**Organic Letters**

**Supporting Information to Accompany:**

# Asymmetric Synthesis of the Tricyclic Core of Cyathane Diterpenes via a Transition Metal Catalyzed [5+2] Cycloaddition

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## Experimental Section

**General:** Unless otherwise noted all reactions were run under an argon atmosphere, distilled solvents and reagents were transferred by syringe or stainless steel cannula. Diethyl ether was purified as described in the procedure published by Grubbs and co-workers in: *Organometallics* **1996**, *15*, 1518-1520. Tetrahydrofuran (THF) was distilled from sodium / benzophenone immediately before use; $CH_2Cl_2$ was distilled from $CaH_2$; 1,2-dichloroethane was dried and stored over 4Å molecular sieves. Final reaction mixture solutions were dried over $MgSO_4$. Melting points are uncorrected. Analytical thin-layer chromatography (TLC) was performed by using glass or aluminum-backed silica plates coated with a 0.2 mm thickness of silica gel 60 $F_{254}$ (Merck), visualized with UV light, iodine, *p*-anisaldehyde solution, potassium permanganate solution and ceric ammonium molybdate solution. Chromatography was performed using Kieselgel 60 (230-400 mesh). Infra-red spectra were recorded on a Perkin-Elmer 1600 Series Fourier Transform Spectrometer and are reported in wavenumbers ($cm^{-1}$). Unless otherwise noted, $^1H$ NMR (500 MHz) and $^{13}C$ NMR (125 MHz) spectra were recorded in $CDCl_3$ on a Varian Inova Spectrometer. Chemical shifts are reported in ppm (δ units) downfield of internal tetramethylsilane ($(CH_3)_4Si$), or residual $CHCl_3$; coupling constants are reported in hertz. Multiplicities are reported as follows: s =

singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dsep = doublet of septet, td = triplet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are within error limits of ±13 millimass units. Elemental analyses were determined by Desert Analytics, Tucson, Arizona. Reported atomic percentages are within error limits of ±0.4%.

**(5*R*)-Isopropyl-2-methyl-cyclopent-1-enecarbaldehyde**

Freshly distilled (*S*)-limonene (50.0 g, 0.37 mol) and $PtO_2$ (100 mg, 0.44 mmol) were introduced in a Parr hydrogenation reactor. The mixture was hydrogenated at 2 atm (206.8 kPa, 30 psi) and the exothermic reaction was monitored by $^1$H NMR spectroscopy. After 1.5 h, the mixture was filtered through a plug of diatomaceous earth to give (4*S*)-isopropyl-1-methyl-cyclohexene: 47.6 g, 94%, colorless oil, $[\alpha]_D^{23}$ –78.8 (*c* 1.09, $CHCl_3$); $^1$H NMR (200 MHz) δ 5.39-5.42 (m, 1 H), 1.70-2.06 (m, 5 H), 1.67 (s, 3 H), 1.44-1.53 (m, 1 H), 1.20-1.31 (m, 2 H), 0.93 (d, 3 H, *J* = 6.0), 0.91 (d, 3 H, *J* = 6.0). HRMS calcd for $C_{10}H_{18}$ [$M^+$]: 138.1409, found: 138.1404.

A stirred solution of (4*S*)-isopropyl-1-methylcyclohexene (13.0 g, 94 mmol) in THF (250 mL) and water (120 mL) at rt was treated with a solution of $OsO_4$ (5 mL, 0.94 mmol, 1 mol%, 4% wt in water). The solution became black instantly and $NaIO_4$ (49.8 g, 235 mmol, 250 mol%) was added in portions over 15 min. The thick mixture was stirred at rt for 48 h, filtered through diatomaceous earth and the filter cake was washed thoroughly with EtOAc. The layers were separated and the organic layer was washed with brine, dried and evaporated to a residue that was filtered through a plug of silica gel eluting with EtOAc. Evaporation of the filtrate gave (3*S*)-isopropyl-6-oxoheptanal: 15.5 g, 97%, colored oil; TLC $R_f$ = 0.27 (1:4 $Et_2O$ : pentane); IR (neat) 3419, 2960, 2876, 2722, 1720, 1368, 1164, 1023. $^1$H NMR δ 9.79 (d, 1 H, *J* = 2.2), 2.44 (m, 3 H), 2.25 (m, 1 H), 2.16 (s, 3 H), 1.90 (bm, 1 H), 1.64-1.78 (m, 2 H), 1.51 (m, 1 H), 0.90 (d, 3 H, *J* = 6.8), 0.87 (d, 3 H, *J* = 6.8); $^{13}$C NMR δ 208.5, 202.9, 45.4, 41.6, 37.7, 30.1, 29.9, 25.4, 19.6, 18.2. HRMS calcd for $C_{10}H_{18}O_2$ [$M^+$]: 170.1307, found: 170.1307.

