Two-Phase Synthesis of (–)-Taxuyunnanine D

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SUPPORTING INFORMATION

Part 1: Experimental Procedures and Characterization Data

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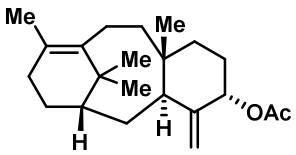
General Experimental. All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Dry acetonitrile (MeCN), dichloromethane (DCM), diethyl ether (Et_2O), tetrahydrofuran (THF), toluene (PhMe) and triethylamine (Et_3N) were obtained by passing the previously degassed solvents through activated alumina columns. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light as the visualizing agent and an acidic solution of *p*-anisaldehyde and heat, ceric ammonium molybdate and heat, or $KMnO_4$ and heat as developing agents. Flash silica gel chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm), flash alumina chromatography was performed using Brockmann Grade 1 aluminum oxide (activated, basic, 58 Å, 60 mesh powder), and flash Florisil® chromatography was conducted using Acros magnesium silicate (activated, 60–100 mesh). Chiral HPLC was performed using a Hitachi LaChrom Elite HPLC system. NMR spectra were recorded on Bruker DRX-600 and AMX-400 instruments and were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H-NMR, 77.16 ppm ^{13}C-NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. IR experiments were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Optical rotations were obtained on a Perkin-Elmer 341 polarimeter. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected. Cr(V) reagent **9** was prepared according to Roček and Krumpolc (*J. Am. Chem. Soc.* **1979**, *101*, 3206-

3209). 1-Hydroxy-1-methyl-2-cyclohexene **17** was prepared according to Wieser *et al*. (U.S. patent: US4994268 A1, **1991**, Experimental: example 1).



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5α-Acetoxy-taxa-4(20),11-diene 4. To a flame-dried 100 mL flask equipped with a stir bar were added taxadiene **1** (381.0 mg, 1.398 mmol, 1 equiv), *p*-benzoquinone (332.52 mg, 3.076 mmol, 2.2 equiv) and palladium(II) acetate (62.8 mg, 0.280 mmol, 20 mol%). The vial was evacuated and filled back with argon, followed by adding glacial acetic acid (38.1 mL) and anisole (0.607 mL, 5.59 mmol, 4 equiv). The flask was sealed with a septum cap and heated to 50ºC for 18 hr, after which palladium(II) acetate (31.4 mg, 0.140 mmol, 10 mol%) was added. Stirring at 50°C for another 8 hr completed the reaction. The yellow-orange, homogeneous reaction mixture was diluted with ca. 100 mL hexanes and 60 mL water. This mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with 2 × 40 mL hexanes. The organic layers were combined, washed with 100 mL saturated aqueous sodium bicarbonate, 100 mL water, and 100 mL saturated aqueous sodium chloride, dried over sodium sulfate, filtered, and concentrated by rotary evaporation. Purification by silica gel flash chromatography (gradient from hexanes to a mixture of hexanes/ethyl acetate 30:1) gave 5α-acetoxytaxa-4(20),11(12)-diene (+)-**4** (226.6 mg, 49% yield).

Data for **5α-acetoxytaxa-4(20),11-diene (+)-4**:

Appearance: Colorless, viscous liquid that solidifies upon standing to an amorphous white solid.

TLC: R_f = 0.51 (1:10 EtOAc/hexanes, slightly UV active but stains blue upon *p*-anisaldehyde staining).

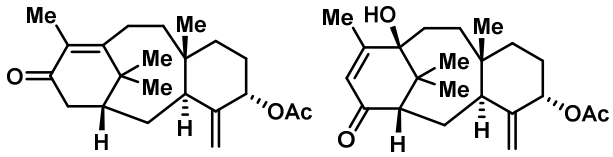
^{1}H NMR (600 MHz, $CDCl_3$): δ 5.32 (t, *J* = 3.0 Hz, 1H), 5.07 (s, 1H), 4.75 (s, 1H), 3.11 (dd, *J* = 6.0, 1.2 Hz, 1H), 2.81 (td, *J* = 13.6, 5.3 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.18 – 2.06 (m with s at 2.08, 5H), 2.06 – 1.98 (m, 2H), 1.88 (ddd, *J* = 18.6, 10.5, 3.1 Hz, 1H), 1.84 (s, 3H), 1.82 – 1.78 (m, 2H), 1.77 – 1.73 (m, 1H), 1.64 (ddd, *J* = 15.4, 5.9, 2.2 Hz, 1H), 1.56 (ddd, *J* = 15.4, 5.3, 2.0 Hz, 1H), 1.34 (s, 3H), 1.29 – 1.22 (m, 2H), 1.06 (dt, *J* = 13.6, 4.1 Hz, 1H), 1.04 (s, 3H), 0.63 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.1, 150.6, 137.2, 129.9, 111.5, 76.7, 43.5, 40.0, 39.6, 39.2, 37.1, 33.3, 30.8, 30.3, 28.3, 28.1, 25.4, 24.7, 22.8, 22.3, 21.9, 21.3 ppm.

IR (neat): $\tilde{\nu}$ = 2929, 1734, 1648, 1450, 1367, 1237 ($\tilde{\nu}_{max}$), 1000, 965, 897 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{22}H_{34}O_2$ [M + H^+] 331.2631, found 331.2624.

Optical rotation: $[\alpha]_D^{20}$ (c 1.0, $CHCl_3$) = +100.5º, taken on a >93% ee sample.



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5α-Acetoxytaxa-4(20),11(12)-dien-13-one 5 and 5α-Acetoxy-11β-hydroxytaxa-4(20),12(13)-dien-14-one 10. Thus, to a flame-dried 50 mL flask equipped with a stir bar were added 5α-acetoxytaxa-4(20),11-diene **4** (105.4 mg, 0.319 mmol, 1 equiv), Cr(V) reagent **9** (515.4 mg, 1.595 mmol, 5 equiv) and manganese(IV) oxide (1.386 g, 15.95 mmol, 50 equiv). The flask was evacuated and filled back with argon, followed by adding α,α,α -trifluorotoluene (21.1 mL) and 15-crown-5 (0.422 mL). The vial was sealed with a septum cap and heated to 80 ºC until

completion of the reaction (typically 12h). The black reaction mixture was diluted with ethyl acetate (ca. 30 mL) and filtered through a two-layered plug of silica and celite. This solution was concentrated by rotary evaporation and purified by silica gel flash chromatography (gradient elution from 100% toluene to 7% acetone in toluene) gave 5α-acetoxytaxa-4(20),11(12)-dien-13-one **5** (58.5 mg, 53% yield) and 5α-acetoxy-11β-hydroxytaxa-4(20),12(13)-dien-14-one **10** (40.5 mg, 35% yield).

Data for **5α-Acetoxytaxa-4(20),11(12)-dien-13-one 5**:

Appearance: Colorless, viscous liquid that solidifies upon standing to an amorphous white solid.

TLC: R_f = 0.49 (1:3 EtOAc/hexanes, UV active and stains blue upon *p*-anisaldehyde staining).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.27 (t, *J* = 2.6 Hz, 1H), 5.08 (s, 1H), 4.73 (s, 1H), 3.13 (d, *J* = 4.4 Hz, 1H), 2.97 (td, *J* = 12.8, 4.9 Hz, 1H), 2.87 (dd, *J*= 19.2, 7.2 Hz, 1H), 2.37 (broad d, *J* = 13.4 Hz, 1H), 2.23 – 2.16 (m, 2H), 2.08 – 2.02 (m, 1H), 2.00 (s, 3H), 1.97 (s, 3H), 1.92 (d, *J* = 19.2 Hz, 1H), 1.80 – 1.76 (m, 2H), 1.76 – 1.72 (m, 2H), 1.46 (s, 3H), 1.43 (ddd, *J* = 15.5, 5.2, 3.1 Hz, 1H), 1.14 (s, 3H), 1.12 (dt, *J* = 13.5, 3.4 Hz, 1H), 0.68 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.0, 170.4, 162.4, 149.9, 132.9, 111.5, 75.8, 40.9, 40.4, 40.3, 39.8, 38.2, 36.9, 36.7, 33.2, 28.1, 26.9, 26.6, 24.5, 22.1, 21.5, 13.4 ppm.

IR (neat): $\tilde{\nu}$ = 2939, 1734 ($\tilde{\nu}_{max}$), 1660, 1437, 1373, 1305, 1236, 1200, 1134, 1115, 1046, 1020, 1000, 962, 904, 883 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}O_3$ [M + H^+] 345.2424, found 345.2428.

Optical rotation: $[\alpha]_D^{20}$ (c 0.5, $CHCl_3$) = +103.0º, taken on a >93% ee sample.

Data for **5α-Acetoxy-11β-hydroxytaxa-4(20),12(13)-dien-14-one 10**:

Appearance: Colorless, viscous liquid that solidifies upon standing to an amorphous white solid.

TLC: R_f = 0.10 (1:3 EtOAc/hexanes, UV active and stains pink upon *p*-anisaldehyde staining).

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.04 (s, 1H), 5.24 (t, *J* = 2.9 Hz, 1H), 5.10 (s, 1H), 4.74 (s, 1H), 2.55 (d, *J* = 11.0 Hz, 1H), 2.28 (dd, *J* = 15.6, 10.3 Hz, 1H), 2.19 (dd, *J* = 15.5, 11.5 Hz, 1H), 2.05 – 2.01 (m with s at 2.03, 4H), 1.95 (s, 3H), 1.82 (dd, *J* = 15.6, 11.3 Hz, 1H), 1.74 (ddt, *J* = 14.3, 4.9, 2.6 Hz, 1H), 1.68 (tt, *J* = 14.0, 3.9 Hz, 1H), 1.59 – 1.51 (m, 3H), 1.46 – 1.40 (m, 1H), 1.34 (dd, *J* = 15.8, 10.3 Hz, 1H), 1.21 (s, 3H), 1.12 (s, 3H), 1.03 (ddd, *J* = 13.5, 4.6, 2.4 Hz, 1H), 0.78 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.9, 170.4, 163.9, 149.5, 127.9, 112.4, 79.3, 76.1, 56.0, 41.9, 41.2, 39.6, 38.7, 38.0, 30.6, 29.6, 28.2, 25.8, 21.5, 21.4, 19.5, 15.9 ppm.

IR (neat): $\tilde{\nu}$ = 3439, 2934, 1733, 1644, 1436, 1372, 1242 ($\tilde{\nu}_{max}$), 1158, 1071, 1018, 999, 967, 913, 877 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}O_4$ [M + H^+] 361.2373, found 361.2373.

Optical rotation: $[\alpha]_D^{20}$ (c 0.5, $CHCl_3$) = –29.4º, taken on a >93% ee sample.

