## Supporting Information

**for**

# Studies for the Synthesis of Xenicane Diterpenes. A Stereocontrolled Total Synthesis of 4-Hydroxydictyolactone

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## General Information

Optical rotations were obtained on a Perkin Elmer 241 polarimeter at 589 nm (sodium D line) using a 10 cm path length and a 1.0 mL volume. Concentrations (c) are given in g/100 mL. Infrared spectra were recorded on a Nicolet Avatar 360 spectrometer and are reported in wavenumbers ($cm^{-1}$). Proton nuclear magnetic resonance ($^1H$ NMR) spectra were measured on a Varian VXR-400 (400 MHz) or a Varian INOVA-400 (400 MHz). Carbon nuclear magnetic resonance ($^{13}C$ NMR) spectra were measured on a VXR-400 (101 MHz) or an INOVA-400 (101 MHz). $^1H$ NMR and $^{13}C$ NMR spectra were acquired as solutions in $CDCl_3$ and are reported in parts per million (ppm) downfield (δ) from tetramethylsilane using residual chloroform ($CHCl_3$) as an internal standard set to δ 7.26 and δ 77.00, respectively. Proton NMR data are reported in the form: δ (multiplicity, coupling constants, number of protons). Mass spectral data (MS and HRMS) were recorded on a Kratos MS-80 RFA mass spectrometer by use of chemical ionization (CI) with methane or electron impact (EI).

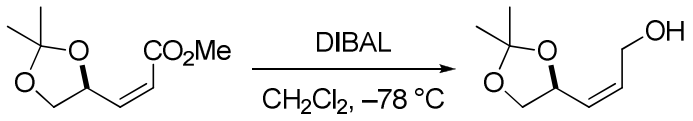
Analytical thin-layer chromatography (TLC) was performed using glass-backed 0.25 mm thickness silica gel 60 ($F_{254}$) plates (EM Science) which were visualized under UV light and/or staining with ethanolic *p*-anisaldehyde. Flash chromatography was performed using Merck silica gel 60 (Kiesegel 60) (E. M. Science; 230–400 mesh ASTM) or similar products from Whatman Scientific or Sorbent Technologies and pressure was obtained using an airline bleed.

All reagents and solvents were reagent grade and used as received unless noted otherwise. Bulk grade hexanes and ethyl acetate (EtOAc) for chromatography were distilled before use. Diethyl ether ($Et_2O$) and tetrahydrofuran (THF) were distilled under nitrogen from sodium/benzophenone ketyl immediately before use. Methylene chloride ($CH_2Cl_2$),

diisopropylethylamine (DIPEA) and triethylamine ($Et_3N$) were distilled from $CaH_2$ under dry air immediately before use.

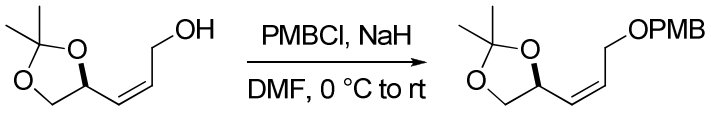
Unless otherwise noted, all reactions were conducted in flame or oven-dried glassware under an atmosphere of argon. All non-volatile samples were pumped to a constant weight under high vacuum (0.1–0.2 mmHg) at ambient temperature following removal of solvents by rotary evaporation.

## Experimental Procedures



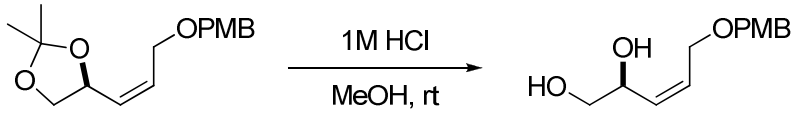

**12** **S1**

**(S,Z)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)prop-2-en-1-ol (S1)** Allylic alcohol **S1** was prepared according to the procedure described by Marshall and coworkers.[1] To a solution of **12** (26.43 g, 142.03 mmol) in $CH_2Cl_2$ (710 mL) at –78 °C, DIBAL (1.0 M in hexanes, 327 mL, 327 mmol) was slowly added. The reaction stirred for 1.5 h and was quenched at –78 °C with the addition of a saturated aqueous solution of sodium potassium tartrate (700 mL). The resulting mixture warmed to room temperature and stirred overnight. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The organic extracts were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated to give a colorless oil. Crude product was purified via flash chromatography (Hexanes/EtOAc (5:2)) providing **S1** (22.13 g, 98%) as a clear oil: $R_f$ 0.23 (Hexanes/EtOAc (1:1)); $[\alpha]_D^{22}$ +14.1° (c 1.18, $CHCl_3$); IR (film) 3404, 2987, 2358, 1372, 1215, 1156, 1059 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.78–5.69 (m, 1H), 5.47 (dt, *J* = 9.4, 1.6 Hz, 1H), 4.78 (m, 1H), 4.24–4.15 (m, 1H), 4.12–4.04 (m, 1H), 4.02 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.48 (dd, *J* = 8.6, 7.8 Hz, 1H), 3.00–2.86 (m, 1H), 1.35 (s, 3H), 1.31 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 135.1, 129.0, 109.2, 71.7, 69.3, 58.1, 26.5, 25.7; HRMS-CI (calcd. for $C_8H_{15}O_3$ $[M+H]^+$) 159.1016, found 159.1016.



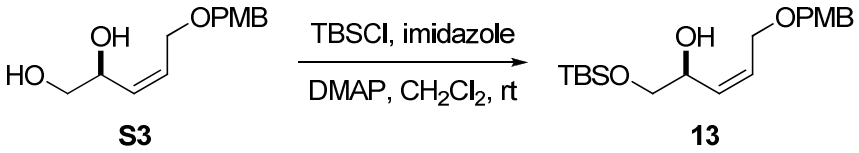

**S1** **S2**

**(S,Z)-4-(3-(4-Methoxybenzyloxy)prop-1-enyl)-2,2-dimethyl-1,3-dioxolane (S2)** To a solution of **S1** (19.50 g, 123.27 mmol) in DMF (615 mL) at 0 °C was added NaH (60% suspension in mineral oil, 5.92 g, 147.92 mmol). The mixture was stirred vigorously for 30 minutes and PMBCl (18.50 mL, 135.60 mmol) was then added dropwise. The solution was allowed to warm to ambient temperature with stirring overnight. The reaction was quenched with $H_2O$ and was diluted in $Et_2O$. Aqueous layer was extracted with $Et_2O$ (3 x 750 mL) and combined organic extracts were washed with saturated aqueous $NH_4Cl$ and brine. Organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow oil. Crude product was purified via flash chromatography (Hexanes/EtOAc (17:3)), providing **S2** (33.26 g, 97%) as a clear oil: $R_f$ 0.52 (Hexanes/EtOAc (3:1)); $[\alpha]_D^{23}$ –9.8° (c 1.04, $CHCl_3$); IR (film) 2985, 2360, 2340, 1513, 1248, 1059 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 6.92–6.86 (m, 2H), 5.89–5.74 (m, 1H), 5.71–5.55 (m, 1H), 4.81 (dd, *J* = 15.1, 7.7 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.09 (dd, *J* = 6.4, 1.3 Hz, 2H), 4.05 (dd, *J* = 8.1, 6.2 Hz, 1H), 3.81 (s, 3H), 3.55 (app. t, *J* = 8.0 Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 159.2, 130.6, 130.5, 130.0, 129.3 (2 C), 113.7 (2 C), 109.2, 71.9, 71.8, 69.3, 65.1, 55.1, 26.6, 25.8; HRMS-CI (calcd. for $C_{16}H_{21}O_4$ [M–H]) 277.1434, found 277.1433.




**S2** **S3**

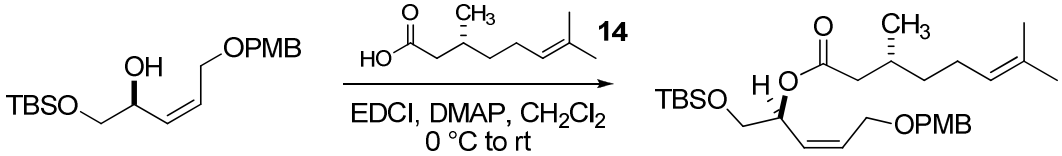
**(S,Z)-5-(4-Methoxybenzyloxy)pent-3-ene-1,2-diol (S3)** To a solution of **S2** (33.26 g, 119.49 mmol) in MeOH (400 mL) was added HCl (1.0 M in $H_2O$, 200 mL, 200 mmol). The reaction was allowed to stir for 3 h and was then neutralized with the slow addition of NaOH (1.0 M in $H_2O$, 200 mL, 200 mmol). The solution was extracted with $CH_2Cl_2$ (4 x 500 mL) and combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give an opaque oil. Crude product was purified via flash chromatography ($Et_2O$/MeOH (40:1)), providing **S3** (28.46 g, 100%) as a white solid: $R_f$ 0.11 (Hexanes/EtOAc (1:3)); $[\alpha]_D^{21}$ +4.5° (c 0.91, $CHCl_3$); IR (film) 3386 (br), 2932, 2862, 1612, 1514, 1249, 1073, 1033 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 6.92–6.86 (m, 2H), 5.84–5.76 (m, 1H), 5.67–5.58 (m, 1H), 4.53–4.44 (m, 3H), 4.14 (ddd, *J* = 12.4, 6.3, 1.1 Hz, 1H), 4.05 (ddd, 12.4, 5.9, 0.9 Hz, 1H), 3.82 (s, 3H), 3.64–3.55 (m, 1H), 3.55–3.47 (m, 1H), 2.59 (br. s, 1H), 2.03 (br. s, 1H)); $^{13}C$ (101 MHz, $CDCl_3$) δ 159.2, 131.9, 129.6, 129.4 (2 C), 129.2, 113.7 (2 C), 72.1, 68.6, 65.9, 65.4, 55.1; HRMS-CI (calcd. for $C_{13}H_{19}O_4$ $[M+H]^+$) 239.1273, found 239.1278




**S3** **13**

**(S,Z)-1-(tert-Butyldimethylsilyloxy)-5-(4-methoxybenzyloxy)pent-3-en-2-ol (13)** To a solution of **S3** (25.73 g, 107.98 mmol) in $CH_2Cl_2$ (540 mL) at 0 °C was added imidazole (9.56 g, 140.48 mmol), followed by TBSCl (16.27 g, 107.98 mmol). The mixture was allowed to slowly warm to room temperature and was stirred for an additional 8 h. The reaction was quenched with the addition of saturated aqueous $NaHCO_3$ and aqueous layer was extracted with $CH_2Cl_2$ (3 x 500 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and

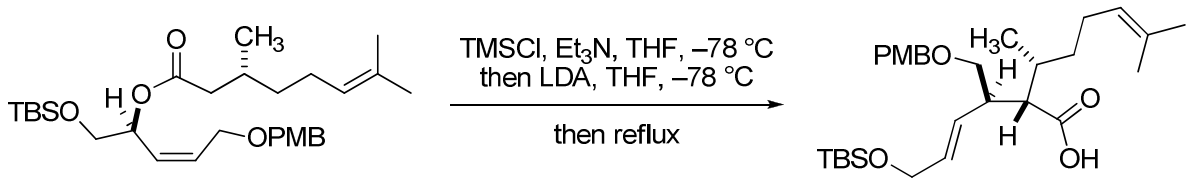
concentrated *in vacuo* to give a clear oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (17:3)), providing **13** (35.48 g, 93%) as a clear oil: $R_f$ 0.26 (Hexanes/EtOAc (3:1)); $[\alpha]_D^{24}$ +22.8° (c. 0.98, $CHCl_3$); IR (film) 3430 (br), 2928, 2856, 1613, 1513, 1464, 1249, 1073 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H), 6.91–6.85 (m, 2H), 5.81–5.72 (m, 1H), 5.60–5.52 (m, 1H), 4.45–4.38 (m, 3H), 4.16–4.04 (m, 2H), 3.81 (s, 3H), 3.56 (dd, *J* = 10.0, 3.9 Hz, 1H), 3.45 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.63 (d, *J* = 2.8 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$), δ 159.2, 131.4, 130.1, 129.9, 129.4 (2 C), 113.8 (2 C), 72.0, 68.5, 66.8, 65.6, 55.2, 25.8 (3 C), 18.3, –5.3, –5.4; HRMS-CI (calcd. for $C_{19}H_{33}O_4Si$ $[M+H]^+$) 353.2143, found 353.2154.




**13** **15**

**(R)-((S,Z)-1-(tert-Butyldimethylsilyloxy)-5-(4-methoxybenzyloxy)pent-3-en-2-yl) 3,7-dimethyloct-6-enoate (15)** To a solution of **13** (28.24 g, 80.10 mmol) in $CH_2Cl_2$ (400 mL) was added (*R*)-citronellic acid (**14**) (15.00 g, 88.11 mmol). The solution was chilled to 0 °C and EDCI (46.07 g, 240.3 mmol) was added, followed by DMAP (11.74 g, 96.12 mmol). The reaction was allowed to slowly warm to ambient temperature with stirring overnight. Saturated aqueous $NH_4Cl$ (400 mL) was added and the layers were separated. The aqueous layer was extracted with $Et_2O$ and combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a slightly yellow oil. The crude product was purified via flash chromatography, (Hexanes/EtOAc (19:1)), providing **15** (39.15 g, 97%) as a clear oil: $R_f$ 0.68 (Hexanes/EtOAc (3:1)); $[\alpha]_D^{23}$ –22.4° (c 0.91, $CHCl_3$); IR (film) 2928, 2856, 1736, 1513,

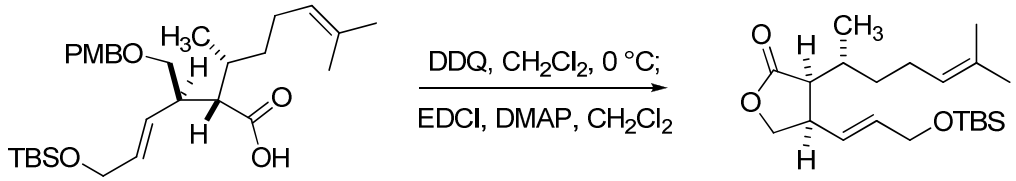
1249 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 6.91–6.84 (m, 2H), 5.80 (dt, *J* = 11.7, 6.3 Hz, 1H), 5.60–5.53 (m, 1H), 5.52–5.46 (m, 1H), 5.13–5.05 (m, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.25–4.14 (m, 2H), 3.79 (s, 3H), 3.69 (dd, *J* = 10.9 Hz, 7.0 Hz, 1H), 3.63 (dd, *J* = 10.9, 4.7 Hz, 1H), 2.30 (dd, *J* = 14.9, 6.3 Hz, 1H), 2.11 (dd, *J* = 14.9, 8.6 Hz, 1H), 2.06–1.90 (m, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.41–1.30 (m, 1H), 1.29–1.15 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 172.2, 159.1, 131.7, 131.3, 130.2, 129.3 (2 C), 127.5, 124.2, 113.7 (2 C), 72.0, 70.7, 66.0, 64.6, 55.1, 41.9, 36.7, 30.0, 25.7 (3 C), 25.6, 25.3, 19.5, 18.2, 17.5, –5.5 (2 C); HRMS-CI (calcd. for $C_{29}H_{47}O_5Si$ $[M-H]^+$) 503.3187, found 503.3208.




**15** **16**

**(2S,3R)-2-((R,E)-6-(tert-Butyldimethylsilyloxy)-1-(4-methoxybenzyloxy)hex-4-en-2-yl)-3,7-dimethyloct-6-enoic acid (16)** To a solution of **15** (1.02 g, 2.02 mmol) in THF (40 mL) at −78 °C was added a premixed solution of $Et_3N$ (1.30 mL, 9.09 mmol) and TMSCl (1.30 mL, 10.10 mmol). The solution was allowed to stir for 5 min and then a solution of LDA (1.0 M in THF, 3.03 mL, 3.03 mmol) was pre-cooled to −78 °C and was added dropwise via cannula. The reaction was allowed to stir for 90 min and then at ambient temperature for 2 h. Additional THF (20 mL) was added, and the reaction was heated to reflux for 2 h. The solution was cooled to ambient temperature and diluted in EtOAc (50 mL) and brine (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 25 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude

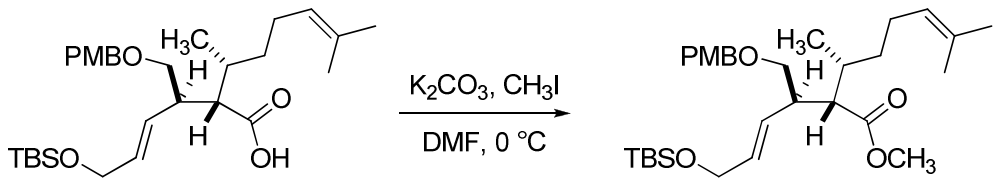
product was purified via flash chromatography, (Hexanes/EtOAc (9:1 to 4:1)), providing **16** (871 mg, 85%) as a clear oil: $R_f$ 0.09 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{22}$ +11.6° (c 1.01, $CHCl_3$); IR (film) 2956, 2929, 2856, 1703, 1514, 1249 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (m, 2H), 6.89–6.84 (m, 2H), 5.73 (dd, *J* = 15.5, 8.9 Hz, 1H), 5.65 (dt, *J* = 15.4, 4.8 Hz, 1H), 5.11–5.03 (m, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.19–4.07 (m, 2H), 3.80 (s, 3H), 3.49–3.38 (m, 2H), 2.79–2.71 (m, 1H), 2.59 (t, *J* = 7.2 Hz, 1H), 2.08–1.88 (m, 2H), 1.87–1.73 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.54–1.42 (m, 1H), 1.22–1.10 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 179.3, 159.1, 132.4, 131.5, 130.3, 129.2 (2 C), 128.3, 124.3, 113.7 (2 C), 72.8, 71.5, 63.7, 55.2, 51.0, 41.8, 34.3, 31.6, 25.9 (3 C), 25.7, 25.2, 18.4, 17.6, 16.4, –5.1, –5.2; HRMS-CI (calcd. for $C_{29}H_{49}O_5Si$ $[M+H]^+$) 505.3344, found 505.3349.




**16** **18**

**(3S,4R)-4-((E)-3-(tert-butyldimethylsilyloxy)prop-1-enyl)-3-((R)-6-methylhept-5-en-2-yl)dihydrofuran-2(3H)-one (18)** To a solution of acid **16** (15 mg, 0.030 mmol) in $CH_2Cl_2/H_2O$ (300 μL, 18:1) at 0 °C was added DDQ (17.6 mg, 0.078 mmol) in a single portion. The reaction was stirred for 3 h and was then quenched with saturated aqueous $NH_4Cl$ (1 mL). The mixture was diluted in $CH_2Cl_2$ (5 mL) and the layers were separated. The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to give a yellow residue. The residue was dissolved in $CH_2Cl_2$ (1 mL) and excess EDCI and DMAP were added. After 1 h, TLC analysis

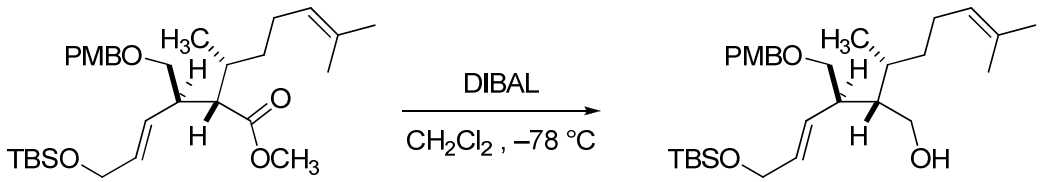
revealed complete consumption of the starting material and the reaction was diluted in $CH_2Cl_2$ (3 mL) and washed with saturated aqueous $NH_4Cl$ (2 x 5 mL) and brine (2 x 5 mL). The organic layer was then dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow film. The crude product was purified via flash chromatography, (Hexanes/EtOAc (9:1)), providing **18** (8.1 mg, 73%) as a clear oil: $[\alpha]_D^{22}$ +55.2° (c 0.21, $CHCl_3$); IR (film) 2956, 2928, 2856, 1776, 1128 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.78–5.68 (m, 2H), 5.12–5.06 (m, 1H), 4.31 (A of ABX, $J_{AB}$ = 9.0 Hz, $J_{AX}$ = 6.8 Hz, 1H), 4.20–4.17 (m, 2H), 4.08 (B of ABX, $J_{BA}$ = 9.0 Hz, $J_{BX}$ = 5.1 Hz, 1H), 3.32–3.26 (m, 1H), 2.51 (dd, *J* = 8.1, 6.7 Hz, 1H), 2.10–2.01 (m, 1H), 2.01–1.99 (m, 1H), 1.99–1.78 (m, 1H), 1.70 (s, 3H), 1.61 (s, 3H), 1.35–1.26 (m, 2H), 1.13 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.09 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 177.7, 133.8, 131.9, 125.1, 124.2, 71.5, 63.2, 48.5, 42.6, 35.2, 30.9, 26.1, 25.9, 25.4, 18.6, 17.9, 16.9, –5.1; HRMS-CI (calcd. for $C_{21}H_{38}O_3Si$ $[M+H]^+$) 367.2668, found 367.2672.