A solution of (3*S*)-isopropyl-6-oxoheptanal (7.0 g, 41.1 mmol) in diethyl ether (230 mL) was treated with piperidine (1.40 mL, 14.1 mmol) and the solution was stirred at rt for 15 min. Glacial acetic acid (1.40 mL, 24.5 mmol) was added and the mixture was heated at a reflux for 24 h. After cooling to rt, evaporation of the volatiles and chromatography of the residue using 20% ethyl acetate in pentane as eluant gave (5*R*)-isopropyl-2-methyl-cyclopent-1-enecarbaldehyde **4**: 4.69 g, 75%, colorless oil, TLC $R_f$ = 0.67 (1:4 $Et_2O$ : pentane); $[\alpha]_D^{22}$ +6.74 (*c* 1.0, $CHCl_3$); IR (neat) 3312, 2957, 2870, 1667, 1632, 1466, 1380, 1279. $^1$H NMR δ 10.01 (s, 1 H), 3.05 (bm, 1 H), 2.52 (m, 1 H), 2.42 (m, 1 H), 2.14 (s, 3 H), 1.80 (m, 1 H), 1.70 (m, 1 H), 0.89 (d, 3 H, *J* = 6.8), 0.65 (d, 3 H, *J* = 6.8); $^{13}$C NMR δ 188.5, 163.7, 139.9, 49.7, 40.0, 28.7, 21.9, 21.2, 16.2, 14.3. HRMS calcd for $C_{10}H_{16}O$ [$M^+$]: 152.1201, found: 152.1203.

**(5*R*)-(5-Isopropyl-2-methyl-cyclopent-1-enyl)methanol**

A solution of aldehyde **4** (5.60 g, 36.9 mmol) in diethyl ether (80 mL) at 0˚C was treated with DIBAL-H (40.6 mL, 40.6 mmol, 1.0 M in hexanes). The solution was stirred at 0˚C for 5 min, quenched with acetone (2 mL) and saturated aqueous $NaHCO_3$ (5 mL). Solid sodium-potassium tartrate (5.60 g) was added and the mixture was stirred vigorously for 1 h at rt. The solution was then diluted with EtOAc and filtered on a pad of diatomaceous earth. The filter cake was washed thoroughly with EtOAc and the filtrate was washed with brine. The organic layer was dried and evaporated to a residue that was filtered through a plug of silica gel. Evaporation of the filtrate afforded (5*R*)-(5-isopropyl-2-methyl-cyclopent-1-enyl)methanol: 5.44 g, 96%, TLC $R_f$ = 0.33 (1:4 $Et_2O$ : pentane); $[\alpha]_D^{23}$ –10.9 (*c* 1.05, $CHCl_3$); IR (neat) 3326, 2955, 2871, 1466, 1383, 1366, 1007. $^1$H NMR δ 4.26 (d, 1 H, *J* = 12.0), 4.02 (d, 1 H, *J* = 12.0), 2.85 (bt, 1 H, *J* = 1.7), 2.24 (m, 2 H), 2.00 (m, 1 H), 1.76 (m, 1 H), 1.71 (s, 3 H), 1.61 (m, 1 H), 0.93 (d, 3 H, *J* = 6.8), 0.67 (d, 3 H, *J* = 7.1); $^{13}$C NMR δ 137.3, 136.2, 57.3, 51.7, 37.8, 28.6, 21.6, 21.3, 15.8, 13.8. HRMS calcd for $C_{10}H_{18}O$ [$M^+$]: 154.1358, found: 154.1355. Anal. calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.49; H, 11.96.

