Short Enantioselective Synthesis of (-)-Sclerophytin A by a Stereoconverging Epoxide Hydrolysis

Bin Wang, Armando P. Ramirez, Justin J. Slade and James P. Morken *

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Supporting Information

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General Information

^{1}H NMR spectra were recorded on Varian VNMRS 600 MHz, Varian VNMRS 500 MHz**,** Varian Unity Inova 500 MHz and Varian Gemini 400 MHz spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and assignment. $^{13}C\{^1H\}$NMR spectra were recorded on Varian VNMRS 600 MHz, Varian VNMRS 500 MHz, Varian Unity Inova 500 MHz and Varian Gemini 400 MHz spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.23 ppm). Infrared (IR) spectra were recorded on a Bruker α-P Spectrometer or a Galaxy series FTIR 5000 of Madison Instrument, Inc. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (ESI) was performed at Boston College, Chestnut Hill, MA. Elemental analysis was performed by Robertson Microlit Laboratories. Melting points are reported uncorrected.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), and potassium permanganate ($KMnO_4$).

All reactions were conducted in oven- or flame-dried glassware. Benzene, acetonitrile, methylene chloride, and diethyl ether were purified using commercial solvent purification systems, by passing the solvent through two activated alumina columns after being purged with argon unless it was mentioned. Pentane, triethyl amine, and diisopropylamine were distilled from calcium hydride under nitrogen immediately prior to use. Tetrahydrofuran is purified by distillation from sodium with benzophenone as color indicator immediately prior to use.

Magnesium turnings, (+)-B-methoxydiisopinocampheylborane, methylallyl chloride, (-)-menthol, 1,10-phenanthroline, *tert*-butyl vinyl ether, palladium(II) acetate, copper(II) acetate, diisopropylamine, iodine, *n*-butyllithium in hexane, hydrogen chloride in diethyl ether, triphenyltin hydride, 2,2'-azobisisobutyronitrile, indium(III) chloride, sodium borohydride, DIBAL-H, DMAP, triethylamine, acetic anhydride, scandium trifluoromethanesulfonate, trimethylsilyl cyanide, 4-bromo-1-butene, DMSO, *m*-chloroperoxybenzoic acid, and dimethylsulfide was purchased from Aldrich and used without further purification. methylmagnesium chloride was purchased from Acros. The 2nd generation Grubbs catalyst (G2) was from Materia and used without further purification. All other reagents were purchased from Aldrich or Fisher and used without further purification.

Geranial (**S12**) was prepared from geraniol (Aldrich) based on a literature procedure to prepare neral.[1] Jones reagent was prepared based on a literature procedure.[2]

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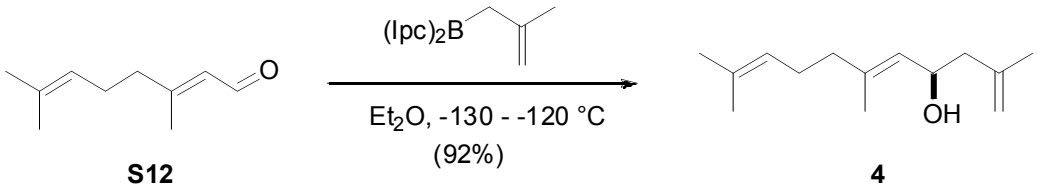
[1] Piancatelli, G.; Leonelli, F.; Do, N.; Ragan, J. *Org. Synth.* **2006**, *83*, 18.

[2] Freeman, F. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, **1995**; Vol. 2, p 1261.

Experimental Procedures



S12 **4**

Magnesium turnings (7.05 g, 290 mmol) were crushed with a mortar and pestle and transferred to a Schlenk tube together with a Teflon-coated stirrer bar. The system was sealed with a pressure-equalized addition funnel, flame-dried under vacuum, and filled with N_2. The turnings were stirred vigorously for 3 d over which time some of the magnesium turned black. Diethyl ether (15 mL) was added to cover the magnesium, the solution cooled to 0 °C under N_2, and a solution of methylallyl chloride (7.10 mL, 72.5 mmol) in diethyl ether (120 mL) was added dropwise to the center of the vortex over 4.5 h. The resulting mixture was stirred for 1 h at 0 °C and the clear solution then transferred to a dry reagent bottle by cannula and titrated (versus menthol with 1,10-phenanthroline as a color indicator). The titration indicated that the concentration of methylallyl magnesium chloride was 0.37 M.[3]

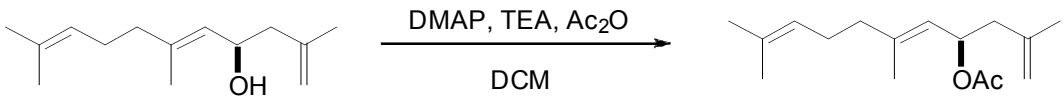
Methylallyl magnesium chloride in ether prepared above (95 mL, 0.37 M, 35.1 mmol) was added dropwise to a stirred solution of the (+)-B-methoxydiisopinocampheylborane (11.59 g, 36.6 mmol) in Et_2O (33 mL) at 0 ºC. Following addition, the reaction mixture was vigorously stirred under N_2 at rt for 1 h during which time a white slurry formed. The Et_2O was removed under vacuum and the residue was treated with pentane (62 mL). The resulting suspension was filtered under nitrogen using Schlenk line techniques, the solids washed with pentane (40 mL), and the pentane removed under high vacuum. The residue was dissolved in Et_2O (54 mL) to form a clear solution which was cooled to -130 - -120 ºC in an ethanol and liquid N_2 bath. To the borane solution (cloudy at low temperature), a cooled (ethanol/liquid N_2) Et_2O (46 mL) solution of geranial (**S12**) (4.61 g, 30.3 mmol) was added slowly dropwise via cannula down the side of the flask (if the geranial solution solidified upon prolonged cooling, it was slightly warmed to liquify). After addition was complete, the reaction mixture was stirred at -130 - -120 ºC for 1 h. Methanol (2 mL) and water (2 mL) were added at -120 ºC and the flask allowed warming to rt. Then reaction mixture was then treated with aqueous NaOH solution (16 mL, 3 M) and 30% aqueous H_2O_2 (32 mL). and the mixture heated to reflux for 3 h. The mixture was cooled to ambient temperature and the aqueous and organic layers were separated. The aqueous layer was washed with Et_2O (20 mL, 3 times) and the combined organic layers washed with water (10 mL), brine (10 mL), and dried over $MgSO_4$. After filtration and removal of solvent, the mixture was purified by flash chromatography [silica gel, hexanes / EtOAc (30/1 to 20/1) as eluent] to give allylic alcohol **4** (5.8 g, 27.8 mmol, 92 % yield) as a colorless oil.[4]

Allylic alcohol 4**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 – 5.17 (m, 1H), 5.12 – 5.05 (m, 1H), 4.89 – 4.85 (m, 1H), 4.82 – 4.79 (m, 1H), 4.55 – 4.47 (m, 1H), 2.25 (ddd, *J* = 13.6, 8.4, 0.8 Hz, 1H), 2.16 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.13 – 2.06 (m, 2H), 2.05 – 1.98 (m, 2H), 1.78 (s, 3H), 1.70 (d, *J* = 1.2 Hz, 3H), 1.68 (d, *J* = 1.2 Hz, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.8, 131.9, 127.4, 124.2, 113.7, 66.3, 46.5, 39.7, 26.6, 25.9, 22.8, 17.9, 16.8. IR (neat): 3365

[3] Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698.
[4] Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401.

(br s), 1668 (w), 1647 (m); HRMS-(ESI+) for $C_{14}H_{23}$ [M+H - H_2O]: calculated: 191.1800, found: 191.1801; $[\alpha]_D^{20}$ = +19.2 (c = 6.5, $CHCl_3$); R_f= 0.19 (hexanes / EtOAc = 20 / 1, stain in PMA).

Determination of Selectivity:

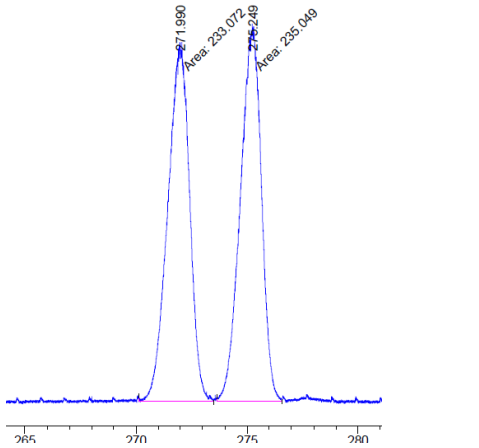


4 **S13**

To a vial containing allylic alcohol **4** (0.03 g, 0.14 mmol) in dichloromethane (0.72 mL), was added DMAP (1.76 mg, 0.014 mmol), triethylamine (0.16 mL, 1.15 mmol), and acetic anhydride (0.054 mL, 0.57 mmol). The resulting mixture was stirred at rt overnight. The mixture was purified by flash chromatography [silica gel, hexanes / EtOAc (50 /1 to 20/1) eluent] to give allylic acetate **S13** as a colorless oil.

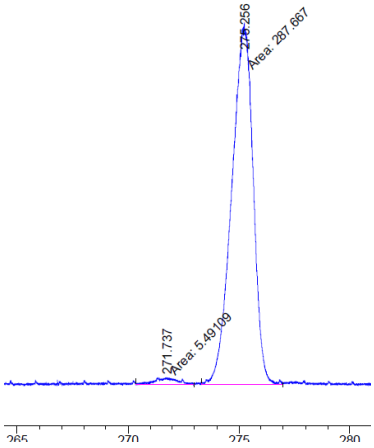
***Allylic acetate S13*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (ddd, *J* = 8.8, 7.2, 6.0 Hz, 1H), 5.12 (ddd, *J* = 8.8, 2.4, 1.2 Hz, 1H), 5.09 – 5.03 (m, 1H), 4.77 (d, *J* = 1.2 Hz, 1H), 4.74 – 4.68 (m, 1H), 2.37 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.18 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.13 – 1.97 (m, 4H), 2.01 (s, 3H), 1.75 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.67 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.6, 140.8, 131.9, 124.0, 123.6, 113.5, 77.6, 77.2, 76.9, 69.8, 43.7, 39.7, 26.5, 25.9, 22.9, 21.5, 17.9, 17.0; IR (neat): 1733 (s), 1670 (w), 1651 (w); HRMS-(ESI+) for $C_{16}H_{27}O_2$ [M+H]: calculated: 251.2011, found: 251.2009; $[\alpha]_D^{20}$ = +23.75 (c = 0.8, $CHCl_3$); R_f= 0.29 (hexanes / EtOAc = 50 / 1, stain in PMA). Enantioselectivity was determined by comparison to racemic material prepared from Grignard addition to geranial and acetylation.