**16** **S4**

**(2S,3R)-Methyl 2-((R,E)-6-(tert-butyldimethylsilyloxy)-1-(4-methoxybenzyloxy)hex-4-en-2-yl)-3,7-dimethyloct-6-enoate (S4)** To a solution of **16** (319 mg, 0.63 mmol) in DMF (3.15 mmol) at 0 °C was added anhydrous $K_2CO_3$ (157 mg, 1.14 mmol), followed by $CH_3I$ (0.18 mL, 2.84 mmol). The reaction mixture was allowed to warm to ambient temperature with stirring for 2 h and was then diluted in $CH_2Cl_2$ and washed with saturated aqueous $NH_4Cl$. The aqueous layer was extracted with $CH_2Cl_2$ (3 x 10 mL) and the combined organic extracts were washed

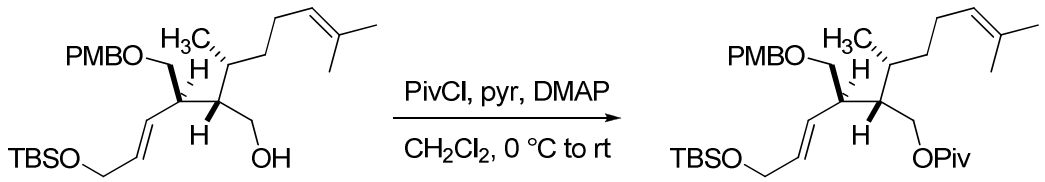
with $H_2O$, dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (19:1)) providing **S4** (320 mg, 97%) as a clear oil: $R_f$ 0.41 (Hexanes/EtOAc (17:3)) $[\alpha]_D^{20}$ +11.0° (c 1.10, $CHCl_3$); IR (film) 2953, 2929, 2855, 1733, 1514, 1249 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.27–7.20 (m, 2H), 6.89–6.83 (m, 2H), 5.72 (dd, *J* = 15.5, 8.8 Hz, 1H), 5.61 (dt, *J* = 15.5, 4.8 Hz, 1H), 5.12–5.02 (m, 1H), 4.45–4.35 (m, 2H), 4.12 (br. d, *J* = 4.8 Hz, 2H), 3.80 (s, 3H), 3.57 (s, 3H), 3.44–3.33 (m, 2H), 2.78–2.66 (m, 1H), 2.58 (t, *J* = 7.4 Hz, 1H), 2.06–1.86 (m, 2H), 1.83–1.71 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.49–1.35(m, 1H), 1.19–1.02 (m, 1H), 0.93–0.86 (m, 12H), 0.05 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 174.4, 159.1, 132.1, 131.5, 130.5, 129.1 (2 C), 128.9, 124.4, 113.7 (2 C), 72.8, 71.5, 63.8, 55.3, 51.1, 50.8, 42.1, 34.5, 31.9, 25.9 (3 C), 25.7, 25.2, 18.4, 17.6, 16.2, –5.2 (2 C); HRMS-CI (calcd. for $C_{30}H_{51}O_5Si$ $[M+H]^+$) 519.3500, found 519.3507.




**S4** **S5**

**(2S,3R)-2-((R,E)-6-(tert-Butyldimethylsilyloxy)-1-(4-methoxybenzyloxy)hex-4-en-2-yl)-3,7-dimethyloct-6-en-1-ol (S5)** To a solution of **S4** (862 mg, 1.66 mmol) in $CH_2Cl_2$ (33.2 mL) at –78 °C was added DIBAL (1.0 M in Hexanes, 4.98 mL, 4.98 mmol) slowly. The reaction was stirred for 1.5 h and then was quenched at –78 °C with the addition of a saturated aqueous solution of sodium potassium tartrate (30 mL). The resulting mixture was allowed to stir overnight, after which time, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 50 mL). Organic extracts were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated to give a colorless oil. Crude product was purified via flash chromatography

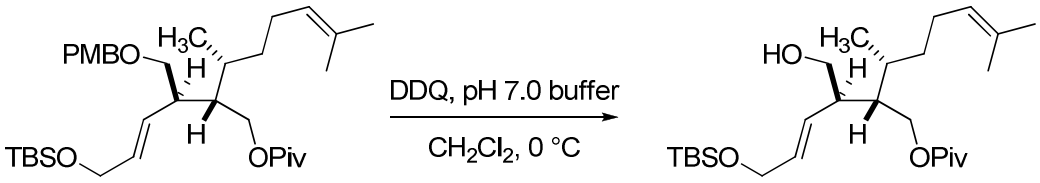
(Hexanes/EtOAc (9:1)) providing **S5** (813 mg, 100%) as a clear oil: $R_f$ 0.19 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{23}$ +27.9° (0.88, $CHCl_3$); IR (film) 3448 (br), 2928, 2855, 1513, 1249 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 2H), 6.90–6.86 (m, 2H), 5.79 (dd, *J* = 15.5, 9.1 Hz, 1H), 5.66 (dt, *J* = 15.5, 5.1 Hz, 1H), 5.11–5.04 (m, 1H), 4.48–4.39 (m, 2H), 4.14 (br. d, *J* = 5.0 Hz, 2H), 3.80 (s, 3H), 3.66–3.55 (m, 2H), 3.51 (dd, *J* = 9.1, 5.4 Hz, 1H), 3.48 (dd, *J* = 9.1, 5.1 Hz, 1H), 2.59–2.48 (m, 2H), 2.07–1.84 (m, 2H), 1.67 (s, 3H), 1.65–1.55 (m, 2H), 1.59 (s, 3H), 1.48–1.36 (m, 1H), 1.28–1.16 (m, 1H), 0.90 (s, 9H), 0.88 (d, *J* = 6.7 Hz, 3H), 0.06 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 159.2, 131.3 (2 C), 130.9, 130.0, 129.3 (2 C), 124.6, 113.8 (2 C), 73.2, 72.9, 63.7, 61.7, 55.2, 47.1, 44.0, 35.3, 33.6, 25.9 (3 C), 25.8, 25.7, 18.3, 17.7, 16.4, –5.2 (2 C); HRMS-ESI (calcd. for $C_{29}H_{50}O_4SiNa$ $[M+Na]^+$) 513.3376, found 513.3352.




**S5** **S6**

**(2S,3R)-2-((R,E)-5-(tert-Butyldimethylsilyloxy)-1-(4-methoxybenzyloxy)pent-3-en-2-yl)-3,7-dimethyloct-6-enyl pivalate (S6)** To a solution of **S5** (994 mg, 2.03 mmol), pyridine (0.82 mL, 10.14 mmol), and DMAP (50 mg, 0.41 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C was added pivaloyl chloride (1.25 mL, 10.14 mmol). The mixture was allowed to slowly warm to ambient temperature and was stirred for 5 h. The reaction was diluted with $CH_2Cl_2$ (50 mL) and saturated, aqueous $NH_4Cl$ (30 mL) was added. The aqueous layer was then separated and extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (9:1)), providing **S6** (1.11g, 95%) as a colorless oil: $R_f$ 0.42

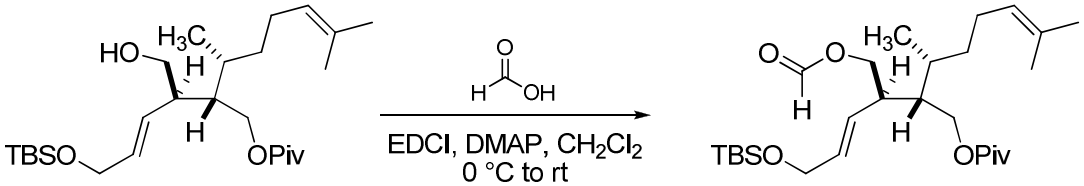
(Hexanes/EtOAc (17:3)); $[\alpha]_D^{22}$ +17.0° (c 1.01, $CHCl_3$); IR (film) 2957, 2929, 2856, 1727, 1514, 1249 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 (m, 2H), 6.89–6.83 (m, 2H), 5.61–5.56 (m, 2H), 5.12–5.06 (m, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 4.18–4.10 (m, 2H), 4.09–3.99 (m, , 2H), 3.80 (s, 3H), 3.46 (d, *J* = 5.9 Hz, 2H), 2.63–2.53 (m, 1H), 2.07–1.85 (m, 2H), 1.84–1.77 (m, 1H), 1.72–1.65 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.49-1.36 (m, 1H), 1.35-1.22 (m, 1H), 1.17 (s, 9H), 0.92–0.86 (m, 12 H), 0.05 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 178.3, 159.0, 131.6, 131.2, 130.5, 130.1, 129.0 (2 C), 124.5, 113.6 (2 C), 72.6, 72.1, 63.7, 63.4, 55.1, 42.8, 41.8, 38.5, 35.4, 32.6, 27.1 (3 C), 25.9 (3 C), 25.7, 25.6, 18.3, 17.6, 16.2, –5.2 (2 C); HRMS-CI (calcd for $C_{34}H_{57}O_5Si$ $[M-H]^+$) 573.3970, found 573.3979.




**S6** **19**

**(2S,3R)-2-((R,E)-5-(tert-Butyldimethylsilyloxy)-1-hydroxypent-3-en-2-yl)-3,7-dimethyloct-6-enyl pivalate (19)** To a solution of **S6** (1.42 g, 2.47 mmol) in $CH_2Cl_2$ (25 mL) and pH 7.0 buffer (2.5 mL) at 0 °C was added DDQ (841 mg, 3.71 mmol) in one portion to give a green suspension. The reaction was stirred for 10 min and then warmed to ambient temperature. After 2 h, the orange reaction mixture was diluted by the addition of saturated aqueous $NaHCO_3$. The layers were separated and the aqueous layer was then extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic extracts were combined, dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (9:1)), providing **19** (853 mg, 76%) as a colorless oil: $R_f$ 0.19 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{24}$ +7.9° (c 0.82, $CHCl_3$); IR (film) 3479 (br), 2958, 2929, 2857, 1729, 1159 $cm^{-1}$;

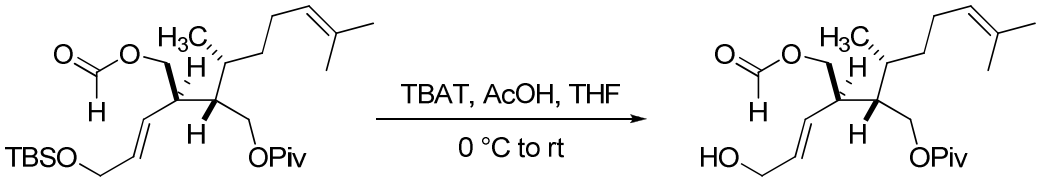
$^1$H NMR (400 MHz, $CDCl_3$) δ 5.67 (td, *J* = 15.4, 4.8 Hz, 1H), 5.50 (dd, *J* = 15.4, 9.5 Hz, 1H), 5.09–5.02 (m, 1H), 4.16–4.12 (m, 2H), 4.10 (dd, *J* = 11.7, 4.6 Hz, 1H), 4.01 (dd, *J* = 11.61, 5.18 Hz, 1H), 3.72–3.63 (m, 1H), 3.54-3.42 (m, 1H), 2.48 (ddd, *J* = 14.6, 8.8, 6.0 Hz, 1H), 2.10-1.85 (m, 2H), 1.85-1.72 (m, 1H), 1.72–1.60 (m, 2 H), 1.67 (s, 3H), 1.59 (s, 3H), 1.49-1.35 (m, 1H), 1.32-1.23 (m, 1H), 1.21-1.13 (m, 9H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.5, 133.9, 131.5, 129.0, 124.4, 64.3, 63.5, 63.4, 45.8, 42.1, 38.6, 35.2, 33.0, 27.2 (3 C), 25.9 (3 C), 25.7, 25.6, 18.3, 17.7, 16.2, –5.2 (2 C); HRMS-CI (calcd for $C_{26}H_{51}O_4Si$ $[M+H]^+$) 455.3551, found 455.3560.




**19** **S7**

**(2S,3R)-2-((R,E)-5-(tert-Butyldimethylsilyloxy)-1-(formyloxy)pent-3-en-2-yl)-3,7-dimethyloct-6-enyl pivalate (S7)** Formic acid (90 μL, 1.93 mmol), EDCI (1.00 g, 5.24 mmol), and DMAP (257 mg, 2.10 mmol) were sequentially added to a solution of alcohol **19** (795 mg, 1.75 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C. The reaction was allowed to warm to ambient temperature and was then stirred for 3 h. The reaction mixture was diluted in saturated aqueous $NH_4Cl$ (10 mL). The layers were immediately separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic extracts were washed with water (30 mL) and brine (30 mL) and then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (97:3)), providing **S7** (814 mg, 96%) as a colorless oil: $R_f$ 0.44 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{22}$ +7.9° (c 0.95, $CHCl_3$);

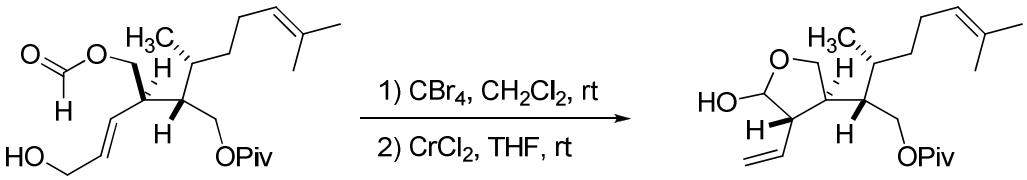
IR (film) 2958, 2929, 2857, 1729, 1156 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 5.63 (dt, *J* = 15.4, 4.7 Hz, 1H), 5.54 (dd, *J* = 15.4, 8.9 Hz, 1H), 5.13-5.01 (m, 1H), 4.28–4.15 (m, 2H), 4.10 (d, *J* =4.4 Hz, 2H), 4.08–3.99 (m, 2H), 2.74–2.55 (m, 1H), 2.10–1.85 (m, 2H), 1.76–1.68 (m, 1H), 1.68–1.58 (m, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.46–1.33 (m, 1H), 1.33–1.21 (m, 1H), 1.17 (m, 9H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.91–0.87 (s, 9H), 0.19–0.08 (s, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 178.2, 160.7, 133.1, 131.5, 127.9, 124.2, 65.7, 63.3, 63.1, 41.9, 41.8, 38.5, 35.2, 32.6, 27.1 (3 C), 25.8 (3 C), 25.6, 25.6, 18.3, 17.6, 16.1, –5.3, –5.3; HRMS-CI (calcd for $C_{27}H_{51}O_5Si$ $[M+H]^+$) 483.3500, found 483.3517.




**S7** **S8**

**(2S,3R)-2-((R,E)-1-(Formyloxy)-5-hydroxypent-3-en-2-yl)-3,7-dimethyloct-6-enyl pivalate (S8)** Acetic acid (1.52 mL, 26.58 mmol) and tetrabutylammonium triphenyldifluorosilicate (TBAT, 9.37 g, 17.36 mmol) were sequentially added to a solution of **S7** (4.19 g, 8.68 mmol) in THF (90 mL) at 0 °C. The reaction was then allowed to warm to ambient temperature and was stirred for 12 h. The reaction was quenched with the addition of water (40 mL) and was diluted in $Et_2O$ (100 mL). The aqueous layer was then separated and extracted with $Et_2O$ (3 x 50 mL). The combined organic extracts were washed with water (2 x 50 mL) and brine (2 x 50 mL) and then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (4:1)), providing **S8** (3.17 g, 99%) as a colorless oil: $R_f$ 0.16 (Hexanes/EtOAc (3:1)); $[\alpha]_D^{23}$ +2.9° (c 0.90, $CHCl_3$); IR (film) 3431,

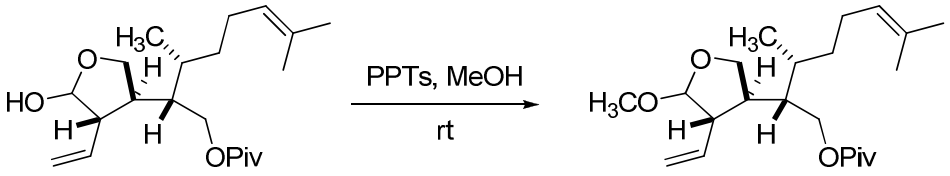
2964, 2917, 1723, 1715, 1157 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 5.68 (td, *J* = 15.4, 5.5 Hz, 1H), 5.54 (dd, *J* = 15.4, 9.2 Hz, 1H), 5.08-4.99 (m, 1H), 4.22-4.13 (m, 3H), 4.12-3.99 (m, 4H), 2.67–2.56 (m, 1H), 2.07-1.84 (m, 3H), 1.76–1.68 (m, 1H), 1.68-1.60 (m, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.45–1.33 (m, 1H), 1.32-1.23 (m, 1H), 1.15 (s, 9H), 0.90 (d, *J* = 6.9 Hz, 3H);$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 178.5, 160.9, 132.7, 131.6, 130.2, 124.1, 65.5, 63.1, 62.9, 41.9, 41.9, 38.6, 35.3, 32.4, 27.1 (3 C), 25.6, 25.6, 17.6, 16.0; HRMS-CI (calcd for $C_{21}H_{35}O_4$ [M-OH]$^+$) 351.2530, found 351.2526.




**S8** **22**

**(2S,3R)-2-((3S,4S)-5-Hydroxy-4-vinyltetrahydrofuran-3-yl)-3,7-dimethyloct-6-enyl pivalate (22)** To a solution of $CBr_4$ (2.34 g, 7.05 mmol) and $PPh_3$ (2.44 g, 9.31 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C was added a solution of **S8** (980 mg, 2.66 mmol) in $CH_2Cl_2$ (17 mL). The reaction was allowed to stir for 20 min and was then diluted in hexanes (50 mL) and passed through a plug of silica gel followed by a wash with 15% EtOAc in hexanes (100 mL). The filtrate was concentrated *in vacuo* and then dissolved in THF (175 mL). To the solution was added $CrCl_2$ (689 mg, 5.61 mmol), resulting in a green-gray suspension. After 10 h, the purple homogeneous solution was quenched with water (150 mL) and then diluted in EtOAc (200 mL). The aqueous layer was separated and extracted with EtOAc (3 x 200 mL). The combined organic extracts were then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (17:3)), providing **22** (863 mg, 92%) as a 2:1 mixture of inseparable C-19 diastereomers: $R_f$ 0.26 (Hexanes/EtOAc (3:1)); IR (film) 3424 (br), 2965, 2930, 1727, 1480, 1284, 1157 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.86–5.64 (m,

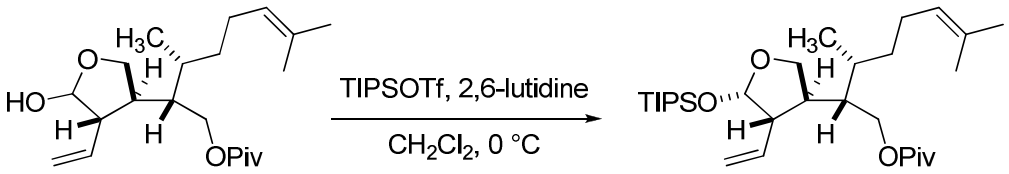
1H), 5.29 (dd, *J* = 4.2, 3.4 Hz, 0.3H), 5.23–4.98 (m, 3.7H), 4.25 (t, *J* = 8.3 Hz, 0.3H), 4.15–3.99 (m, 2.7H), 3.77 (dd, *J* = 9.8, 8.6 Hz, 0.7H), 3.64 (t, *J* = 8.2 Hz, 0.3H), 2.71–2.49 (m, 1.3H), 2.33–2.21 (m, 0.7H), 2.02–1.86 (m, 2H), 1.83–1.74 (m, 0.7H), 1.71–1.61 (m, 0.3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.52–1.24 (m, 3H), 1.19–1.14 (m, 9H), 0.91–0.84 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.3, 138.7, 136.6, 131.6, 124.1, 117.4, 116.4, 103.8, 100.5, 72.0, 71.0, 63.0, 62.8, 56.2, 53.6, 44.9, 44.8, 44.3, 40.7, 38.5, 35.9, 35.7, 33.7, 33.6, 27.2, 25.9, 25.8, 25.6, 17.7, 25.9, 15.6; HRMS-CI (calcd for $C_{21}H_{35}O_3$ $[M\text{-}OH]^+$) 335.2581, found 335.2572.




**22** **23**

**(2S,3R)-2-((3S,4S)-5-methoxy-4-vinyltetrahydrofuran-3-yl)-3,7-dimethyloct-6-enyl pivalate (23)** To a solution of lactol **22** (440 mg, 1.25 mmol) in MeOH (13 mL) at ambient temperature was added PPTs (32 mg, 0.125 mmol). After stirring for 12 h, the reaction solution was diluted in $Et_2O$ (25 mL) and washed with $H_2O$ (3 x 15 mL) and brine (15 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (19:1)), providing **23** (456 mg, 100%) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.87 (Hexanes/EtOAc (3:1)); IR (film) 2966, 2927, 1729, 1283, 1159, 1033 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.83–5.66 (m, 1H), 5.17–4.98 (m, 3H), 4.79 (d, *J* = 4.1 Hz, 0.4H), 4.72 (d, *J* = 2.2 Hz, 0.6H), 4.19–3.98 (m, 3H), 3.70–3.65 (m, 0.4H), 3.61 (dd, *J* = 10.1, 8.5 Hz, 0.6H), 3.34 (s, 0.6H), 3.32 (s, 0.4H), 2.61–2.54 (m, 1.4H), 2.25 (tt, *J* = 10.2, 7.4 Hz, 0.6H), 2.04–1.86 (m, 2.4H), 1.81–1.72 (m, 0.6H), 1.68 (s, 3H), 1.60 (s, 3H), 1.54–1.44 (m, 1H), 1.42–1.27 (m, 2H), 1.20–1.17 (m, 9H), 0.90 (d, *J* = 7.0 Hz, 1.2H), 0.89 (d, *J*

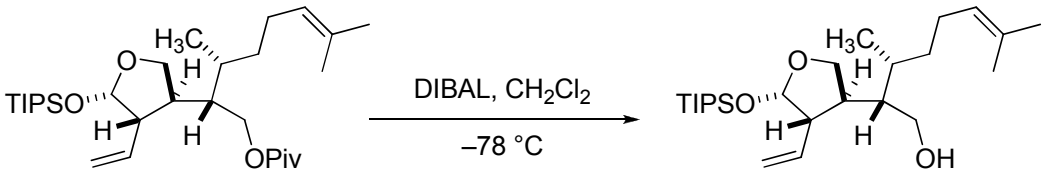
= 6.9 Hz, 1.8H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.2, 139.1, 136.8, 131.6, 124.2, 124.1, 116.8, 115.9, 110.5, 107.3, 71.8, 70.8, 63.0, 62.8, 55.5, 54.9, 54.6, 53.6, 45.1, 44.9, 44.3, 41.1, 38.5, 35.9, 35.7, 33.7, 33.6, 27.2 (3 C), 25.9, 25.8, 25.6, 17.6, 15.9, 15.6; HRMS-CI (calcd for $C_{22}H_{37}O_4$ $[M–H]^+$) 365.2686, found 365.2670.