Crystallographic data for 5α-Acetoxy-11β-hydroxytaxa-4(20),12(13)-dien-14-one 10:

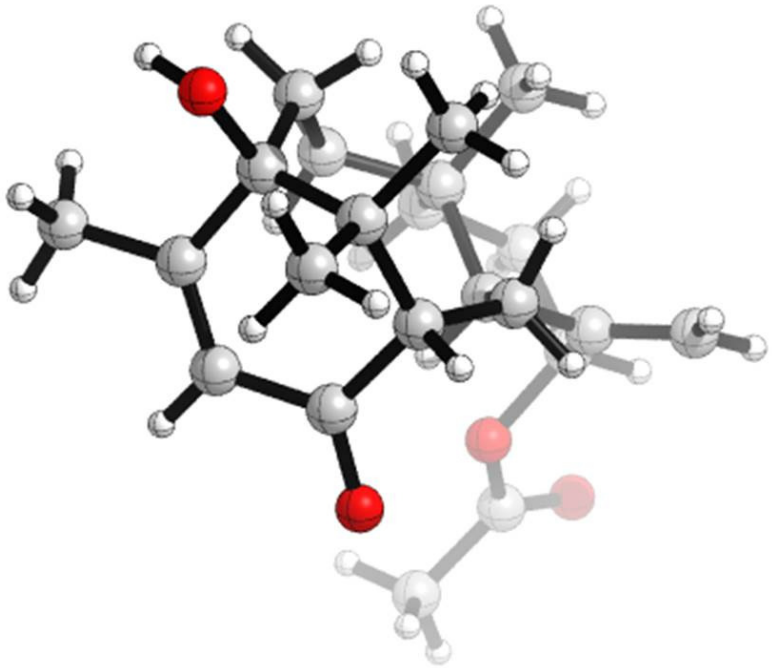


Table S1. Crystal data and structural refinement for CCDC # 986369

Identification code	CCDC # 986369	
Empirical formula	C22 H32 O4	
Molecular formula	C22 H32 O4	
Formula weight	360.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.5652(13) Å	α = 90°.
	b = 14.8496(19) Å	β = 100.665(6)°.
	c = 8.9503(15) Å	γ = 90°.
Volume	988.1(3) $Å^3$	
Z	2	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	392	
Crystal size	0.35 x 0.20 x 0.20 mm^3	
Crystal color, habit	colourless BLOCK	

Theta range for data collection	2.32 to 27.90°.
Index ranges	-9<=h<=9, -19<=k<=19, -11<=l<=11
Reflections collected	16364
Independent reflections	4570 [R(int) = 0.0513]
Completeness to theta = 25.00°	100.0 %
Absorption correction	mulit-scan / sadabs
Max. and min. transmission	0.9839 and 0.9720
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4570 / 1 / 245
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.0904
R indices (all data)	R1 = 0.0583, wR2 = 0.0966
Absolute structure parameter	0.6(9)
Largest diff. peak and hole	0.236 and -0.222 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for CCDC # 986369. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6870(2)	6058(1)	5502(2)	24(1)
O(2)	13628(2)	7030(1)	5056(2)	22(1)
O(3)	4961(2)	4400(1)	1335(2)	21(1)
O(4)	2760(2)	3638(1)	-175(2)	27(1)
C(1)	8361(3)	6254(1)	5230(2)	17(1)
C(2)	9926(3)	5711(1)	5837(2)	18(1)
C(3)	11563(3)	5858(1)	5510(2)	17(1)
C(4)	11920(3)	6621(1)	4473(2)	16(1)
C(5)	10553(3)	7398(1)	4474(2)	18(1)
C(6)	8586(3)	7047(1)	4219(2)	17(1)
C(7)	7519(3)	6883(1)	2575(2)	18(1)
C(8)	7410(2)	5946(1)	1829(2)	15(1)
C(9)	5682(3)	5892(1)	634(2)	18(1)
C(10)	5197(3)	4963(1)	37(2)	20(1)
C(11)	6705(3)	4577(1)	-671(2)	22(1)

C(12)	8513(3)	4657(1)	416(2)	20(1)
C(13)	8998(3)	5613(1)	1079(2)	17(1)
C(14)	10769(3)	5451(1)	2220(2)	18(1)
C(15)	12040(3)	6217(1)	2900(2)	19(1)
C(16)	13099(3)	5234(1)	6075(2)	22(1)
C(17)	10775(3)	8129(1)	3314(3)	28(1)
C(18)	10899(3)	7859(1)	6049(2)	26(1)
C(19)	4703(3)	6585(1)	20(2)	21(1)
C(20)	9325(3)	6245(1)	-196(2)	21(1)
C(21)	3680(3)	3758(1)	1053(2)	18(1)
C(22)	3565(3)	3239(1)	2462(2)	25(1)

Table S3. Bond lengths [Å] and angles [°] for CCDC # 986369.

O(1)-C(1)	1.233(2)	C(7)-H(7A)	0.9900
O(2)-C(4)	1.436(2)	C(7)-H(7B)	0.9900
O(2)-H(2)	0.85(3)	C(8)-C(9)	1.530(3)
O(3)-C(21)	1.349(2)	C(8)-C(13)	1.561(3)
O(3)-C(10)	1.469(2)	C(8)-H(8)	1.0000
O(4)-C(21)	1.201(2)	C(9)-C(19)	1.326(3)
C(1)-C(2)	1.453(3)	C(9)-C(10)	1.500(3)
C(1)-C(6)	1.513(3)	C(10)-C(11)	1.516(3)
C(2)-C(3)	1.343(3)	C(10)-H(10)	1.0000
C(2)-H(2A)	0.9500	C(11)-C(12)	1.529(3)
C(3)-C(16)	1.498(3)	C(11)-H(11A)	0.9900
C(3)-C(4)	1.520(3)	C(11)-H(11B)	0.9900
C(4)-C(15)	1.548(3)	C(12)-C(13)	1.557(3)
C(4)-C(5)	1.551(3)	C(12)-H(12A)	0.9900
C(5)-C(17)	1.532(3)	C(12)-H(12B)	0.9900
C(5)-C(18)	1.545(3)	C(13)-C(20)	1.533(3)
C(5)-C(6)	1.553(3)	C(13)-C(14)	1.545(3)
C(6)-C(7)	1.561(2)	C(14)-C(15)	1.540(3)
C(6)-H(6)	1.0000	C(14)-H(14A)	0.9900
C(7)-C(8)	1.540(3)	C(14)-H(14B)	0.9900

C(15)-H(15A)	0.9900	C(18)-H(18C)	0.9800
C(15)-H(15B)	0.9900	C(19)-H(19A)	0.9500
C(16)-H(16A)	0.9800	C(19)-H(19B)	0.9500
C(16)-H(16B)	0.9800	C(20)-H(20A)	0.9800
C(16)-H(16C)	0.9800	C(20)-H(20B)	0.9800
C(17)-H(17A)	0.9800	C(20)-H(20C)	0.9800
C(17)-H(17B)	0.9800	C(21)-C(22)	1.494(3)
C(17)-H(17C)	0.9800	C(22)-H(22A)	0.9800
C(18)-H(18A)	0.9800	C(22)-H(22B)	0.9800
C(18)-H(18B)	0.9800	C(22)-H(22C)	0.9800

C(4)-O(2)-H(2)	110.1(19)	C(5)-C(6)-C(7)	120.33(16)
C(21)-O(3)-C(10)	116.28(15)	C(1)-C(6)-H(6)	103.9
O(1)-C(1)-C(2)	120.45(18)	C(5)-C(6)-H(6)	103.9
O(1)-C(1)-C(6)	120.74(17)	C(7)-C(6)-H(6)	103.9
C(2)-C(1)-C(6)	118.79(17)	C(8)-C(7)-C(6)	121.78(15)
C(3)-C(2)-C(1)	123.31(17)	C(8)-C(7)-H(7A)	106.9
C(3)-C(2)-H(2A)	118.3	C(6)-C(7)-H(7A)	106.9
C(1)-C(2)-H(2A)	118.3	C(8)-C(7)-H(7B)	106.9
C(2)-C(3)-C(16)	121.01(17)	C(6)-C(7)-H(7B)	106.9
C(2)-C(3)-C(4)	121.96(17)	H(7A)-C(7)-H(7B)	106.7
C(16)-C(3)-C(4)	116.91(16)	C(9)-C(8)-C(7)	108.69(15)
O(2)-C(4)-C(3)	110.04(15)	C(9)-C(8)-C(13)	108.02(14)
O(2)-C(4)-C(15)	107.12(16)	C(7)-C(8)-C(13)	119.24(16)
C(3)-C(4)-C(15)	108.30(15)	C(9)-C(8)-H(8)	106.8
O(2)-C(4)-C(5)	103.86(15)	C(7)-C(8)-H(8)	106.8
C(3)-C(4)-C(5)	111.17(16)	C(13)-C(8)-H(8)	106.8
C(15)-C(4)-C(5)	116.12(16)	C(19)-C(9)-C(10)	118.99(18)
C(17)-C(5)-C(18)	106.46(16)	C(19)-C(9)-C(8)	126.08(19)
C(17)-C(5)-C(4)	111.73(17)	C(10)-C(9)-C(8)	114.70(16)
C(18)-C(5)-C(4)	109.25(16)	O(3)-C(10)-C(9)	107.42(15)
C(17)-C(5)-C(6)	111.15(16)	O(3)-C(10)-C(11)	109.04(16)
C(18)-C(5)-C(6)	106.19(16)	C(9)-C(10)-C(11)	110.06(17)
C(4)-C(5)-C(6)	111.75(15)	O(3)-C(10)-H(10)	110.1
C(1)-C(6)-C(5)	112.63(15)	C(9)-C(10)-H(10)	110.1
C(1)-C(6)-C(7)	110.24(16)	C(11)-C(10)-H(10)	110.1

C(10)-C(11)-C(12)	111.01(16)	C(5)-C(17)-H(17A)	109.5
C(10)-C(11)-H(11A)	109.4	C(5)-C(17)-H(17B)	109.5
C(12)-C(11)-H(11A)	109.4	H(17A)-C(17)-H(17B)	109.5
C(10)-C(11)-H(11B)	109.4	C(5)-C(17)-H(17C)	109.5
C(12)-C(11)-H(11B)	109.4	H(17A)-C(17)-H(17C)	109.5
H(11A)-C(11)-H(11B)	108.0	H(17B)-C(17)-H(17C)	109.5
C(11)-C(12)-C(13)	115.65(16)	C(5)-C(18)-H(18A)	109.5
C(11)-C(12)-H(12A)	108.4	C(5)-C(18)-H(18B)	109.5
C(13)-C(12)-H(12A)	108.4	H(18A)-C(18)-H(18B)	109.5
C(11)-C(12)-H(12B)	108.4	C(5)-C(18)-H(18C)	109.5
C(13)-C(12)-H(12B)	108.4	H(18A)-C(18)-H(18C)	109.5
H(12A)-C(12)-H(12B)	107.4	H(18B)-C(18)-H(18C)	109.5
C(20)-C(13)-C(14)	110.35(16)	C(9)-C(19)-H(19A)	120.0
C(20)-C(13)-C(12)	109.50(15)	C(9)-C(19)-H(19B)	120.0
C(14)-C(13)-C(12)	102.94(15)	H(19A)-C(19)-H(19B)	120.0
C(20)-C(13)-C(8)	111.69(15)	C(13)-C(20)-H(20A)	109.5
C(14)-C(13)-C(8)	114.06(15)	C(13)-C(20)-H(20B)	109.5
C(12)-C(13)-C(8)	107.84(16)	H(20A)-C(20)-H(20B)	109.5
C(15)-C(14)-C(13)	123.21(16)	C(13)-C(20)-H(20C)	109.5
C(15)-C(14)-H(14A)	106.5	H(20A)-C(20)-H(20C)	109.5
C(13)-C(14)-H(14A)	106.5	H(20B)-C(20)-H(20C)	109.5
C(15)-C(14)-H(14B)	106.5	O(4)-C(21)-O(3)	123.43(18)
C(13)-C(14)-H(14B)	106.5	O(4)-C(21)-C(22)	125.52(18)
H(14A)-C(14)-H(14B)	106.5	O(3)-C(21)-C(22)	111.05(17)
C(14)-C(15)-C(4)	120.54(16)	C(21)-C(22)-H(22A)	109.5
C(14)-C(15)-H(15A)	107.2	C(21)-C(22)-H(22B)	109.5
C(4)-C(15)-H(15A)	107.2	H(22A)-C(22)-H(22B)	109.5
C(14)-C(15)-H(15B)	107.2	C(21)-C(22)-H(22C)	109.5
C(4)-C(15)-H(15B)	107.2	H(22A)-C(22)-H(22C)	109.5
H(15A)-C(15)-H(15B)	106.8	H(22B)-C(22)-H(22C)	109.5
C(3)-C(16)-H(16A)	109.5		
C(3)-C(16)-H(16B)	109.5		
H(16A)-C(16)-H(16B)	109.5		
C(3)-C(16)-H(16C)	109.5		
H(16A)-C(16)-H(16C)	109.5		
H(16B)-C(16)-H(16C)	109.5		