Chiral GLC (CD-GTA, Supelco, 70° C for 80 min, ramp 0.1° C/min to 130° C, 130° C for 10 min, 20 psi) analysis of ***S13****.*



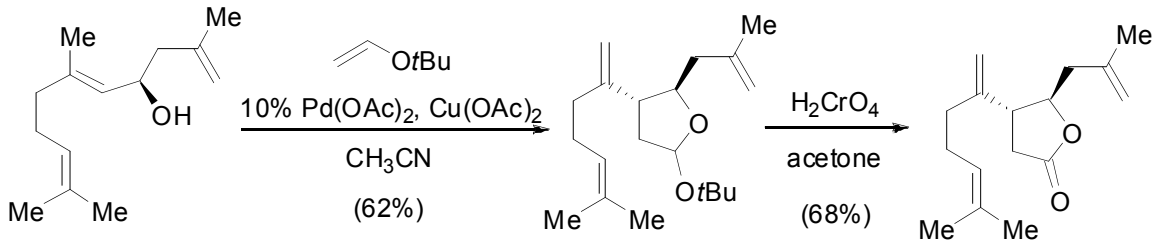
Racemic

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	271.990	MM	1.1348	233.07184	3.42312	49.78882
2	275.249	MM	1.0889	235.04898	3.59762	50.21118



Chiral

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	271.737	MM	1.1145	5.49109	8.21135e-2	1.87308
2	275.256	MM	1.1167	287.66681	4.29353	98.12692

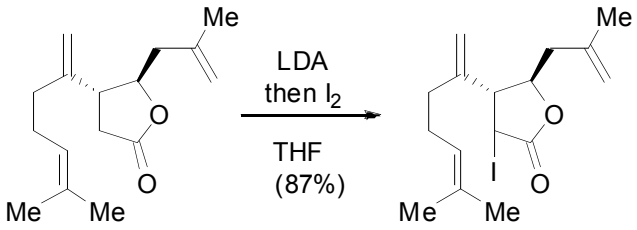


To a round bottom flask containing allylic alcohol **4** (4.28 g, 20.54 mmol) was added *tert*-butyl vinyl ether (10.83 mL, 82 mmol) and acetonitrile (20.54 mL). Then palladium (II) acetate (0.462 g, 2.054 mmol) and copper (II) acetate (9.33 g, 51.4 mmol) were added to the flask. The mixture was purged with nitrogen for 15 min and vigorously stirred for 22 h at 75-80°C (oil bath temperature). At the end of this time period, the reaction mixture was diluted with 400 mL of pentane-ether (v/v, 3/1). The resulting precipitate was filtered through celite. The filtration cake was washed with 300 mL of pentanes-ether (v/v, 3/1). After solvent was removed by rotovap, the crude mixture was purified by column chromatography [silica gel, first pentane, then pentane / Et_2O (100/1 → 50/1 → 30/1 → 10/1) was used as eluent] to give lactal **3** (3.9 g, 12.73 mmol, 61.9 % yield) as a mixture of two epimers (ratio = 1/1) containing some solvent and trace impurity.

Lactal 3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 and 5.36 (dd, J = 5.6, 3.6 Hz and dd, J = 4.8, 1.6 Hz, 1H), 5.15 – 5.07 (m, 1H), 4.90 and 4.87 (s, 1H), 4.85 – 4.81 (m, 1H), 4.81 – 4.75 (m, 2H), 4.07 and 3.96 (td, J = 8.8, 2.8 Hz and td, J = 8.0, 4.8 Hz, 1H), 2.75 and 2.18 – 1.91 (dt, J = 10.4, 8.0 Hz and m, 6H), 2.37 – 2.25 (m, 3H), 1.77 (d, J = 1.2 Hz, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.24 and 1.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 143.8, 131.9, 124.3, 111.8, 110.9, 98.1, 78.8, 74.2, 51.7, 42.2, 40.8, 34.3, 29.2, 28.3, 27.1, 25.9, 23.2 (149.0, 144.0, 132.0, 124.2, 112.2, 110.3, 98.4, 81.9, 74.0, 49.8, 45.1, 40.7, 34.5, 29.3, 28.2, 27.0, 23.0, 18.0); IR (neat): 1643 (w); Anal. Calcd. For $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.36; H, 11.03. HRMS-(ESI+) for $C_{20}H_{35}O_2$ [M+H]: calculated: 307.2637, found: 307.2631; R_f= 0.58 (hexanes / EtOAc = 10 / 1, stain in PMA).

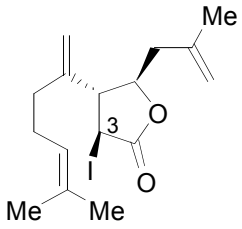
To a stirred solution of above lactal **3** (3.9 g, 12.73 mmol) in acetone (118 ml) at 0 °C, Jones reagent (chromic acid) (6.58 ml, 2.9 M, 19.09 mmol) was added dropwise. The resulting mixture was stirred for 10 min at 0 °C. The reaction was then quenched by slow addition of 2-propanol (4.90 ml, 63.6 mmol) and sat. sodium bicarbonate solution (85 mL, 76 mmol) (caution – vigorous reaction) and solid sodium bicarbonate (8.02 g, 95 mmol). The blue precipitate was removed by filtration and the filtration cake washed with EtOAc. The filtrate was diluted with EtOAc (400 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (100 mL). The combined organic layers were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The crude product was purified by column chromatography [silica gel, hexanes / EtOAc (15/1) as eluent] to give lactone **S14** (2.134 g, 8.66 mmol, 67.5 % yield) as colorless oil.

Lactone S14: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (t, *J* = 6.5 Hz, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.88 (s, 1H), 4.81 (s, 1H), 4.51 (td, *J* = 7.5, 5.0 Hz, 1H), 2.81 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.71 (dd, *J* = 17.5, 9.0 Hz, 1H), 2.47 (dd, *J* = 17.5, 9.0 Hz, 1H), 2.42 – 2.31 (m, 2H), 2.15 (dd, *J* = 14.5, 7.0 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.78 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 141.0, 132.7, 123.4, 114.0, 111.8, 82.7, 47.1, 42.6, 35.0, 34.4, 26.5, 25.9, 23.0, 18.0; IR (neat): 1781 (s), 1646 (w); HRMS-(ESI+) for $C_{16}H_{25}O_2$ [M+H]: calculated: 249.1855, found: 249.1851; $[\alpha]_D^{20}$ = +43.6 (c = 1.0, $CHCl_3$); R_f= 0.3 (hexanes / EtOAc = 10 / 1, stain in PMA).



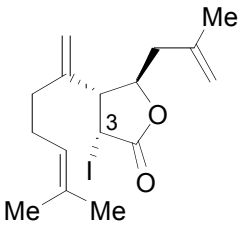
S14 **5**

To a solution of freshly distilled diisopropylamine (0.705 mL, 4.95 mmol) in THF (31.2 mL) at 0 ºC was added *n*-butyllithium in hexane (2.00 mL, 2.27 M, 4.55 mmol). The mixture was stirred at 0 ºC for 5 min and then cooled to -78 ºC. Lactone **S14** (0.983 g, 3.96 mmol) in THF (6 mL) was added dropwise at -78 ºC and the resulting mixture was stirred at -78 ºC for 90 min. The resulted mixture was then transferred by cannula to a cooled (-78 ºC) solution of iodine (1.507 g, 5.94 mmol) in THF (22 mL) over 15 min. The mixture was stirred at -78 °C for 1 h. The reaction was quenched by sequential dropwise addition of 2 M HCl in Et_2O (5 mL), EtOAc (5 mL), and water (10 mL) at -78 °C. After the mixture was allowed to warm to rt, it was further diluted with EtOAc (100 mL) and 1M HCl (10 mL); the organic layer was separated and the aqueous layer was extracted with EtOAc (10 mL). The combined organic layers were washed with 20% aqueous sodium thiosulfate (25 mL), saturated $NaHCO_3$ (5 mL), and brine (20 mL); they were then dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography [silica gel, hexanes / EtOAc (20/1) as eluent] afforded iodo lactone **5** (1.293 g, 3.45 mmol, 87 % yield) (a mixture of (3*S*)-**5** and (3*R*)-**5**; dr=2.4/1) as a colorless oil.



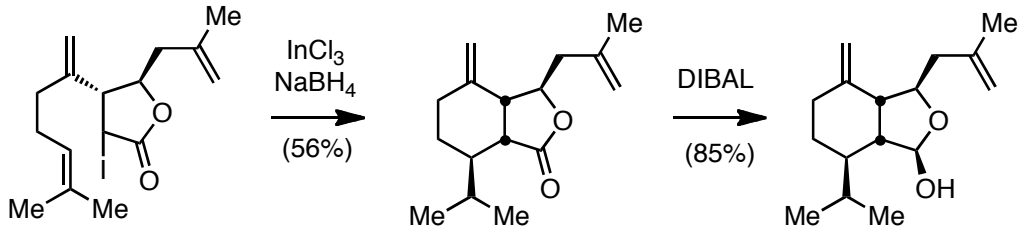
(3*S*)-**5**

Iodo lactone (3S)-5**:** colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 – 5.07 (m, 2H), 5.05 (s, 1H), 4.91 – 4.89 (m, 1H), 4.84 – 4.81(m, 1H), 4.63 (d, *J* = 9.5 Hz, 1H), 4.57 (td, *J* = 8.0, 5.0 Hz, 1H), 3.09 (dd, *J* = 9.5, 8.0 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.21 – 2.16 (m, 2H), 2.09 – 2.06 (m, 2H), 1.77 (t, *J* = 1.0 Hz, 3H), 1.70 (d, *J* = 1.0 Hz, 3H), 1.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 144.4, 140.5, 133.1, 123.1, 114.8, 114.5, 82.9, 59.5, 42.1, 33.5, 26.6, 25.9, 22.9, 18.1, 16.3; IR (neat): 1775 (s), 1645 (w); HRMS-(ESI+) for $C_{16}H_{24}IO_2$ [M+H]: calculated: 375.0821, found: 375.0824; R_f = 0.48 (hexanes / EtOAc = 10 / 1, stain in PMA).



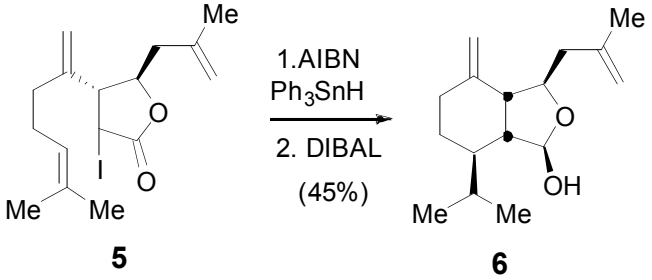
(3*R*)-**5**

Iodo lactone (3R)-5**:** colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (q, *J* = 1.5 Hz, 1H), 5.13 – 5.09 (m, 1H), 4.93 (t, *J* = 1.5 Hz, 1H), 4.85 (d, *J* = 1.0 Hz, 1H), 4.77 (s, 1H), 4.66 – 4.62 (m, 1H), 6.54 (d, *J* = 6.0 Hz, 1H), 2.60 (d, *J* = 15.0 Hz, 1H), 2.36 (dd, *J* = 15.0, 9.5 Hz, 1H), 2.23 – 2.05 (m, 4H), 1.99 – 1.91 (m, 1H), 1.85 (s, 3H), 1.72 (d, *J* = 1.0 Hz, 3H), 1.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 144.5, 141.1, 132.9, 123.3, 114.4, 113.1, 80.7, 51.6, 40.3, 36.4, 26.0, 25.9, 23.9, 23.3, 18.0; IR (neat): 1765 (s), 1648 (w); HRMS-(ESI+) for $C_{16}H_{24}IO_2$ [M+H]: calculated: 375.0821, found: 375.0813; R_f = 0.46 (hexanes / EtOAc = 10 / 1, stain in PMA).