**22** **24**

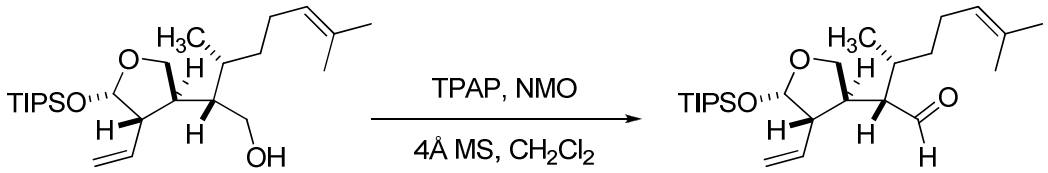
**(2S,3R)-3,7-Dimethyl-2-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)oct-6-enyl pivalate (24)** To a solution of lactol **22** (2.43 g, 6.89 mmol) in $CH_2Cl_2$ (70 mL) at 0 °C were added 2,6-lutidine (3.20 mL, 27.57 mmol) and TIPSOTf (3.72 mL, 13.79 mmol). The reaction was allowed to stir at 0 °C for 90 minutes and was then diluted in $CH_2Cl_2$ (50 mL) and brine (50 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 50 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (50:1)), providing **24** (3.16 g, 90%) as a 91:9 mixture of inseparable C-19 diastereomers. The major diastereomer was characterized as follows: $R_f$ 0.82 (Hexanes/EtOAc (3:1)); IR (film) 2963, 2941, 2867, 1730, 1157 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.72 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.22 (d, *J* = 1.4 Hz, 1H), 5.14–5.03 (m, 2H), 5.02–4.96 (m, 1H), 4.10 (d, *J* = 4.1 Hz, 2H), 4.05 (t, *J* = 7.9 Hz, 1H), 3.77 (t, *J* = 8.9 Hz, 1H), 2.69–2.57 (m, 1H), 2.27–2.16 (m, 1H), 2.05–1.89 (m, 2H), 1.87–1.79 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.45 (m, 1H), 1.42–1.24 (m, 2H), 1.22–1.15 (m, 9H), 1.12–1.01 (m, 21H), 0.88 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.3, 139.7, 131.6, 124.2, 115.7, 103.8, 70.8, 63.2, 58.0, 44.8, 44.5, 38.6, 35.8,

33.6, 27.2 (3 C), 25.9, 25.7, 17.8 (4 C), 17.7 (3 C), 15.6, 12.0 (3 C); HRMS-ESI (calcd for $C_{30}H_{56}O_4SiNa$ $[M+Na]^+$) 531.3846, found 531.3843.



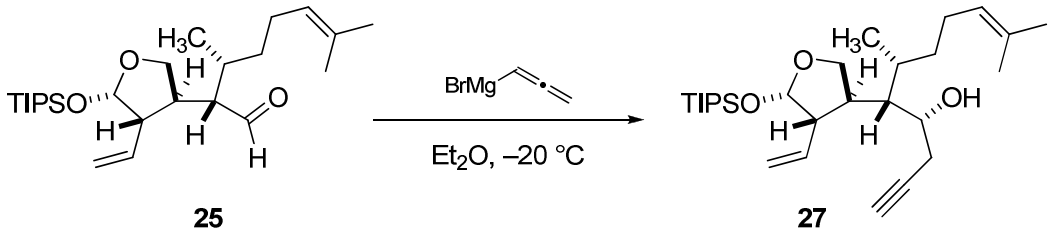

**24** **S9**

**(2S,3R)-3,7-Dimethyl-2-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)oct-6-en-1-ol (S9)** To a solution of alcohol **24** (3.36 g, 6.60 mmol) in $CH_2Cl_2$ (140 mL) at −78 °C was added DIBAL (1.0 M in hexanes, 16.51 mL, 16.51 mmol). The reaction was allowed to stir for 1 h and was then quenched at −78 °C with the addition of a saturated aqueous solution of potassium sodium tatrate (200 mL). Mixture was warmed to ambient temperature and stirred vigorously overnight. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 200 mL). Combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (19:1)), providing **S9** (2.70g, 96%) as a 91:9 mixture of inseparable C-19 diastereomers. The major diastereomer was characterized as follows: $R_f$ 0.64 (Hexanes/EtOAc (3:1)); IR (film) 3438 (br), 2940, 2866, 2360, 2342, 1457, 1027 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.81 (dt, $J$ = 17.2, 9.5 Hz, 1H), 5.26–5.21 (m, 1H), 5.21–5.03 (m, 3H), 4.05 (t, $J$ = 8.1 Hz, 1H), 3.88–3.77 (m, 1H), 3.77–3.63 (m, 2H), 2.77–2.67 (m, 1H), 2.24–2.13 (m, 1H), 2.10–1.81 (m, 3H), 1.68 (s, 3H), 1.63–1.55 (m, 1H), 1.59 (s, 3H), 1.54–1.35 (m, 2H), 1.34–1.23 (m, 1H), 1.14–1.01 (m, 21H), 0.87 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 140.3, 131.5, 124.4, 115.9, 104.0, 71.5, 61.5, 57.1, 47.5, 45.4, 35.7, 34.0, 26.0, 25.7, 17.9, 17.8 (3 C), 17.7, (3 C), 15.7, 12.0 (3 C); HRMS-ESI (calcd for $C_{25}H_{48}O_3SiNa$ $[M+Na]^+$) 447.3270, found 447.3256.




**S9** **25**

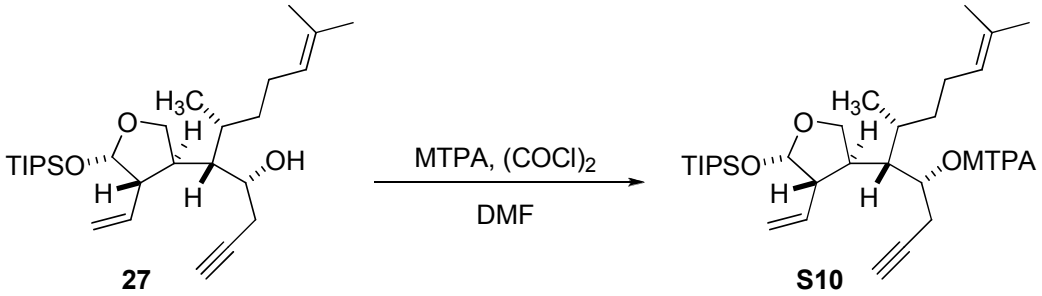
**(2S,3R)-3,7-Dimethyl-2-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)oct-6-enal (25)** To a solution of alcohol **S9** (381 mg, 0.90 mmol, 10:1 mixture of C-19 diastereomers) in $CH_2Cl_2$ (9.0 mL) were added powdered, activated 4Å MS (500 mg) and NMO (157 mg, 1.34 mmol). The suspension was allowed to stir for 10 min and then TPAP (31 mg, 0.09 mmol) was added in one portion. The reaction was allowed to stir for 45 minutes and was then filtered through a plug of silica gel. The filtrate was concentrated *in vacuo* to give a dark oil that was purified via flash chromatography (Hexanes/EtOAc (49:1)), providing **25** (375 mg, 99%) as a 91:9 inseparable mixture of diastereomers. The major diastereomer was characterized as follows: $R_f$ 0.62 (Hexanes/EtOAc (17:3)); IR (film) 2924, 2866, 1723, 1463, 1027 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.70 (d, $J$ = 3.6 Hz, 1H), 5.80–5.64 (m, 1H), 5.23 (d, $J$ = 1.4 Hz, 1H), 5.13–4.97 (m, 3H), 4.14–4.03 (m, 1H), 3.82–3.71 (m, 1H), 2.59-2.42 (m, 3H), 2.08–1.96 (m, 2H), 1.74–1.65 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.51–1.37 (m, 1H), 1.35–1.18 (m, 1H), 1.12–1.01 (m, 21H), 1.01–0.95 (m, 3H) ; $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 205.2, 138.2, 132.1, 123.7, 116.7, 103.4, 69.7, 59.0, 58.1, 42.4, 35.7, 33.6, 25.7, 25.6, 17.8 (3 C), 17.7 (3 C), 17.7 15.4, 11.9 (3 C); HRMS-CI (calcd for $C_{25}H_{47}O_3Si$ $[M+H]^+$) 423.3289, found 423.3286.




**25** **27**

**(4R,5S,6R)-6,10-Dimethyl-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)undec-9-en-1-yn-4-ol (27)** Allenylmagnesium bromide was prepared according to the procedure described by Kleinschroth and coworkers.[2] To a 2-neck round-bottom flask was added a stir bar, freshly polished magnesium turnings (750 mg, 30.73 mmol), and $HgCl_2$ (17 mg, 0.06 mmol). The flask was fitted with a condenser and placed under high-vacuum. The system was then flame-dried, cooled and back-filled with argon. To the flask were added $Et_2O$ (50 mL) and propargyl bromide (80% in toluene, 1.20 mL, 10.80 mmol). The reaction was heated to reflux to initiate Grignard formation and then cooled to −20 °C. Additional propargyl bromide (80% in toluene, 1.70 mL, 15.30 mmol) was added and reaction was stirred for 1 h. Next, a solution of aldehyde **25** (2.57 g, 6.09 mmol, 10:1 mixture of C-19 diastereomers) in $Et_2O$ (120 mL) was added over 30 minutes (syringe pump). The reaction was allowed to stir an additional 2 h and was the quenched with saturated aqueous ammonium chloride (100 mL). Mixture was warmed to ambient temperature and stirred vigorously until complete consumption of magnesium was observed. The aqueous layer was then extracted with $Et_2O$ (3 x 100 mL) and the combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (50:1)), providing **27** as a single diastereomer and the other C-4 and C-19 diastereomers as an inseparable mixture (combined yield: 2.70g, 96%): $R_f$ 0.33 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{24}$ +24.2° (c 0.95, $CHCl_3$); IR (film) 3460 (br), 3312, 2942, 2926, 2866, 1463, 1025 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.72 (td, $J$ = 17.7, 9.4 Hz,1H), 5.23 (d, $J$ = 2.0 Hz, 1H), 5.13–5.06 (m, 3H), 4.06 (t, $J$ = 8.0 Hz,

1H), 3.99–3.92 (m, 1H), 3.90 (dd, *J* = 9.6, 8.6 Hz, 1H), 2.58 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 1H), 2.45 (ddd, *J* = 16.6, 7.9, 2.6 Hz, 1H), 2.34 (ddd, *J* = 16.6, 5.3, 2.6 Hz, 1H), 2.28-2.17 (m, 1H), 2.24 (d, *J* = 4.5 Hz, 1H), 2.03 (t, *J* = 2.55 Hz, 1H), 2.00-1.90 (m, 2H), 1.76-1.66 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.33-1.16 (m, 2H), 1.16-0.99 (m, 21H), 0.95 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.4, 131.7, 124.3, 116.6, 103.0, 81.3, 70.7, 70.6, 69.0, 57.5, 46.5, 43.8, 36.0, 32.1, 27.0, 26.1, 25.7, 17.9 (3 C), 17.8 (3 C), 17.7, 17.4, 12.0 (3 C) ; HRMS-ESI (calcd for $C_{28}H_{50}O_3SiNa$ $[M+Na]^+$) 485.3427, found 485.3438.




**27** **S10**

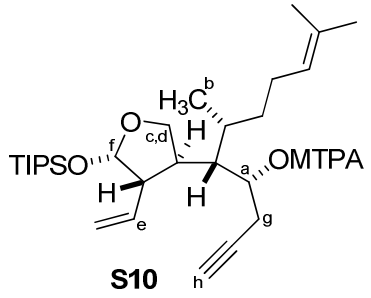
**General Procedure for the Formation of C-4 Mosher Esters (S10):** To a solution of (*S*)-(–)-α-methoxy-α-trifluoromethylphenylacetic acid (19 mg, 0.081 mmol) and DMF (10 μL, 0.081 mmol) in hexanes (4 mL) was added oxalyl chloride (70 μL, 0.081 mmol) at ambient temperature. The reaction was allowed to stir for 2 h and was then filtered and concentrated *in vacuo*. The acid chloride was then placed under argon and a solution of alcohol **27** (15 mg, 0.032 mmol) in $CH_2Cl_2$ (4 mL) was added via syringe, followed by DMAP (20 mg, 0.162 mmol). The reaction was allowed to stir for 12 h and was then diluted in $H_2O$ (3 mL) and $CH_2Cl_2$ (3 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 5 mL). The combined organic extracts were then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to give the crude (*S*)-Mosher ester **(*S*)-S10**. In a separate flask, (*R*)-(+)-α-

methoxy-α-trifluoromethylphenylacetic acid was employed in an identical procedure to give **(*R*)-S10**. Both esters were then used in crude form for 1H-NMR analysis :

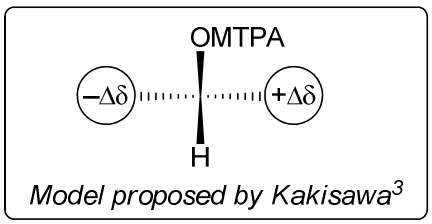
**Selected Proton Shifts:**

**(*S*)-S10**: $^1$H NMR (400 MHz, $CDCl_3$) δ 5.62 (ddd, *J* = 17.1, 9.8, 9.6 Hz, 1H, H(e)), 5.30–5.23 (m, 1H, H(a)), 5.15 (d, *J* = 2.4 Hz, 1H H(f)), 3.76 (dd, *J* = 7.9, 7.8 Hz, 1H, H(c)), 3.53 (dd, *J* = 10.1, 8.4 Hz, 1H, H(d)), 2.55 (ddd, *J* = 16.5, 6.6, 2.5 Hz, 1H, H(g)), 1.98 (dd, *J* = 2.5, 2.5 Hz, 1H, H(h)), 0.44 (d, *J* = 7.0 Hz, 3H, H(b))

**(*R*)-S10**: $^1$H NMR (400 MHz, $CDCl_3$) δ 5.63 (ddd, *J* = 17.1, 9.8, 9.6 Hz, 1H, H(e)), 5.35–5.28 (m, 1H, H(a)), 5.16 (d, *J* = 2.4 Hz, 1H, H(f)), 3.79 (dd, *J* = 7.7, 7.7 Hz, 1H, H(c)), 3.69–3.63 (m, 1H, H(d)), 2.37 (ddd, *J* = 16.5, 8.0, 2.6 Hz, 1H, H(g)), 1.93 (dd, *J* = 2.6, 2.5 Hz, 1H, H(h)), 0.73 (d, *J* = 7.0 Hz, 1H, H(b))

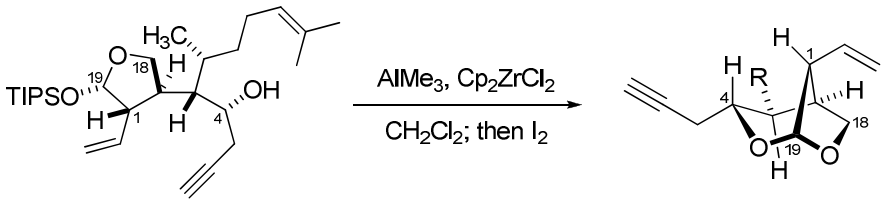



**S10**




*Model proposed by Kakisawa*[3]

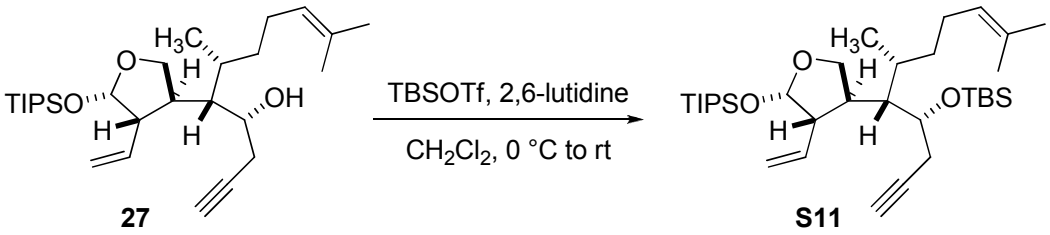
| Proton | $\delta_S$ (Hz) | $\delta_R$ (Hz) | $\Delta\delta$ ($\delta_S$–$\delta_R$) |
|---|---|---|---|
| a | 2105 | 2126 | –21 |
| b | 176 | 293 | –117 |
| c | 1505 | 1517 | –12 |
| d | 1412 | 1464 | –52 |
| e | 2248 | 2251 | –3 |
| f | 2058 | 2065 | –7 |
| g | 1025 | 944 | +81 |
| h | 793 | 770 | +23 |




**27** **29**

**(1R,3R,4S,5S,8S)-4-((R)-6-methylhept-5-en-2-yl)-3-(prop-2-ynyl)-8-vinyl-2,7-dioxabicyclo[3.2.1]octane (29)** To a solution of $Cp_2ZrCl_2$ (100 mg, 0.34 mmol) in $CH_2Cl_2$ (0.85 mL) was added neat $AlMe_3$ (100 μL, 1.03 mmol). The resulting yellow solution was allowed to stir for 20 min at ambient temperature and was then cooled to –25 °C. Next, $H_2O$ (6 μL, 0.34 mmol) and a solution of homopropargylic alcohol **27** (80 mg, 0.17 mmol) in $CH_2Cl_2$ (0.75 mL) were added sequentially and the reaction was left to stir at –25 °C for 18 h and then –5 °C for 6 h. The reaction was then cooled to –20 °C and a solution of $I_2$ (431 mg, 1.7 mmol) in THF (1.7 mL) was added dropwise. The resulting mixture was warmed to 0 °C over 1 h and then quenched with the addition of ice. The mixture was diluted in saturated, aqueous $K_2CO_3$ and then stirred for 30 min. The layers were separated and the aqueous layer was extracted with CH2Cl2 (3 x 3 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated to give an orange oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (49:1)), providing **29** (31 mg, 62%) as a colorless oil: $R_f$ 0.35 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{22}$ +59.8° (c 0.67, $CHCl_3$); IR (film) 3310, 2964, 2925, 1085 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.66 (ddd, *J* = 17.5, 10.4, 7.3 Hz, 1H), 5.27 (s, 1H), 5.19 (dt, *J* = 17.4, 1.1 Hz, 1H), 5.12 (dt, *J* = 10.3, 1.1 Hz, 1H), 5.10–5.04 (m, 1H), 3.99 (dd, *J* = 8.2, 4.4 Hz, 1H), 3.68 (d, *J* = 8.2 Hz, 1H), 3.68–3.61 (m, 1H), 2.77 (d, *J* = 7.2 Hz, 1H), 2.54 (ddd, *J* = 17.0, 5.1, 2.6 Hz, 1H), 2.44 (ddd, *J* = 17.0, 6.1, 2.6 Hz, 1H), 2.29 (br. d, *J* = 4.3 Hz, 1H), 2.16–2.04 (m, 1H), 2.03 (t, *J* = 2.6 Hz, 1H), 1.98–1.86 (m, 1H), 1.76–1.70 (m, 1H), 1.70 (s, 3H), 1.61 (s,

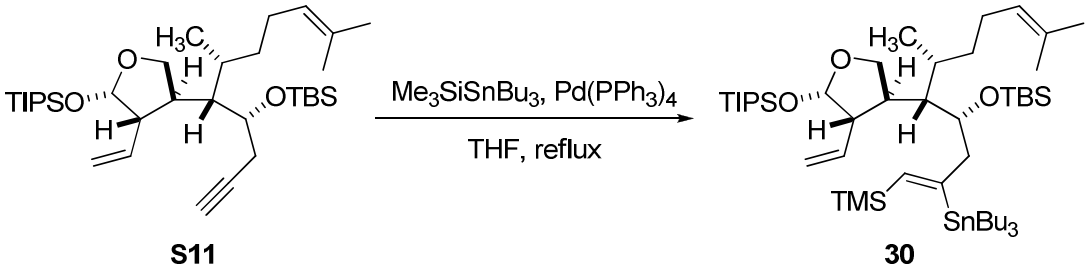
3H), 1.62–1.50 (m, 2H), 1.23–1.11 (m, 1H), 1.00 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 134.8, 132.0, 124.1, 116.9, 101.5, 81.3, 73.0, 70.0, 68.7, 52.5, 45.9, 38.1, 34.2, 31.9, 26.1, 25.7 (2 C), 18.1, 17.7; HRMS-CI (calcd for $C_{19}H_{29}O_2$ $[M+H]^+$) 289.2162, found 289.2162.