**(1*R*,3*R*)-(3-Isopropyl-1-methyl-2-methylene-cyclopentyl)-acetaldehyde (5)**

A solution of alcohol (5*R*)-(5-isopropyl-2-methyl-cyclopent-1-enyl)methanol (5.40 g, 35 mmol) in ethyl vinyl ether (50 mL) was treated with $Hg(OAc)_2$ (558 mg, 1.75 mmol, 5 mol%) and heated at a reflux for 20 h. The mixture was filtered on basic alumina and the volatiles were removed under vacuum to give (3*R*)-isopropyl-1-methyl-2-vinyloxymethyl-cyclopentene: 6.23 g, 99%, colorless oil; TLC $R_f$ = 0.89 (5:95 $Et_2O$ : pentane); $[\alpha]_D^{23}$ +8.27 (*c* 1.0, $CHCl_3$); IR (neat) 2956, 1633, 1608, 1466, 1316, 1196, 1046, 810. $^1$H NMR δ 6.51 (dd, 1 H, *J* = 6.8, 14.4), 4.33 (d, 1 H, *J* = 11.4), 4.24 (dd, 1 H, *J* = 1.95, 14.4), 4.14 (dd, 1 H, *J* = 11.4), 4.02 (dd, 1 H, *J* = 6.8, 1.95), 2.55 (m, 1 H), 2.28 (dd, 1 H, *J* = 7.0, 7.6), 1.97 (m, 1 H), 1.81 (m, 1 H), 1.74 (s, 3 H), 1.62 (m, 1 H), 0.93 (d, 3 H, *J* = 6.8), 0.70 (d, 3 H, *J* = 6.8); $^{13}$C NMR δ 151.9, 139.3, 132.5, 86.3, 63.0, 52.1, 37.9, 28.6, 21.7, 21.3, 15.9, 14.1. HRMS calcd for $C_{12}H_{20}O$ [$M^+$]: 180.1514, found: 180.1517. The residue was dissolved in toluene (5 mL), placed in a resealable pressure tube. The solution was degassed with argon bubbles for 10 min, the tube was sealed and the solution was then heated at 200˚C for 2 h behind a blast shield. After cooling to rt, the reaction mixture was chromatographed using 0-5% diethyl ether in pentane as eluant. Evaporation of the collected fractions gave aldehyde **5**: 5.70 g, 90%, colorless oil, TLC $R_f$ = 0.55 (5:95 $Et_2O$ : pentane), $[\alpha]_D^{23}$ +90.8 (*c* 1.07, $CHCl_3$); IR (neat) 3425, 2958, 2873, 2731, 1723, 1646, 1465, 1384, 885. $^1$H NMR δ 9.71 (t, 1 H, *J* = 2.9), 4.89 (d, 1 H, *J* = 2.9), 4.87 (d, 1 H, *J* = 2.4), 2.46-2.48 (m, 3 H), 1.95-2.01 (m, 1 H), 1.55-1.70 (m, 3 H), 1.41-1.51 (m, 1 H), 1.09 (s, 3 H), 0.97 (d, 3 H, *J* = 6.8), 0.78 (d, 3 H, *J* = 6.8); $^{13}$C NMR δ 203.6, 161.1, 105.0, 54.3, 50.7, 44.1, 37.5, 28.8, 27.7, 23.0, 21.8, 16.4. HRMS calcd for $C_{12}H_{20}O$ [$M^+$]: 180.1514, found: 180.1518. Anal. calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.48; H, 11.21.