A vial with a stirr bar was charged with anhydrous indium(III) chloride (0.165 g, 0.53 mmol) and sodium borohydride (14.1 mg, 0.37 mmol) in a drybox. The vial was sealed with a septum and removed from the drybox. Acetonitrile (4.8 mL) was added and the mixture was stirred at rt for 5 min and then cooled to -78 °C. After cooling bath was removed, and the mixture was then slowly warmed to rt, stirred for 5 min, and iodolactone **5** (0.199 g, 0.53 mmol – mixture of stereoisomers) in acetonitrile (0.5 mL) was added. The mixture was stirred at rt for 2 h at which time TLC analysis indicated the UV active iodo lactone **5** was consumed (UV inactive product lactone has same R_f as iodo lactone **5**). The reaction mixture was diluted with EtOAc (25 mL) and water (25 mL). After separation of the organic layer, the aqueous layer was extracted with EtOAc (25 mL, twice) and the combined organic layers were dried over $MgSO_4$ and concentrated to give an oil. The crude product was purified by flash chromatography [silica gel, hexanes / EtOAc (20/1) as eluent] to give lactone **S15** (74 mg, 0.30 mmol, 56% yield) as an oil. Lactone **S15** (74 mg, 0.30 mmol) in a 20 mL vial with stir bar was flushed three times with N_2. Then CH_2Cl_2 (3 mL) was added and the solution was cooled to -78 °C. To this dichloromethane solution at -78 °C, was added dropwise DIBAL-H (0.16 mL, 0.89 mmol). After stirring at -78 °C for 3 h, the reaction mixture was quenched with a saturated aqueous sodium potassium tartrate (3 mL) at -78 °C and the solution allowed to warm to rt and stir overnight. The organic layer was separated and the aqueous solution was extracted with CH_2Cl_2 (3 mL, twice) and EtOAc (3 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to a crude oil. The crude product was purified by flash chromatography [silica gel, hexanes / EtOAc (15/1) as eluent] to give lactol **6** (63.1 mg, 0.25 mmol, 85% yield) as a white solid. The overall yield from iodolactone **5** to lactol **6** is 48%.

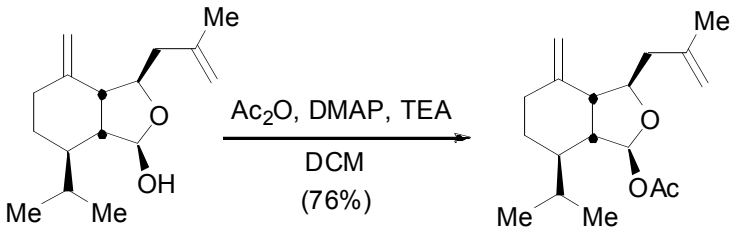
Alternative procedure for radical cyclization of lactone 5:



A solution of triphenyltin hydride (4.35 g, 12.38 mmol) in benzene (179 mL) was added to a 250 mL flask containing iodolactone **5** (2.317 g, 6.19 mmol) and a stir bar. 2, 2'-Azobisisobutyronitrile (0.712 g, 4.33 mmol) was added and the mixture was heated at 60 °C for 1.5 h. ^{1}HNMR of reaction mixture showed that iodolactone **5** has been consumed. After the solvent was removed under reduced pressure, the remaining white solid was dissolved in CH_2Cl_2

(80 mL) cooled to -78 ºC and treated with DIBAL (4.38 mL, 24.76 mmol) dropwise. After stirring at -78 ºC for 5 h, the reaction mixture was quenched with a saturated aqueous solution of sodium potassium tartrate (41 mL) at -78 ºC and then allowed to stir at ambient temperature overnight. The organic layer was separated and the aqueous solution was extracted three times with EtOAc (20 mL). The combined organic layers were concentrated, redissolved in CH_2Cl_2 (25 mL) and EtOAc (25 mL) and treated with saturated KF (25 mL). The mixture was stirred at rt for 1 h and the white precipitate formed was then removed by filtration. The filtration cake was washed by EtOAc (30 mL) and the filtrate diluted with EtOAc (30 mL) and water (30 mL). The layers were separated, the aqueous layer washed with EtOAc (40 mL), and the organic layers combined, washed with brine (10 mL) and dried over $MgSO_4$, filtrated, and concentrated. The crude product was purified by flash chromatography [silica gel, hexanes / DCM (3/2, 750 mL) until UV active organic stannane was eluted, then hexanes / EtOAc (20/1, 700 mL) and hexanes / EtOAc (15/1 900 mL)] to furnish lactol **6** (0.690 g, 2.76 mmol, 44.5 % yield) as a white solid.

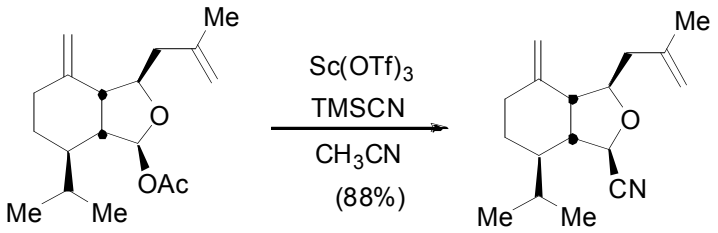
***Lactol 6*:** Mp = 62-63 ºC (enantiomerically enriched); Mp = 85-86 ºC (racemic); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (d, *J* = 2.0 Hz, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 4.80 (s, 1H), 4.78 (s, 1H), 4.10 (td, *J* = 9.5, 2.5 Hz, 1H), 2.90 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.46 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.37 (d, *J* = 14.5 Hz, 1H), 2.29 (d, *J* = 14.0 Hz, 1H), 2.19 (dd, *J* = 15.0, 9.5 Hz, 1H), 2.09 (dd, *J* = 12.0, 6.0 Hz, 2H), 1.87 – 1.79 (m, 1H), 1.77 (s, 3H), 1.75 – 1.72 (m, 1H), 1.31 (t, *J* = 12.5 Hz, 1H), 1.08 – 0.99 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 143.8, 112.0, 111.6, 101.4, 80.1, 51.4, 50.3, 45.0, 40.2, 31.6, 29.0, 25.4, 23.2, 22.0, 16.2; IR (neat): 3418 (w), 1646 (w); HRMS-(ESI+) for $C_{16}H_{25}O$ [M+H - H_2O]: calculated: 233.1905, found: 233.1897; $[\alpha]_D^{20}$ = -8.8 (c = 0.9, $CHCl_3$); R_f = 0.19 (hexanes / EtOAc = 10 / 1, stain in PMA).



6 **S16**

To the solution of lactol **6** (0.610 g, 2.436 mmol), DMAP (0.060 g, 0.487 mmol), and triethylamine (2.105 mL, 15.11 mmol) in dichloromethane (18.74 mL) at -45 °C, acetic anhydride (0.690 mL, 7.31 mmol) was added dropwise. The resulting mixture was stirred at -45 °C for 3.5 h and quenched with MeOH (1 mL). After 0.5 h of continued stirring at -45 °C, the mixture was warmed to rt and diluted with 25 mL CH_2Cl_2 and washed with 10% $KHSO_4$ (15 mL), saturated $NaHCO_3$ (16 mL), and brine (15 mL). The organic layer was then was dried over Na_2SO_4, filtered, and concentrated to give a crude product. The crude product was purified by flash chromatography [silica gel, hexanes / EtOAc (50/1) as eluent] to give acetate **S16** (0.543 g, 1.857 mmol, 76 % yield) as a colorless oil.

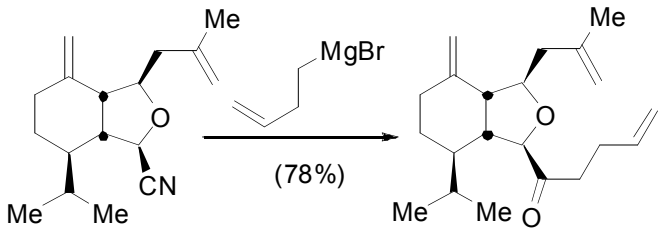
***Acetate S16*:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (s, 1H), 4.83 – 4.81 (m, 2H), 4.80 – 4.77 (m, 2H), 4.13 (td, *J* = 9.0, 3.0 Hz, 1H), 2.81 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.34 (dd, *J* = 14.0, 2.5 Hz, 1H), 2.30 (dt, *J* = 13.5, 3.5 Hz, 1H), 2.18 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.13 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.09 – 2.03 (m, 1H), 2.04 (s, 3H), 1.96 (dtd, *J* = 14.0, 7.0, 2.5 Hz, 1H), 1.75 (s, 3H), 1.79 – 1.72 (m, 1H), 1.35 (tt, *J* = 12.5, 3.0 Hz, 1H), 1.04 (ddd, *J* = 26.5, 13.0, 3.5 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 145.0, 143.1, 112.5, 112.0, 101.8, 81.2, 50.6, 50.0, 44.3, 40.2, 31.5, 28.7, 25.2, 23.2, 21.9, 21.8, 16.1; IR (neat): 1733 (s), 1648 (w); HRMS-(ESI+) for $C_{18}H_{32}NO_3$ [M+NH_4]: calculated: 310.2382, found: 310.2375; $[\alpha]_D^{20}$ = +1.5 (c = 0.8, $CHCl_3$); R_f = 0.47 (hexanes / EtOAc = 10 / 1, stain in PMA).



S16 **7**

Scandium trifluoromethanesulfonate (0.024 g, 0.048 mmol) in acetonitrile (1 mL) was added dropwise to a solution of acetate **S16** (0.506 g, 1.730 mmol) and TMSCN (0.580 mL, 4.33 mmol) in acetonitrile (13.31 mL) at -22 °C. After being stirred for 10 h at -22 °C (TLC and ^{1}HNMR show complete reaction), the mixture was treated with saturated sodium bicarbonate solution (12 mL) at -22 °C. The mixture was diluted with CH_2Cl_2 (20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL, 3 times). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude product. The crude mixture was purified by flash chromatography [silica gel, hexanes / EtOAc (50/1) as eluent] to give nitrile **7** (0.395 g, 1.523 mmol, 88 % yield) as a colorless oil.

***Nitrile 7*:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (t, *J* = 2.0 Hz, 1H), 4.85 (dd, *J* = 4.0, 2.0 Hz, 2H), 4.83 – 4.81 (m, 1H), 4.62 (s, 1H), 4.08 (td, *J* = 9.5, 3.0 Hz, 1H), 2.94 (dd, *J* = 10.0, 6.5 Hz, 1H), 2.42 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.36 – 2.24 (m, 3H), 2.11 – 2.03 (m, 1H), 1.77 (s, 3H), 1.82 – 1.68 (m, 2H), 1.39 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.09 (ddd, *J* = 26.5, 13.0, 3.5 Hz, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.8, 120.0, 113.0, 112.8, 81.0, 69.4, 52.5, 50.9, 43.1, 41.3, 31.3, 29.1, 25.5, 23.2, 21.8, 16.1; IR (neat): 2236 (w), 1649 (s); HRMS-(ESI+) for $C_{17}H_{26}NO$ [M+1]: calculated: 260.2014, found: 260.2016; $[\alpha]_D^{20}$ = +19.6 (c = 0.52, $CHCl_3$); R_f = 0.51 (hexanes / EtOAc = 10 / 1, stain in PMA).

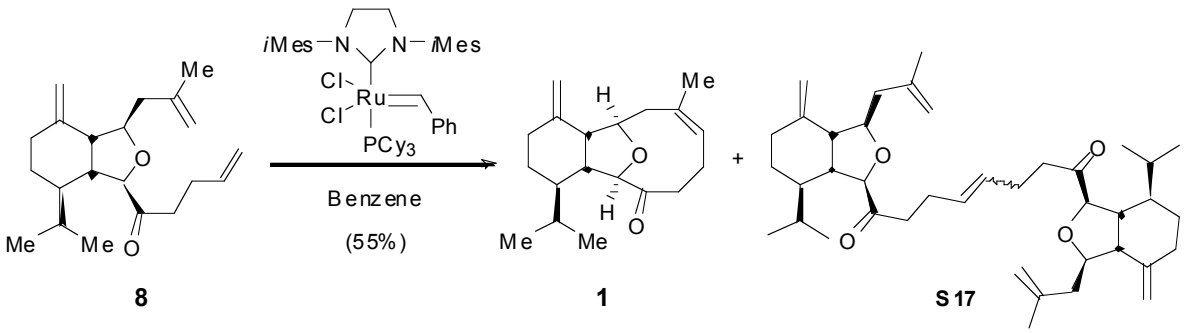


7 **8**

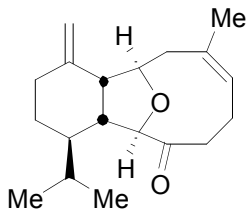
To an oven-dried two-neck flask equipped with a stir bar and condenser, freshly crushed magnesium turnings (6.70 g, 276 mmol) were added. The flask was flame-dried three times. Then iodine (5.00 mg, 0.020 mmol) was added and the system was flushed with N_2 twice. After addition of THF (65.7 mL), 4-bromo-1-butene (4 mL, 39.4 mmol) was dropwise added with stirring. The mixture was refluxed for 0.5 h and then stirred at rt for 1 h. The clear solution was transferred to a dried reagent bottle. Titration of the solution with (-)-menthol and 1,10-phenanthroline indicated the concentration of the resulting 3-butenyl magnesium bromide was 0.467 M.