**27** **S11**

**tert-Butyl((4R,5S,6R)-6,10-dimethyl-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)undec-9-en-1-yn-4-yloxy)dimethylsilane (S11)** To a solution of alcohol **27** (169 g, 0.37 mmol) in $CH_2Cl_2$ (8.0 mL) at 0 °C were added 2,6-lutidine (0.51 mL, 4.38 mmol) and TBSOTf (0.49 mL, 1.83 mmol), sequentially. The reaction was then warmed to ambient temperature and stirred for an additional 3 h. The reaction was quenched with the addition of $H_2O$ (10 mL), the layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 15 mL). The combined organic extracts were washed with a saturated aqueous solution of $CuSO_4$ (3 x 15 mL), $H_2O$ (20 mL) and brine (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (99:1)), providing **S11** (196 mg, 93%) as a colorless oil: $R_f$ 0.70 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{20}$ +22.0° (c 0.96, $CHCl_3$); IR (film) 3314, 2929, 2866, 2360, 2340, 1464, 1095 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.72 (td, $J$ = 17.0, 9.8 Hz, 1H), 5.21 (d, $J$ = 2.4 Hz, 1H), 5.14–5.05 (m, 3H), 4.06–3.99 (m, 2H), 3.84 (dd, $J$ = 10.3, 8.5 Hz, 1H), 2.51 (dt, $J$ = 9.1, 2.2 Hz, 1H), 2.35 (ddd, $J$ = 16.5, 7.6, 2.6 Hz, 1H), 2.27 (ddd, $J$ = 16.5, 6.0, 2.6 Hz, 1H),

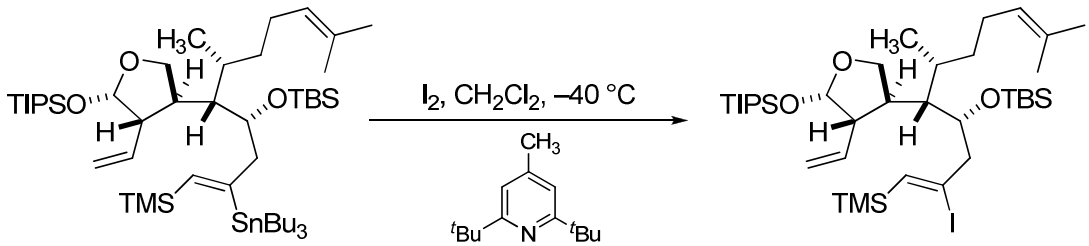
2.21-2.09 (m, 1H), 2.04–1.95 (m, 2H), 1.92 (t, *J* = 2.6 Hz, 1H), 1.89-1.84 (m, 1H), 1.84-1.73 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.48-1.33 (m, 1H), 1.29-1.14 (m, 1H), 1.14-0.97 (m, 21H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.2, 131.4, 124.5, 116.5, 102.7, 81.9, 71.3, 70.1, 59.0, 46.6, 44.6, 35.8, 30.7, 26.1, 26.0 (3 C), 25.7, 25.6, 19.1, 18.1, 17.9 (3 C), 17.8 (3 C), 17.7, 12.0 (3 C), –3.9, –4.3; HRMS-CI (calcd for $C_{34}H_{63}O_3Si_2$ $[M-H]^+$) 575.4310, found 575.4318.




**S11** **30**

**tert-Butyl((4R,5S,6R,Z)-6,10-dimethyl-2-(tributylstannyl)-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)-1-(trimethylsilyl)undeca-1,9-dien-4-yloxy)dimethylsilane (30)** To a solution of alkyne **S11** (195 g, 0.34 mmol) in THF (3.5 mL) were added $Me_3SiSnBu_3$ (0.59 mL, 1.69 mmol) and $Pd(PPh_3)_4$ (78 mg, 0.07 mmol), sequentially. The reaction was heated to reflux for 12 h and then cooled to ambient temperature, diluted in hexanes (10 mL) and filtered through a plug of silica. The filtrate was concentrated *in vacuo* to give crude **30** as a orange oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (99:1)), providing **30** (271 mg, 85%) as a colorless oil: $R_f$ 0.41 (Hexanes/EtOAc (19:1)); $[\alpha]_D^{23}$ +24.9° (c 1.24, $CHCl_3$); IR (film) 2956, 2971, 2867, 1463, 1247, 1047 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 6.46 (s, 1H), 5.67 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.18 (d, *J* = 2.5 Hz, 1H), 5.15–4.96 (m, 3H), 4.24–4.17 (m, 1H), 4.07 (t, *J* = 7.9 Hz, 1H), 3.87 (dd, *J* = 10.4, 8.6 Hz, 1H), 2.51 (ddd, *J* = 18.4, 9.2, 2.3 Hz, 1H), 2.48-2.34 (m, 2H), 2.22-2.11 (m, 1H),

2.10–1.98 (m, 1H), 1.98-1.79 (m, 2H), 1.71-1.63 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.56-1.39 (m, 7H), 1.39-1.25 (m, 7H), 1.11–1.03 (m, 21H), 0.99-0.85 (m, 27H), 0.13-0.06 (m, 15H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.2, 145.0, 139.6, 131.2, 124.7, 116.6, 102.7, 71.1, 70.2, 59.2, 44.9, 36.5, 30.9, 29.3, 29.2 (3 C), 29.1, 27.5 (3 C), 26.3, 26.2 (3 C), 25.6, 19.5, 18.2, 17.9 (3 C), 17.8 (3 C), 17.7, 13.6 (3 C), 12.1 (3 C), 11.4 (3 C), 0.4 (3 C), –3.4, –3.6; HRMS-CI (calcd for $C_{49}H_{99}O_3Si_3Sn$ $[M-H]^+$) 939.5918, found 939.5945.

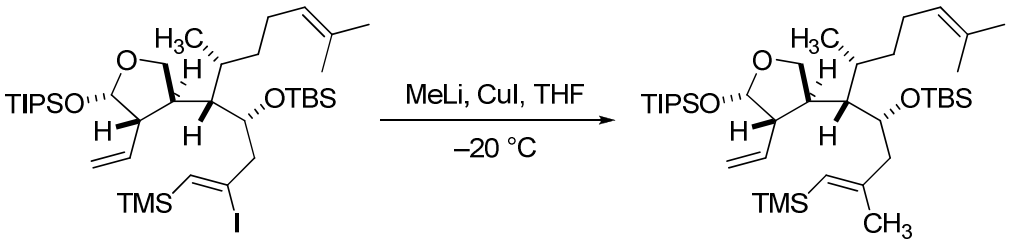



**30** **S12**

**tert-Butyl((4R,5S,6R,Z)-2-iodo-6,10-dimethyl-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)-1-(trimethylsilyl)undeca-1,9-dien-4-yloxy)dimethylsilane (S12)**

Di-*t*-butyl-4-methylpyridine (187 mg, 0.91 mmol) and $I_2$ (77 mg, 0.30 mmol) were sequentially added to a solution of vinylstannane **30** (286 mg, 0.30 mmol) in $CH_2Cl_2$ (6.0 mL) at −40 °C. The reaction was allowed to stir for 3 h and was then quenched with a saturated aqueous solution of $Na_2S_2O_3$ (10 mL). The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 15 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (199:1)), providing **S12** (220 mg, 93%) as a colorless oil: $R_f$ 0.55 (Hexanes/EtOAc (19:5)); $[\alpha]_D^{22}$ +23.8° (c, $CHCl_3$); IR (film) 2927, 2865, 2360, 1463, 1249, 1028 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H), 5.73 (td, *J* = 17.0, 9.8 Hz, 1H), 5.20 (d, *J* = 2.5 Hz, 1H), 5.15–5.03 (m, 3H), 4.17 (t, *J* = 6.6 Hz, 1H), 4.06 (t, *J* = 7.9 Hz, 1H), 3.86 (dd, *J*

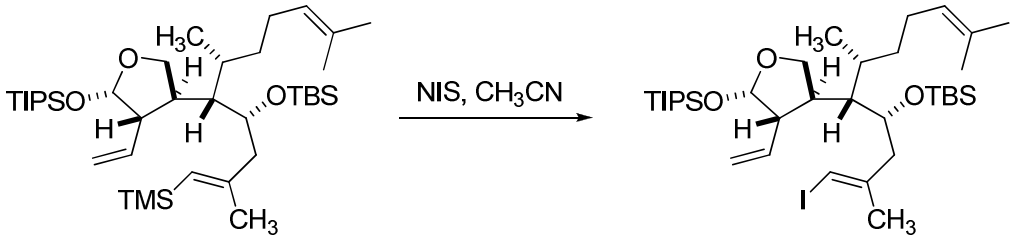
= 10.4, 8.7 Hz, 1H), 2.65 (d, *J* = 6.6 Hz, 2H), 2.47 (dt, *J* = 9.3, 2.3 Hz, 1H), 2.22–2.11 (m, 1H), 2.03–1.89 (m, 2H), 1.87–1.77 (m, 1H), 1.68 (s, 3H), 1.66–1.63 (m, 1H), 1.61 (s, 3H), 1.47–1.35 (m, 1H), 1.31–1.19 (m, 1H), 1.11–1.04 (m, 21H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.90-0.85 (s, 9H), 0.16 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.6, 139.8, 131.7, 124.7, 118.6, 117.3, 102.5, 70.7, 69.9, 59.4, 56.1, 45.3, 37.1, 30.4, 30.2, 26.4 (3 C), 26.2, 25.9, 19.4, 18.3, 18.1 (3 C), 18.0 (3 C), 18.0, 12.3 (3 C), –1.1 (3 C), –3.3, –3.5; HRMS-CI (calcd for $C_{37}H_{72}O_3Si_3I$ $[M-H]^+$) 775.3828, found 775.3812.




**S12** **S13**

**tert-Butyldimethyl((4R,5S,6R,E)-2,6,10-trimethyl-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)-1-(trimethylsilyl)undeca-1,9-dien-4-yloxy)silane (S13)** To a flame-dried flask under argon was added CuI (2.61 g, 13.72 mmol) and $Et_2O$ (13.5 mL). The suspension was then cooled to –20 °C and MeLi (1.6 M in $Et_2O$, 17.3 mL, 27.70 mmol) was added dropwise. Next, a solution of vinyl iodide **S12** (2.09 g, 2.69 mmol) in $Et_2O$ (13.5 mL) was added dropwise via syringe. The reaction was allowed to warm slowly to 0 °C and then stirred an additional 1 h at this temperature. Filtration through a plug of silica gel and concentration of the filtrate provided crude **S13** as a yellow oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (99:1)), providing **S13** (1.73g, 98%) as a colorless oil: $R_f$ 0.55 (Hexanes/EtOAc (19:1)); $[\alpha]_D^{20}$ +32.4° (c 1.13, $CHCl_3$); IR (film) 2956, 2866, 1463, 1248, 836 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.72 (td, *J* = 17.0, 9.8 Hz, 1H), 5.22 (s, 1H), 5.19 (d, *J* =

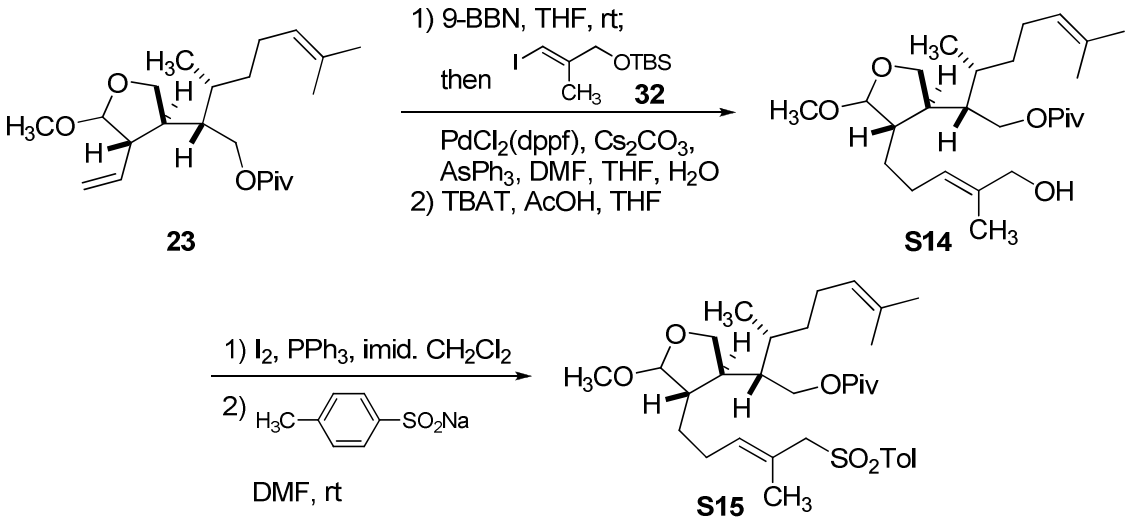
2.4 Hz, 1H), 5.13–5.02 (m, 3H), 4.06 (t, *J* = 7.8 Hz, 1H), 4.03–3.97 (m, 1H), 3.85 (dd, *J* = 10.4, 8.6 Hz, 1H), 2.49 (dt, *J* = 9.4, 2.1 Hz, 1H), 2.29–2.10 (m, 3H), 2.05–1.88 (m, 2H), 1.87–1.79 (m, 1H), 1.74 (s, 3H), 1.68 (s, 3H), 1.66–1.62 (m, 1H), 1.60 (s, 3H), 1.37-1.24 (m, 1H), 1.19–0.99 (m, 22H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.09–0.04 (m, 15H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.8, 139.7, 131.5, 127.7, 124.6, 116.8, 102.6, 70.9, 70.1, 59.4, 48.5, 44.9, 36.4, 30.2, 30.0, 26.2 (3 C), 26.1, 25.7, 22.2, 19.6, 18.1, 17.9 (3 C), 17.8 (3 C), 17.7, 12.1 (3 C), 0.0 (3 C), –3.8, –3.9; HRMS-CI (calcd for $C_{37}H_{73}O_3Si_3$ $[M\text{-}CH_3]^+$) 649.4862, found 649.4842.




**S13** **31**

**tert-butyl((4R,5S,6R,E)-1-iodo-2,6,10-trimethyl-5-((3S,4S,5S)-5-(triisopropylsilyloxy)-4-vinyltetrahydrofuran-3-yl)undeca-1,9-dien-4-yloxy)dimethylsilane (31)** To a solution of vinylsilane **S13** (1.73 g, 2.60 mmol) in $CH_3CN$ (52 mL) was added NIS (878 mg, 3.90 mmol). The reaction flask was capped, covered in tin foil, and stirred for 12 h. A saturated aqueous solution of $Na_2S_2O_3$ (40 mL) was then added and the mixture was diluted in EtOAc (50 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The crude product was purified via flash chromatography (Hexanes/EtOAc (199:1)), providing **31** (1.54g, 82%) as a colorless oil: $R_f$ 0.66 (Hexanes/EtOAc (9:1)); $[\alpha]_D^{25}$ +36.4° (c 0.99, $CHCl_3$); IR (film) 2928, 2865, 1638, 1463, 1255, 1047 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ ; $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.1, 131.9, 124.6, 117.0, 102.9, 78.8, 70.6, 70.5, 59.8, 45.0, 35.8,

30.1, 26.4, 26.2 (3 C), 25.9, 24.5, 20.5, 18.2, 18.1 (3 C), 18.0 (6 C), 12.2 (3 C), –3.8, –3.9; HRMS-CI (calcd for $C_{35}H_{66}O_3Si_2I$ $[M-H]^+$) 717.3590, found 717.3619.



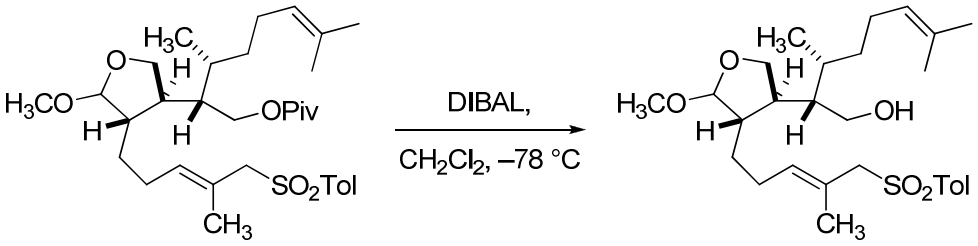

**(2S,3R)-2-((3S,4S)-5-methoxy-4-((E)-4-methyl-5-tosylpent-3-enyl)tetrahydrofuran-3-yl)-3,7-dimethyloct-6-enyl pivalate (S15)** To a solution of 9-BBN dimer (91 mg, 0.37 mmol) in THF (0.9 mL), was added a solution of alkene **23** (137 mg, 0.37 mmol) in THF (0.6 mL). After stirring for 3 h at ambient temperature, TLC analysis revealed complete consumption of **23** and $H_2O$ (0.1 mL) was added. The resulting mixture was allowed to stir vigorously for 15 min and was then transferred via cannula to a flask containing vinyl iodide **32**[4] (175 mg, 0.56 mmol), $PdCl_2$(dppf) (61 mg, 0.2 mmol), $Cs_2CO_3$ (244 mg, 0.75 mmol), and $AsPh_3$ (23 mg, 0.075 mmol) in $H_2O$ (0.2 mL) and DMF (2.5 mL). The reaction was allowed to stir for 2 h and was then diluted in $Et_2O$ (10 mL) and washed with $H_2O$ (3 x 5 mL) and brine (5 mL). The organic layer was then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to give an orange oil which was taken up in THF (2.2 mL) and cooled to 0 °C. To the solution were added AcOH (40 μL, 0.72 mmol) and TBAT (287 mg, 0.53 mmol). The reaction was allowed to warm slowly and was stirred overnight at ambient temperature. Dilution with $H_2O$ (3 mL) and $CH_2Cl_2$ (5 mL) was followed by separation of the layers and extraction of the aqueous layer with $CH_2Cl_2$ (3 x 5 mL).

The combined organic extracts were then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to afford crude **S14** as an orange oil. Filtration through a plug of silica gel then gave **S14** (92 mg, 56% from **23**) as an oil of moderate purity that could be utilized without further purification in the next reaction.

**S14:** $^1$H NMR (400 MHz, $CDCl_3$) δ 5.44–5.35 (m, 1H), 5.10–5.02 (m, 1H), 4.86 (d, *J* = 4.7 Hz, 0.4H), 4.69 (br. s, 0.6H), 4.21–4.13 (m, 1H), 4.06–3.95 (m, 4H), 3.64 (dd, *J* = 8.4, 6.5 Hz, 0.4H), 3.56 (dd, *J* = 8.9, 8.6 Hz, 0.6H), 3.35 (s, 1.2H), 3.32 (s, 1.8H), 2.20–1.85 (m, 7H), 1.78–1.55 (m, 3H), 1.68 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H), 1.53–1.30 (m, 2H), 1.21–1.17 (m, 9H), 0.94–0.84 (m, 3H).

Imidazole (23 mg, 0.33 mmol), $PPh_3$ (67 mg, 0.26 mmol) and $I_2$ (84 mg, 0.33 mmol) were sequentially added to a solution of alcohol **S14** (56 mg, 0.128 mmol) in $CH_2Cl_2$ (2.6 mL) at 0 °C. The reaction was allowed to stir for 10 min in the dark and was then diluted in hexanes and passed through a plug of silica gel. The filtrate was washed with saturated, aqueous $Na_2S_2O_3$, dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting oil was then taken up in DMF (2.6 mL) and sodium tolylsulfinate was added. The reaction was covered in aluminum foil, stirred overnight, diluted in $Et_2O$ (15 mL), and washed with $H_2O$ (3 x 10 mL) and brine (15 mL). The organic layer was then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (17:3)), providing **S15** (63 mg, 86% from **S14**) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.58 (Hexanes/EtOAc (3:1)); IR (film) 2921, 1725, 1480, 1456, 1316, 1285, 1157, 1033 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 2H), 7.34–7.30 (m, 2H), 5.12–5.01 (m, 2H), 4.78 (d, *J* = 4.7 Hz, 0.4H), 4.63 (d, *J* = 0.9 Hz, 0.6H), 4.09–3.96 (m, 3H), 3.71–3.67 (m, 2H), 3.63 (dd, *J* = 8.5, 6.6 Hz, 0.4H), 3.55 (dd, *J* = 8.9, 8.9 Hz, 0.6H), 3.32 (s,

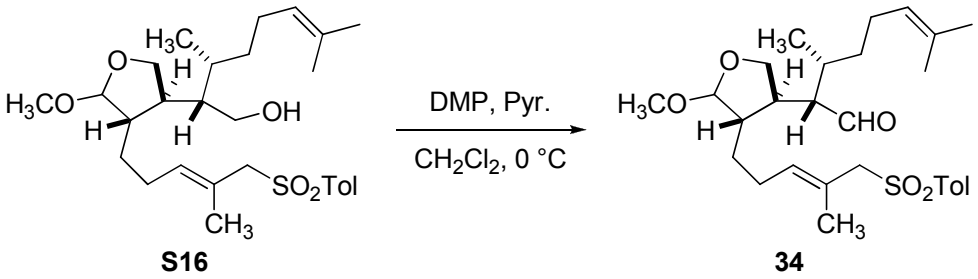
1.2H), 3.30 (s, 1.8H), 2.44 (s, 3H), 2.20–2.09 (m, 0.6H), 2.08–1.77 (m, 6.4H), 1.74 (s, 1.2H), 1.73 (s, 1.8H), 1.68 (s, 3H), 1.59 (s, 3H), 1.64–1.55 (m, 1H), 1.44–1.20 (m, 4H), 1.78–1.64 (m, 9H), 0.87 (d, $J$ = 6.9 Hz, 1.2H), 8.86 (d, $J$ = 6.8 Hz, 1.8H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.4, 144.4, 135.8, 135.1, 131.8, 131.7, 129.6, 128.5, 124.2, 123.8, 109.8, 105.4, 70.8, 70.4, 66.2, 63.8, 63.7, 54.6, 45.4, 49.6, 47.1, 44.9, 44.5, 44.4, 42.6, 38.7, 36.3, 35.9, 33.4, 33.3, 29.7, 28.2, 27.2, 27.0, 26.0, 25.8, 25.7, 21.6, 17.7, 16.8, 16.6, 15.8, 15.4; HRMS-CI (calcd for $C_{32}H_{49}O_5S$ $[M–OCH_3]^+$) 545.3295, found 545.3275.