**(1*R*, 3*R*)-2-(3-Isopropyl-1-methyl-2-methylene-cyclopentyl)ethanol**

A solution of aldehyde **5** (4.63 g, 25.66 mmol) in MeOH (116 mL) at 0˚C was treated with a solution of $NaBH_4$ (1.46 g, 38.49 mmol, 150 mol%) in $H_2O$ (19 mL). The mixture was let warm to rt over 5 h, quenched with brine and extracted thoroughly with EtOAc. The organic layer was dried and evaporated to a residue that was filtered through a pad of silica gel using ethyl

acetate as the eluant. Evaporation of the filtrate gave (1*R*, 3*R*)-2-(3-isopropyl-1-methyl-2-methylene-cyclopentyl)ethanol: 4.12 g, 88%, TLC $R_f$ = 0.70 (3:7 EtOAc : pentane), $[\alpha]_D^{25}$ +90.2 (*c* 1.05, $CHCl_3$); IR (neat) 3326, 2956, 1645, 1465, 1367, 1050, 881. $^1$H NMR δ 4.89 (d, 1 H, *J* = 2.8), 4.82 (d, 1 H, *J* = 2.8), 3.71 (m, 2 H), 2.45 (m, 1 H), 1.99 (dsep, 1 H, *J* = 4.4, 6.8), 1.81 (ddd, 1 H, *J* = 5.9, 8.1, 13.8), 1.68-1.74 (m, 1 H), 1.54-1.67 (m, 3 H), 1.38-1.46 (m, 2 H), 1.01 (s, 3 H), 0.99 (d, 3 H, *J* = 6.8), 0.79 (d, 3 H, *J* = 6.8); $^{13}$C NMR δ 162.7, 103.7, 60.3, 50.7, 44.6, 44.0, 37.2, 28.8, 27.5, 22.9, 21.9, 16.4. HRMS calcd for $C_{12}H_{22}O$ [$M^+$]: 182.1671, found: 182.1672. Anal. calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.74; H, 12.01.

**(1*R*,3*R*)-*tert*-Butyl-[2-(3-isopropyl-1-methyl-2-methylene-cyclopentyl)-ethoxy]-dimethyl-silane** A solution of (1*R*, 3*R*)-2-(3-isopropyl-1-methyl-2-methylene-cyclopentyl)ethanol (8.59 g, 47.2 mmol) in DMF (75 mL) at 0˚C was treated with imidazole (3.85 g, 56.6 mmol) and *tert*-butyldimethylsilyl chloride (7.82 g, 51.9 mmol). The solution was stirred at 0˚C for 1 h and overnight at rt. The reaction mixture was diluted with diethyl ether, quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The organic layer was dried and the volatiles were removed under vacuum. Chromatography of the residue using 5% EtOAc in hexanes as eluant gave (1*R*,3*R*)-*tert*-butyl-[2-(3-isopropyl-1-methyl-2-methylene-cyclopentyl)-ethoxy]-dimethyl-silane: 14.9 g, 84%, TLC $R_f$ = 0.70 (5:95 $Et_2O$ : pentane), $[\alpha]_D^{23}$ +46.3 (*c* 5.0, $CHCl_3$); IR (neat) 2956, 2859, 1472, 1385, 1255, 1093, 836. $^1$H NMR δ 4.84 (d, 1 H, *J* = 2.8), 4.79 (d, 1 H, *J* = 2.8), 3.67 (m, 2 H), 2.42 (m, 1 H), 1.98 (dsep, 1 H, *J* = 4.4, 6.8), 1.74-1.80 (m, 1 H), 1.53-1.67 (m, 3 H), 1.37-1.46 (m, 2 H), 1.00 (d, 3 H, *J* = 6.8), 0.99 (s, 3 H), 0.91 (s, 9 H), 0.79 (d, 3 H, *J* = 6.8), 0.07 (s, 6 H); $^{13}$C NMR δ 162.5, 103.4, 60.6, 50.8, 44.5, 44.2, 37.3, 28.8, 27.3, 25.9, 23.1, 21.9, 18.3, 16.5, -5.2, -5.3. HRMS calcd for $C_{18}H_{36}Osi$ [$M^+$]: 296.2535, found: 296.2537. Anal. calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 73.06; H, 12.30.