To the solution of nitrile **7** (0.353 g, 1.361 mmol) in benzene (9.86 mL) at 40 °C, 3-butenyl magnesium bromide (0.467M, 11.66 mL, 5.44 mmol) prepared above was added. The resulting mixture was stirred at 40 °C for 9 h. Subsequently, the reaction mixture was cooled to 0 ºC and 1 M aqueous HCl (8 mL) was added dropwise. The solution was stirred at rt for 15 min and then extracted with EtOAc (10 mL, 3 times). The organic phase was then washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL). The combined two aqueous washing solutions were back extracted with CH_2Cl_2 (10 mL, twice) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography [silica gel, hexanes/EtOAc (100/1 to 50/1) as eluent] to give ketone **8** (0.337 g, 1.065 mmol, 78 % yield) as a light yellow oil.

***Ketone 8*:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.04 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H), 4.98 (ddd, *J* = 10.2, 2.8, 1.2 Hz, 1H), 4.84 (s, 2H), 4.81 (t, *J* = 2.0 Hz, 1H), 4.71 (t, *J* = 1.6 Hz, 1H), 4.30 (s, 1H), 4.11 (td, *J* = 10.0, 2.0 Hz, 1H), 2.73 (dt, *J* = 18.0, 7.6 Hz, 1H), 2.60 (dt, *J* = 18.0, 7.6 Hz, 1H), 2.41 – 2.15 (m, 7H), 2.07 (tt, *J* = 13.6, 2.0 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.80 (s, 3H), 1.79 – 1.73 (m, 1H), 1.47 (tt, *J* = 12.0, 2.4 Hz, 1H), 1.06 (ddd, *J* = 26.0, 12.8, 3.2 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 145.1, 143.6, 137.4, 115.4, 112.2, 112.1, 87.8, 80.0, 52.6, 47.9, 43.0, 42.9, 38.3, 31.9, 28.4, 27.5, 25.7, 23.2, 22.0, 15.6; IR (neat): 1714 (s), 1644 (s); HRMS-(ESI+) for $C_{21}H_{33}O_2$ [M+1]: calculated: 317.2481, found: 317.2475; $[\alpha]_D^{20}$ = +20.54 (c = 0.68, $CHCl_3$); R_f= 0.34 (hexanes / EtOAc = 20 / 1, stain in PMA).

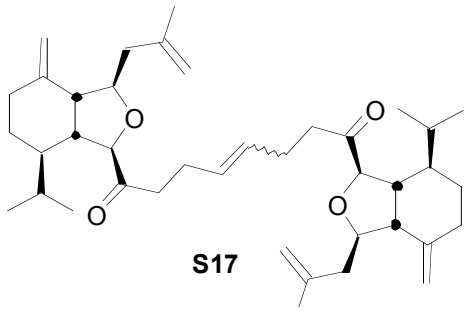


Ketone **8** (0.324 g, 1.024 mmol) was dissolved in benzene (788 mL) and the mixture sparged with N_2 for 0.5 h. The solution was then heated to reflux under N_2 and the G2 catalyst (0.087 g, 0.102 mmol) dissolved in benzene (20 mL) was added by cannula. The reaction mixture was stirred at reflux for 5 h, cooled to rt, opened to air, and treated with DMSO (0.363 mL, 5.12 mmol). After stirring overnight, the solvent was removed and the mixture purified by column chromatography [silica gel, hexanes / EtOAc (100/1 → 50/1 → 20/1) to give diene **1** (colorless oil, 0.122 g, 0.423 mmol, 41.3 % yield), dimer **S17** (colorless oil, 0.073 g, trans / cis = 4.7 /1), and unreacted ketone **8** (89 mg) with impurities. The recovered ketone **8** (89 mg) was resubjected to the above conditions (0.1 eq G2 catalyst, reflux in benzene for 5 h) to yield additional 17 mg diene **1.** The dimer **S17** (0.073 g, 0.121 mmol) was also resubjected to the reaction conditions to with the G2 catalyst (20 mg, 0.024 mmol) for 6 h followed by additional loading of catalyst G2 (10 mg, 0.012 mmol) for 10 h to give additional diene **1** (0.022 g, 0.076 mmol) as a colorless oil. The overall yield for conversion of ketone **8** to diene **1** was 55 %.



1

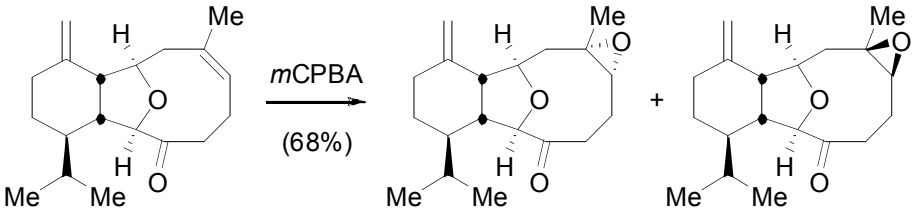
***Diene 1*:** ^{1}H NMR (500 MHz $CDCl_3$) δ 5.53 (dd, *J* = 11.5, 6.0 Hz, 1H), 4.78 (t, *J* = 2.0 Hz, 1H), 4.72 (t, *J* = 2.0 Hz, 1H), 4.27 (dt, *J* = 9.5, 3.5 Hz, 1H), 4.17 (s, 1H), 3.36 (qd, *J* = 12.5, 6.0 Hz, 1H), 2.91 – 2.86 (m, 1H), 2.84 (ddd, *J* = 12.5, 6.0, 2.5 Hz, 1H), 2.65 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.55 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.42 (td, *J* = 12.5, 6.5 Hz, 1H), 2.27 (dt, *J* = 14.0, 3.0 Hz, 1H), 2.14 – 2.06 (m, 2H), 1.84 (dd, *J* = 15.0, 3.5 Hz, 1H), 1.78 (t, *J* = 1.5 Hz, 3H), 1.77 – 1.72 (m, 1H), 1.71 – 1.64 (m, 1H), 1.35 (tt, *J* = 12.5, 3.0 Hz, 1H), 1.06 (ddd, *J* = 26.0, 13.0, 3.5 Hz, 1H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4, 146.3, 133.8, 127.5, 111.2, 89.4, 83.1, 47.1, 45.8, 43.1, 41.3, 34.8, 32.0, 29.2, 28.4, 27.0, 25.9, 22.0, 16.2; IR (neat): 1708 (s), 1646 (w); HRMS-(ESI+) for $C_{19}H_{29}O_2$ [M+1]: calculated: 289.2168, found: 289.2162; $[\alpha]_D^{20}$ = -2.08 (c = 0.39, $CHCl_3$); R_f= 0.47 (hexanes / EtOAc = 10 / 1, stain in PMA).



S17

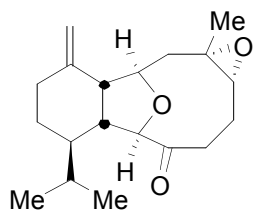
***Dimer S17*:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 – 5.39 (m, 1H) (trans) or 5.38 – 5.31 (m, 1H) (cis), 4.83 (s, 2H), 4.81 (t, *J* = 2.0 Hz, 1H), 4.71 (t, *J* = 2.0 Hz, 1H), 4.28 (d, *J* = 1.5 Hz, 1H), 4.10 (td, *J* = 10.0, 2.0 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.59 – 2.48 (m, 1H), 2.40 – 2.15 (m, 7H), 2.12 – 2.01 (m, 1H), 1.94 – 1.84 (m, 1H), 1.80 (s, 3H), 1.79 – 1.72 (m, 1H), 1.46 (tt, *J* = 12.0, 2.5 Hz, 1H), 1.06 (ddd, *J* = 26.0, 13.0, 3.5 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 212.0, 145.1, 143.7, 129.8 (trans) or 129.4 (cis), 112.3, 112.1, 87.7, 79.9, 52.5, 47.8, 42.9, 42.8, 38.8, 31.8, 28.3, 26.4, 25.7, 23.1, 22.0, 15.6; IR (neat): 1713 (s), 1646 (w); HRMS-(ESI+) for $C_{40}H_{61}O_4$ [M+1]: calculated: 605.4570, found: 605.4573; $[\alpha]_D^{20}$ = +15.38 (c = 0.33, $CHCl_3$); R_f= 0.40 (hexanes / EtOAc = 10 / 1, stain in PMA).



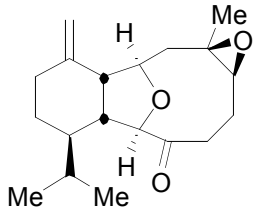
1 **α-9** **β-9**

To a vial containing diene **1** (0.050 g, 0.173 mmol) in $CHCl_3$ (10.3 mL) at -12 °C, a precooled (0 ºC) solution of *m*-chloroperoxybenzoic acid (77%, measured by iodometric titration,[5] 0.058 g, 0.260 mmol) in $CHCl_3$ (7 mL) was added dropwise and the mixture was stirred at -12 °C for 24 h. The mixture was quenched by addition of dimethylsulfide (0.076 mL, 1.040 mmol) at -13 ºC. After the mixture was stirred for 30 min at -13 ºC, the mixture was diluted with $CHCl_3$ (3 mL) and immediately washed with saturated $NaHCO_3$ (5 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude mixture was purified by column chromatography [silica gel, hexanes / EtOAc (50/1 → 20/1 → 15/1)] to give a mixture of **α-9** and **β-9** (0.036 g, 0.118 mmol, 68 % yield) as a colorless oil (dr = 1.8/1).



α-9

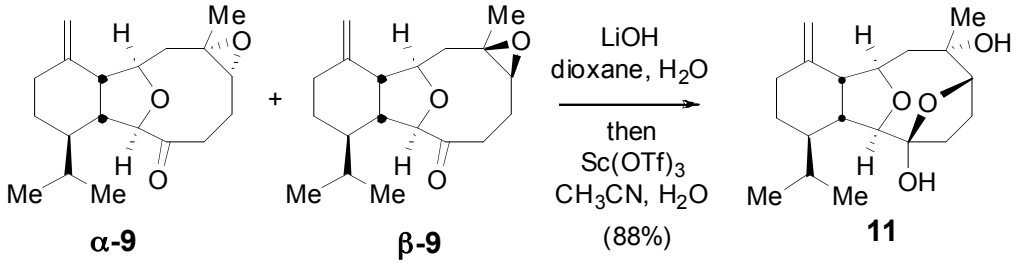
***Epoxide α-9*:** white solid; Mp = 105-106 ºC (racemic); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (t, *J* = 1.5 Hz, 1H), 4.75 (s, 1H), 4.35 (s, 1H), 4.18 (dt, *J* = 10.5, 3.0 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.78 (dd, *J* = 11.0, 3.0 Hz, 1H), 2.70 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.56 – 2.43 (m, 2H), 2.30 – 2.22 (m, 2H), 2.14 – 2.07 (m, 2H), 1.77 (ddd, *J* = 12.5, 7.0, 3.5 Hz, 1H), 1.72 – 1.65 (m, 2H), 1.45 (s, 3H), 1.38 (tt, *J* = 12.5, 3.0 Hz, 1H), 1.09 (ddd, *J* = 26.0, 13.0, 3.5 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 145.6, 111.6, 88.4, 79.9, 62.8, 59.6, 46.4, 45.2, 40.6, 40.5, 37.4, 31.6, 29.0, 28.5, 28.3, 25.7, 22.0, 16.1; IR (neat): 1699 (s), 1648 (w); HRMS-(ESI+) for $C_{19}H_{29}O_3$ [M+1]: calculated: 305.2117, found: 305.2121; R_f = 0.64 (hexanes / EtOAc = 3 / 1, stain in PMA).



