2.65
2.65
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

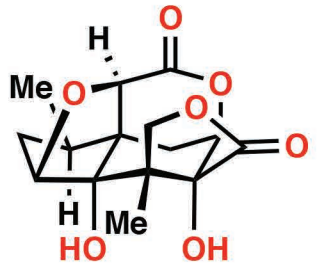

HO
H
O
O
O
Me
O
H
HO
H
Me
HO
OH

(–)-majucin (**1**)

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



(–)-jiadifenoxolane A (**2**)



(–)-jiadifenoxolane A (**2**)