**(2*R*,5*R*)-2-[2-(*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-5-isopropyl-2-methyl-cyclopentanone (6)** To a –78˚C solution of (1*R*,3*R*)-*tert*-butyl-[2-(3-isopropyl-1-methyl-2-methylene-cyclopentyl)-ethoxy]-dimethyl-silane (1.0 g, 3.37 mmol) in $CH_2Cl_2$ (30 mL) was bubbled ozone

until the solution became *very slightly* blue. Argon was then bubbled until the solution was colorless and methyl sulfide (1.24 mL, 16.85 mmol, 500 mol%) was added. The solution was let warm to rt overnight. The volatiles were removed under vacuum and the residue was chromatographed using 0-5% EtOAc in pentane as eluant. First to elute was ketone **6**: 650 mg, 65%, colorless oil, TLC $R_f$ = 0.63 (1:9 EtOAc : petroleum ether). IR (neat) 2957, 2930, 2859, 1733, 1472, 1464, 1387, 1370, 1255, 1185, 1103, 1042, 1001, 523, 837, 812, 776, 662. $^1$H NMR δ 3.64-3.72 (m, 2H), 2.13-2.20 (m, 2H), 1.85-1.96 (m, 2H), 1.63-1.78 (m, 4H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.94 (s, 3H), 0.89 (s, 9H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.048 (s, 3H), 0.041 (s, 3H). $^{13}$C NMR δ 223.7(223.1), 59.6(59.5), 55.2(54.4), 47.4(47.6), 39.9(37.7), 33.2(34.5), 27.0(27.6), 25.9, 21.6(22.6), 21.1(21.2), 20.5(20.8), 18.3(18.6), 18.2, -5.46(-5.37), -5.48(-5.39). HRMS calcd for $C_{13}H_{25}O_2Si$ [$M^+ - C_4H_9$]: 241.1624, found: 241.1630. Anal. calcd for $C_{17}H_{34}O_2Si$: C: 68.39. H: 11.48. Si: 9.41. Found: C: 68.56. H: 11.22. Si: 9.17.

**(1*RS*,2*R*,5*R*)-2-[2-*tert*-Butyl-dimethyl-silanyloxy)-ethyl]-1-cyclopropylethynyl-5-isopropyl-2-methyl-cyclopentanol (7)** To a stirred solution of 1-ethynylcyclopropane (188 mg, 2.84 mmol, 220 mol%) in THF (2.8 mL) at 0 °C was added dropwise *n*-BuLi (1.8 mL, 2.84 mmol, 220 mol%, 1.6 M in hexanes). The solution was stirred for 15 min at 0˚C and transferred via cannula into a suspension of $CeCl_3$ (700 mg, 2.84 mmol, 220 mol%; Note: commercially available anhydrous $CeCl_3$ was dried further *in vacuo* at 160 °C overnight and stirred vigorously in THF overnight before use) in THF (3.0 mL) at 0 °C. The bright yellow solution was stirred for 2 h at 0 °C and a solution of ketone **6** (385 mg, 1.29 mmol, 100 mol%) in THF (3.5 mL) was added via cannula. The resulting solution was stirred for 45 min at 0˚C. The reaction was quenched with saturated aqueous $NaHCO_3$ (15 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (4 × 25 mL). The combined organic layers were dried, filtered, and evaporated to a residue that was chromatographed using 3% EtOAc in petroleum ether as eluant gave **7** as a mixture of diastereoisomers: 430 mg, 91%, light-yellow oil, $R_f$ = 0.53 (1:9 EtOAc : petroleum ether). IR (neat): 3412, 2955, 2870, 1472, 1386, 1362, 1256, 1090, 1029, 968, 928, 837, 811, 775. $^1$H NMR (characteristic cyclopropyl signals) δ

0.74-0.78 (m, 2H), 0.64-0.67 (m, 2H). HRMS calcd for $C_{22}H_{40}O_2Si$ [$M^+$]: 364.2798, found: 364.2806. Anal. calcd for $C_{22}H_{40}O_2Si$: C: 72.47. H: 11.06. Si: 7.70. Found: C: 72.49. H: 11.23. Si: 7.59.