β-9

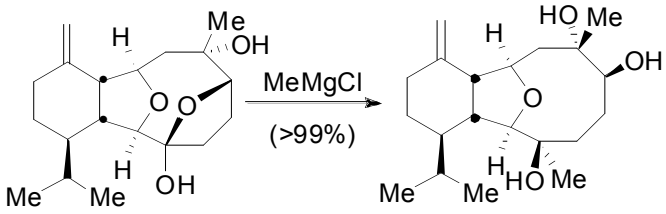
***Epoxide β-9*:** colorless oil**;** ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.66 (s, 1H), 4.20 (s, 1H), 4.10 – 4.05 (m, 1H), 2.93 – 2.85 (m, 2H), 2.68 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.32 – 2.25 (m, 2H), 2.16 (dd, *J* = 14.8, 4.8 Hz, 1H), 2.06 (t, *J* = 12.6 Hz, 1H), 1.78 – 1.73 (m, 1H), 1.71 – 1.66 (m, 1H), 1.43 (s, 3H), 1.41 – 1.31 (m, 1H), 1.23 (dd, *J* = 15.0, 11.4 Hz, 1H), 1.09 (ddd, *J* = 25.2, 12.6, 3.6 Hz, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.5, 145.6, 110.9, 87.5, 78.9, 63.7, 60.0, 53.8, 44.4, 41.7, 40.2, 34.7, 31.6, 29.4, 27.0, 25.2, 22.3, 22.0, 16.5; IR (neat): 1713 (s), 1648 (w); HRMS-(ESI+) for $C_{19}H_{29}O_3$ [M+1]: calculated: 305.2117, found: 305.2109; R_f = 0.56 (hexanes / EtOAc = 3 / 1, stain in PMA).

[5] McDonald, R. N.; Steppel, R. N.; Dorsey, J. E.; Washburn, W. N.; Breslow, R. *Org. Synth.* **1970**, 50, 15.



To a vial containing a mixture of epoxide **α-9** and **β-9** (0.014 g, 0.046 mmol) in 1,4-dioxane (0.493 mL), a lithium hydroxide solution (1M, 0.493 mL, 0.493 mmol) was added. The mixture was stirred at rt for 70 min (at 45 min TLC indicated that epoxide **α-9** was comsumed). Then potassium hydrogensulfate (0.069 g, 0.509 mmol) in water (0.493 mL) was added and mixture was stirred for 15 min. Then scandium trifluoromethanesulfonate (3.23 mg, 6.57 μmol) in acetonitrile (2.465 mL) was added and the mixture was stirred at rt for 5 h (TLC indicated that there is a detectable amount of **β-9** left). Additional scandium trifluoromethanesulfonate (3.23 mg, 6.57 μmol) was added and mixture was stirred for an additional 1 h. The mixture was diluted with water (3 mL) and saturated sodium bicarbonate (1 mL), extracted with $CHCl_3$ (3 mL, 4 times). The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed. The crude product was purified by flash pipette chromatography [silica gel, hexanes / EtOAc (50/1 → 20/1 → 5/1 → 1/1)] to give hemiketal **11** (0.013 g, 0.040 mmol, 88 % yield) as a white solid.

***Hemiketal 16*:** Mp = 165-166 ºC (enantiomerically enriched); Mp = 170-172 ºC (racemic); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (t, *J* = 2.0 Hz, 1H), 4.69 (s, 1H), 4.21 (dd, *J* = 7.6, 6.4 Hz, 1H), 4.14 – 4.07 (m, 1H), 3.87 (s, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 2.45 – 2.29 (m, 3H), 2.28 – 2.21 (m, 2H), 2.12 – 1.99 (m, 3H), 1.91 – 1.82 (m, 2H), 1.81 – 1.68 (m, 2H), 1.51 (s, 3H), 1.29 – 1.20 (m, 1H), 1.02 (ddd, *J* = 26.0, 13.2, 2.8 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 110.2, 107.6, 87.7, 85.9, 81.6, 74.8, 48.3, 45.0, 43.3, 42.5, 38.9, 31.9, 31.6, 29.3, 26.5, 25.3, 22.1, 15.9; IR (neat): 3384 (w), 1645 (w); HRMS-(ESI+) for $C_{19}H_{29}O_3$ [M+H-H_2O]: calculated: 305.2117, found: 305.2106; $[\alpha]_D^{20}$ = +2.04 (c = 1.7, $CHCl_3$); R_f= 0.47 (hexanes / EtOAc = 1 / 2, stain in PMA).



11 *sclerophytin A*

In a dry box, a vial containing hemiketal **11** (0.013 g, 0.040 mmol) in THF (0.40 mL) was charged with methylmagnesium chloride (22 wt% solution in THF, 2.97M) (0.584 mL, 1.734 mmol) was added. The vial was sealed with a polypropylene cap, removed from the dry box, and stirred at 52 °C for 22 h. The mixture was cooled to 0 ºC and slowly treated with wet THF (prepared by washing THF with saturated NH_4Cl solution) (1 mL), then saturated NH_4Cl (1 mL) (exothermic). The resulting slurry was diluted with water (2 mL) and EtOAc (6 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 times, 6 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude mixture was purified by flash pipette chromatography [silica gel, hexanes / EtOAc (1/1 to 1/2)] to give sclerophytin A (0.014 g, 0.041 mmol, >99 % yield) as a white solid.

Sclerophytin A[6]: Mp = 185-186 ºC (enantiomerically enriched); Mp = 129-130 ºC (racemic); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (t, *J* = 2.0 Hz, 1H), 4.64 (s, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.63 (s, 1H), 2.97 (t, *J* = 6.8 Hz, 1H), 2.31 – 2.20 (m, 2H), 2.16 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.09 – 1.67 (m, 8H), 1.32 – 1.24 (m, 1H), 1.20 (s, 3H), 1.16 (s, 3H), 1.06 (ddd, *J* = 24.8, 12.8, 2.8 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz,$CDCl_3$) δ 148.1, 109.4, 90.7, 80.3, 78.3, 75.1, 53.2, 45.5, 45.4, 43.9, 40.2, 31.8, 30.5, 29.5, 29.3, 25.0, 22.2, 16.2; IR (neat): 3403 (w), 1646 (w); HRMS-(ESI+) for $C_{20}H_{33}O_3$ [M+H-H_2O]: calculated: 321.2430, found: 321.2425; $[\alpha]_D^{20}$ = -3.0 (c = 1.0, $CHCl_3$), $[\alpha]_D^{20}$ = -4.0 (c = 0.4, $CHCl_3$); R_f= 0.43 (hexanes / EtOAc = 1 / 3, stain in $KMnO_4$).

[6] (a) Sharma, P.; Alam, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2537. (b) Chen, S.-P.; Sung, P.-J.; Duh, C.-Y.; Dai, C.-F.; Sheu, J.-H. *J. Nat. Prod.* **2001**, *64*, 1241. (c) Gallou, F.; MacMillan, D. W. C.; Overman, L. E.; Paquette, L. A.; Pennington, L. D.; Yang, J. *Org. Lett.* **2001**, *3*, 135.

bw01113G-p-1-H4H

Sample Name:
bw01113G-p-1-H4H
Archive directory:

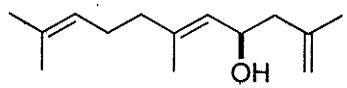
Sample directory:

FidFile: Proton

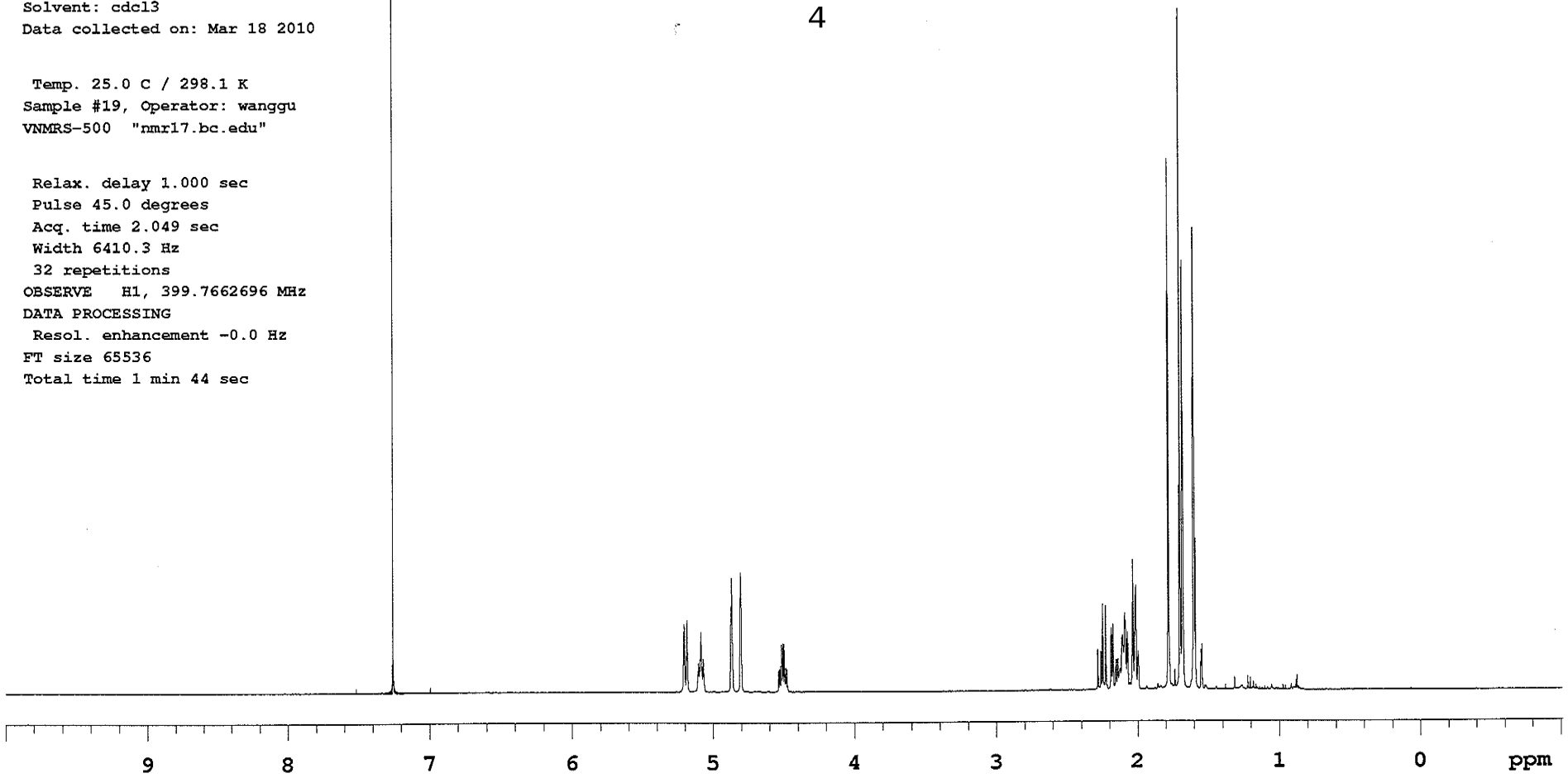
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2010