Symmetry transformations used to generate equivalent atoms:

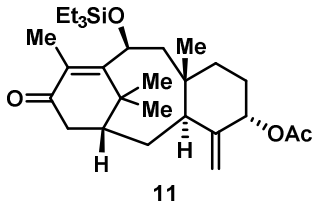
Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CCDC # 986369. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	14(1)	32(1)	26(1)	1(1)	6(1)	-1(1)
O(2)	12(1)	24(1)	29(1)	-6(1)	1(1)	-2(1)
O(3)	18(1)	24(1)	18(1)	2(1)	0(1)	-4(1)
O(4)	27(1)	22(1)	28(1)	-5(1)	-3(1)	-3(1)
C(1)	16(1)	22(1)	14(1)	-5(1)	3(1)	-1(1)
C(2)	17(1)	21(1)	14(1)	2(1)	3(1)	1(1)
C(3)	15(1)	21(1)	13(1)	-5(1)	0(1)	1(1)
C(4)	11(1)	19(1)	19(1)	-4(1)	2(1)	-3(1)
C(5)	14(1)	17(1)	22(1)	-2(1)	3(1)	-1(1)
C(6)	14(1)	17(1)	20(1)	-2(1)	4(1)	3(1)
C(7)	13(1)	19(1)	20(1)	1(1)	2(1)	2(1)
C(8)	14(1)	17(1)	14(1)	3(1)	2(1)	1(1)
C(9)	14(1)	26(1)	14(1)	0(1)	6(1)	-2(1)
C(10)	19(1)	25(1)	13(1)	3(1)	0(1)	-3(1)
C(11)	23(1)	25(1)	16(1)	-3(1)	1(1)	0(1)
C(12)	20(1)	22(1)	18(1)	-3(1)	2(1)	3(1)
C(13)	15(1)	20(1)	14(1)	0(1)	3(1)	2(1)
C(14)	18(1)	21(1)	15(1)	-4(1)	2(1)	4(1)
C(15)	13(1)	25(1)	18(1)	0(1)	6(1)	4(1)
C(16)	16(1)	28(1)	21(1)	6(1)	3(1)	5(1)
C(17)	21(1)	18(1)	43(1)	4(1)	6(1)	1(1)
C(18)	18(1)	26(1)	34(1)	-13(1)	3(1)	2(1)
C(19)	15(1)	29(1)	19(1)	2(1)	1(1)	0(1)
C(20)	16(1)	29(1)	17(1)	1(1)	4(1)	1(1)
C(21)	14(1)	15(1)	26(1)	-5(1)	3(1)	3(1)
C(22)	23(1)	23(1)	31(1)	2(1)	6(1)	0(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for CCDC # 986369.

	x	y	z	U(eq)
H(2)	14470(40)	6653(19)	5050(30)	53(9)
H(2A)	9783	5227	6499	21
H(6)	7909	7544	4616	20
H(7A)	6267	7082	2563	21
H(7B)	8026	7297	1896	21
H(8)	7282	5500	2640	18
H(10)	4055	4981	-732	23
H(11A)	6764	4904	-1625	26
H(11B)	6453	3935	-927	26
H(12A)	9473	4459	-128	24
H(12B)	8512	4235	1273	24
H(14A)	10442	5120	3089	22
H(14B)	11495	5033	1719	22
H(15A)	11867	6719	2159	22
H(15B)	13286	5997	2958	22
H(16A)	12678	4738	6641	32
H(16B)	14052	5565	6744	32
H(16C)	13571	4992	5209	32
H(17A)	10568	7867	2291	41
H(17B)	11997	8375	3553	41
H(17C)	9902	8612	3355	41
H(18A)	12119	8109	6254	40
H(18B)	10773	7416	6833	40
H(18C)	10025	8345	6058	40
H(19A)	3711	6489	-786	25
H(19B)	4993	7177	385	25
H(20A)	10356	6029	-615	31
H(20B)	9573	6854	212	31
H(20C)	8254	6257	-1002	31

H(22A)	2440	2895	2306	38
H(22B)	3593	3656	3314	38
H(22C)	4587	2824	2690	38



11

5α-acetoxy-10β-triethylsiloxytaxa-4(20),11(12)-dien-13-one 11. To a flame-dried vial was added silver trifluoromethanesulfonate (61.9 mg, 0.241 mmol, 10 equiv). This was dried by adding benzene (1.5 mL) and concentrating by rotary evaporation, repeating three times, followed by drying under vacuum at 100°C overnight. A separate pyrex vessel was flame dried, and to this was added 5α-acetoxytaxa-4(20),11(12)-dien-13-one **5** (8.3 mg, 0.0241 mmol, 1 equiv), *N*-bromosuccinimide (4.4 mg, 0.247 mmol, 1.03 equiv. Note: using more equivalents of NBS results in overbromination.), benzoyl peroxide (1.0 mg, 0.0041 mmol, 0.17 equiv), and carbon tetrachloride (1.6 mL). This vessel was heated to reflux using a pre-heated oil bath, and after 1 hr the reaction was deemed complete by thin layer chromatography (5% acetone in toluene gives superior resolution to ethyl acetate/hexanes for this bromide product). The reaction was concentrated by rotary evaporation, triethyl silanol (0.83 mL) was added, and this mixture was dried by adding benzene (1.5 mL) and concentrating by rotary evaporation, repeating five times. This mixture was then added to another dry flask containing activated 4Å molecular sieves (350 mg) and using toluene (0.3 mL) to rinse once. This mixture was cooled to 0°C. The dried silver trifluoromethanesulfonate was purged with argon and dissolved in 1.66 mL toluene, and this solution was added dropwise over 1 min to the bromide mixture described above. After stirring at 0°C for 30 min, the reaction was deemed complete by thin-layer chromatography, and

was quenched with saturated aqueous sodium bicarbonate (3.0 mL). This mixture was diluted with ethyl acetate (3.0 mL), and the aqueous phase was extracted with ethyl acetate (3 x 2.0 mL). The collected organic portions were washed with water (2 x 3.0 mL) and saturated aqueous sodium chloride (2 x 3.0 mL), followed by drying over sodium sulfate. Filtration and concentration yielded the crude mixture, which was purified by first leaving under vacuum for 3 hr to remove excess triethyl silanol (but not hexaethyldisiloxane), and then by silica gel flash chromatography (gradient elution from 100% hexanes to 20% ethyl acetate in hexanes) to afford 5α-acetoxy-10β-triethylsiloxy-Taxa-4(20),11(12)-dien-13-one **11** (9.2 mg, 80% yield).

Data for 5α-acetoxy-10β-triethylsiloxytaxa-4(20),11(12)-dien-13-one 11:

Appearance: Colorless, viscous liquid.

TLC: R_f = 0.59 (25% EtOAc in hexanes, stains with cerium molybdate stain, UV active)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.27 (t, *J* = 3.0 Hz, 1H), 5.11 (dd, *J* = 11.4, 5.7 Hz, 1H), 5.11 (s, 1H), 2.94 (d, *J* = 6.1 Hz, 1H), 2.90 (dd, *J* = 19.5, 7.2 Hz, 1H), 2.41 (dd, *J* = 14.8, 11.4 Hz, 1H), 2.11 (t, *J* = 5.1 Hz, 1H), 2.05 (s, 3H), 1.95 (s, 3H), 1.92 (d, *J* = 19.5 Hz, 2H), 1.85 – 1.74 (m, 3H), 1.70 (ddd, *J* = 15.9, 5.3, 1.8 Hz, 1H), 1.61 (s, 3H), 1.58 (dd, *J* = 14.9, 5.8 Hz, 1H), 1.28 – 1.19 (m, 2H), 1.16 (s, 3H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.72 (s, 3H), 0.62 (q, *J* = 7.8 Hz, 6H) ppm.

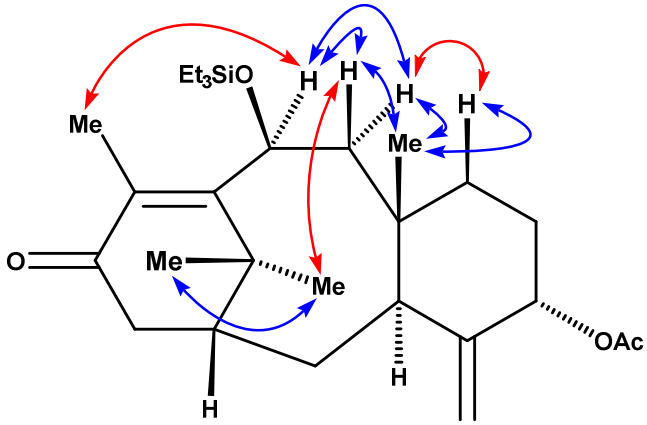
^{13}C NMR: (151 MHz, $CDCl_3$) δ 201.4, 170.4, 160.8, 149.9, 132.4, 112.2, 75.9, 69.1, 48.3, 41.8, 40.1, 38.3, 37.6, 35.9, 34.2, 28.2, 27.0, 24.8, 22.2, 21.6, 13.7, 7.0, 5.2 ppm.

IR (neat): $\tilde{\nu}$ = 2952, 2876, 1734, 1666 ($\tilde{\nu}_{max}$), 1233, 1047, 1003, 743, 671 cm^{-1}.

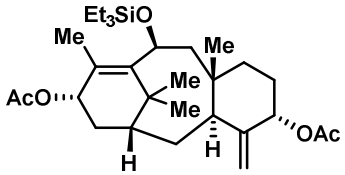
HRMS (ESI-TOF): calc'd for $C_{28}H_{46}O_4Si$ [M+H] 475.3244; found 475.3244.

Optical rotation: $[\alpha]_D^{20}$ (c 0.615, $CHCl_3$) = +110.0º, taken on a >93% ee sample.

NOESY analysis:



All arrows are selected observed NOE correlations. Red arrows are those deemed diagnostic for assigning the triethylsiloxy group to the β-position.



12

5α,13α-diacetoxy-10β-triethylsiloxytaxa-4(20),11(12)-diene 12. To a flame-dried reaction vial was added taxa-4(20),11(12)-dien-5α-acetoxy-10β-triethylsiloxy-13-one **11** (24.6 mg, 0.0518 mmol, 1 equiv) and toluene (5.47 mL). After cooling to -78ºC, diisobutylaluminumhydride (0.259 mL of a 1.0 M solution in hexanes, 0.259 mmol, 5 equiv) was added dropwise, and this was stirred for 30 min. This was warmed to 0ºC and stirred for another 30 min, upon which time starting material was determined to be consumed by thin-layer chromatography. Methanol (21.0 μL, 0.518 mmol, 10 equiv) was added dropwise, and this solution was warmed to room temperature and stirred for 1 hr. This solution was cooled to 0ºC, and triethylamine (0.650 mL, 4.664 mmol, 90 equiv) and acetic anhydride (0.294 mL, 3.109 mmol, 60 equiv) were added successively and dropwise. 4-dimethylaminopyridine (6.3 mg, 0.0518 mmol, 1 equiv) was then added, and this solution was warmed to room temperature and stirred for 20 hr. The reaction was

deemed incomplete by thin-layer chromatography, so another batch of 4-dimethylaminopyridine (6.3 mg, 0.0518 mmol, 1 equiv) was then added and the resulting solution was stirred another 24 hr at room temperature. The reaction was deemed complete by thin-layer chromatography, and was slowly quenched with saturated aqueous sodium bicarbonate (5 mL) and diluted with ethyl acetate (20 mL). The phases were separated, the aqueous phase was extracted with ethyl acetate (3 x 10 mL), and the combined organic extractions were washed with water (30 mL) and saturated aqueous sodium chloride (30 mL). After drying over sodium sulfate and filtering, the reaction was concentrated by rotary evaporation. The crude material was purified by silica column flash chromatography (gradient elution from 0% to 20% ethyl acetate in hexanes) to afford 5α,13α-diacetoxy-10β-triethylsiloxytaxa-4(20),11(12)-diene **12** (22.3 mg, 80% yield).