**S15** **S16**

**(2S,3R)-2-((3S,4S)-5-methoxy-4-((E)-4-methyl-5-tosylpent-3-enyl)tetrahydrofuran-3-yl)-3,7-dimethyloct-6-en-1-ol (S16)** To a solution of **S15** (73 mg, 0.126 mmol) in $CH_2Cl_2$ (2.5 mL) at –78 °C was added DIBAL (1.0M in Hexanes, 316 μL, 0.316 mmol). The reaction was allowed to stir for 30 min and was then quenched at –78 °C with a saturated aqueous solution of sodium potassium tartrate (3 mL). The mixture was allowed to warm to ambient temperature and was then allowed to stir vigorously for 3 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 10 mL). The combined organic extracts were then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (3:1)), providing **S16** (61 mg, 98%) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.63 (Hexanes/EtOAc (1:1)); IR (film) 3504 (br), 2923, 1457, 1314, 1133, 1086 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 2H), 7.35–7.31 (m,

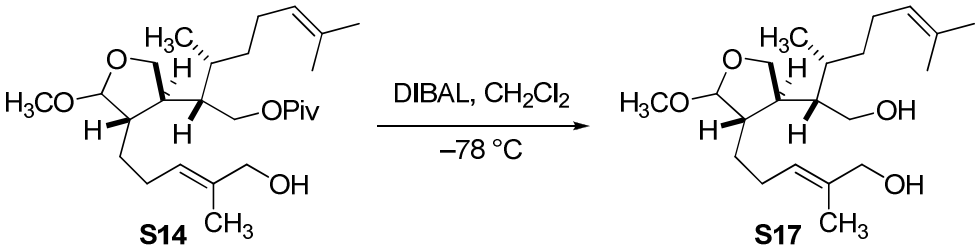
2H), 5.26–5.19 (m, 1H), 5.11–5.04 (m, 1H), 4.79 (d, $J$ = 4.7 Hz, 0.4H), 4.65 (d, $J$ = 0.5 Hz, 0.6H), 4.05–3.97 (m, 1H), 3.73–3.57 (m, 5H), 3.33 (s, 1.2H), 3.32 (s, 1.8H), 2.44 (s, 3H), 2.19–1.84 (m, 7H), 1.73 (s, 1.2H), 1.71 (s, 1.8H), 1.68 (s, 3H), 1.60 (s, 3H), 1.61–1.24 (m, 6H), 0.89–0.83 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.5, 136.3, 136.0, 135.9, 135.5, 131.6, 131.6, 129.6, 128.5, 124.4, 124.3, 123.9, 123.4, 109.9, 105.6, 76.3, 71.4, 71.2, 66.3, 62.0, 61.9, 54.6, 54.4, 48.4, 47.9, 47.8, 46.4, 45.3, 42.6, 36.4, 35.8, 34.0, 33.3, 27.9, 27.1, 27.0, 26.0, 25.9, 25.7, 21.6, 17.7, 16.8, 16.7, 15.8, 15.4; HRMS-CI (calcd for $C_{27}H_{41}O_4S$ $[M–OCH_3]^+$) 461.2720, found 461.2702.




**S16** **34**

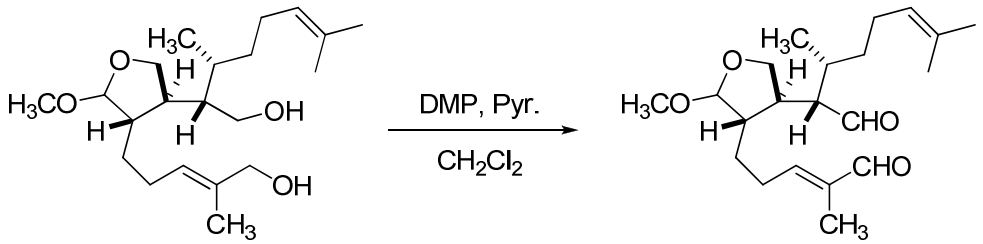
**(2S,3R)-2-((3R,4S)-5-methoxy-4-((E)-4-methyl-5-tosylpent-3-enyl)tetrahydrofuran-3-yl)-3,7-dimethyloct-6-enal (34)** Pyridine (25 μL, 0.31 mmol) and Dess-Martin periodinane (20 mg, 0.05 mmol) were sequentially added to a solution of alcohol **S16** (15 mg, 0.03 mmol) in $CH_2Cl_2$ (0.7 mL) at 0 °C and the reaction was allowed to stir 1 h. The reaction was diluted in $Et_2O$ (3 mL) and washed with a saturated, aqueous solutions of $NaHCO_3$ (2 x 2 mL), $Na_2S_2O_3$ (2 x 2 mL), $CuSO_4$ (3 mL), $H_2O$ (3 mL), and brine (3 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (17:3)), providing **34** (14.3 mg, 96%) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.50 (Hexanes/EtOAc (3:1)); IR (film) 2959, 2922, 2854, 1717, 1315, 1133, 1087 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, $J$ = 3.3 Hz, 0.6H), 9.69 (d,

*J* = 5.0 Hz, 0.4H), 7.74–7.69 (m, 2H), 7.36–7.31 (m, 2H), 5.09–4.99 (m, 2H), 4.75 (d, *J* = 4.6 Hz, 0.4H), 4.62 (br. s, 0.6H), 4.08 (dd, *J* = 8.4, 8.4 Hz, 0.4H), 4.01 (dd, *J* = 8.3, 8.3 Hz, 0.6H), 3.69 (s, 1.2H), 3.68 (s, 1.8H), 3.56 (dd, *J* = 8.5, 7.3 Hz, 0.4H), 3.53 (dd, *J* = 8.5, 8.5 Hz, 0.6H), 3.33 (s, 1.2H), 3.29 (s, 1.8H), 2.62–2.50 (m, 1H), 2.47–2.42 (m, 3H), 2.30–1.76 (m, 6H), 1.73 (s, 3H), 1.69 (s, 1.8H), 1.68 (s, 1.2H), 1.66–1.43 (m, 5H), 1.42–1.10 (m, 2H), 1.02 (d, *J* = 7.1 Hz, 1.2H), 0.94 (d, *J* = 7.0 Hz, 1.8H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 205.4, 205.0, 144.4, 135.7, 135.5, 135.2, 132.2, 129.6, 128.5, 124.1, 124.0, 123.6, 109.3, 105.2, 69.9, 69.3, 66.3, 66.2, 59.7, 59.4, 54.7, 54.4, 50.3, 48.2, 41.7, 40.0, 35.8, 35.7, 33.8, 33.5, 32.7, 29.7, 27.3, 26.9, 26.8, 25.7, 25.6, 25.4, 21.6, 17.7, 16.7, 16.6, 15.5, 15.3; HRMS-ESI (calcd for $C_{28}H_{42}O_5NaS$ $[M+Na]^+$) 513.2651, found 513.2628.




**(2S,3R)-2-((3S,4S)-4-((E)-5-hydroxy-4-methylpent-3-enyl)-5-methoxytetrahydrofuran-3-yl)-3,7-dimethyloct-6-en-1-ol (S17)** To a solution of **S14** (44 mg, 0.10 mmol) in $CH_2Cl_2$ (2 mL) at –78 °C was added DIBAL (1.0M in Hexanes, 0.25 mL, 0.25 mmol). The reaction was allowed to stir for 45 min and was then quenched at –78 °C with a saturated aqueous solution of sodium potassium tartrate (3 mL). The mixture was allowed to warm to ambient temperature and was then allowed to stir vigorously for 12 h. The layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 10 mL). The combined organic extracts were then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash

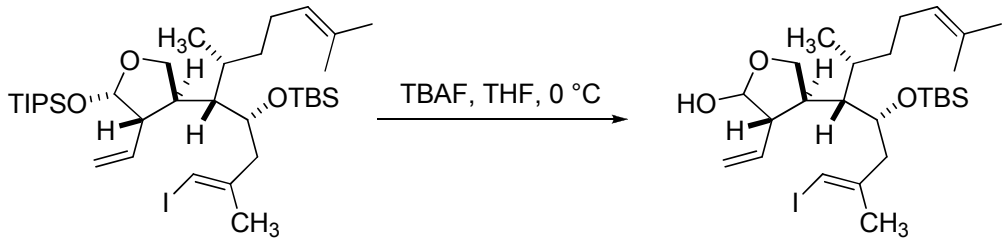
chromatography (Hexanes/EtOAc (3:1)), providing **S17** (34 mg, 97%) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.34 (Hexanes/EtOAc (1:1)); IR (film) 3393 (br), 2920, 2359, 2342, 1449, 1375, 1021 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.47–5.38 (m, 1H), 5.11–5.04 (m, 1H), 4.87 (d, *J* = 4.7 Hz, 0.4H), 4.72 (br. s, 0.6H), 4.07–3.96 (m, 3H), 3.75–3.57 (m, 3H), 3.35 (s, 1.2H), 3.34 (s, 1.8H), 2.24–1.80 (m, 7H), 1.68 (br. s, 3H), 1.67 (s, 3H), 1.61 (s, 3H), 1.59–1.20 (m, 6H), 0.93–0.80 (m, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 135.6, 135.1, 131.6, 126.2, 125.4, 124.4, 110.0, 110.0, 105.7, 71.5, 71.0, 69.0, 68.9, 62.1, 62.0, 54.7, 54.4, 48.0, 47.9, 47.7, 46.6, 45.3, 42.6, 39.2, 36.5, 35.7, 34.1, 33.9, 33.2, 28.5, 26.4, 26.1, 26.0, 25.9, 25.7, 17.7, 15.9, 15.4, 13.7, 13.6; HRMS-CI (calcd for $C_{21}H_{37}O_3$ $[M–OH]^+$) 337.2737, found 337.2731.




**S17** **36**

**(2S,3R)-2-((3R,4S)-5-methoxy-4-((E)-4-methyl-5-oxopent-3-enyl)tetrahydrofuran-3-yl)-3,7-dimethyloct-6-enal (36)** Pyridine (103 μL, 1.29 mmol) and Dess-Martin periodinane (90 mg, 0.212 mmol) were sequentially added to a solution of diol **S17** (12.0 mg, 0.043 mmol) in $CH_2Cl_2$ (0.86 mL) at 0 °C and the reaction was allowed to stir 1 h. The reaction was diluted in $Et_2O$ (3 mL) and washed with saturated, aqueous solutions of $Na_2S_2O_3$ (2 x 2 mL), $CuSO_4$ (3 mL), $H_2O$ (3 mL), and brine (3 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo.* The crude product was purified via flash chromatography (Hexanes/EtOAc (22:3)), providing **36** (11.0 mg, 92%) as a 58:42 inseparable mixture of C-19 diastereomers: $R_f$ 0.55 (Hexanes/EtOAc (3:1)); IR (film) 2925, 2359, 2342, 1720, 1687, 1450,

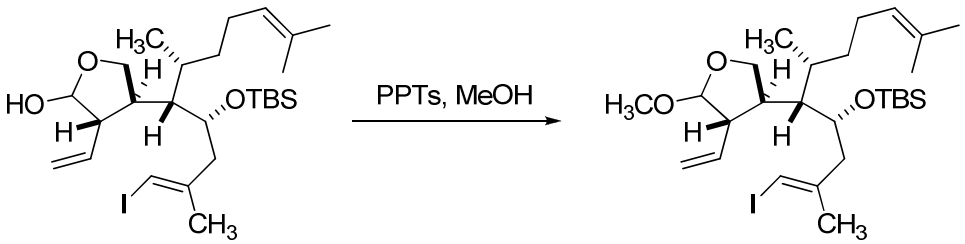
1378, 1103, 1024 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.80 (d, *J* = 2.9 Hz, 0.6H), 9.75 (d, *J* = 4.9 Hz, 0.4H), 9.40 (s, 0.6H), 9.39 (s, 0.4H), 6.47–6.40 (m, 1H), 5.11–5.01 (m, 1H), 4.84 (d, *J* = 4.6 Hz, 0.4H), 4.70 (br. s, 0.6H), 4.11 (dd, *J* = 8.5, 8.4 Hz, 0.4H), 4.04 (dd, *J* = 8.4, 8.4 Hz, 0.6H), 3.60 (dd, *J* = 8.6, 6.9 Hz, 0.4H), 3.56 (dd, *J* = 8.7, 8.5 Hz, 0.6H), 3.35 (s, 1.2H), 3.30 (s, 1.8H), 2.65–2.58 (m, 1H), 2.43–2.17 (m, 3H), 2.15–1.95 (m, 3H), 1.88–1.46 (m, 3H), 1.74 (s, 1.8H), 1.73 (s, 1.2H), 1.69 (s, 1.8H), 1.68 (s, 1.2H), 1.62 (s, 1.8H), 1.60 (s, 1.2H), 1.45–1.20 (m, 2H), 1.04 (d, *J* = 7.1 Hz, 1.2H), 0.94 (d, *J* = 7.0 Hz, 1.8H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 205.1, 195.2, 153.3, 139.8, 132.3, 123.5, 109.2, 104.9, 69.3, 59.5, 54.5, 50.5, 41.6, 35.8, 33.5, 32.0, 27.5, 25.8, 25.7, 25.4, 22.6, 17.7, 15.3, 9.2; HRMS-CI (calcd for $C_{20}H_{31}O_3$ $[M–OCH_3]^+$) 319.2268, found 319.2263.




**31** **S18**

**(3S,4S)-4-((4R,5S,6R,E)-4-(tert-butyldimethylsilyloxy)-1-iodo-2,6,10-trimethylundeca-1,9-dien-5-yl)-3-vinyltetrahydrofuran-2-ol (S18)** To a solution of acetal **31** (1.21 g, 1.68 mmol) in THF (35 mL) at −40 °C was added TBAF (1.0 M in THF, 1.68 mL, 1.68 mmol) dropwise. The reaction was allowed to warm to −15 °C over 3 h and then quenched with $H_2O$ (30 mL). The mixture was diluted with $Et_2O$ (30 mL) and the layers were separated. The aqueous layer was extracted with $Et_2O$ (3 x 25 mL) and the combined organic extracts were dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography

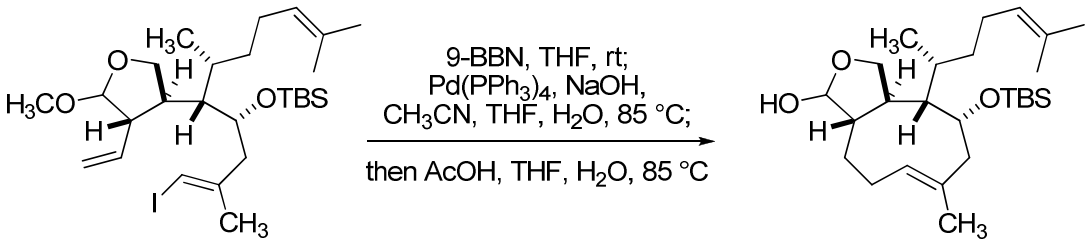
(Hexanes/EtOAc (9:1)), providing **S18** (900 mg, 95%) as a 1:1 inseparable mixture of C-19 diastereomers: $R_f$ 0.20 (Hexanes/EtOAc (17:3)); IR (film) 3387, 2957, 2928, 2857, 2360, 1462, 1255, 1071, 1045 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.90 (s, 0.5H), 5.88 (s, 0.5 H), 5.83–5.64 (m, 1H), 5.31–5.27 (m, 0.5H), 5.25–5.03 (m, 3.5H), 4.22 (t, *J* = 8.6 Hz, 0.5H), 4.08 (t, *J* = 7.7 Hz, 0.5H), 4.05–3.95 (m, 1H), 3.86 (dd, *J* = 10.3, 8.5 Hz, 0.5H), 3.80 (t, *J* = 8.4 Hz, 0.5H), 3.51 (br. s, 0.5H), 3.22 (br. s, 0.5H), 2.62–2.32 (m, 2.5H), 2.31–2.23 (m, 1H), 2.23–2.12 (m, 0.5H), 2.03–1.86 (m, 2H), 1.86–1.75 (m, 0.5H), 1.77 (s, 3H), 1.74–1.65 (m, 0.5H), 1.68 (s, 3H), 1.63–1.56 (m, 0.5H), 1.60 (s, 3H), 1.49–1.44 (m, 0.5H), 1.34–1.19 (m, 1H), 1.19–1.06 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 1.5H), 0.90 (d, *J* = 7.0 Hz, 1.5H), 0.87 (s, 9H), 0.08–0.02 (m, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.6, 144.3, 138.7, 136.8, 132.0, 124.5, 124.5, 118.8, 118.2, 102.7, 99.0, 79.3, 79.1, 70.7, 70.6, 70.0, 69.9, 57.1, 54.2, 45.7, 45.1, 40.1, 36.9, 36.2, 30.3, 30.2, 26.4, 26.3, 26.2, 26.0, 24.4, 24.3, 20.1, 19.6, 18.3, 18.1, 17.9, –3.6, –3.7, –3.8; HRMS-ESI (calcd for $C_{26}H_{47}O_3SiINa$ $[M+Na]^+$) 585.2237, found 585.2261.




**S18** **39**

**tert-butyl((4R,5S,6R,E)-1-iodo-5-((3S,4S)-5-methoxy-4-vinyltetrahydrofuran-3-yl)-2,6,10-trimethylundeca-1,9-dien-4-yloxy)dimethylsilane (39)** To a solution of lactol **S18** (900 mg, 1.60 mmol) in MeOH (80 mL) at ambient temperature was added PPTs (40 mg, 0.16 mmol). The reaction flask was capped, covered in aluminum foil, and stirred for 18 h. Next, the reaction solution was diluted in $Et_2O$ (100 mL) and washed with $H_2O$ (3 x 50 mL) and brine (50 mL).

The organic layer was dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (99:1)), providing **39** (912 mg, 99%) as a 1:1 inseparable mixture of C-19 diastereomers: $R_f$ 0.58 (Hexanes/EtOAc (17:3)); IR (film) 2956, 2928, 2856, 1462, 1254, 1049 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.87 (br. s, 1H), 5.80–5.67 (m, 1H), 5.21–5.04 (m, 3H), 4.77 (d, *J* = 4.1 Hz, 0.5H), 4.69 (d, *J* = 3.1 Hz, 0.5H), 4.11–3.94 (m, 2H), 3.86–3.79 (m, 0.5H), 3.70 (dd, *J* = 10.5, 8.4 Hz, 0.5H), 3.36 (s, 1.5H), 3.34 (s, 1.5H), 2.55–2.33 (m, 2.5H), 2.31–2.22 (m, 1H), 2.19–2.08 (m, 0.5H), 2.04–1.86 (m, 2H), 1.85–1.75 (m, 0.5H), 1.78 (d, *J* = 0.8 Hz, 3H), 1.74–1.66 (m, 0.5H), 1.69 (s, 3H), 1.60 (s, 3H), 1.59–1.56 (m, 0.5H), 1.46–1.41 (m, 0.5H), 1.36–1.02 (m, 2H), 0.96 (d, *J* = 6.8 Hz, 1.5H), 0.90 (d, *J* = 7.0 Hz, 1.5H), 0.87 (s, 9H), 0.07–0.03 (m, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 144.4, 144.1, 138.8, 136.7, 131.7, 124.3, 124.2, 118.1, 117.6, 109.4, 105.5, 79.0, 78.8, 70.4, 69.9, 69.8, 56.1, 55.4, 54.6, 54.1, 45.4, 44.9, 40.3, 36.5, 36.0, 30.1, 30.0, 29.7, 26.2, 26.0, 25.7, 24.2, 24.1, 19.9, 19.4, 18.0, 17.8, –3.8, –4.0, –4.1; HRMS-CI (calcd for $C_{27}H_{48}O_3SiI$ $[M-H]^+$) 575.2412, found 575.2406.