Temp. 25.0 C / 298.1 K
Sample #19, Operator: wanggu
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 399.7662696 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min 44 sec



4



bw01113G-p-1-C4H

Sample Name:
bw01113G-p-1-C4H
Archive directory:

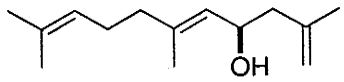
Sample directory:

FidFile: Carbon

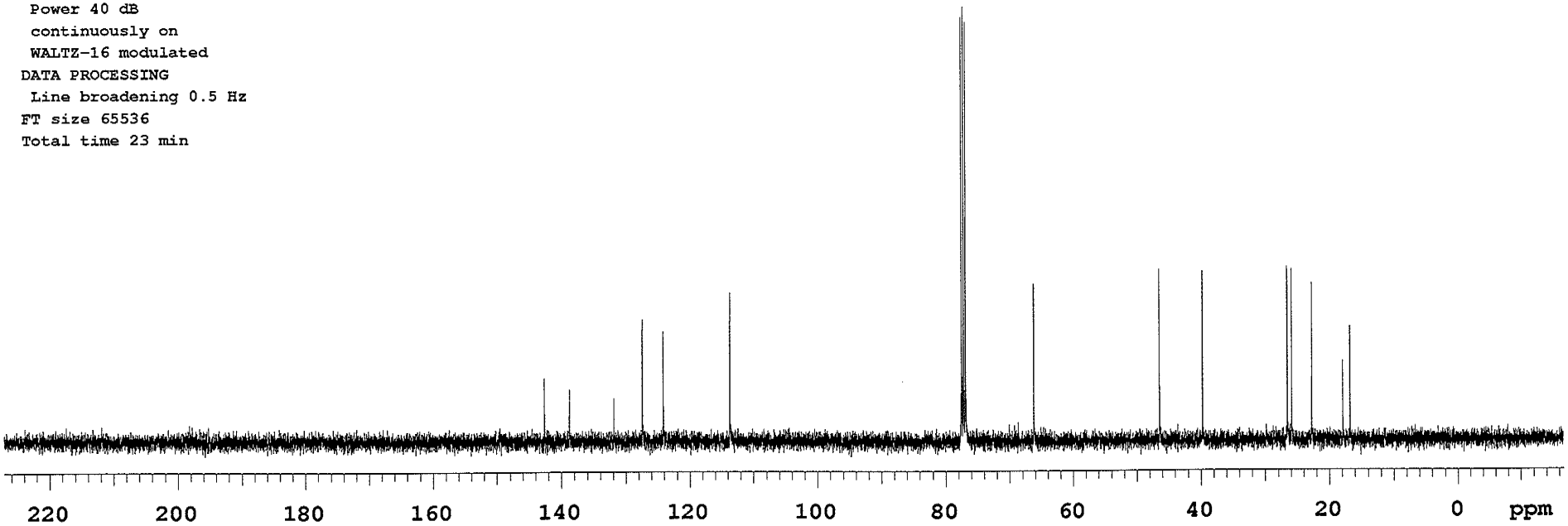
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2010

Temp. 25.0 C / 298.1 K
Sample #19, Operator: wanggu
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
600 repetitions
OBSERVE C13, 100.5212848 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 23 min



4



bw0190H-p-1-H4H

Sample Name:
bw0190H-p-1-H4H
Archive directory:

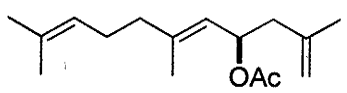
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Mar 24 2010

Temp. 25.0 C / 298.1 K
Sample #6, Operator: wanggu
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7662696 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 30 sec



S13

bw0190H-p-1-C4H

Sample Name:
bw0190H-p-1-C4H
Archive directory:

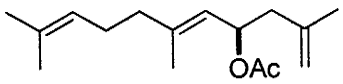
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Mar 24 2010

Temp. 25.0 C / 298.1 K
Sample #6, Operator: wanggu
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
10000 repetitions
OBSERVE C13, 100.5212848 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 23 min



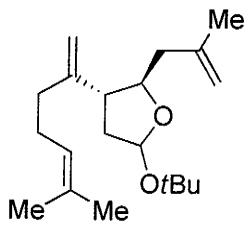
S13

bw01115G-p-1-whole-H4H

Sample: bw01115G-p-1-H4H
Sample ID: s_20100717_wanggu_17_01
File: /home/walkup/wanggu/bw01115G-p-1-whole-H4H.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Sample #17, Operator: wanggu
File: bw01115G-p-1-whole-H4H
VNMRS-400 "nmr14"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 32 repetitions
OBSERVE H1, 399.7662698 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min, 44 sec



3

Sample Name:
bw01115G-p-1
Archive directory:

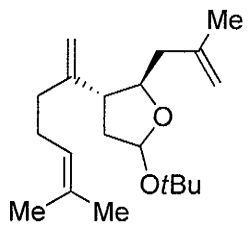
Sample directory:

FidFile: bw01115G-p-1_Apt5J_01

Pulse Sequence: Apt (APT)
Solvent: cdcl3
Data collected on: Jul 11 2010

Operator: Morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 30487.8 Hz
15000 repetitions
OBSERVE C13, 125.6962461 MHz
DECOUPLE H1, 499.8878615 MHz
Power 40 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 hr, 23 min



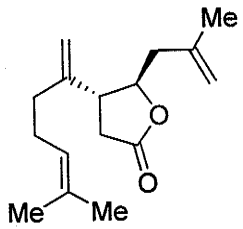
3

bw01117C-SM-H5

File: /home/jpm/binwang/bw01117C-SM-H5.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: jpm
File: bw01117C-SM-H5
INOVA-500 "nmr11"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 88 repetitions
OBSERVE H1, 499.7720264 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 7 hr, 7 min, 45 sec



S14

STANDARD CARBON PARAMETERS

Sample Name:

Archive directory:

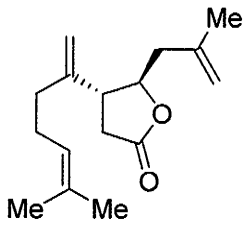
Sample directory:

FidFile: C13

Pulse Sequence: s2pul
Solvent: CDCl3
Data collected on: Nov 19 2008

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 2.000 sec
Pulse 42.0 degrees
Acq. time 3.000 sec
Width 33361.1 Hz
412 repetitions
OBSERVE C13, 125.6675870 MHz
DECOUPLE H1, 499.7738599 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 262144
Total time 1388923 hr, 35 min



S14

bw01117B-p-1-1-verypure-H5J
PTLC from p-1-1

Sample Name:

Archive directory:

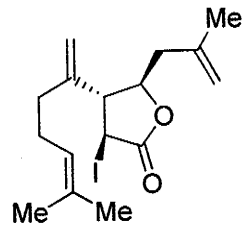
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
112 repetitions
OBSERVE H1, 499.8853683 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 541985 hr, 6 min



(3S)-5

bw01117B-p-1-1-verypure-C5J
PTLC from p-1-1

Sample Name:
bw01117B-p-1-1-verypure-H5J
Archive directory:

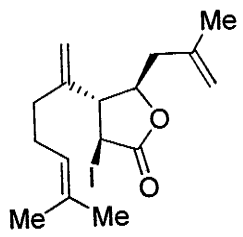
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
13000 repetitions
OBSERVE C13, 125.6962456 MHz
DECOUPLE H1, 499.8878615 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 8 hr, 18 min



(3S)-5

bw01117B-p-1-2-ptlc-1-verypure-H5
from p-1-1

Sample Name:
HYC-4-081-Crude
Archive directory:

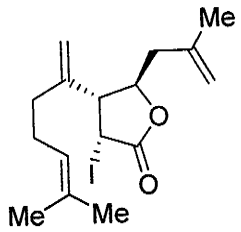
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2010

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
38 repetitions
OBSERVE H1, 499.7720256 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 71112 hr, 14 min



(3R)-5

bw01117B-p-1-2-ptlc-verypure-C5J
from p-1-2

Sample Name:

Archive directory:

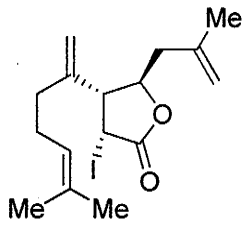
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Mar 28 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
14308 repetitions
OBSERVE C13, 125.6962456 MHz
DECOUPLE H1, 499.8878615 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 639 hr, 3 min



(3R)-5

STANDARD PROTON PARAMETERS

Sample Name:

Archive directory:

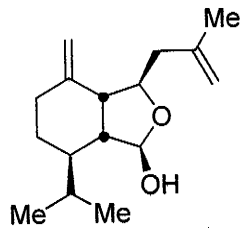
Sample directory:

FidFile: H1

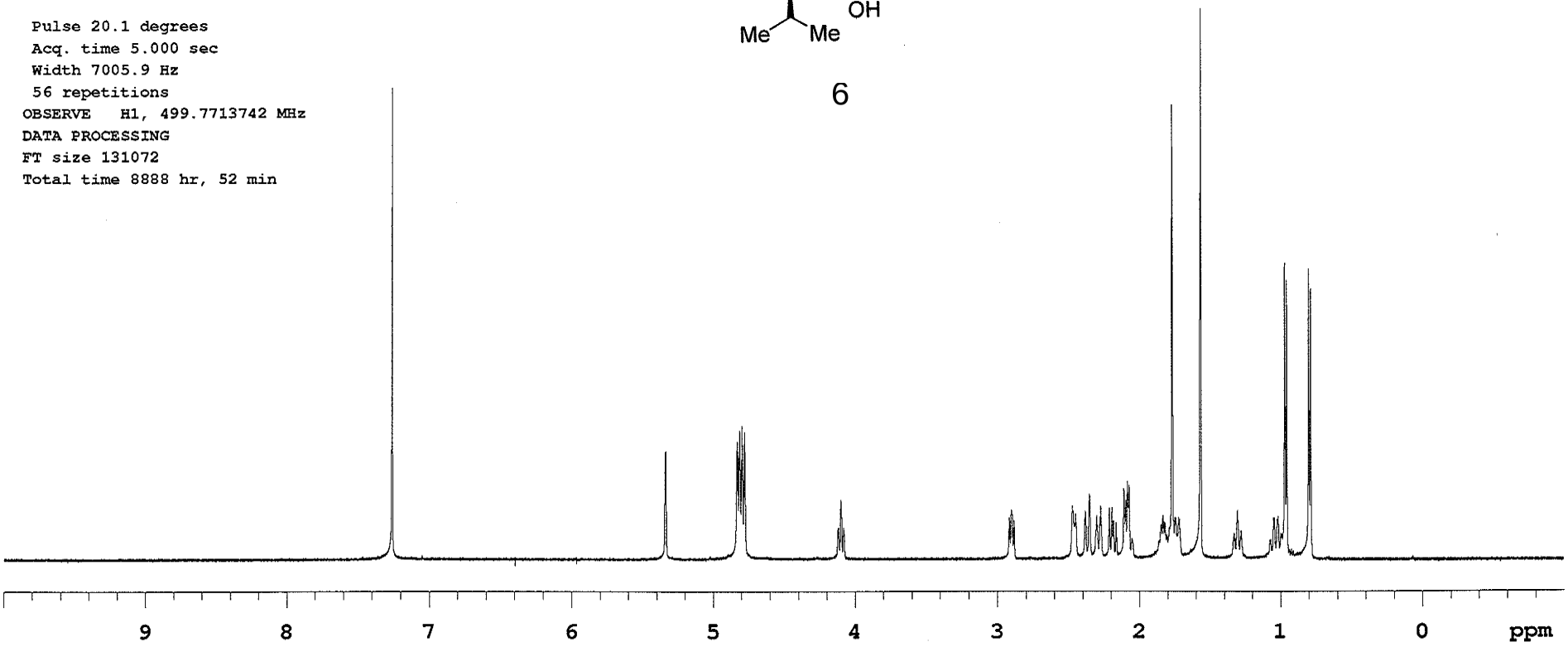
Pulse Sequence: s2pul
Solvent: CDCl3
Data collected on: Jul 3 2009