**(1*R*,2*R*,5*R*)-1-((*E*)-2-cyclopropyl-vinyl)-2-(hydroxyethyl)-5-isopropyl-2-methyl-cyclopentanol (8)** To a stirred solution of $LiAlH_4$ (189 mg, 5.06 mmol, 500 mol%) in THF (30 mL) was added sodium methoxide (327 mg, 6.06 mmol, 600 mol%) portion-wise at rt. After stirring for 5 min, a solution of alkyne **7** (369 mg, 1.01 mmol) in THF (10 mL) was added via cannula. The resulting suspension was heated at a reflux for 3 h, cooled to 0˚C and quenched with $H_2O$ (0.2 mL), NaOH (0.2 mL, 15% aqueous) and $H_2O$ (0.6 mL). After stirring at rt overnight, the mixture was filtered through a plug of diatomaceous earth and the filter cake was washed thoroughly with diethyl ether. The filtrate was evaporated and the residue was chromatographed using 20% EtOAc in petroleum ether as eluant to provide diol **8**: 174 mg, 69%, light yellow oil, $[\alpha]_D^{25.6}$ +50.8 (*c* 1.04, $CH_2Cl_2$), TLC $R_f$ = 0.43 (2:5 EtOAc : petroleum ether). IR (thin film, $CDCl_3$) 3391, 3081, 2953, 2871, 1662, 1468, 1371, 1127, 1046, 1016, 974, 946, 809. $^1$H NMR (300 MHz) δ 5.58 (d, 1 H, *J* = 15.6), 5.14 (dd, 1 H, *J* = 15.6, 8.7), 3.68 (t, 2 H, *J* = 7.4), 1.74-1.88 (m, 2H), 1.32-1.68 (m, 6H), 1.26 (s, 1H), 0.89 (d, 6 H, *J* = 6.3), 0.84 (s, 3H), 0.65-0.71 (m, 2H), 0.33-0.37 (m, 2H). $^{13}$C NMR (75 MHz) δ 132.32, 132.25, 84.8, 60.3, 53.6, 50.2, 39.3, 33.1, 29.7, 26.7, 22.9, 22.5, 17.4, 13.6, 6.7, 6.5. HRMS calcd. for $C_{16}H_{28}O_2$ [$M^+$]: 252.2089, found: 252.2086. Anal. calcd for $C_{16}H_{28}O_2$: C: 76.14. H: 11.18. Found: C: 76.12. H: 11.46.

**(1*R*,2*R*,5*R*)-1-((*E*)-2-cyclopropyl-vinyl)-2-(2-hydroxy-pent-3-ynyl)-5-isopropyl-2-methyl-cyclopentanol (9)** To a stirred solution of diol **8** (60 mg, 0.24 mmol) in $CH_2Cl_2$ (2.5 mL) at rt was added $NaHCO_3$ (60 mg, 0.72 mmol, 300 mol%) and Dess-Martin periodinane (141 mg, 0.33 mmol, 140 mol%). The reaction was stirred for 20 min and quenched by addition of a solution of $NaHCO_3$ and $Na_2S_2O_3$ (2.5 mL, 1:1, saturated aqueous). The resulting solution was stirred for 1 h and diluted with diethyl ether (25 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (4 × 2.5 mL). The combined organic layers