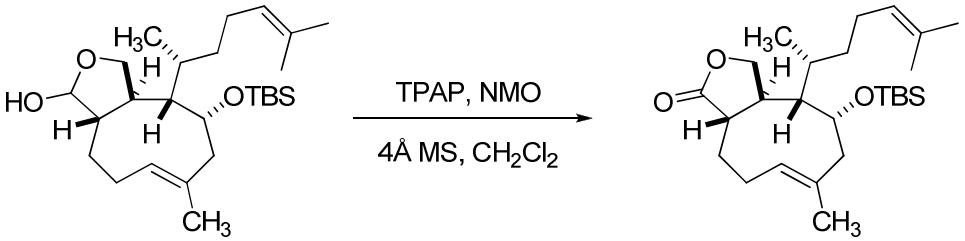



**39** **38**

**(3aS,4S,5R,10aS,E)-5-(tert-butyldimethylsilyloxy)-7-methyl-4-((R)-6-methylhept-5-en-2-yl)-3,3a,4,5,6,9,10,10a-octahydro-1H-cyclonona[c]furan-1-ol (38)** To neat **39** (78 mg, 0.135 mmol) was added 9-BBN (0.5 M in THF, 405 μL, 0.203 mmol). The reaction was allowed to stir overnight and was then quenched with degassed $H_2O$ (750 μL) and stirred vigorously for 15

min. The mixture was diluted in degassed THF (2.25 mL) and then added via syringe to a solution of $Pd(PPh_3)_4$ (78 mg, 0.068 mmol) and NaOH (27 mg, 0.676 mmol) in degassed $CH_3CN$ (25.3 mL) and degassed $H_2O$ (1.70 mL) at ambient temperature. The reaction was then heated to 85 °C and was stirred for 18 h. The reaction was cooled to ambient temperature and filtered through Celite. The filtrate was washed with $H_2O$ (3 x 10 mL) and brine (3 x 10 mL). The organic layer was then dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude mixture was taken up in hexanes (30 mL), filtered and concentrated *in vacuo* to give an orange oil. This crude material was dissolved in THF (3.8 mL) and to the resulting solution was added $H_2O$ (5.7 mL) and glacial acetic acid (1.9 mL). The mixture was heated to 85 °C, stirred for 4 h, cooled to 0 °C and slowly quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL). The mixture was diluted in $Et_2O$ (10 mL), the layers were separated and the aqueous layer was extracted with $Et_2O$ (3 x 10 mL). The combined organic extracts were then washed with saturated aqueous $NaHCO_3$ (2 x 20 mL), $H_2O$ (20 mL) and brine (20 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (50:1 to 93:7)), providing **38** (39 mg, 66%) as a 80:20 inseparable mixture of C-19 diastereomers: $R_f$ 0.32 (Hexanes/EtOAc (17:3)); IR (film) 3389, 2928, 2856, 2359, 2342, 1462, 1253, 1050 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.35–5.27 (m, 1H), 5.24 (dd, *J* = 9.0, 6.3 Hz, 0.2H), 5.17–5.09 (m, 0.8H), 5.09–5.05 (m, 0.2H), 5.01 (br. s, 0.8H), 4.20–4.06 (m, 1H), 4.02 (t, *J* = 8.6 Hz, 0.2H), 3.94 (t, *J* = 8.3 Hz, 0.8H), 3.87 (dd, *J* = 9.2, 8.7 Hz, 0.8H), 3.68 (dd, *J* = 8.3, 6.3 Hz, 0.2H), 2.68–2.51 (m, 1H), 2.51–2.30 (m, 2H), 2.26–2.12 (m, 1.6H), 2.11–1.86 (m, 4.4H), 1.83–1.65 (m, 4H), 1.79 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H), 1.47–1.31 (m, 1H), 1.29–1.09 (m, 1H), 0.93–0.87 (m, 9H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.19–0.14 (m, 3H), 0.09–0.04 (m, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 134.8, 134.0, 131.4,

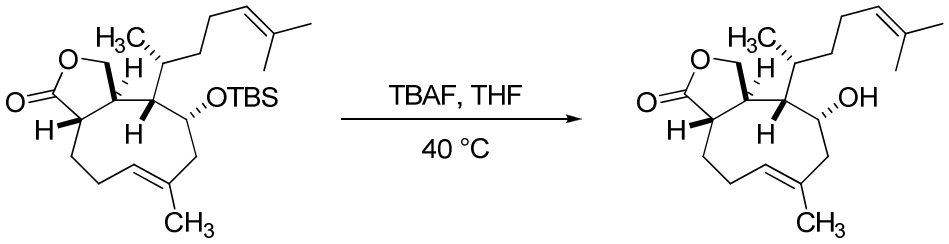
131.3, 128.1, 126.3, 124.6, 124.5, 104.6, 100.1, 71.6, 71.4, 69.6, 68.7, 54.4, 49.9, 48.4, 48.3, 47.4, 46.9, 43.8, 39.4, 37.1, 36.9, 31.7, 31.5, 31.4, 29.7, 26.5, 26.2, 26.1, 26.0, 25.7, 24.8, 20.2, 18.6, 18.3, 18.0, 17.7, –2.3, –2.6, –5.0, ; HRMS-ESI (calcd for $C_{26}H_{48}O_3SiNa$ $[M+Na]^+$) 459.3270, found 459.3274.




**38** **43**

**(3aS,4S,5R,10aS,E)-5-(tert-butyldimethylsilyloxy)-7-methyl-4-((R)-6-methylhept-5-en-2-yl)-3,3a,4,5,6,9,10,10a-octahydro-1H-cyclonona[c]furan-1-one (43)** To a solution of lactol **38** (47 mg, 0.108 mmol) in $CH_2Cl_2$ (11 mL) were added powdered, activated 4Å MS (60 mg) and NMO (19 mg, 0.162 mmol). The suspension was allowed to stir for 10 min and then TPAP (3.8 mg, 0.011 mmol) was added in one portion. The reaction was allowed to stir for 45 minutes and was then filtered through a plug of silica gel. The filtrate was concentrated *in vacuo* to give a dark oil. The crude product was purified via flash chromatography (Hexanes/EtOAc (50:1)), providing **43** (37 mg, 79%) as a colorless oil: $R_f$ 0.46 (Hexanes/EtOAc (17:3)); $[\alpha]_D^{22}$ –24.0° (c 0.59, $CHCl_3$); IR (film) 2956, 2927, 2856, 2359, 1770, 1039 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.30–5.19 (m, 1H), 5.13–5.02 (m, 1H), 4.26 (t, *J* = 9.5 Hz, 1H), 4.23-4.19 (m, 1H), 4.04 (dd, *J* = 8.8, 7.5 Hz, 1H), 2.72–2.60 (m, 1H), 2.54-2.42 (m, 1H), 2.40–2.23 (m, 2H), 2.28-2.23 (m, 1H), 2.23–2.10 (m, 1H), 2.09–1.97 (m, 3H), 1.97–1.84 (m, 2H), 1.79 (s, 3H), 1.69–1.63 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.28-1.14 (m, 1H), 1.12-1.01 (m, 1H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 9H), 0.14 (s, 3H), 0.05 (s, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 180.7, 135.1, 132.3, 126.2,

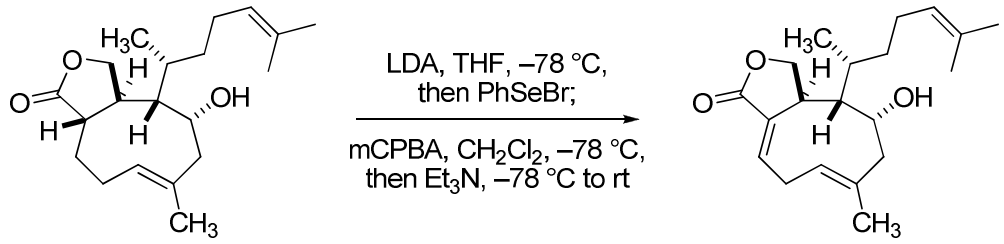
123.7, 71.8, 69.6, 50.1, 48.0, 47.7, 39.3, 35.4, 31.0, 29.8, 26.0 (3 C), 25.6, 25.6, 25.0, 20.3, 18.3, 17.9, 17.7, –3.3, –4.5; HRMS-ESI (calcd for $C_{26}H_{46}O_3SiNa$ $[M+Na]^+$) 457.3114, found 457.3135.




**43** **S19**

**(3aS,4S,5R,10aS,E)-5-hydroxy-7-methyl-4-((R)-6-methylhept-5-en-2-yl)-3,3a,4,5,6,9,10,10a-octahydro-1H-cyclonona[c]furan-1-one (S19)** To a solution of **43** (11.8 mg, 0.027 mmol) in THF (1.0 mL) at ambient temperature was added TBAF (1.0 M in THF, 0.20 mL, 0.200 mmol). The reaction was then warmed to 40 °C and stirred for 10 h. The reaction was cooled to ambient temperature and quenched with $H_2O$ (1 mL) and diluted in $Et_2O$ (2 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 x 2 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash chromatography (Hexanes/EtOAc (50:1 to 93:7)), providing **S19** (7.2 mg, 83%) as a colorless oil: $R_f$ 0.30 (Hexanes/EtOAc (3:1)); $[\alpha]_D^{25}$ +14.0° (c 0.72, $CHCl_3$); IR (film) 3477 (br), 2916, 2854, 1756, 1445, 1003 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.18–5.03 (m, 2H), 4.33 (t, *J* = 8.1 Hz, 1H), 4.20–4.13 (m, 1H), 3.96 (dd, *J* = 9.7, 8.6 Hz, 1H), 2.74–2.61 (m, 1H), 2.42–2.04 (m, 8H), 2.03–1.95 (m, 2H), 1.82 (s, 3H), 1.80–1.74 (m, 1H), 1.69 (s, 3H), 1.68-1.64 (m, 1H), 1.62 (s, 3H), 1.35-1.17 (m, 2H), 0.90 (d, *J* = 6.7 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 179.3, 133.7, 132.1, 128.9, 123.9, 70.2 (2 C), 49.1, 44.8, 44.1, 39.1, 36.9, 31.2,

27.1, 26.1, 25.7, 25.4, 20.2, 17.8, 17.6; HRMS-CI (calcd for $C_{20}H_{33}O_3$ $[M+H]^+$) 321.2424, found 321.2411.



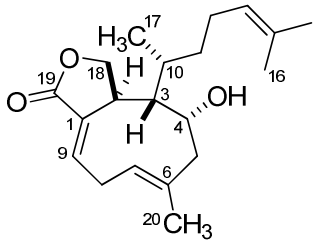

**S19** **4**

**4-Hydroxydictyolactone (4)** To a solution of **S19** (7.2 mg, 0.022 mmol) in THF (440 μL) at –78 °C was added freshly prepared lithium diisopropylamide (1.0M in THF, 135 μL, 0.135 mmol) dropwise. The reaction was allowed to stir for 30 min and then a solution of PhSeBr (13 mg, 0.055 mmol) in THF (50 μL) was added slowly. After 45 minutes at –78 °C, the reaction was diluted with a saturated aqueous solution of $NH_4Cl$ (500 μL) and $Et_2O$ (1 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 x 2 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo* to afford the crude α-selenylester that was used without purification in the next reaction.

To a solution of the α-selenylester in $CH_2Cl_2$ (1.3 mL) at –78 °C was added a solution of *m*CPBA (3.4 mg, 0.020 mmol) in $CH_2Cl_2$ (100 μL). The reaction was allowed to stir for 1 h and then $Et_3N$ (50 μL) was added. The reaction was allowed to warm to ambient temperature and was stirred for 24 h. The reaction was partitioned between $H_2O$ (1 mL) and $Et_2O$ (2 mL) and the layers were separated. The aqueous layer was extracted with $Et_2O$ (3 x 2 mL) and the combined organic extracts were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The crude product was then purified by preparative TLC (Hexanes/EtOAc (13:7)) to give synthetic 4-hydroxydictyolactone (**4**) (3.4 mg, 55% from **S19**) as a white foam: $R_f$ 0.21 (Hexanes/EtOAc

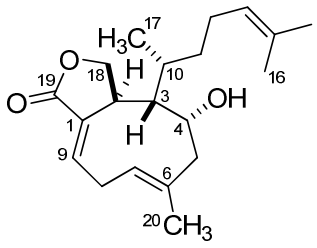
(3:1)); $[\alpha]_D^{23}$ –175.2 (c 0.13, $CCl_4$); IR (film) 3448 (br), 2917, 1735, 1637, 1183 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.92 (dt, *J* = 7.6, 2.0 Hz, 1H), 5.30 (br. dd, *J* = 11.7, 4.1 Hz, 1H), 5.01 (appt. t, *J* = 7.0 Hz, 1H), 4.43 (dd, *J* = 9.5, 1.0 Hz, 1H), 4.31–4.27 (m, 1H), 4.08 (dd, *J* = 9.7, 7.9 Hz, 1H), 3.39 (br. d, *J* = 7.3 Hz, 1H), 3.18 (ddt, *J* = 17.5, 11.6, 1.8 Hz, 1H), 2.95 (ddd, *J* = 17.4, 7.3, 4.3 Hz, 1H), 2.31 (br. d, *J* = 12.8 Hz, 1H), 2.17 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.02 (br. s, 1H), 1.95–1.84 (m, 2H), 1.88 (br. s, 3H), 1.71–1.63 (m, 1H), 1.65 (br. s, 3H), 1.55 (br. s, 3H), 1.22–1.10 (m, 2H), 1.06 (d, *J* = 6.7 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 173.4, 139.4, 136.1, 135.4, 131.9, 125.3, 123.9, 72.7, 68.7, 51.0, 49.1, 37.9, 35.7, 32.3, 29.4, 25.9, 25.6, 20.0, 18.1, 17.7; HRMS-CI (calcd for $C_{20}H_{31}O_3$ $[M+H]^+$) 319.2268, found 319.2255.

# Comparison of $^{1}H$ and $^{13}C$ NMR Spectra of Natural and Synthetic 4-Hydroxydictyolactone (4) (Major Conformer)




**4** (4-hydroxydictyolactone)

| H | Natural[5] | Synthetic |
|---|---|---|
| 2 | 3.39 (br. d, *J* = 7.8 Hz) | 3.39 (br. d, *J* = 7.3 Hz) |
| 3 | 2.02 (br. s) | 2.02 (br. s) |
| 4 | 4.28 (m) | 4.31–4.27 (m) |
| 5α | 2.17 (dd, *J* = 12.8, 2.0 Hz) | 2.17 (dd, *J* = 13.0, 4.0 Hz) |
| 5β | 2.32 (dd, *J* = 12.8, 4.3 Hz) | 2.31 (br. d, *J* = 12.8 Hz) |
| 7 | 5.30 (br. dd, *J* = 11.4, 4.2 Hz) | 5.30 (br. dd, *J* = 11.7, 4.1 Hz) |
| 8α | 3.19 (ddt, *J* = 17.6, 11.4, 2.3 Hz) | 3.18 (ddt, *J* = 17.5, 11.6, 1.8 Hz) |
| 8β | 2.94 (ddd, *J* = 17.6, 7.5, 4.2 Hz) | 2.95 (ddd, *J* = 17.4, 7.3, 4.3 Hz) |
| 9 | 6.92 (dt, *J* = 7.5, 2.3 Hz) | 6.92 (dt, *J* = 7.6, 2.0 Hz) |
| 10 | 1.61 (m) | 1.71–1.63 (m) |
| 11 | 1.22–1.17 (m) | 1.22–1.10 (m) |
| 12 | 1.92 (m) | 1.95–1.84 (m) |
| 13 | 5.02 (sept. t, *J* = 7.2, 1.5 Hz) | 5.01 (appt. t, *J* = 7.0 Hz) |
| 15 | 1.66 (br. s) | 1.65 (br. s) |
| 16 | 1.56 (br. s) | 1.55 (br. s) |
| 17 | 1.06 (d, *J* = 6.7 Hz) | 1.06 (d, *J* = 6.7 Hz) |
| 18α | 4.09 (dd, *J* = 9.5, 7.8 Hz) | 4.08 (dd, *J* = 9.7, 7.9 Hz) |
| 18β | 4.44 (dd, *J* = 9.5, 1.2 Hz) | 4.43 (dd, *J* = 9.5, 1.0 Hz) |
| 20 | 1.89 (d, *J* = 1.3 Hz) | 1.88 (br. s) |




**4** (4-hydroxydictyolactone)

| C | Natural[5] | Synthetic | Δ (δ ppm) |
|---|---|---|---|
| 1 | 136.08 | 136.07 | 0.01 |
| 2 | 35.74 | 35.75 | 0.01 |
| 3 | 50.97 | 50.99 | 0.02 |
| 4 | 72.71 | 72.74 | 0.03 |
| 5 | 49.05 | 49.06 | 0.01 |
| 6 | 135.36 | 135.38 | 0.02 |
| 7 | 125.28 | 125.30 | 0.02 |
| 8 | 29.42 | 29.43 | 0.01 |
| 9 | 139.39 | 139.36 | 0.03 |
| 10 | 32.25 | 32.26 | 0.01 |
| 11 | 37.86 | 37.88 | 0.02 |
| 12 | 25.87 | 25.89 | 0.02 |
| 13 | 123.90 | 123.91 | 0.01 |
| 14 | 131.87 | 131.87 | 0.00 |
| 15 | 25.64 | 25.64 | 0.00 |
| 16 | 17.69 | 17.69 | 0.00 |
| 17 | 18.13 | 18.14 | 0.01 |
| 18 | 68.73 | 68.72 | 0.01 |
| 19 | 173.39 | 173.36 | 0.03 |
| 20 | 20.00 | 19.99 | 0.01 |

## References

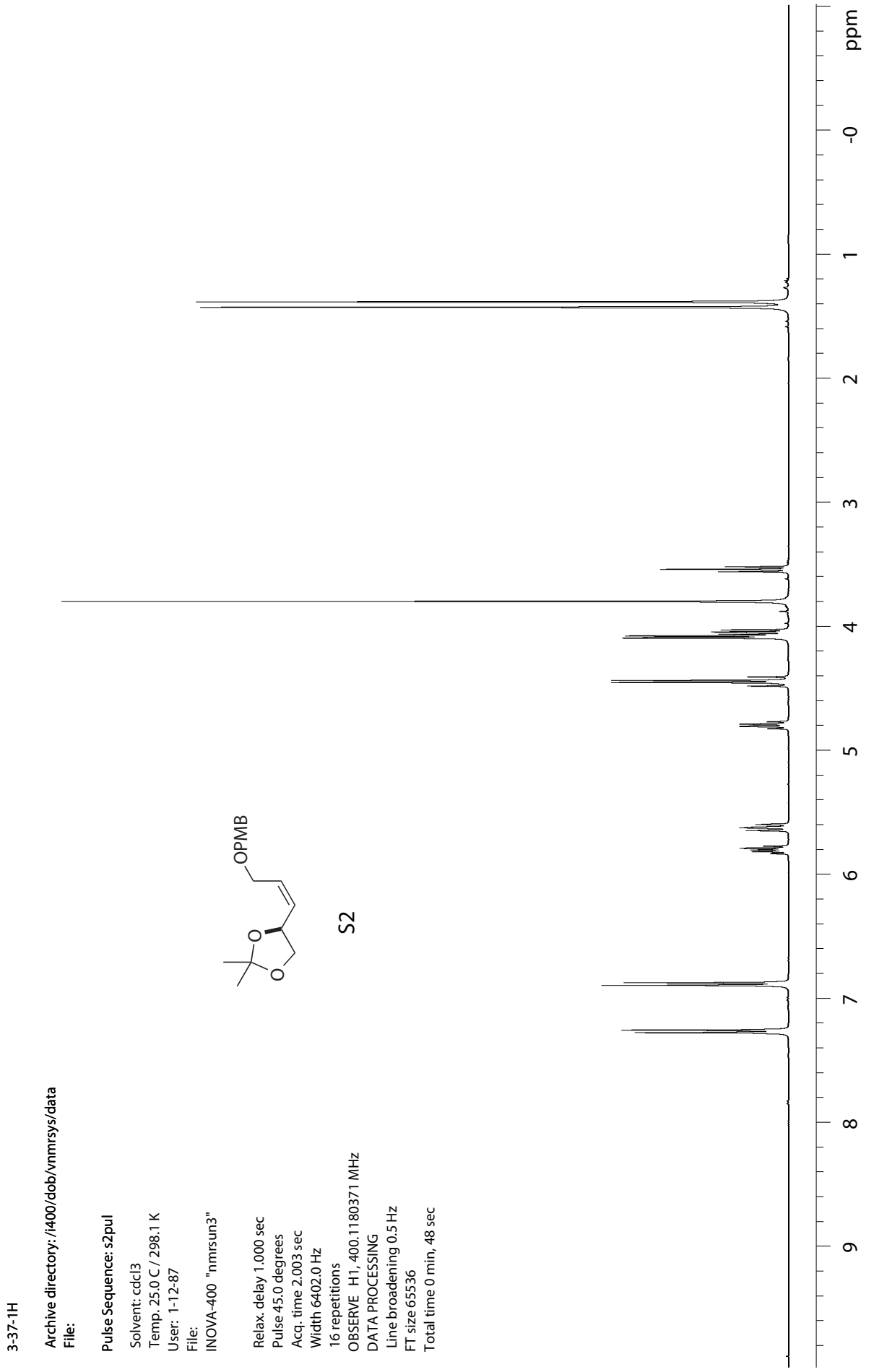
(1) Marshall, J. M.; Trometer, J. D.; Cleary, D. G. *Tetrahedron* **1989**, *45*, 391–402.

(2) Hopf, H.; Böhm, I.; Kleinschroth, J. *Org. Synth.* **1981**, *60*, 41.

(3) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.

(4) Lipshutz, B. H.; Lee, C.-T.; Servesko, J. M. *Org. Lett*. **2007**, *9*, 4713–4716.

(5) Guella, G.; Chiasera, G.; N'Diaye, I.; Pietra, F. *Helv. Chim. Acta* **1994**, *77*, 1203–1221.