Data for 5α,13α-diacetoxy-10β-triethylsiloxytaxa-4(20),11(12)-diene 12:

Appearance: Colorless, viscous liquid.

TLC: R_f = 0.60 (25% EtOAc in hexanes, stains with cerium molybdate stain, very slightly UV active)

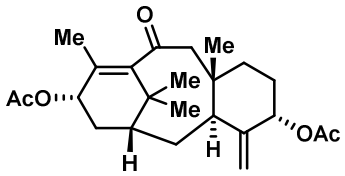
^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 10.2, 7.3, 1.7 Hz, 1H), 5.32 (t, *J* = 2.9 Hz, 1H), 5.11 (s, 1H), 5.03 (dd, *J* = 11.5, 5.7 Hz, 1H), 4.77 (s, 1H), 2.99 (d, *J* = 6.7 Hz, 1H), 2.67 (dt, *J* = 14.5, 9.8 Hz, 1H), 2.37 (dd, *J* = 14.9, 11.5 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 2.02 – 1.94 (m, 1H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.82 – 1.73 (m, 3H), 1.70 (ddd, *J* = 15.6, 6.7, 2.3 Hz, 1H), 1.60 – 1.53 (m, with singlet at 1.57, 4H), 1.49 (dd, *J* = 15.0, 5.7 Hz, 1H), 1.19 (dt, *J* = 13.2, 3.6 Hz, 1H), 1.12 (s, 3H), 1.08 (ddd, *J* = 14.4, 7.3, 1.2 Hz, 1H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.70 (s, 3H), 0.58 (q, *J* = 8.0, 1.2 Hz, 6H) ppm.

^{13}C NMR: (151 MHz, $CDCl_3$) δ 170.8, 170.2, 150.3, 141.9, 129.5, 112.9, 76.7, 71.3, 67.8, 49.4, 41.1, 39.6, 38.1, 36.6, 34.9, 32.4, 31.5, 29.0, 28.3, 26.7, 22.3, 22.0, 21.7, 14.7, 7.1, 5.2 ppm.

IR (neat): $\tilde{\nu}$ = 2950, 2874, 1733, 1456, 1371, 1237 ($\tilde{\nu}_{max}$), 1046, 1003, 745, 669 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{30}H_{50}O_5Si$ [M+Na] 541.3325; found 541.3322.

Optical rotation: $[\alpha]_D^{20}$ (c 0.41, $CHCl_3$) = +61.5°, taken on a >93% ee sample.



3: (–)-taxuyunnanine D

Taxuyunnanine D 3. To a flame-dried reaction vial was added 5α,13α-diacetoxy-10β-triethylsiloxytaxa-4(20),11(12)-diene **12** (16.7 mg, 0.0322 mmol, 1 equiv), DMSO (6.7 mL), and IBX (27.1 mg, 0.0968 mmol, 3 equiv). After all IBX had dissolved, the reaction was heated to 80°C and stirred under argon for 16 hr. The reaction was then deemed complete by thin layer chromatography. This was diluted with water (15 mL) and extracted with ethyl ether (4 x 10 mL). The combined organic portions were washed with brine (3 x 20 mL), dried over sodium sulfate, filtered, and concentrated by rotary evaporation. The crude material was purified by silica column flash chromatography (gradient elution from 10% to 30% ethyl acetate in hexanes) to afford taxuyunnanine D **3** (11.4 mg, 88% yield).

Data for taxuyunnanine D 3:

Appearance: Amorphous white solid.

TLC: R_f = 0.52 (40% EtOAc in hexanes, stains with cerium molybdate stain, UV active)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 10.3, 7.7, 1.6 Hz, 1H), 5.35 (s, 1H), 5.21 (s, 1H), 4.87 (s, 1H), 3.07 (d, *J* = 6.0 Hz, 1H), 2.97 (d, *J* = 16.0 Hz, 1H), 2.75 (dt, *J* = 14.6, 9.8 Hz, 1H), 2.34 (d, *J* = 16.1 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.02 – 1.96 (m, 2H), 1.90 (d, *J* = 1.5 Hz, 3H), 1.85 (ddd, *J* = 15.8, 6.8, 2.3 Hz, 1H), 1.80 – 1.73 (m, 3H), 1.36 (s, 3H), 1.30 – 1.26 (m, 1H), 1.20 (ddd, *J* = 14.5, 7.7, 1.4 Hz, 1H), 1.16 (s, 3H), 0.78 (s, 3H) ppm.

^{13}C NMR: (151 MHz, $CDCl_3$) δ 205.6, 170.5, 170.0, 149.5, 146.0, 135.2, 113.9, 76.2, 70.1, 58.9, 40.2, 39.9, 37.7, 36.9, 36.8, 32.2, 30.0, 29.3, 28.4, 28.0, 21.9, 21.5, 21.5, 14.7 ppm.

IR (neat): $\tilde{\nu}$ = 2925, 1731, 1671, 1372, 1235 ($\tilde{\nu}_{max}$), 1018, 749, 667 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{24}H_{34}O_5$ [M+H] 403.2479; found 403.2476.

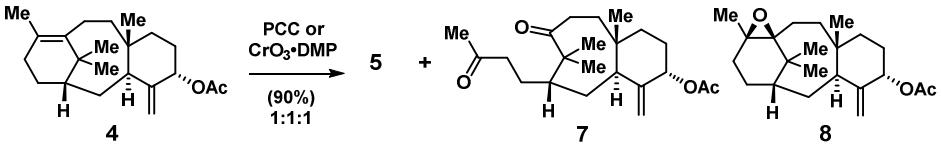
Optical rotation: $[\alpha]_D^{20}$ (c 0.240, $CHCl_3$) = –57.2°.

Table comparing tabulated NMR spectra from taxuyunnanine D isolation and synthesis:

Isolated **3** NMR	Synthetic **3** NMR
^{1}H	
0.80 (s)	0.78 (s)
1.17 (s)	1.16 (s)
1.21 (dd, *J* = 14.1, 6.3 Hz)	1.20 (ddd, *J* = 14.5, 7.7, 1.4 Hz)
~1.29 (m)	1.26-1.30 (m)
1.36 (s)	1.36 (s)
~1.75 (m) ~1.75 (m) ~1.77 (m)	1.80 – 1.73 (m, 3H)
1.77-1.87 (m)	1.85 (ddd, *J* = 15.8, 6.8, 2.3 Hz)
1.91 (d, *J* = 1.5 Hz)	1.90 (d, *J* = 1.5 Hz)
2.01 (m)	2.02 – 1.96 (m)
2.09 (s)	2.08 (s)
2.17 (s)	2.14 (s)
2.34 (d, *J* = 16.1 Hz)	2.34 (d, *J* = 16.1 Hz)
2.76 (dt, *J* = 14.1, 9.8 Hz)	2.75 (dt, *J* = 14.6, 9.8 Hz)
2.98 (d, *J* = 16.1 Hz)	2.97 (d, *J* = 16.0 Hz)
3.08 (d, *J* = 5.9 Hz)	3.07 (d, *J* = 6.0 Hz)
4.87 (s)	4.87 (s)
5.22 (s)	5.21 (s)
5.36 (br s)	5.35 (s)
5.89 (br t, *J* = 8.8 Hz)	5.88 (ddd, *J* = 10.3, 7.7, 1.6 Hz)

^{13}C	
14.58	14.72
21.34	21.47
21.34	21.50
21.73	21.89
27.87	28.02
28.20	28.36
29.17	29.31
29.83	29.97
32.02	32.18
36.65	36.83
36.74	36.90
37.55	37.69
39.74	39.89
40.03	40.18
58.69	58.85
69.93	70.09
76.06	76.21
113.72	113.86
135.08	135.22
145.88	146.03
149.30	149.46
169.88	170.04
170.32	170.48
205.40	205.57

Note: The authors of the isolation paper used tetramethylsilane to reference their spectra, while the authors of this paper used ^{13}C and residual ^{1}H from the NMR solvent ($CDCl_3$). This accounts for the consistent differences in the ^{13}C spectrum.



Treating 5α-Acetoxy-taxa-4(20),11-diene 4 with pyridinium chlorochromate. This procedure follows that of Nicolaou *et al*. (*J. Am. Chem. Soc.* **1995**, *117*, 624-633). Thus, to a flame-dried flask was added celite (97.7 mg) and sodium acetate (40.9 mg, 0.498 mmol, 33 equiv), and this was heated with a heat gun for 20 seconds under vacuum. Pyridinium chlorochromate (97.7 mg,

0.453 mmol, 30 equiv) was independently dried under vacuum for 30 min and then added to the celite and sodium acetate. After purging with argon, 5α-Acetoxy-taxa-4(20),11-diene **4** (5.0 mg, 0.0151 mmol, 1 equiv) was added as a solution in benzene (2 x 2.5 mL). This was stirred for 18 hr under argon at room temperature, upon which time the reaction was deemed complete by thin-layer chromatography. The reaction mixture was diluted with ethyl acetate (5 mL) and run through a silica plug. Concentration by rotary evaporation and purification by basic alumina flash chromatography gave **5**, **7**, and **8** (4.7 mg, *ca.* 90% yield, *ca.* 1:1:1 by crude NMR).

Data for diketone 7:

Appearance: White foam

TLC: R_f = 0.18 (25% ethyl acetate in hexanes, stains blue upon *p*-anisaldehyde staining)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.22 (t, *J* = 3.3 Hz, 1H), 5.10 (s, 1H), 4.73 (s, 1H), 2.79 (ddd, *J* = 15.0, 6.5, 3.2 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.46 (ddd, *J* = 16.4, 8.7, 6.8 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.33 (d, *J* = 12.1 Hz, 1H), 2.27 (ddd, *J* = 15.2, 12.9, 6.5 Hz, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 2.05 – 1.96 (m, 2H), 1.86 – 1.68 (m, 3H), 1.53 (ddd, *J* = 15.1, 6.7, 3.3 Hz, 1H), 1.28 – 1.24 (m, 1H), 1.20 – 1.13 (m, 1H), 1.16 (s, 3H), 0.99 (ddd, *J* = 13.4, 4.6, 2.7 Hz, 1H), 0.93 (s, 3H), 0.78 (s, 3H).

^{13}C NMR: (151 MHz, $CDCl_3$) 217.89, 208.80, 170.58, 148.57, 111.78, 75.24, 51.60, 42.41, 39.90, 38.92, 38.82, 38.06, 32.65, 30.24, 30.11, 29.85, 27.82, 27.23, 26.01, 21.51, 20.20, 17.17. ppm.

IR (neat): $\tilde{\nu}$ = 2923, 2856, 1733, 1717, 1681, 1456, 1370, 1236 ($\tilde{\nu}_{max}$), 1018, 962, 904, 754, 669 cm^{-1}.