were dried, filtered, and evaporated to a residue that was used in the next step without further purification. An analytical sample was obtained by chromatography using a gradient of 5-10% EtOAc in petroleum ether to give (1*R*,2*R*,3*R*)-[2-((*E*)-2-cyclopropyl-vinyl)-2-hydroxy-3-isopropyl-1-methyl-cyclopentyl]-acetaldehyde as a colorless oil: $[\alpha]_D^{25.8}$ +49.8 (*c* 0.45, $CH_2Cl_2$). $R_f$ = 0.35 (1:9 EtOAc : petroleum ether). IR (thin film, $CDCl_3$) 3501, 3082, 2954, 2872, 2739, 1716, 1669, 1468, 1374, 1158, 1022, 975, 946, 810. $^1$H NMR δ 9.79 (t, 1 H, *J* = 2.8), 5.49 (d, 1 H, *J* = 15.8), 5.23 (dd, 1 H, *J* = 15.8, 8.5), 2.30 (ddd, 1 H, *J* = 15.2, 2.8, 1.0), 2.25 (dd, 1 H, *J* = 15.2, 2.8), 1.89-1.97 (m, 1H), 1.62-1.81 (m, 4H), 1.51-1.58 (m, 1H), 1.42 (m, 1H), 1.36 (s, 1H), 1.11 (s, 3H), 0.94 (d, 3H, *J* = 3.0), 0.93 (d, 3 H, *J* = 3.0), 0.71-0.75 (m, 2H), 0.36-0.41 (m, 2H). $^{13}$C NMR δ 203.7, 133.7, 131.6, 84.2, 53.9, 51.3, 50.3, 34.7, 29.7, 26.6, 22.8, 22.5, 18.4, 13.6, 6.7, 6.6. HRMS calcd. for $C_{16}H_{26}O_2$ [$M^+$]: 250.1933, found: 250.1935.

To a stirred solution of crude (1*R*,2*R*,3*R*)-[2-((*E*)-2-cyclopropyl-vinyl)-2-hydroxy-3-isopropyl-1-methyl-cyclopentyl]-acetaldehyde (0.24 mmol) in THF (5.0 mL) at –78˚C was added 1-propynylmagnesium bromide (1.4 mL, 0.71 mmol, 300 mol%, 0.5 M in THF). The reaction was allowed to warm to 0 °C, stirred for 1 h and quenched with saturated aqueous $NH_4Cl$ (3.0 mL). The resulting solution was diluted with diethyl ether (30 mL), the layers were separated and the aqueous layer was extracted with diethyl ether (4 × 5 mL). The combined organic layers were dried, filtered, and evaporated to a residue that was chromatographed using a gradient of 10-20% EtOAc in petroleum ether to provide alcohol **9** as a 1:1 mixture of diastereoisomers: 52 mg, 75% over two steps, yellow oil, $R_f$ = 0.25 (1:9 EtOAc : petroleum ether). IR (thin film, $CDCl_3$) 3436, 3081, 2953, 2871, 1661, 1468, 1372, 1045, 1023, 973, 946, 810. $^1$H NMR δ 5.57-5.62 (m, 1H), 5.14-5.20 (m, 1H), 4.39-4.43 (m, 1H), 1.86-1.92 (m, 5H), 1.69-1.82 (m, 2H), 1.55-1.65 (m, 3H), 1.39-1.49 (m, 2H), 0.96 (s, 3H), 0.91-0.93 (m, 6H), 0.69-0.72 (m, 2H), 0.37-0.39 (m, 2H). $^{13}$C NMR δ 132.6 (132.4), 131.9 (132.2), 85.0 (84.8), 81.9 (81.8), 81.0 (80.9), 60.5 (60.4), 53.5 (53.6), 50.8 (50.6), 44.74 (44.70), 33.07 (32.96), 29.76 (29.81), 26.68 (26.65), 22.9, 22.6 (22.5), 17.5 (17.7), 13.7, 6.7, 6.6, 3.6. HRMS calcd for $C_{19}H_{30}O_2$ [$M^+$]: 290.2246, found: 290.2242. Anal. calcd for $C_{19}H_{30}O_2$: C: 78.57. H: 10.41. Found: C: 78.44. H: 10.70.