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Pulse 20.1 degrees
Acq. time 5.000 sec
Width 7005.9 Hz
56 repetitions
OBSERVE H1, 499.7713742 MHz
DATA PROCESSING
FT size 131072
Total time 8888 hr, 52 min



6



13C OBSERVE

Sample Name:

Archive directory:

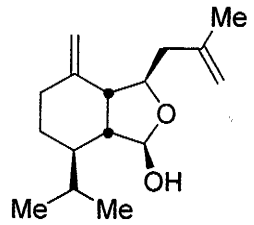
Sample directory:

FidFile: std13c

Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Jan 20 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 4.000 sec
Pulse 64.8 degrees
Acq. time 0.640 sec
Width 25683.4 Hz
6696 repetitions
OBSERVE C13, 100.5868021 MHz
DECOUPLE H1, 400.0288163 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1288909 hr, 13 min



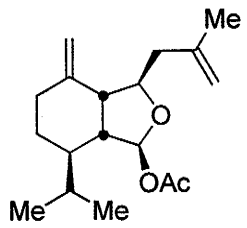
6

bw01119A-p-1-repurified-H5J

Sample: bw01119A-p-1-repurified-H5J
File: exp

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr15"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 24 repetitions
OBSERVE H1, 499.8853680 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 54198 hr, 30 min, 40 sec



S16

13C OBSERVE

Sample Name:

Archive directory:

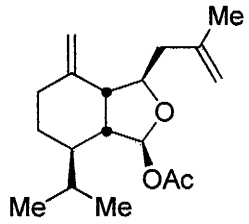
Sample directory:

FidFile: std13c

Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Feb 28 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 4.000 sec
Pulse 64.8 degrees
Acq. time 0.640 sec
Width 25683.4 Hz
6212 repetitions
OBSERVE C13, 100.5868021 MHz
DECOUPLE H1, 400.0288163 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1288909 hr, 13 min



S16

bw01120A-p-1-whole-H5J

Sample Name:

Archive directory:

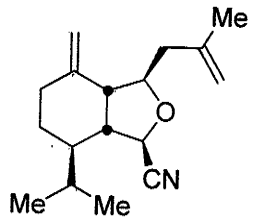
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Apr 3 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
78 repetitions
OBSERVE H1, 499.8853680 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 54198 hr, 30 min



7

13C OBSERVE

Sample Name:

Archive directory:

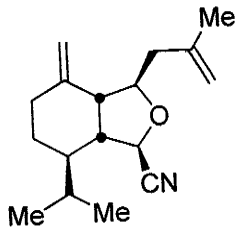
Sample directory:

FidFile: std13c

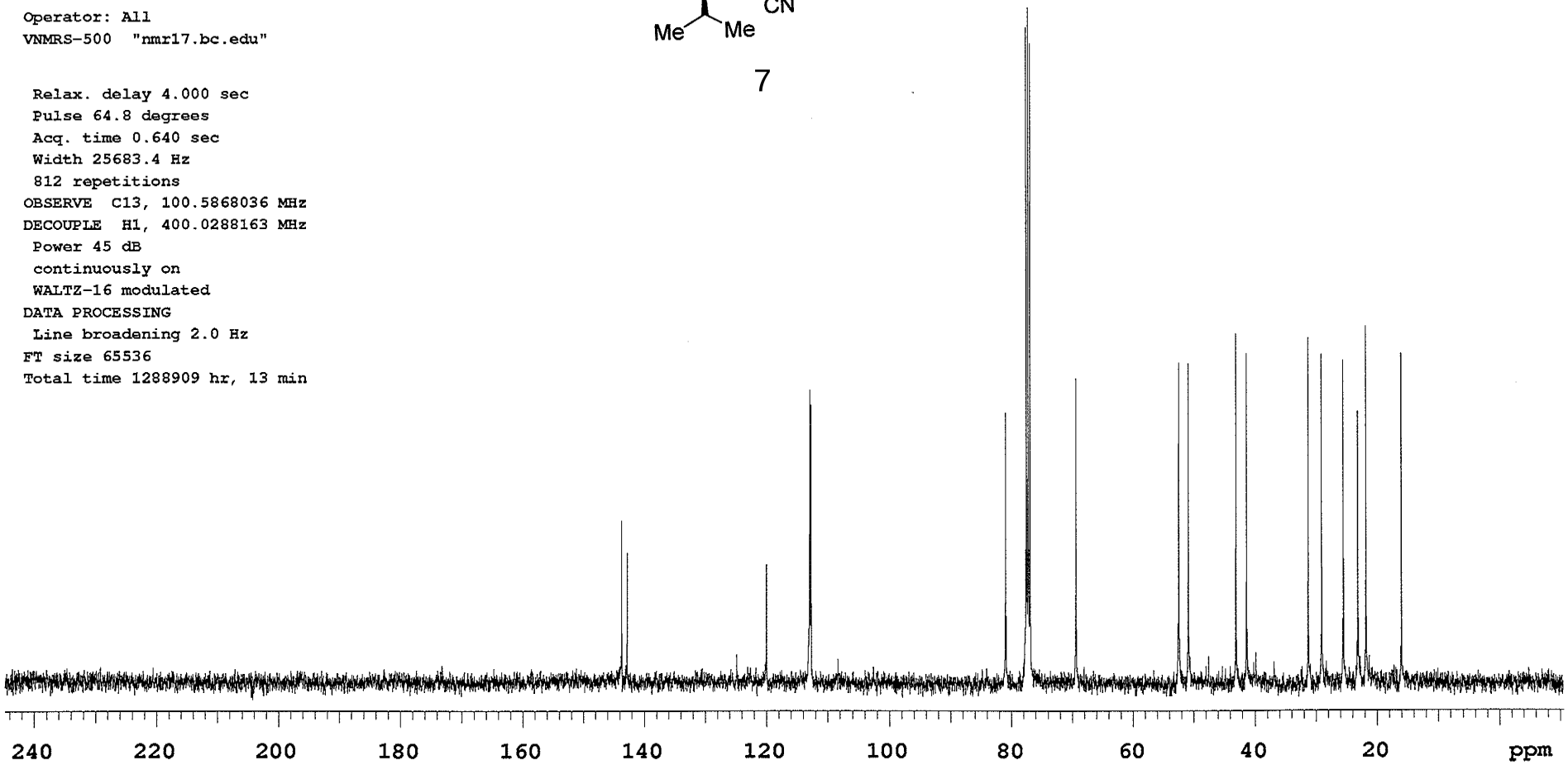
Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Apr 3 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 4.000 sec
Pulse 64.8 degrees
Acq. time 0.640 sec
Width 25683.4 Hz
812 repetitions
OBSERVE C13, 100.5868036 MHz
DECOUPLE H1, 400.0288163 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1288909 hr, 13 min



7



STANDARD 1H OBSERVE

Sample Name:

Archive directory:

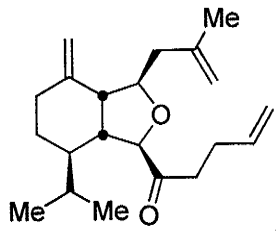
Sample directory:

FidFile: std1h

Pulse Sequence: std1h (s2pul)
Solvent: CDCl3
Data collected on: Jul 10 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.256 sec
Pulse 42.9 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
14 repetitions
OBSERVE H1, 399.7662713 MHz
DATA PROCESSING
FT size 65536
Total time 888887 hr, 6 min



8

13C OBSERVE

Sample Name:

Archive directory:

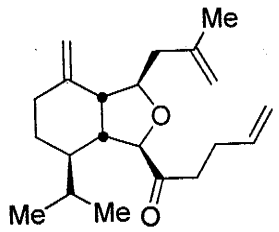
Sample directory:

FidFile: std13c

Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Apr 7 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 4.000 sec
Pulse 64.8 degrees
Acq. time 0.640 sec
Width 25683.4 Hz
5508 repetitions
OBSERVE C13, 100.5868013 MHz
DECOUPLE H1, 400.0288163 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1288909 hr, 13 min



8

bw01122A-p-1-PTLC-1-H5

Sample Name:

Archive directory:

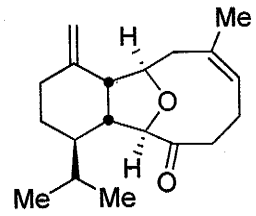
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: May 31 2010

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
54 repetitions
OBSERVE H1, 499.7720254 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 711122 hr, 20 min



1

13C OBSERVE

Sample Name:

Archive directory:

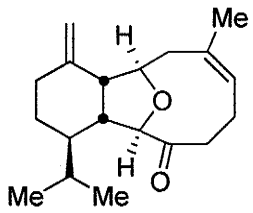
Sample directory:

FidFile: std13c

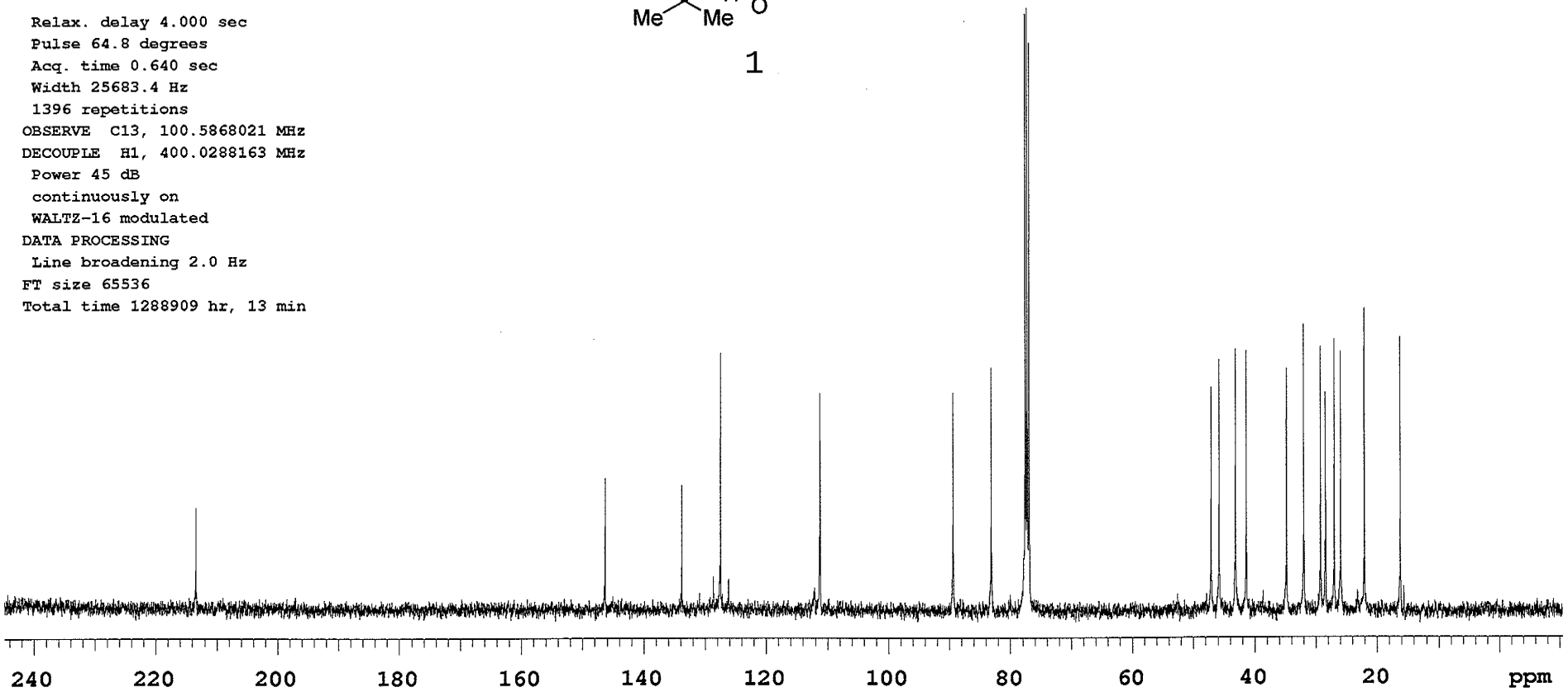
Pulse Sequence: std13c (s2pul)
Solvent: CDCl3
Data collected on: Apr 7 2009