HRMS: calc'd $C_{22}H_{34}O_4$ [M+H] 363.2535; found 363.2529.

Optical rotation: $[\alpha]_D^{20}$ (c 0.28, $CHCl_3$) = +6.1º, taken on a >93% ee sample.

Data for epoxide 8:

Appearance: White foam

TLC: R_f = 0.51 (25% ethyl acetate in hexanes, stains blue upon *p*-anisaldehyde staining)

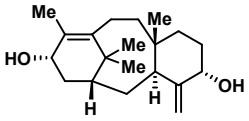
^{1}H NMR: (600 MHz, $CDCl_3$) δ 5.46 (dd, J = 4.3, 1.8 Hz, 1H), 5.21 (d, 1H), 4.91 (s, 1H), 2.62 (s, 1H), 2.20 – 2.12 (m, 2H), 2.09 (s, 3H), 2.02 – 1.95 (m, 2H), 1.90 – 1.84 (m, 1H), 1.84 – 1.78 (m, 2H), 1.77 – 1.72 (m, 1H), 1.70 (s, 3H), 1.67 – 1.60 (m, 3H), 1.41 (s, 3H), 1.38 (ddd, J = 15.9, 5.0, 3.4 Hz, 1H), 1.29 – 1.20 (m, 2H), 1.06 (ddd, J = 13.5, 5.3, 2.0 Hz, 1H), 0.87 (s, 3H), 0.70 (s, 3H) ppm.

^{13}C NMR: (151 MHz, $CDCl_3$) δ 170.0, 149.1, 113.3, 76.5, 65.6, 62.0, 41.1, 39.2, 39.1, 39.1, 38.9, 32.7, 30.6, 28.2, 26.8, 26.5, 25.9, 24.8, 23.7, 22.0, 22.0, 22.0.

IR (neat): $\tilde{\nu}$ = 2923, 2854, 1732, 1458, 1372, 1235, 1013, 753 ($\tilde{\nu}_{max}$), 668 cm^{-1}.

HRMS: calc'd $C_{22}H_{34}O_3$ [M+Na] 369.2406; found 369.2403.

Optical rotation: $[\alpha]_D^{20}$ (c 0.05, $CHCl_3$) = –12º, taken on a >93% ee sample.



S1

5α,13α-dihydroxytaxa-4(20),11(12)-diene S1. To a flame-dried 25 mL vial equipped with a stir bar were added 5α-acetoxytaxa-4(20),11-dien-13-one **5** (10 mg, 0.029 mmol, 1 equiv). The vial was evacuated and filled back with argon and toluene (5 mL) was added. The vial was cooled to –78ºC and diisobutylaluminum hydride (1M in hexane, 145 µl, 0.145 mmol, 5 equiv) was added

dropwise over 1 min. The mixture is stirred inside the cooling bath for 1.5 hr (upon which the temperature is –20 ºC). The clear reaction solution was quenched at low temperature with the addition of Rochelle's salt aq. saturated solution (10 mL) and the organic phase was subsequently diluted with ethyl acetate (*ca*. 10 mL) and stirred for 1 hour at room temperature. The organic phase is separated and the aqueous layer is extracted with ethyl acetate (2 x 10 mL). The combined organic fractions were dried with anhydrous sodium sulfate, filtered and finally evaporated to dryness by rotary evaporation. The resulting oil was purified by silica gel thin layer chromatography (elution with hexanes/ethyl acetate 2:1) gave 4.5 mg of **S1** (51% yield) that was indistinguishable from the data previously reported for this compound (see Williams *et al.*, *Tetrahedron* **2008**, *64*, 6561-6567).

Data for 5α,13α-dihydroxytaxa-4(20),11(12)-diene S1:

Appearance: White crystalline solid.

Melting point: 144 – 147 ºC

TLC: R_f = 0.51 (1:1 EtOAc/hexanes, stains blue upon *p*-anisaldehyde staining).

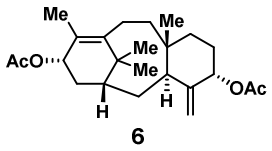
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97 (s, 1H), 4.64 (s, 1H), 4.33 (broad d, *J* = 10.0 Hz, 1H), 4.28 (t, *J* = 2.7 Hz, 1H), 3.53 (s, 1H), 2.84 (td, *J* = 13.4, 5.4 Hz, 1H), 2.79 (dt, *J* = 15.4, 9.7 Hz, 1H), 2.25 (td, *J* = 13.4, 5.1 Hz, 1H), 2.15 (broad d, *J* = 13.5 Hz, 1H), 2.02 – 1.95 (m with s at 1.97, 4H), 1.77 (tdd, *J* = 14.0, 5.1, 3.1 Hz, 1H), 1.73 – 1.71 (m, 1H), 1.71 – 1.57 (m, 3H), 1.34 (s, 3H), 1.29 – 1.22 (m, 2H), 1.02 (ddd, *J* = 13.3, 5.1, 2.1 Hz, 1H), 0.90 (s, 3H), 0.62 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 153.7, 139.5, 132.5, 109.1, 74.7, 68.7, 40.4, 39.6, 39.3, 39.2, 36.3, 35.8, 32.4, 32.1, 31.4, 27.5, 25.4, 25.0, 22.2, 16.3 ppm.

IR (neat): $\tilde{\nu}$ = 3356, 2928 ($\tilde{\nu}_{max}$), 1651, 1446, 1114, 1088, 1039, 1006, 924, 893 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{20}H_{34}O_2$ [M + Na+] 327.2294, found 327.2292.

Optical rotation: $[\alpha]_D^{20}$ (c 0.35, $CHCl_3$) = +104.8º, taken on a >93% ee sample.



6

5α,13α-diacetoxytaxa-4(20),11-diene 6. To a flame-dried 5 mL vial equipped with a stir bar were added **5α,13α-dihydroxytaxa-4(20),11(12)-diene S1** (1.7 mg, 0.0056 mmol, 1 equiv) and 4-dimethylaminopyridine (1 mg, 0.008 mmol, 1.4 equiv). The vial was evacuated and filled back with argon and dichloromethane (1 mL) was added. The vial was cooled to 0 ºC and triethylamine (17 µl, 0.125 mmol, 22 equiv) was added, followed by acetic anhydride (7.8 µl, 0.083 mmol, 15 equiv). The mixture is stirred inside the cooling bath for 5 minutes and then at room temperature until completion of the reaction (typically 12h). The light yellow reaction solution was quenched with the addition of sodium bicarbonate aqueous saturated solution (3 mL) and the organic phase was subsequently diluted with dichloromethane (*ca*. 1 mL). The organic phase is separated and the aqueous layer is extracted with dichloromethane (2 x 2 mL). The combined organic fractions were dried with anhydrous sodium sulfate, filtered and finally evaporated to dryness by rotary evaporation. The resulting oil was purified by silica gel thin layer chromatography (elution with hexanes/ethyl acetate 3:1), which gave 0.7 mg of **6** (32% yield) and 0.3 mg of an unknown (likely rearranged) by-product.

Data for 5α,13α-diacetoxytaxa-4(20),11-diene 6:

Appearance: White foam.

TLC: R_f = 0.59 (3:1 EtOAc/hexanes, stains blue upon *p*-anisaldehyde staining).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.84 (t, *J* = 8.2 Hz, 1H), 5.33 (t, *J* = 3.0 Hz, 1H), 5.09 (s, 1H),

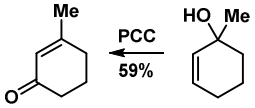
4.76 (s, 1H), 3.19 (d, J = 5.5 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.63 (dt, J = 14.4, 9.6 Hz, 1H), 2.16 (s, 3H), 2.16 – 2.07 (m, 3H), 2.06 (s, 3H), 1.87 (s, 3H), 1.84 – 1.77 (m, 3H), 1.65 (ddd, J = 15.7, 6.1, 2.3 Hz, 1H), 1.60 (ddd, J = 15.7, 5.2, 1.8 Hz, 1H), 1.42 (s, 3H), 1.34 – 1.26 (m, 2H), 1.12 – 1.05 (m with s at 1.09, 4H), 0.67 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.8, 170.2, 150.2, 139.6, 127.9, 112.3, 76.6, 71.4, 40.5, 40.0, 39.9, 39.8, 37.4, 34.0, 31.9, 30.3, 28.5, 28.2, 26.6, 25.2, 22.5, 21.9, 21.6, 14.6 ppm.

IR (neat): $\tilde{\nu}$ = 2924, 2853, 1734, 1453, 1370, 1243 ($\tilde{\nu}_{max}$), 1116, 1022, 906 cm^{-1}.

HRMS (ESI-TOF): calc'd for $C_{24}H_{36}O_4$ [M + Na+] 411.2506, found 411.2504.

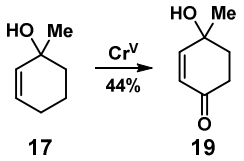
Optical rotation: $[\alpha]_D^{20}$ (c 0.35, $CHCl_3$) = +104.8º, taken on a >93% ee sample.



18 17

3-methyl-2-cyclohexenone 18. This procedure follows the precedent from Danishefsky *et al.* (*J. Am. Chem. Soc.* **2012**, *134*, 16080-16084). Thus, to a flame-dried flask was added 1-hydroxy-1-methylcyclohex-2-ene **16** (10 mg, 0.089 mmol, 1 equiv), dichloromethane (0.45 mL, 0.2 M), and sodium acetate (21.9 mg, 0.267 mmol, 3 equiv). The mixture was cooled to 0ºC, and pyridinium chlorochromate (38.4 mg, 0.178 mmol, 2 equiv) was added in portions over 5 min. After 15 min, the vessel was warmed to room temperature and stirred for 1.5 hr. After the reaction was deemed complete by thin-layer chromatography, it was diluted with 50% ethyl acetate in hexanes (1 mL) and filtered through a plug of celite and silica using 50% ethyl acetate in hexanes as the eluent. After concentration, silica gel flash chromatography (isocratic elution using 25% ethyl acetate in hexanes) yielded 3-methyl-2-cyclohexenone **18** (5.8 mg, 59% yield), which matched an authentic

sample (purchased from Sigma-Aldrich) by both thin-layer chromatography and ^{1}H and ^{13}C NMR. Crude ^{1}H NMR spectrum is reported.



4-hydroxy-4-methylcyclohex-2-enone 19. To a flame-dried reaction vial was added 1-hydroxy-1-methylcyclohex-2-ene **17** (10 mg, 0.0892 mmol, 1 equiv), manganese(IV) oxide (387 mg, 4.457 mmol, 50 equiv), "Cr^{V}" reagent **8** (144 mg, 0.446 mmol, 5 equiv), α,α,α-triflourotoluene (2.00 mL), and 15-crown-5 (0.040 mL) were added successively. This was stirred under argon at 80ºC for 20 hr, after which time the reaction was deemed complete by thin-layer chromatography. This was diluted with 1:1 ethyl acetate : hexanes (4 mL) and passed through a silica and celite plug, using 1:1 ethyl acetate : hexanes to rinse the reaction flask and flush the plug. This rinsate was concentrated by rotary evaporation, and purification by preparatory thin-layer chromatography afforded 4-hydroxy-4-methylcyclohex-2-enone **19** (4.9 mg, 44% yield), which matched literature precedent (Booker-Milburn *et al*., *Org. Lett.* **2003**, *5*, 3309-3312) for both ^{1}H and ^{13}C NMR spectra. Crude ^{1}H NMR spectrum is reported and pure ^{1}H and ^{13}C NMR spectra are tabulated below.