**(1*R*,2*R*,3*R*)-1-[2-((*E*)-2-cyclopropyl-vinyl)-2-hydroxy-3-isopropyl-1-methyl-cyclopentyl]-pent-3-yn-2-one (10)** To a stirred solution of alkynyl-vinylcyclopropane **9** (50 mg, 0.172 mmol) in $CH_2Cl_2$ (2.0 mL) at rt was added $NaHCO_3$ (42 mg, 0.496 mmol, 288 mol%) and Dess-Martin periodinane (98 mg, 0.231 mmol, 134 mol%). The reaction was stirred for 45 min and quenched by addition of a solution of $NaHCO_3$ and $Na_2S_2O_3$ (4.0 mL, 1:1, saturated aqueous). The resulting solution was stirred for 1 h and diluted with diethyl ether (30 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried, filtered, and evaporated to a residue that was chromatographed using 10% EtOAc in petroleum ether as eluant to provide ynone-vinylcyclopropane **10**: 48 mg, 97%, yellow oil, $R_f$ = 0.53 (1:9 EtOAc : petroleum ether), $[\alpha]_D^{25.0}$ +62.3 (*c* 1.14, $CH_2Cl_2$). IR (neat) 3468, 3088, 2954, 2872, 2223, 1660, 1467, 1376, 1303, 1214, 1174, 1131, 1047. $^1$H NMR δ 5.51 (d, 1 H, *J* = 15.7), 5.19 (dd, 1 H, *J* = 15.7, 8.8), 2.55 (d, 1 H, *J* = 14.1), 2.41 (d, 1 H, *J* = 14.1), 2.04 (s, 3H), 1.88-1.97 (m, 2H), 1.61-1.77 (m, 3H), 1.49-1.55 (m, 1H), 1.39-1.46 (m, 1H), 1.06 (s, 3H), 0.93 (d, *J* = 6.5, 6H), 0.70-0.73 (m, 2H), 0.37-0.40 (m, 2H). $^{13}$C NMR δ 188.0, 132.9, 131.6, 89.8, 84.3, 81.9, 53.8, 52.1, 51.2, 33.4, 29.7, 26.8, 22.9, 22.4, 18.1, 13.6, 6.7, 6.6, 4.1. HRMS calcd for $C_{19}H_{28}O_2$ [$M^+$]: 288.2089, found: 288.2090. Anal. calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.15; H, 9.64.

**(1*R*,3*R*,10*R*)-10b-Hydroxy-1-isopropyl-3a,b-dimethyl-2,3,3a,4,7,8,10a,10b-octahydro-1*H*-cyclohept[*e*]-inden-5-one (13)** A stirred solution of ynone-vinylcyclopropane **10** (30 mg, 0.104 mmol) in 1,2-dichloroethane (5.0 mL) was treated with argon bubbles for 15 min and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol, 5 mol%) was added in one portion. The reaction vessel was sealed and heated at 80˚C for 3.5 h. After cooling to room temperature, the solvent was removed *in vacuo*, the residue was dissolved in diethyl ether and filtered through a plug of neutral alumina. Evaporation of the filtrate afforded **14**: 27 mg, 90%, white solid, mp = 108.5-109.0 ˚C, TLC $R_f$ = 0.44 (1:9 EtOAc : petroleum ether), $[\alpha]_D^{24.3}$ +118.1 (*c* 0.95, $CH_2Cl_2$). IR (thin film, $CDCl_3$) 3359, 2951, 1674, 1620, 1429, 1294, 1154, 1115, 824. $^1$H NMR δ 6.13-6.17 (m, 1 H), 5.47 (ddd, 1 H, *J* = 11.3, 7.0, 4.0), 4.35 (m, 1 H), 3.14 (dt, 1 H, *J* = 13.4, 4.7), 2.57 (d, 1 H, *J* =

13.0), 2.32-2.38 (m, 2 H), 2.21 (d, 1 H, *J* = 13.0), 2.11-2.19 (m, 2 H), 2.17 (s, 3 H), 2.03 (ddd, 1 H, *J* = 13.4, 4.0, 1.0), 1.81 (dsep, 1 H, *J* = 7.0, 2.0), 1.38-1.67 (m, 7 H), 1.20 (s, 3 H), 0.98 (d, 3 H, *J* = 7.0), 0.95 (d, 3 H, *J* = 7.0). $^{13}$C NMR δ 201.7, 147.7, 139.4, 128.6, 128.2, 82.0, 54.8, 54.4, 47.8, 43.9, 39.4, 33.6, 27.0, 25.8, 25.0, 24.4, 24.2, 21.2, 20.7. HRMS calcd for $C_{19}H_{28}O_2$ [$M^+$]: 288.2089, found: 288.2093. Anal. calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 79.05; H, 9.71.