Operator: All
VNMRS-500 "nmr17.bc.edu"

Relax. delay 4.000 sec
Pulse 64.8 degrees
Acq. time 0.640 sec
Width 25683.4 Hz
1396 repetitions
OBSERVE C13, 100.5868021 MHz
DECOUPLE H1, 400.0288163 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1288909 hr, 13 min



1



bw01122A-p-2-verypure-H5J

Sample Name:

Archive directory:

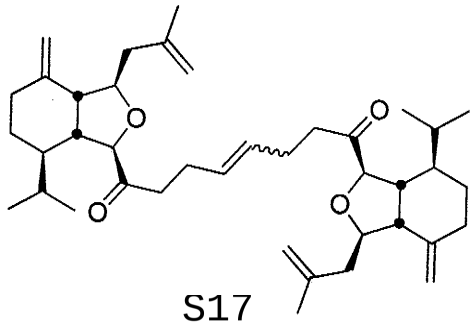
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Apr 11 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
112 repetitions
OBSERVE H1, 499.8853683 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 54198 hr, 30 min



S17

bw01122A-p-2-verypure-C5J

Sample Name:

Archive directory:

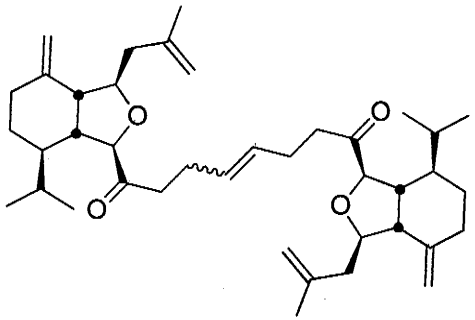
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Apr 11 2010

Temp. 25.0 C / 298.1 K
Operator: morken
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
100 repetitions
OBSERVE C13, 125.6962465 MHz
DECOUPLE H1, 499.8878615 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 63 hr, 54 min



S17

bw0126L-p-1-H5

Sample Name:

Archive directory:

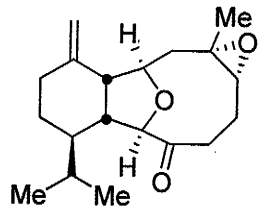
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Oct 2 2009

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 7996.0 Hz
80 repetitions
OBSERVE H1, 499.7720254 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 5419 hr, 56 min



α-9

STANDARD CARBON PARAMETERS

Sample Name:

Archive directory:

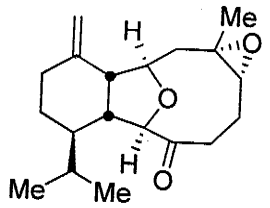
Sample directory:

FidFile: C13

Pulse Sequence: s2pul
Solvent: CDCl3
Data collected on: Apr 12 2009

Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 2.000 sec
Pulse 42.0 degrees
Acq. time 3.000 sec
Width 33361.1 Hz
7580 repetitions
OBSERVE C13, 125.6675832 MHz
DECOUPLE H1, 499.7738599 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 262144
Total time 1388923 hr, 35 min



α-9

Sample Name:
bw0126G-p-4-Apt6
Data Collected on:
nmr12-vnmrs600
Archive directory:

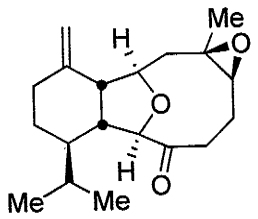
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Sep 16 2009

Temp. 25.0 C / 298.1 K
Operator: jpm

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 9615.4 Hz
42 repetitions
OBSERVE H1, 599.6956589 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 3 min 21 sec



β-9

Sample Name:
bw0126G-p-4-Apt6
Data Collected on:
nmr12-vnmrs600
Archive directory:

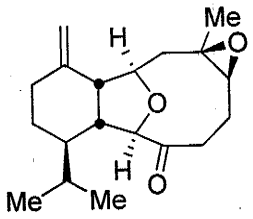
Sample directory:

FidFile: Apt

Pulse Sequence: Apt (APT)
Solvent: cdcl3
Data collected on: Sep 16 2009

Temp. 25.0 C / 298.1 K
Operator: jpm

Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 36764.7 Hz
18512 repetitions
OBSERVE C13, 150.7935577 MHz
DECOUPLE H1, 599.6986656 MHz
Power 46 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 559560 hr, 21 min



β-9

bw0135C-p-1-H4H

Sample Name:

Archive directory:

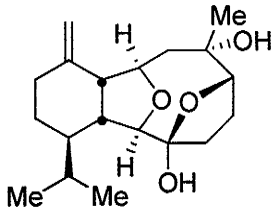
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Oct 18 2009

Temp. 25.0 C / 298.1 K
Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 4807.7 Hz
32 repetitions
OBSERVE H1, 399.7662699 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 5 hr, 25 min



11

bw0135C-p-1-C4H

Sample Name:

Archive directory:

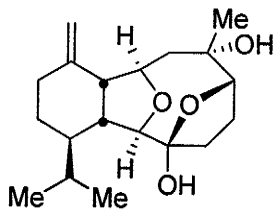
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Oct 18 2009

Temp. 25.0 C / 298.1 K
Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
13112 repetitions
OBSERVE C13, 100.5212848 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 639065 hr, 10 min



11

bw0130T-p-1---H4H

Sample Name:

Archive directory:

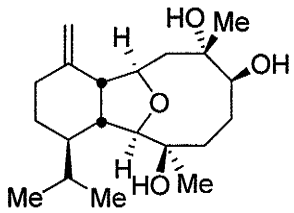
Sample directory:

FidFile: Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Nov 17 2009

Temp. 25.0 C / 298.1 K
Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
640 repetitions
OBSERVE H1, 399.7662698 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 32 min



sclerophytin A

bw0130T-p-1---C5J

Sample Name:

Archive directory:

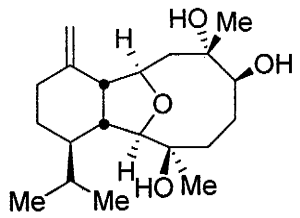
Sample directory:

FidFile: Carbon

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Nov 19 2009

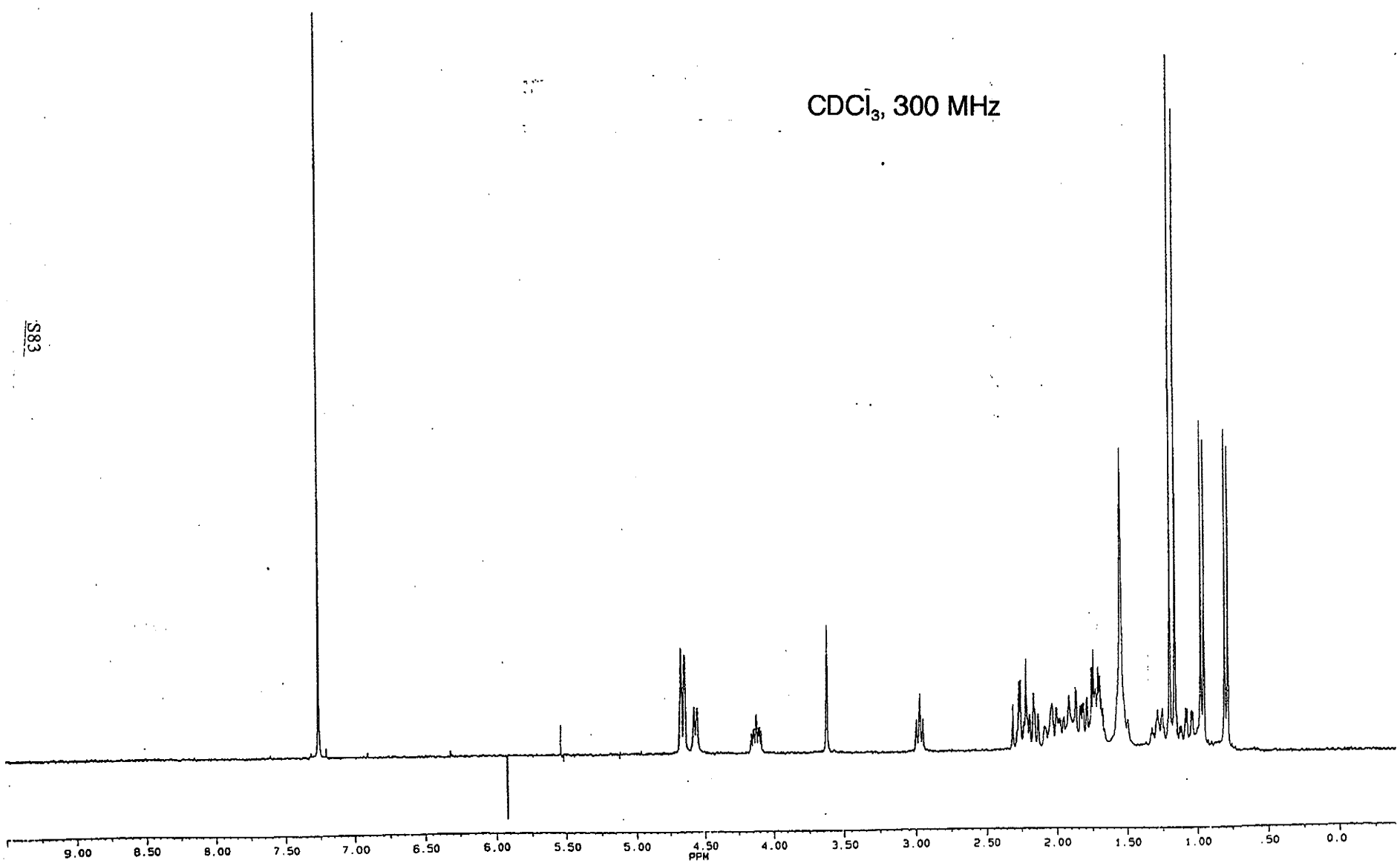
Temp. 25.0 C / 298.1 K
Operator: jpm
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30487.8 Hz
12380 repetitions
OBSERVE C13, 125.6962451 MHz
DECOUPLE H1, 499.8878615 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 639061 hr, 37 min



sclerophytin A

^{1}H NMR Spectrum of Natural Sclerophytin A[1]



(1) Bernardelli, P.; Moradei, O. M.; Friedrich, D.; Yang, J.; Gallou, F.; Dyck, B. P.; Doskotch, R. W.; Lange, T.; Paquette, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 9021.