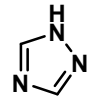
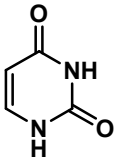
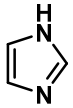
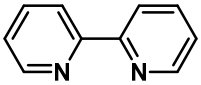
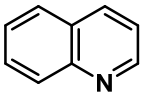
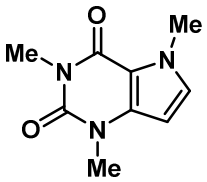
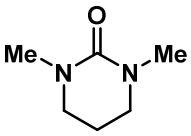
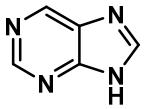
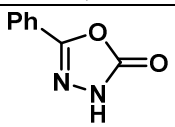
Data for 4-hydroxy-4-methylcyclohex-2-enone 19.

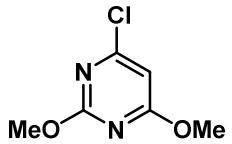
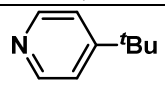
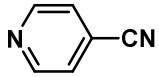
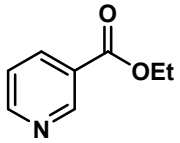
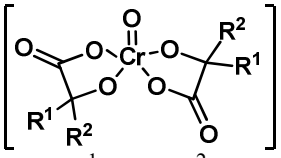
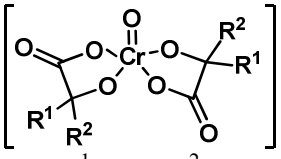
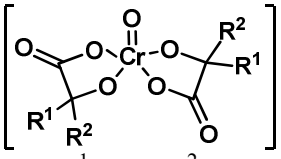
^{1}H NMR: (600 MHz, $CDCl_3$) δ 6.76 (d, *J* = 10.2, 1H), 5.89 (d, *J* = 10.1 Hz, 1H), 2.63 (ddd, *J* = 17.2, 6.7, 5.6 Hz, 1H), 2.43 (ddd, *J* = 17.3, 8.9, 6.2 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.47 (s, 3H) ppm.

^{13}C NMR: (151 MHz, $CDCl_3$) δ 198.9, 154.6, 128.3, 68.7, 37.5, 35.0, 27.3 ppm.

Table S6. Summary of allylic oxidation attempts:

Target Carbon (Substrate)	Conditions	Results, or percent product
C-5 (**1**)	CuBr, $PhCO_3tBu$	Degradation
	$Mn(OAc)_3$, TBHP	Degradation
	O_2, $Pd(O_2CCF_3)$, 2-aminopyridine, Mesitylene, 120°C	No reaction
	$Pd(OAc)_2$, BQ, AcOH, 50°C	35%
	$Pd(OAc)_2$, BQ, 1,3,5-trimethoxybenzene, AcOH, 50°C	41%
	$Pd(OAc)_2$, BQ, 1,3-dimethoxybenzene AcOH, 50°C	45%
	$Pd(OAc)_2$, BQ, Anisole AcOH, 50°C	50%
	$Pd(OAc)_2$, BQ, *N*,*N*-dimethylaniline AcOH, 50°C	Degradation
C-13 (**4**)	PCC, NaOAc, celite, benzene	30%, byproducts **7** and **8**
	CrO_3·DMP, DCM, -20°C	30%, byproducts **7** and **8**
	PCC, NaOAc, celite, MeCN	**5**, byproducts **7** and **8** Low conversion
	PCC, NaOAc, celite, DMF	**5**, byproducts **7** and **8** Low conversion
	PCC, NaOAc, celite, $CHCl_3$	Clean epoxide **8**
	PCC, NaOAc, celite, CCl_4	No conversion
	PCC, NaOAc, celite, C_7F_8	No conversion
	PDC, NaOAc, celite, benzene	No reaction
	Imidazolium dichromate, NaOAc, celite, benzene	No reaction
	Pyr·CrO_3, DCM	**5**, byproducts **7** and **8** Low conversion

	 CrO_3, DCM, -20°C → rt	Mostly **7**, but **8** and **5** also observed
	 CrO_3, DCM, -20°C → rt	Mostly **7**. Trace **5** and no **8**
	 CrO_3, DCM, -20°C → rt	No reaction
	HMPA CrO_3, DCM, -20°C → rt	1:1 **5** and **7**. No **8**. ~60% conversion
	 CrO_3, DCM, -20°C → rt	**7** and **8**. No **5**.
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Mostly **8**.
	 CrO_3, DCM, -20°C → rt	**7** and **8**. No **5**.
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Mostly **7**. ~80% conversion
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. ~50% conversion
	 CrO_3, DCM, -20°C → rt	Very little conversion
	 CrO_3, DCM, -20°C → rt	**7** and **8**. No **5**.

	Urea CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Mostly **7**. ~20% conversion
	 CrO_3, DCM, -20°C → rt	Exclusively **7**
	DMAP CrO_3, DCM, -20°C → rt	Very little conversion
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Very little **5**. ~90% conversion
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Very little **5**. ~90% conversion
	 CrO_3, DCM, -20°C → rt	**5**, **7**, and **8**. Very little **5**. ~100% conversion
	$CuCl$, $BzOOtBu$, Δ	Degradation
	$Pd(OH)_2/C$, TBHP, K_2CO_3	Degradation
	$Mn(OAc)_3$, TBHP	Degradation
	N-hydroxyphthalimide, $(BzO)_2$, $Cu(OAc)_2$	No reaction
	$RuCl_3 \cdot nH_2O$, TBHP	Degradation
	 R^1=Me, R^2=Et MeCN	45%, byproduct **10**
	 R^1=Me, R^2=Me MeCN	~45%, same byproduct **10**
	 R^1=Me, R^2=*t*Bu MeCN	~45%, same byproduct **10**

	NHPI, O_2, $(BzO)_2$, Acetone or EtOAc, reflux	Multiple products
	NBS, $(BzO)_2$, CCl_4, rt	C-11,12 olefin reacted
	$Cu(OAc)_2$, $(BzO)_2$, CCl_4, reflux	Degradation
C-10 (**5**)	$Pd(OH)_2/C$, TBHP, K_2CO_3	Degradation
	TMSCl, EtSH, Et_3N	No reaction
	TMSCl, $[EtSAlMe_3]Li$	No reaction
	TMSCl, PhSH, Et_3N	No reaction
	TMSCl, PhSeNa	No reaction
	TMSCl, $MeSeAlMe_2$	No reaction
	DDQ	No reaction
	Chloranil	No reaction
	IBX	No reaction
	PhSe-Phthl, $(BzO)_2$, CCl_4, reflux	Multiple products
	SeO_2, dioxane, 100°C	C-14 oxidation
	NHPI, $(BzO)_2$, $Cu(OAc)_2$, Benzene or acetone, reflux	No reaction
	$Cu(OAc)_2$, $(BzO)_2$, CCl_4, reflux	Degradation

Computational Procedures:

All calculations were performed using the Gaussian 09 software suite. Geometry minimizations were conducted using the UB3LYP functional[2] with the 6-31+G(d,p) basis set. Spin contamination was low in all cases, with $<S^2>$ before annihilation of the first spin contaminant deviating < 5% from the predicted value. Stationary points were characterized as minima by computing the Hessian matrix and analyzing the vibrational frequencies. All minima were characterized by only real vibrational frequencies. Vibrational analysis was performed to derive thermochemical data. All energies are reported in hartrees/particle and all distances are reported in angstroms (Å) unless otherwise noted. Zero point energies and thermal corrections are used unscaled.

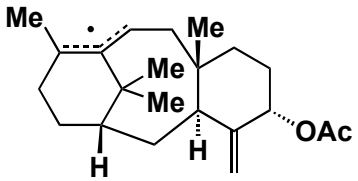
Full Gaussian 09 Citation:

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Computated Structures and Energies:

All energies are reported in hartrees/particle
XYZ coordinates are reported in Å

E(UB3LYP) : UB3LYP/6-31+G(d,p)
ZPE : Zero point correction to energy (UB3LYP/6-31+G(d,p))
TCGFE : Thermal correction to Gibbs free energy (298.15K, UB3LYP/6-31+G(d,p))

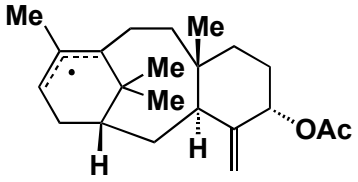


4 C-10

E(UB3LYP) = -1008.65574295
ZPE = 0.506749
TCGFE = 0.453220

C	1.6525000000	1.4093490000	1.8327730000
C	2.1896030000	-0.0191990000	1.4858520000
C	3.0587960000	0.0062160000	0.1989690000
C	2.1495570000	0.6062780000	-0.8956610000
C	1.7729560000	1.9543110000	-0.6890350000
C	1.7725360000	2.4985520000	0.7222970000
C	1.4985240000	-0.1339670000	-1.8823460000
C	1.0858460000	-1.5704830000	-1.7506010000
C	-0.1820540000	-1.7868160000	-0.8247920000
C	-0.1654360000	-0.9230210000	0.5156680000
C	-1.5096470000	-1.1282150000	1.2210590000
C	-2.7182780000	-0.6916360000	0.4232390000
C	-2.7628500000	-1.4194060000	-0.9219710000
C	-1.4194340000	-1.3403960000	-1.6553150000
C	1.0496670000	-1.0889480000	1.4787520000
H	2.8502260000	-0.3338520000	2.3069270000
H	-0.1810370000	0.1185180000	0.1781190000
C	-1.7135320000	-1.7231170000	2.4043190000
C	4.3179820000	0.9069140000	0.3845120000
C	3.6857650000	-1.3819520000	-0.0879160000
O	-2.6014170000	0.7553060000	0.1995340000
C	-3.7495800000	1.4611130000	0.0866890000
C	-3.4648620000	2.9319990000	-0.1053300000
O	-4.8594270000	0.9692140000	0.1406830000
C	1.0828320000	2.7943380000	-1.7285890000
C	-0.2608890000	-3.2977670000	-0.5284660000
H	0.5954260000	1.3244410000	2.1065810000
H	2.1603750000	1.7765310000	2.7311510000
H	2.6462720000	3.1399210000	0.9130530000
H	0.9149190000	3.1796200000	0.8107470000
H	0.9237560000	0.4349680000	-2.6091760000
H	0.8132750000	-1.9682270000	-2.7368320000
H	1.8893560000	-2.2056500000	-1.3885500000
H	-3.6407610000	-0.8591540000	0.9808580000
H	-3.5681080000	-1.0034210000	-1.5371160000
H	-3.0317470000	-2.4632230000	-0.7199820000
H	-1.2602470000	-0.3068890000	-1.9857420000
H	-1.4700500000	-1.9522670000	-2.5649780000
H	0.6663290000	-1.0694640000	2.5019340000
H	1.4892250000	-2.0847900000	1.3663410000

H	-2.7176890000	-1.8256400000	2.8071610000
H	-0.9133000000	-2.1358720000	3.0086520000
H	4.9600030000	0.8225320000	-0.4993450000
H	4.8959940000	0.5588910000	1.2486420000
H	4.1098640000	1.9639750000	0.5302490000
H	3.0179530000	-2.2284120000	0.0564880000
H	4.0811120000	-1.4282640000	-1.1078560000
H	4.5267660000	-1.5332830000	0.5975730000
H	-2.9278900000	3.3237860000	0.7641320000
H	-2.8257940000	3.0826410000	-0.9805820000
H	-4.4045400000	3.4690950000	-0.2327370000
H	1.3910530000	2.5423050000	-2.7472610000
H	-0.0143570000	2.6985170000	-1.6778370000
H	1.3107090000	3.8548220000	-1.5658890000
H	-0.2848600000	-3.8640550000	-1.4669930000
H	0.6128340000	-3.6415020000	0.0358500000
H	-1.1483230000	-3.5676460000	0.0500260000

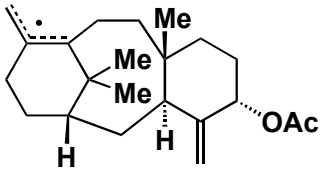


4 C-13

E(UB3LYP) = -1008.67406981
ZPE = 0.506945
TCGFE = 0.454591

C	1.4555310000	1.5963610000	1.7895800000
C	2.1482950000	0.2294460000	1.5506370000
C	3.0733950000	0.3428240000	0.2941130000
C	2.1377590000	0.6439920000	-0.8793580000
C	1.3097670000	1.8023480000	-0.7346840000
C	1.0509200000	2.3013800000	0.5211450000
C	1.8948590000	-0.3481760000	-1.9838560000
C	1.3060970000	-1.7207630000	-1.5332830000
C	-0.0187330000	-1.8214250000	-0.7190330000
C	-0.0826400000	-0.9002530000	0.5728990000
C	-1.4353970000	-1.1235190000	1.2500030000
C	-2.6263050000	-0.7697780000	0.3811620000
C	-2.5801400000	-1.5001300000	-0.9648940000
C	-1.2025530000	-1.4103000000	-1.6359730000
C	1.1405190000	-0.9636490000	1.5350210000
H	2.8030430000	0.0348360000	2.4132180000
H	-0.1476200000	0.1190680000	0.1903010000
C	-1.6596530000	-1.6302760000	2.4693100000
C	4.0804420000	1.5181440000	0.4753300000
C	3.9720610000	-0.9064570000	0.1462610000
O	-2.5750600000	0.6799580000	0.1495320000
C	-3.7522670000	1.3349650000	0.0354660000
C	-3.5332330000	2.8201040000	-0.1312660000
O	-4.8403860000	0.7950070000	0.0796960000
C	0.6507800000	2.4502750000	-1.9404190000
C	-0.1471230000	-3.3149410000	-0.3357590000
H	0.5680880000	1.4599210000	2.4249970000
H	2.1246260000	2.2479810000	2.3720780000
H	0.4608810000	3.2103020000	0.6259090000
H	2.8314340000	-0.5890280000	-2.5093270000
H	1.2372920000	0.0936570000	-2.7380430000
H	1.1468210000	-2.3038580000	-2.4513520000
H	2.0767360000	-2.2654530000	-0.9869920000
H	-3.5644620000	-0.9817500000	0.8959650000
H	-3.3602830000	-1.0966500000	-1.6193600000
H	-2.8448420000	-2.5475600000	-0.7783030000
H	-1.0420560000	-0.3815800000	-1.9800110000
H	-1.1989330000	-2.0427480000	-2.5334040000
H	0.7707790000	-1.0220910000	2.5621000000

H	1.6950260000	-1.8959100000	1.3848180000
H	-2.6727830000	-1.7422140000	2.8464650000
H	-0.8652880000	-1.9566660000	3.1319930000
H	4.8003970000	1.5174990000	-0.3506550000
H	4.6442330000	1.3930300000	1.4080730000
H	3.5983000000	2.4958350000	0.4907290000
H	3.4446710000	-1.8562170000	0.2230910000
H	4.5100310000	-0.8960510000	-0.8077890000
H	4.7252170000	-0.8976150000	0.9419290000
H	-3.1758620000	3.2420300000	0.8140750000
H	-2.7696050000	3.0162590000	-0.8883670000
H	-4.4743340000	3.2963840000	-0.4063040000
H	1.3447860000	2.5566340000	-2.7809620000
H	-0.2105020000	1.8720410000	-2.2978630000
H	0.2839470000	3.4475980000	-1.6795350000
H	-0.1134410000	-3.9426690000	-1.2340160000
H	0.6781730000	-3.6289640000	0.3129430000
H	-1.0751990000	-3.5368030000	0.1953620000

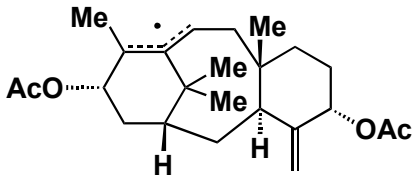


4 C-18

E(UB3LYP) = -1008.66451609
ZPE = 0.507768
TCGFE = 0.455207

C	1.4192320000	1.6551210000	1.7132380000
C	2.1553150000	0.3027640000	1.4946770000
C	3.0646950000	0.3808000000	0.2234550000
C	2.1082330000	0.5939530000	-0.9508050000
C	1.2569820000	1.7326650000	-0.8982030000
C	1.1209700000	2.4844140000	0.4277800000
C	1.8923940000	-0.4775030000	-1.9881720000
C	1.3003680000	-1.8202330000	-1.4599330000
C	-0.0244450000	-1.8675800000	-0.6420390000
C	-0.0647180000	-0.8812380000	0.5994710000
C	-1.4100950000	-1.0515830000	1.3052330000
C	-2.6100560000	-0.7394260000	0.4326470000
C	-2.5811050000	-1.5323770000	-0.8783850000
C	-1.2101480000	-1.4862950000	-1.5684910000
C	1.1764310000	-0.9122910000	1.5369910000
H	2.8295040000	0.1533500000	2.3512160000
H	-0.1246180000	0.1147740000	0.1573110000
C	-1.6208820000	-1.4842910000	2.5550120000
C	4.0624160000	1.5721240000	0.3398930000
C	3.9856940000	-0.8580270000	0.1242560000
O	-2.5637760000	0.6992840000	0.1387660000
C	-3.7446770000	1.3327620000	-0.0405990000
C	-3.5379200000	2.8077060000	-0.2908570000
O	-4.8273300000	0.7821230000	0.0070710000
C	0.5106620000	2.1979120000	-1.9628970000
C	-0.1645470000	-3.3368070000	-0.1792130000
H	0.4804690000	1.4623290000	2.2435740000
H	2.0181790000	2.2750650000	2.3882780000
H	1.7655600000	3.3706750000	0.4071510000
H	0.0992640000	2.8749760000	0.4779930000
H	2.8411260000	-0.7410930000	-2.4770820000
H	1.2435170000	-0.0989420000	-2.7804920000
H	1.1388600000	-2.4521020000	-2.3445600000
H	2.0672980000	-2.3390300000	-0.8833190000
H	-3.5418210000	-0.9287350000	0.9677420000
H	-3.3653880000	-1.1546100000	-1.5427850000
H	-2.8526480000	-2.5674060000	-0.6391170000
H	-1.0416350000	-0.4756450000	-1.9587970000
H	-1.2225020000	-2.1605410000	-2.4350870000

H	0.8347550000	-0.9556700000	2.5742440000
H	1.7406440000	-1.8389540000	1.3910670000
H	-2.6296220000	-1.5678230000	2.9508130000
H	-0.8199830000	-1.7766940000	3.2255670000
H	4.7670580000	1.5445390000	-0.4983770000
H	4.6433410000	1.4860220000	1.2662980000
H	3.5899080000	2.5530030000	0.3305500000
H	3.4746480000	-1.8138900000	0.2246900000
H	4.5342290000	-0.8673290000	-0.8234300000
H	4.7292720000	-0.8107820000	0.9274200000
H	-3.1467480000	3.2828390000	0.6147960000
H	-2.8040990000	2.9600740000	-1.0869830000
H	-4.4896040000	3.2659660000	-0.5597070000
H	0.5827220000	1.7843560000	-2.9619940000
H	-0.1498200000	3.0505850000	-1.8387580000
H	-0.1491420000	-4.0114860000	-1.0432860000
H	0.6652750000	-3.6254220000	0.4756120000
H	-1.0879400000	-3.5190740000	0.3744010000

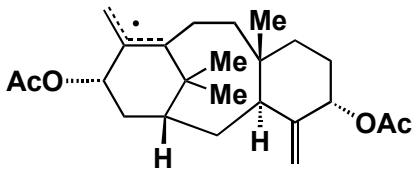


6 C-10

E(UB3LYP) = -1236.54652901
ZPE = 0.549059
TCGFE = 0.487723

C	1.8695740000	-0.1560400000	1.3140050000
C	1.3013010000	-1.6130500000	1.3539440000
C	1.7421370000	-2.4330450000	0.1100660000
C	1.3261200000	-1.5656980000	-1.0963200000
C	2.0359860000	-0.3363530000	-1.2284190000
C	2.6296630000	0.2634890000	0.0285550000
C	0.1960260000	-1.7672320000	-1.8720360000
C	-1.0261560000	-2.5329420000	-1.4627940000
C	-1.9755610000	-1.7429120000	-0.4677330000
C	-1.2124580000	-0.8872610000	0.6450660000
C	-2.2639550000	-0.0650300000	1.3995300000
C	-3.0440410000	0.9100270000	0.5470000000
C	-3.7508000000	0.1696850000	-0.5894000000
C	-2.7878170000	-0.7480640000	-1.3486680000
C	-0.2381250000	-1.6152230000	1.6231980000
H	1.7348670000	-2.1140580000	2.2308440000
H	-0.6283620000	-0.1528830000	0.0799550000
C	-2.6098770000	-0.1961090000	2.6874870000
C	3.2838090000	-2.6653810000	0.0898650000
C	1.1980900000	-3.8825630000	0.1733200000
O	-2.0866450000	1.8724640000	-0.0099190000
C	-2.5365460000	3.1226640000	-0.2608960000
C	-1.4231440000	4.0159070000	-0.7539750000
O	-3.6843460000	3.4811230000	-0.0846010000
C	2.0162720000	0.4978120000	-2.4784070000
C	-2.9205580000	-2.7837370000	0.1648940000
H	1.0427020000	0.5548720000	1.4107370000
H	2.5276820000	0.0180850000	2.1709950000
H	3.7006810000	0.0705890000	0.1346180000
O	2.5197550000	1.7216910000	-0.0853020000
H	0.0399970000	-1.0649530000	-2.6874940000
H	-1.6329200000	-2.7534040000	-2.3501930000
H	-0.7872900000	-3.4971970000	-1.0251420000
H	-3.7617630000	1.4730370000	1.1453720000
H	-4.2149220000	0.8937010000	-1.2677990000
H	-4.5675750000	-0.4107370000	-0.1437930000
H	-2.0799050000	-0.1264400000	-1.9105320000
H	-3.3528820000	-1.3240660000	-2.0922890000
H	-0.3293220000	-1.1207890000	2.5938330000

H	-0.5726680000	-2.6416110000	1.8021220000
H	-3.3830100000	0.4333730000	3.1199930000
H	-2.1614870000	-0.9246070000	3.3538800000
H	3.5390750000	-3.3348660000	-0.7388930000
H	3.5950190000	-3.1544240000	1.0197440000
H	3.8905860000	-1.7712710000	-0.0280110000
H	0.1576750000	-3.9742950000	0.4745550000
H	1.3222430000	-4.3879500000	-0.7898750000
H	1.7833080000	-4.4404730000	0.9126860000
H	-0.8846510000	4.4166720000	0.1119440000
H	-0.7086560000	3.4602590000	-1.3647210000
H	-1.8489750000	4.8487580000	-1.3147830000
H	1.9017470000	-0.1254410000	-3.3694480000
H	1.2079210000	1.2439900000	-2.4799570000
H	2.9517050000	1.0587630000	-2.5783270000
H	-3.4427080000	-3.3440950000	-0.6196560000
H	-2.3686360000	-3.5103740000	0.7710890000
H	-3.6748630000	-2.3280090000	0.8117110000
C	3.5238010000	2.4700060000	0.4283510000
C	3.2364450000	3.9439220000	0.2688080000
O	4.5158140000	2.0119640000	0.9599790000
H	2.8464290000	4.1600020000	-0.7289360000
H	2.4736770000	4.2421800000	0.9961810000
H	4.1475410000	4.5124820000	0.4556870000

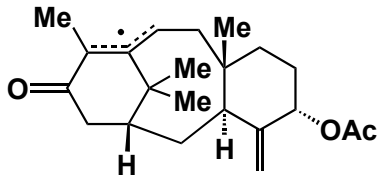


6 C-18

E(UB3LYP) = -1236.55362738
ZPE = 0.549955
TCGFE = 0.490642

C	1.8614220000	0.4122090000	1.3158520000
C	1.8226240000	-1.1443210000	1.3500300000
C	2.5156330000	-1.7535470000	0.0841300000
C	1.7029480000	-1.2181090000	-1.0988670000
C	1.5849850000	0.1974440000	-1.2350610000
C	2.1131950000	1.0410620000	-0.0748030000
C	0.8705310000	-2.1433080000	-1.9498570000
C	-0.2245420000	-2.9586510000	-1.2002500000
C	-1.3247980000	-2.2596280000	-0.3494020000
C	-0.7804320000	-1.1980860000	0.6988720000
C	-1.9811680000	-0.6038230000	1.4391830000
C	-2.9810010000	0.0985610000	0.5417810000
C	-3.4580570000	-0.8101330000	-0.5949200000
C	-2.2929480000	-1.5111830000	-1.3058450000
C	0.3766490000	-1.6688070000	1.6291620000
H	2.4159150000	-1.4716070000	2.2157050000
H	-0.4088630000	-0.3707790000	0.0893900000
C	-2.2517260000	-0.6957340000	2.7477330000
C	4.0130660000	-1.3229880000	-0.0130440000
C	2.6174030000	-3.2952410000	0.2066890000
O	-2.2998790000	1.2630400000	-0.0323450000
C	-3.0483360000	2.3592250000	-0.2863600000
C	-2.2226700000	3.4526430000	-0.9205280000
O	-4.2382040000	2.4429860000	-0.0503180000
C	1.0421080000	0.8399200000	-2.3279140000
C	-2.0771550000	-3.4055050000	0.3676420000
H	0.9082030000	0.8096620000	1.6792750000
H	2.6325620000	0.7874180000	1.9949130000
H	3.1777530000	1.2278370000	-0.2045930000
O	1.4939510000	2.3605550000	-0.1078730000
H	1.5130380000	-2.8873430000	-2.4430670000
H	0.3953030000	-1.5814260000	-2.7559980000
H	-0.7529720000	-3.5369650000	-1.9709850000

H	0.2592670000	-3.7066550000	-0.5744820000
H	-3.8308020000	0.4686220000	1.1170640000
H	-4.0480440000	-0.2181150000	-1.3029080000
H	-4.1435700000	-1.5486100000	-0.1632780000
H	-1.7226920000	-0.7666500000	-1.8742810000
H	-2.6954700000	-2.2239480000	-2.0374680000
H	0.1614590000	-1.3309100000	2.6458810000
H	0.3903820000	-2.7607080000	1.6980420000
H	-3.1440490000	-0.2344990000	3.1625980000
H	-1.6201360000	-1.2275910000	3.4510640000
H	4.5026000000	-1.8983190000	-0.8061620000
H	4.5279560000	-1.5509250000	0.9276340000
H	4.1837390000	-0.2723340000	-0.2356680000
H	1.7085110000	-3.7888500000	0.5428900000
H	2.9174700000	-3.7488730000	-0.7434170000
H	3.3948280000	-3.5376790000	0.9390540000
H	-2.5429580000	4.4188090000	-0.5247150000
H	-1.1568560000	3.2930990000	-0.7551220000
H	-2.4167100000	3.4531130000	-1.9988730000
H	0.7008030000	0.3027990000	-3.2040330000
H	0.9600780000	1.9184790000	-2.3503310000
H	-2.4607130000	-4.1243770000	-0.3658710000
H	-1.4132590000	-3.9535830000	1.0455150000
H	-2.9209150000	-3.0493670000	0.9622280000
C	2.2573110000	3.4048460000	0.2981150000
C	1.4872940000	4.7015860000	0.2346600000
O	3.4092720000	3.3021820000	0.6697260000
H	1.0744630000	4.8538630000	-0.7667590000
H	0.6481230000	4.6693470000	0.9366720000
H	2.1504140000	5.5263770000	0.4945830000

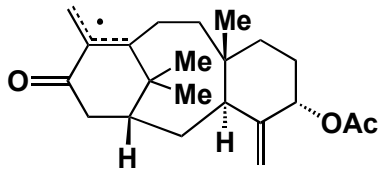


5 C-10

E(UB3LYP) = -1082.69190992
ZPE = 0.488723
TCGFE = 0.436091

C	-1.3607910000	1.4790540000	-1.5942450000
C	-1.8595450000	0.0092170000	-1.5968930000
C	-2.9115360000	-0.1843210000	-0.4676090000
C	-2.1748750000	0.1688460000	0.8344920000
C	-1.7945300000	1.5598950000	0.9611510000
C	-1.3270870000	2.2211280000	-0.2509830000
C	-1.5844380000	-0.7049100000	1.7087940000
C	-1.1239710000	-2.0943020000	1.3889270000
C	0.2792510000	-2.0940150000	0.6558280000
C	0.3837920000	-1.0033230000	-0.4988980000
C	1.8147010000	-1.0199740000	-1.0413990000
C	2.8644960000	-0.6593510000	-0.0083880000
C	2.7869510000	-1.6161440000	1.1812470000
C	1.3583210000	-1.7544140000	1.7235860000
C	-0.7007550000	-1.0362300000	-1.6152440000
C	2.2092100000	-1.3735810000	-2.2706080000
C	-4.0981530000	0.8072720000	-0.6534430000
C	-3.5785510000	-1.5782080000	-0.5235510000
O	2.6138750000	0.6873220000	0.5063970000
C	3.2318470000	1.7255640000	-0.1204150000
C	2.7948530000	3.0454990000	0.4617940000
O	4.0221780000	1.5853950000	-1.0309450000
C	-1.5517380000	2.2494450000	2.2711210000
C	0.4951910000	-3.5205310000	0.1138750000
O	-0.8308160000	3.3594420000	-0.2070090000
H	-0.3522150000	1.5537180000	-2.0164470000
H	-1.9917110000	2.0883780000	-2.2524880000

H	-2.3870390000	-0.1504400000	-2.5484550000
H	-1.1220830000	-0.2621650000	2.5888730000
H	-0.9981710000	-2.6753450000	2.3111860000
H	-1.8377160000	-2.6383670000	0.7759780000
H	0.3040830000	-0.0410320000	0.0157620000
H	3.8593830000	-0.6631810000	-0.4561550000
H	3.4601300000	-1.2676220000	1.9729720000
H	3.1673210000	-2.5879950000	0.8456900000
H	1.0860720000	-0.8130070000	2.2140900000
H	1.3401310000	-2.5284920000	2.5015360000
H	-0.2027780000	-0.8637550000	-2.5725120000
H	-1.1276400000	-2.0403440000	-1.7013970000
H	3.2588310000	-1.3310410000	-2.5467860000
H	1.5239160000	-1.7083700000	-3.0420060000
H	-4.8604220000	0.6228600000	0.1118610000
H	-4.5631630000	0.6502930000	-1.6331050000
H	-3.8149770000	1.8581850000	-0.5800250000
H	-2.8972540000	-2.4011770000	-0.7322690000
H	-4.1043550000	-1.7979920000	0.4114840000
H	-4.3222790000	-1.5803590000	-1.3275390000
H	1.7558890000	3.2483720000	0.1770190000
H	2.8382300000	3.0179600000	1.5541690000
H	3.4366900000	3.8383210000	0.0774810000
H	-2.1590630000	1.8189680000	3.0713970000
H	-0.4958610000	2.2001470000	2.5721850000
H	-1.7840880000	3.3132960000	2.1681700000
H	0.4286810000	-4.2499780000	0.9295530000
H	-0.2662540000	-3.7886270000	-0.6266570000
H	1.4699630000	-3.6381710000	-0.3659430000



5 C-18

E(UB3LYP) = -1082.68867536
ZPE = 0.488355
TCGFE = 0.434915

C	1.3157120000	1.5434530000	1.6402180000
C	2.0786970000	0.2047860000	1.5040520000
C	3.0124050000	0.2684600000	0.2484770000
C	2.0772350000	0.4187130000	-0.9506840000
C	1.2540580000	1.5837920000	-0.9791140000
C	0.9561710000	2.2684320000	0.3401800000
C	1.8852710000	-0.6811250000	-1.9595590000
C	1.3018060000	-2.0148500000	-1.3970650000
C	-0.0396380000	-2.0461180000	-0.6071600000
C	-0.0980880000	-1.0283450000	0.6063780000
C	-1.4574960000	-1.1627860000	1.2891150000
C	-2.6221780000	-0.8298040000	0.3783020000
C	-2.5902150000	-1.6770400000	-0.8983390000
C	-1.2064250000	-1.6845850000	-1.5662980000
C	1.1246700000	-1.0269880000	1.5663190000
C	-1.7014230000	-1.5730530000	2.5397910000
C	3.9537030000	1.5066420000	0.3441000000
C	3.9698860000	-0.9420150000	0.1999360000
O	-2.4901190000	0.5854630000	0.0230330000
C	-3.6237880000	1.3239230000	-0.0659860000
C	-3.3148780000	2.7524070000	-0.4405480000
O	-4.7385230000	0.8753150000	0.1160450000
C	0.6112270000	2.0975660000	-2.0848970000
C	-0.1912000000	-3.5020670000	-0.1102980000
O	0.3777670000	3.3443900000	0.3923300000
H	0.3753350000	1.4134140000	2.1893100000
H	1.8973540000	2.2615770000	2.2285210000
H	2.7381280000	0.1104970000	2.3791430000

H	2.8422940000	-0.9473960000	-2.4309040000
H	1.2395720000	-0.3283150000	-2.7671800000
H	1.1684370000	-2.6769500000	-2.2636370000
H	2.0636010000	-2.5015960000	-0.7861140000
H	-0.1492780000	-0.0481000000	0.1310470000
H	-3.5755340000	-0.9521490000	0.8939600000
H	-3.3522460000	-1.3076460000	-1.5934230000
H	-2.8880500000	-2.6960670000	-0.6238750000
H	-1.0178200000	-0.6928730000	-1.9942300000
H	-1.2150540000	-2.3924700000	-2.4055660000
H	0.7657550000	-1.0543880000	2.5983850000
H	1.7087300000	-1.9448720000	1.4488000000
H	-2.7189030000	-1.6275380000	2.9174870000
H	-0.9195360000	-1.8738240000	3.2293410000
H	4.6636700000	1.4961920000	-0.4898490000
H	4.5303270000	1.4716680000	1.2761990000
H	3.4333130000	2.4652140000	0.3060710000
H	3.4811950000	-1.9099130000	0.2988240000
H	4.5471050000	-0.9495790000	-0.7304920000
H	4.6865490000	-0.8614090000	1.0246010000
H	-2.3936930000	3.1004580000	0.0321170000
H	-3.1754430000	2.8105870000	-1.5260390000
H	-4.1586750000	3.3858160000	-0.1646630000
H	0.7415300000	1.6828920000	-3.0777100000
H	-0.0219370000	2.9697450000	-1.9745610000
H	-0.1573000000	-4.1994380000	-0.9554470000
H	0.6225870000	-3.7742320000	0.5713830000
H	-1.1280910000	-3.6670490000	0.4257210000