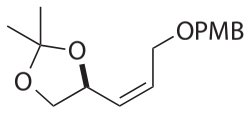

3-37-1H
Archive directory: /l400/dob/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1180371 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec
OPMB
O
O
S2
9
8
7
6
5
4
3
2
1
-0
ppm

3-37-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"




S2

Relax. delay 1.500 sec
Pulse 29.8 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
130 repetitions
OBSERVE C13, 100.6097722 MHz
DECOUPLE H1, 400.1200527 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec

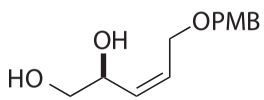
5-299-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

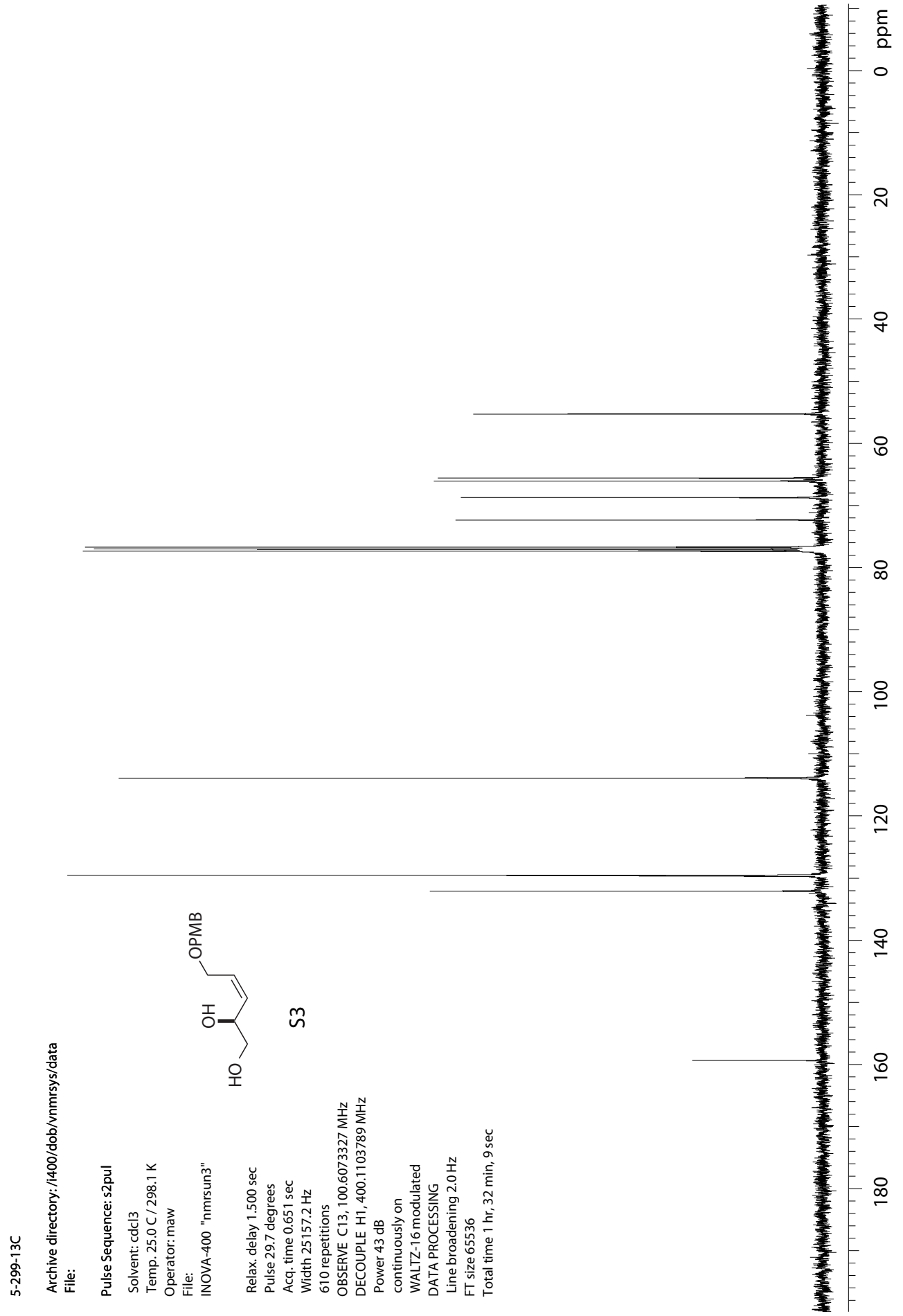
Pulse Sequence: s2pul

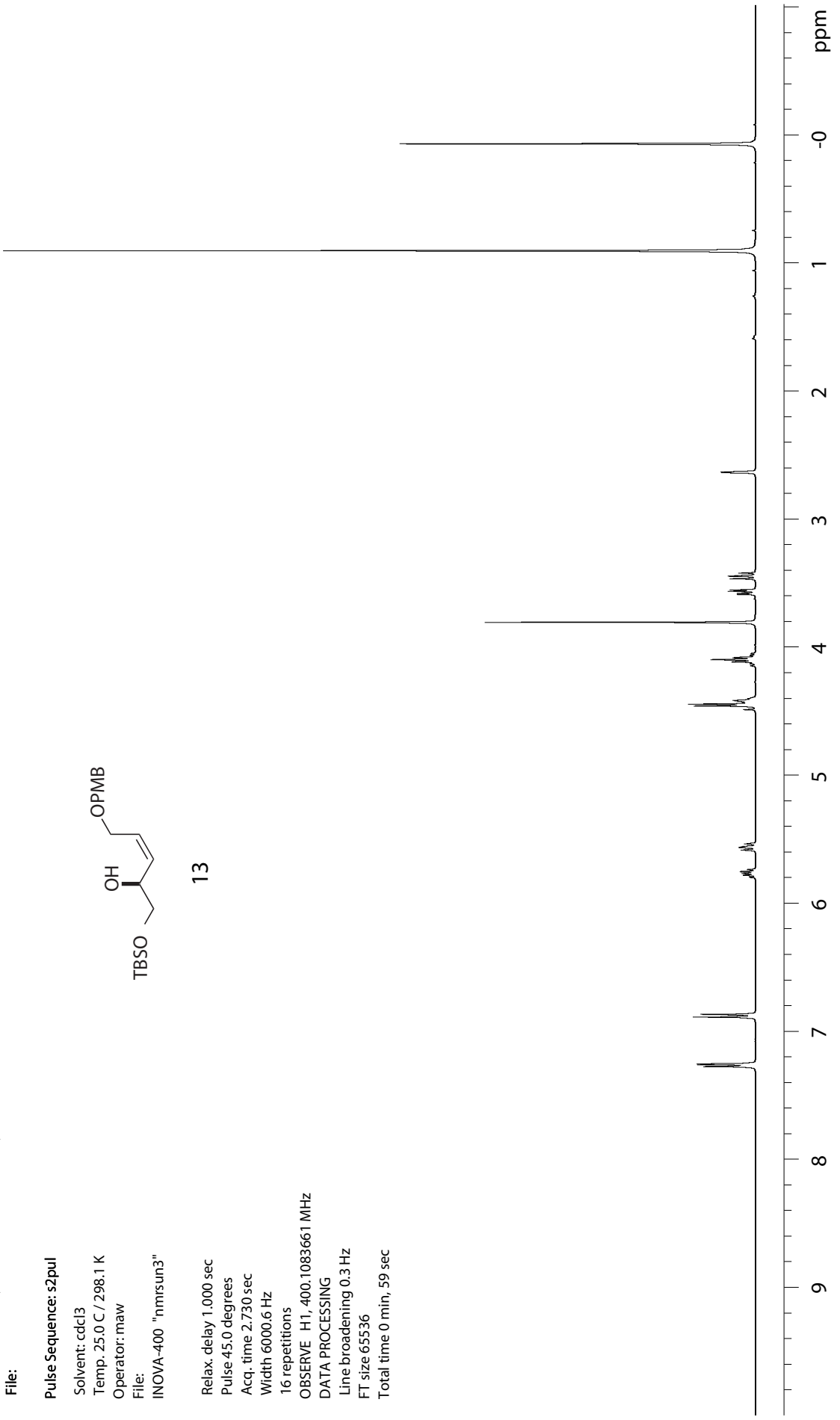
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083663 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




S3


5-299-13C
Archive directory: /l400/dob/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"
Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
610 repetitions
OBSERVE C13, 100.6073327 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec
OPMB
OH
HO
S3
180
160
140
120
100
80
60
40
20
0
ppm

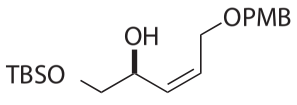

5-301-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083661 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
TBSO
OH
OPMB
13
ppm
9
8
7
6
5
4
3
2
1
-0

5-301-13C

Archive directory: /i400/dob/vnmrsys/data
File:

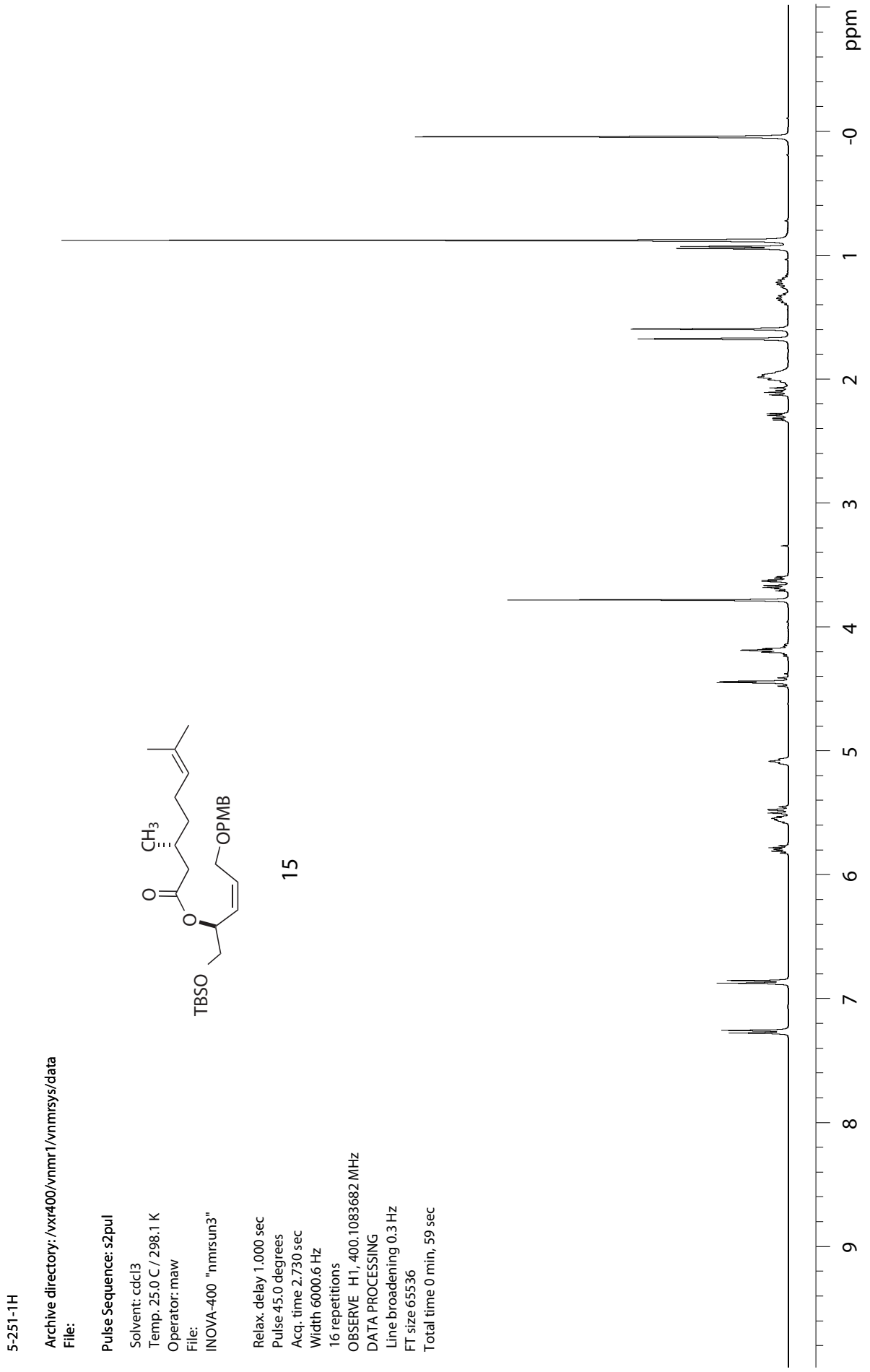
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"




13

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
156 repetitions
OBSERVE C13, 100.6073335 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec

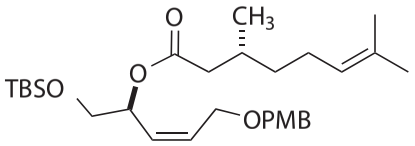

5-251-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083682 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
TBSO
O
O
CH3
OPMB
15
9
8
7
6
5
4
3
2
1
-0
ppm

5-251-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"




15

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
87 repetitions
OBSERVE C13, 100.6073373 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec

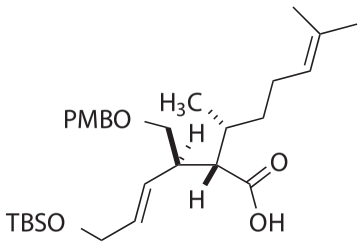
4-295-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1137399 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




16

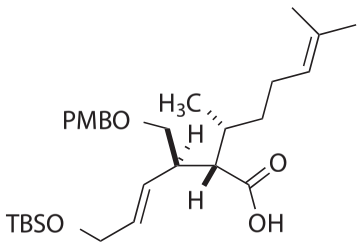
5-101-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
2560 repetitions
OBSERVE C13, 100.6073297 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec



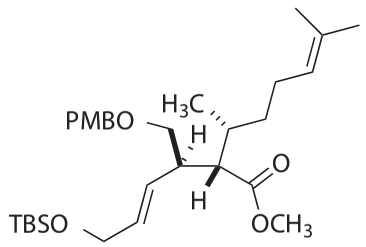

16

2-173-1H

**Pulse Sequence: s2pul**

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0574170 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec



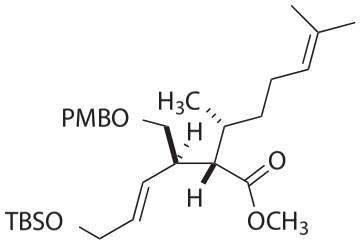

S4

6-16-13C

Archive directory: /i400/dob/vnmrsys/data
File:

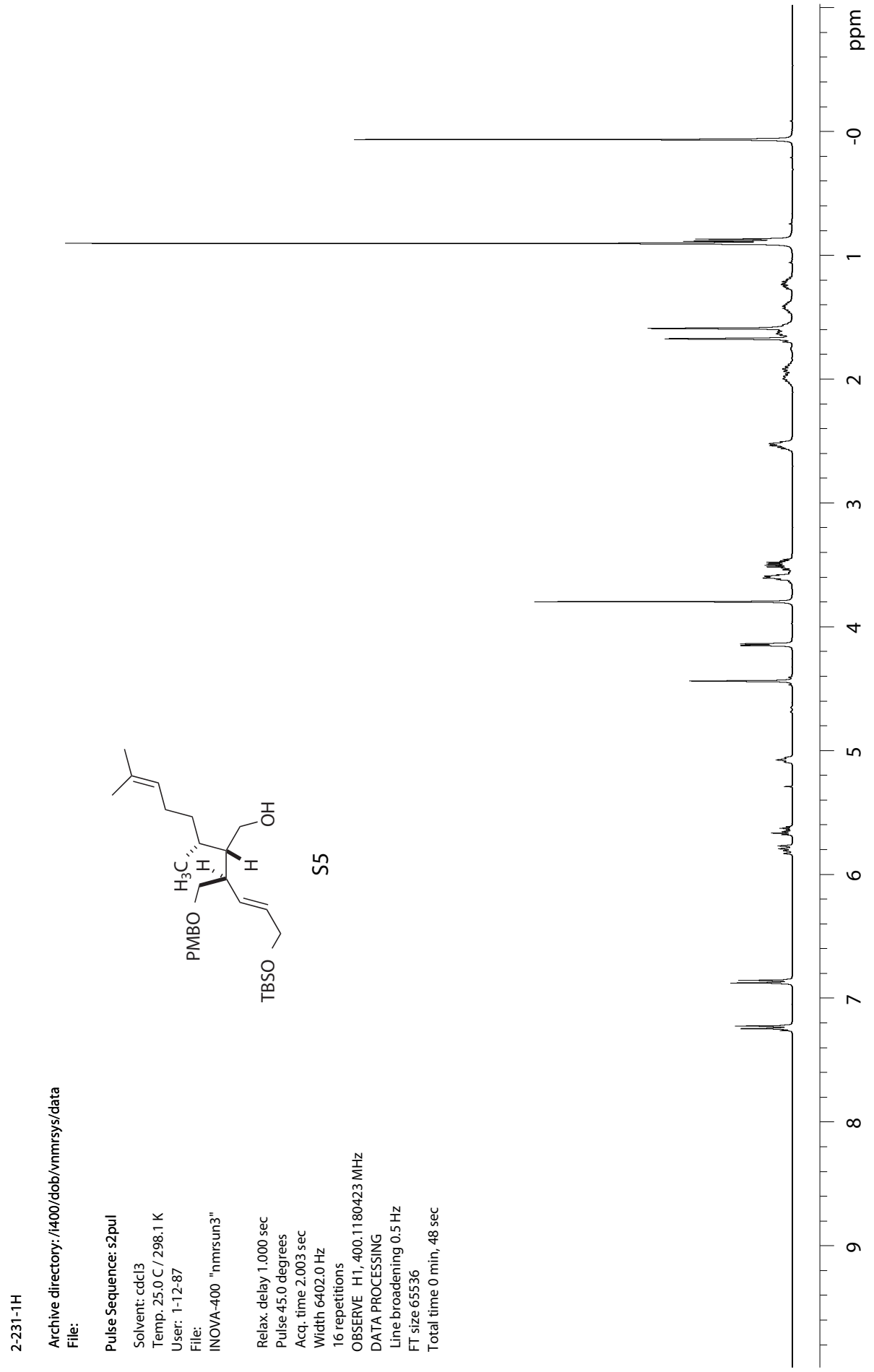
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"




S4

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
159 repetitions
OBSERVE C13, 100.6073312 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec


2-231-1H
Archive directory: /i400/dob/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1180423 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec
PMBO
TBSO
OH
S5
ppm
9
8
7
6
5
4
3
2
1
-0

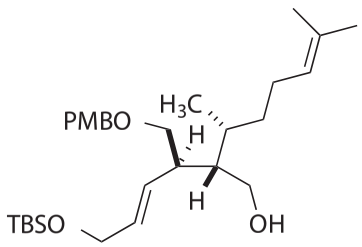
2-187-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.8 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
2624 repetitions
OBSERVE C13, 100.6097614 MHz
DECOUPLE H1, 400.1200527 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 6 hr, 1 sec




S5

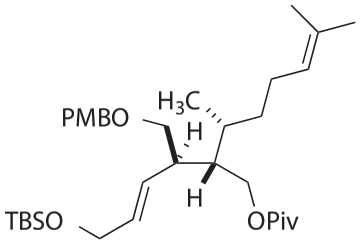
3-221-1H

Archive directory: /vxr400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 5999.7 Hz
16 repetitions
OBSERVE H1, 399.7206759 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec



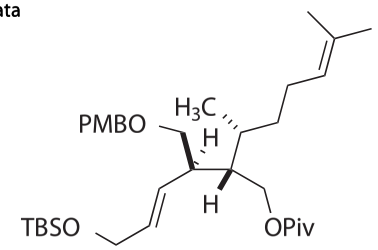

S6

6-22-13C

Archive directory: /i400/dob/vnmrsys/data
File: mjw6_22_13C_p

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw6_22_13C_p
INOVA-400 "nmrsun3"




S6

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
75 repetitions
OBSERVE C13, 100.6073320 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec

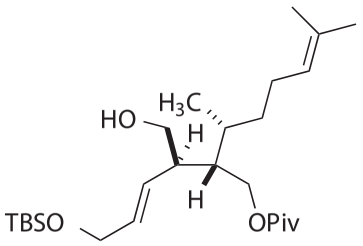
3-251-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137398 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




19

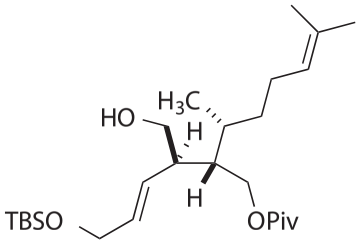
3-250-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
1209 repetitions
OBSERVE C13, 100.6086810 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 55 min, 17 sec




19

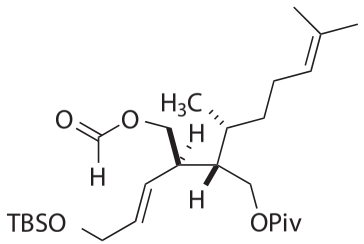
3-252-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137398 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




S7

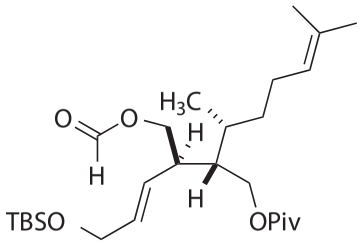
3-252-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
87 repetitions
OBSERVE C13, 100.6086841 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 18 min, 25 sec




S7

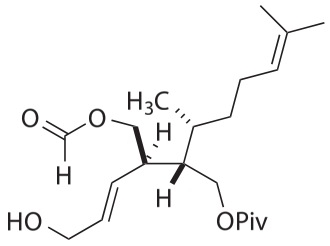
3-254-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137398 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




S8

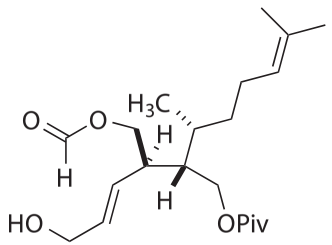
3-227-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
104 repetitions
OBSERVE C13, 100.6086841 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec




S8

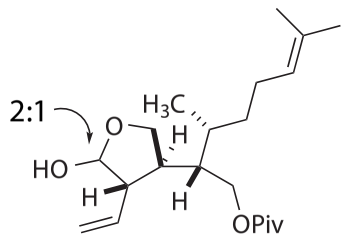
3-261-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137398 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




22

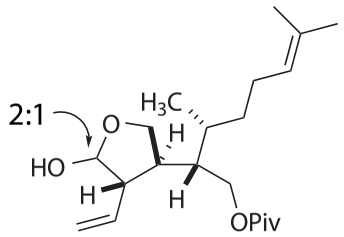
3-261-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
234 repetitions
OBSERVE C13, 100.6086833 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec




22

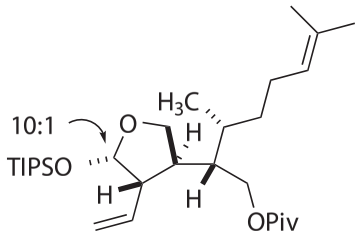
4-165-1H

Archive directory: /vxr400/dob/vnmrsys/data
File:

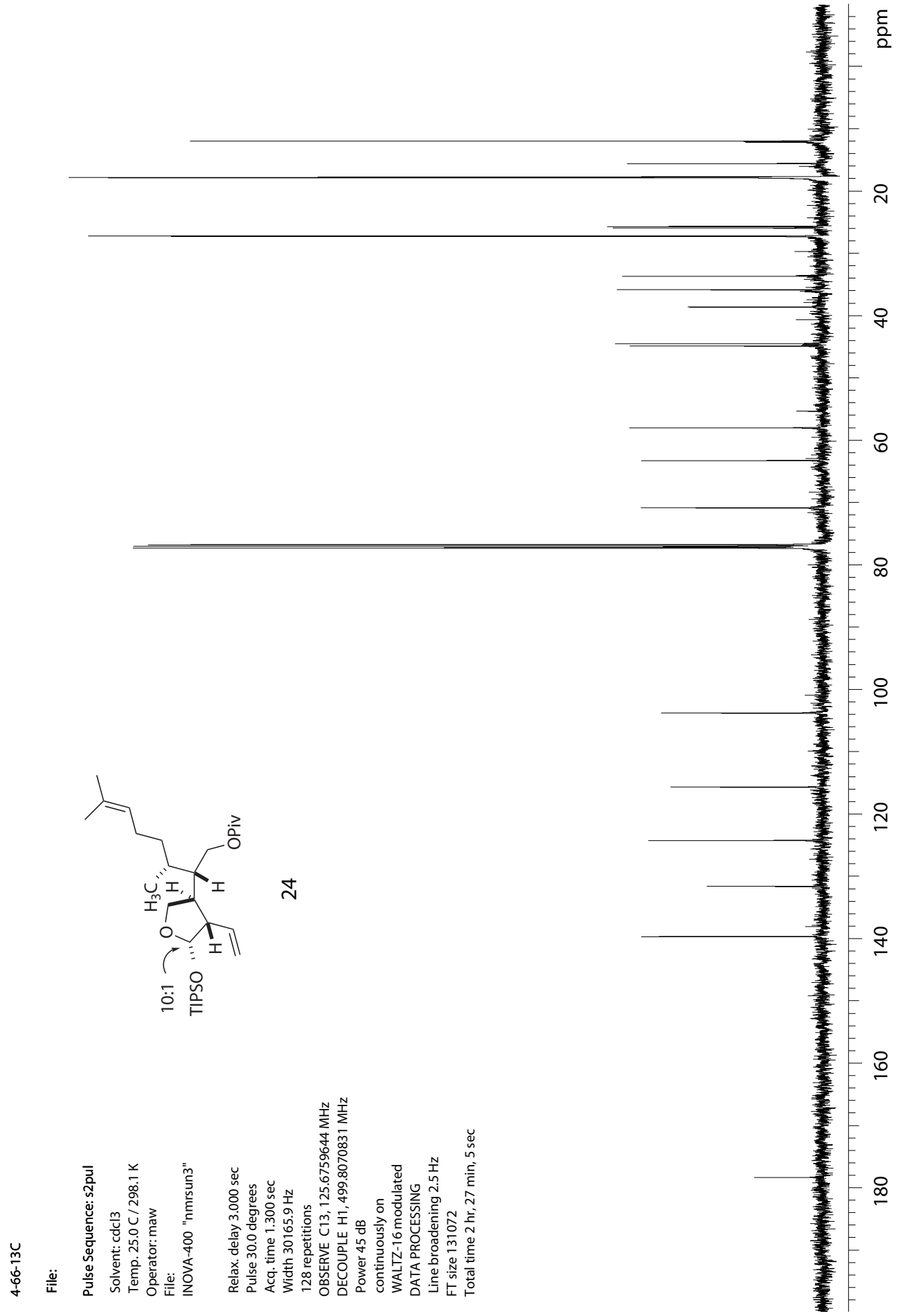
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 5999.7 Hz
16 repetitions
OBSERVE H1, 399.7076472 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




24


4-66-13C
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"
Relax. delay 3.000 sec
Pulse 30.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
128 repetitions
OBSERVE C13, 125.6759644 MHz
DECOUPLE H1, 499.8070831 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.5 Hz
FT size 131072
Total time 2 hr, 27 min, 5 sec
10:1
TIPSO
O
H
H3C
H
OPiv
24
180
160
140
120
100
80
60
40
20
ppm

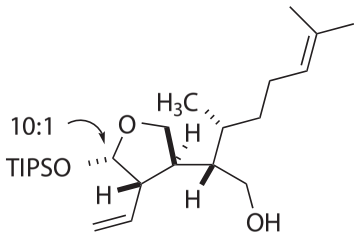
4-280-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1137399 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




S9

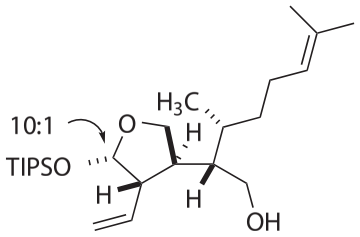
4-280-13C

Archive directory: /i400/dob/vnmrsys/data
File:

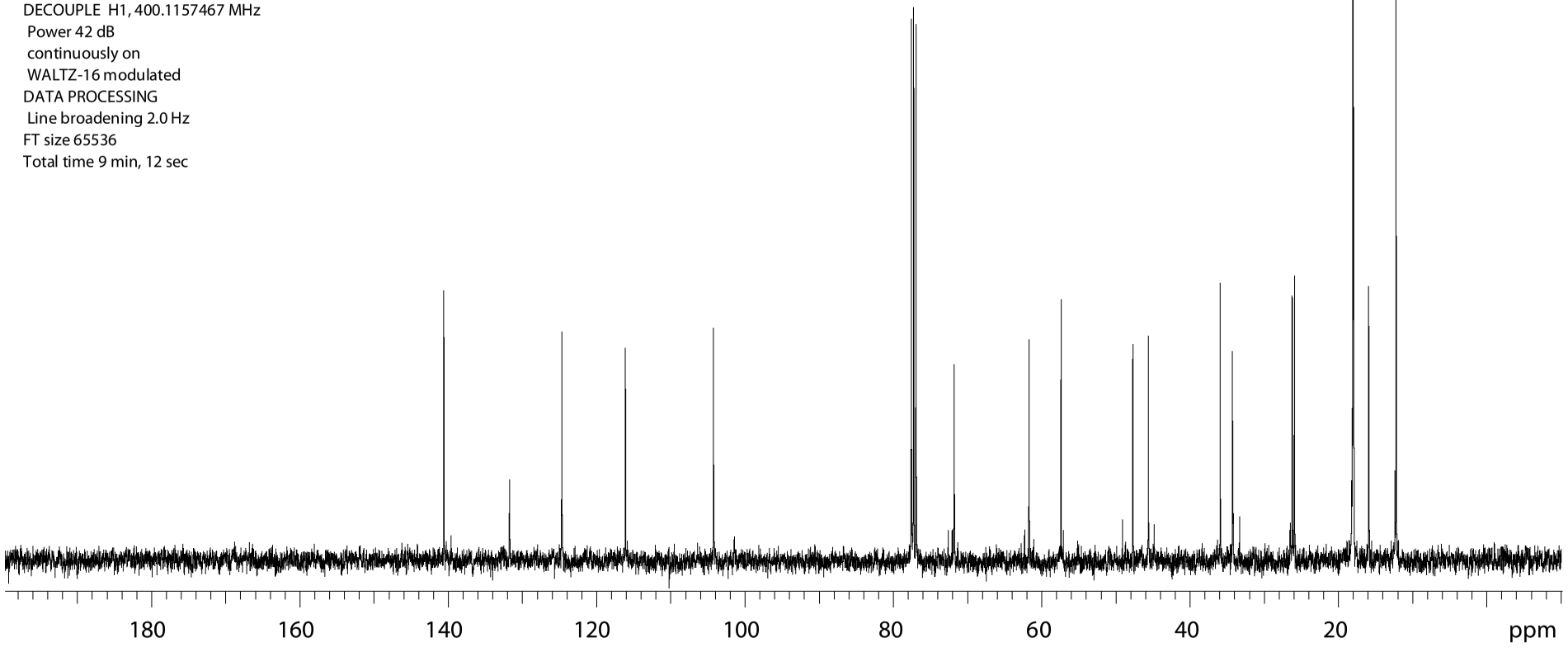
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
256 repetitions
OBSERVE C13, 100.6086574 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec




S9



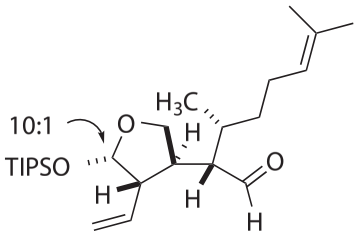
4-82-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-12-87
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137400 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




25

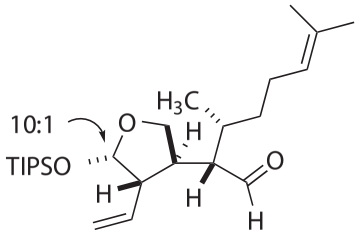
4-224-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
1988 repetitions
OBSERVE C13, 100.6086795 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 13 min, 43 sec




25

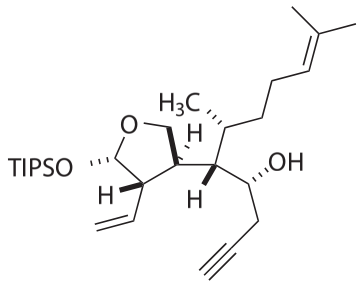
4-179-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137400 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec



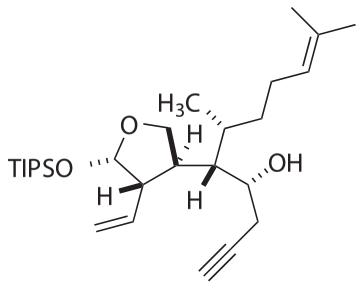

27

4-179-13C

Archive directory: /i400/dob/vnmrsys/data
File:

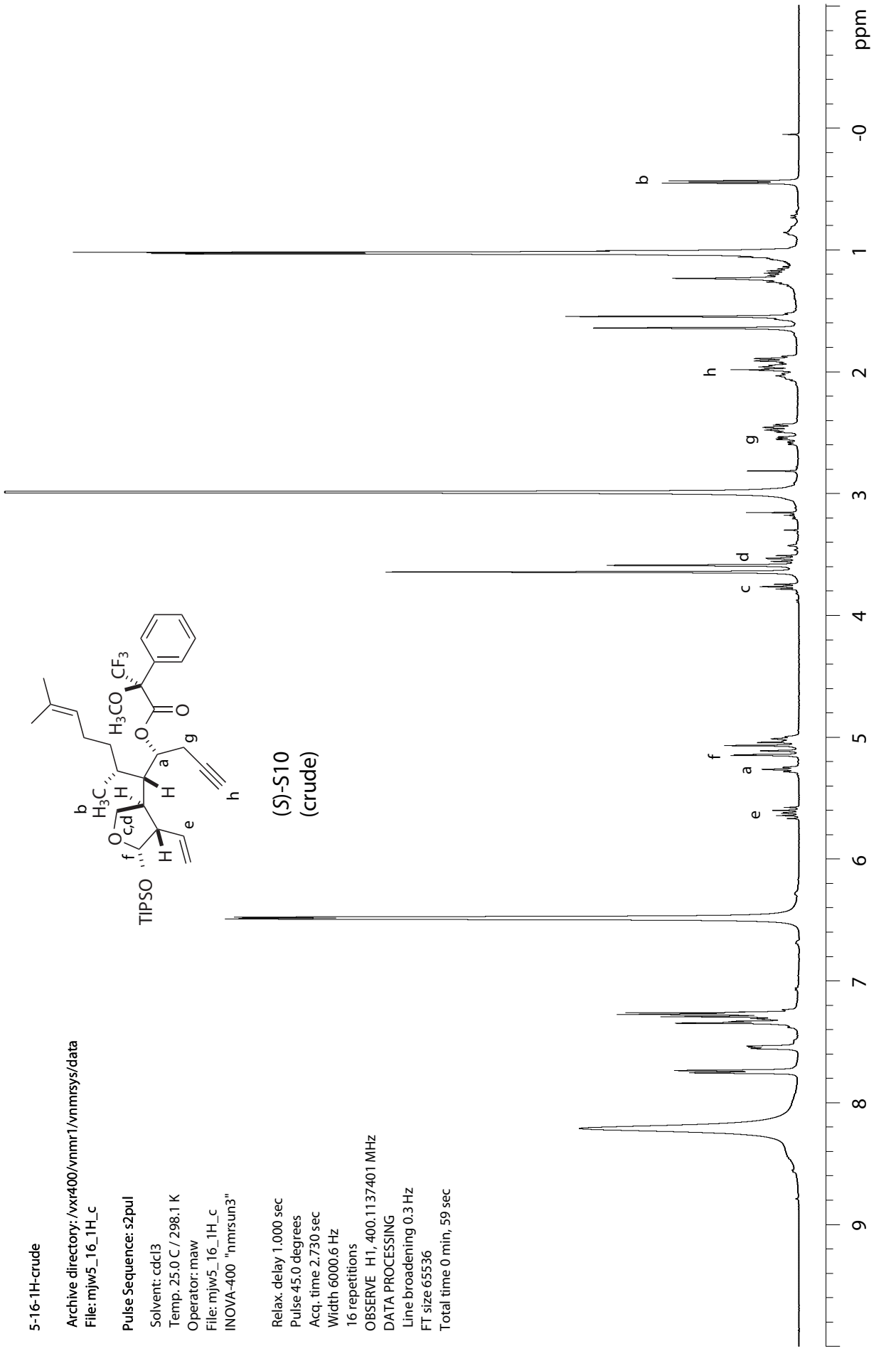
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"




27

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
256 repetitions
OBSERVE C13, 100.6086802 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec


5-16-1H-crude
Archive directory: /vxr400/vnmr1/vnmrsys/data
File: mjw5_16_1H_c
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw5_16_1H_c
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1137401 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
(S)-S10
(crude)
TIPSO
H3C
H3CO
CF3
O
H
a
b
c,d
e
f
g
h
ppm
9
8
7
6
5
4
3
2
1
-0

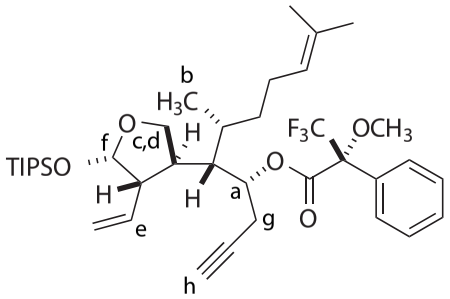
5-15-1H-crude

Archive directory: /vxr400/vnmr1/vnmrsys/data
File: mjw5_15_1H_c

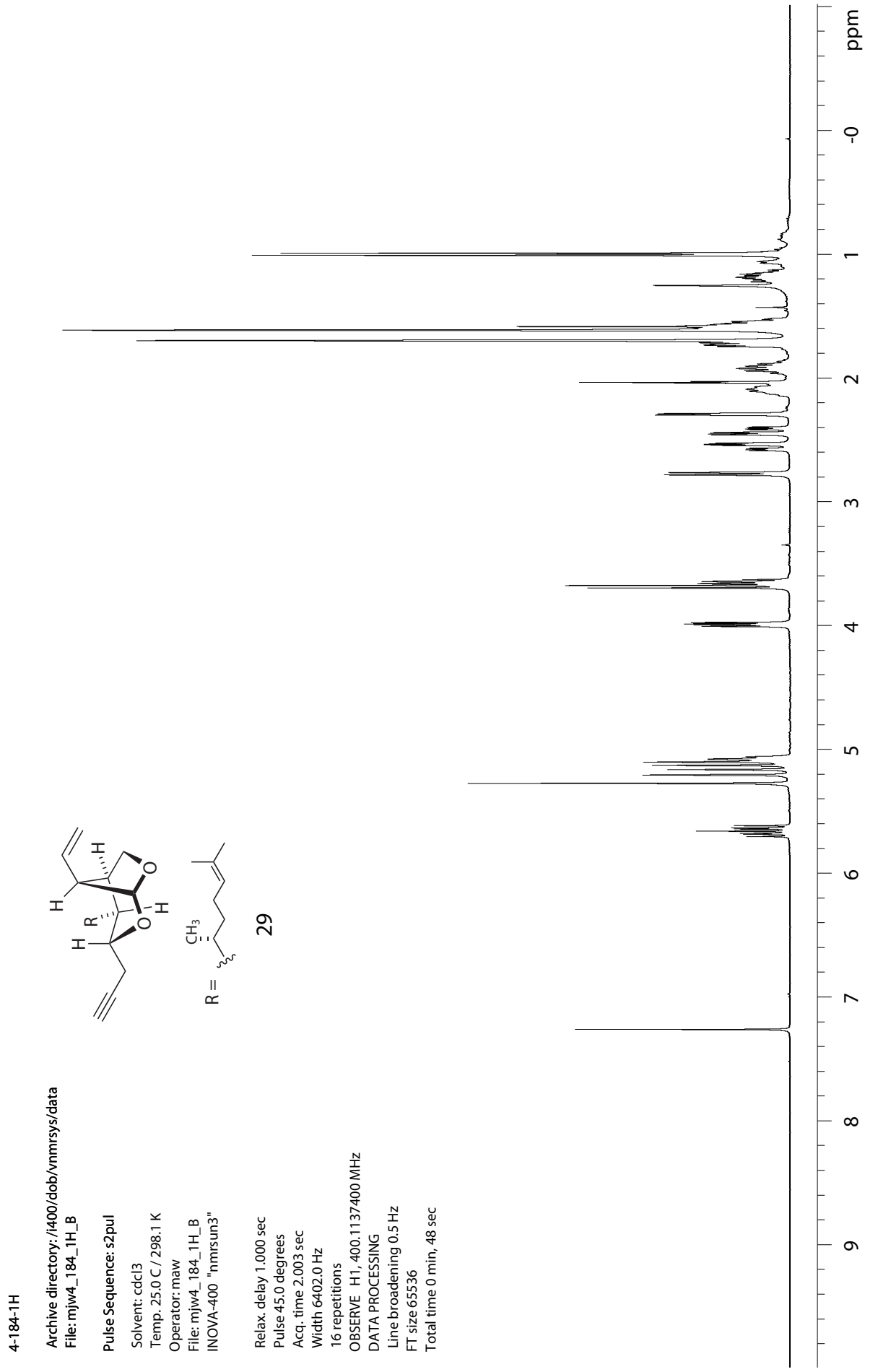
Pulse Sequence: s2pul

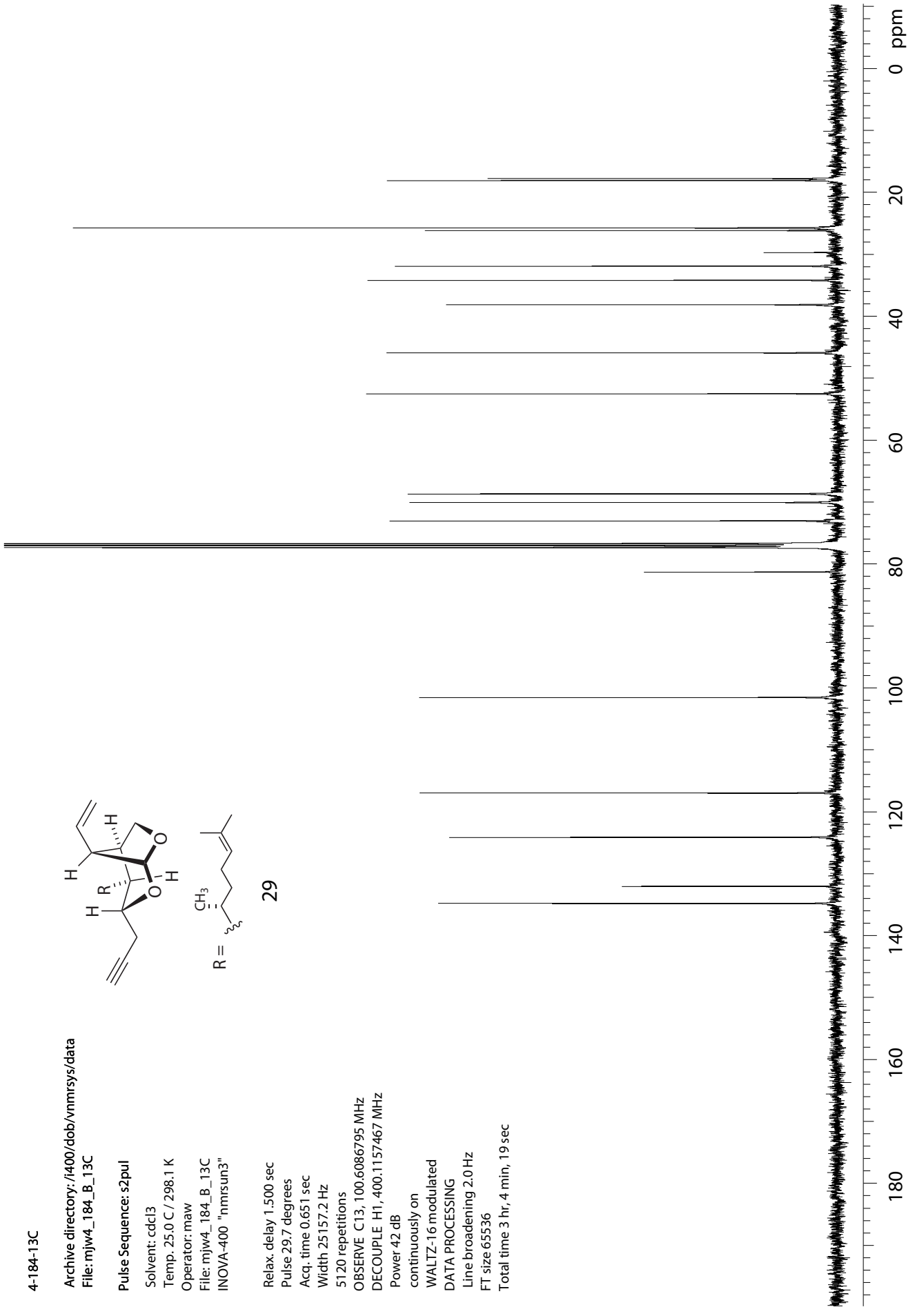
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw5_15_1H_c
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1137395 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




(*R*)-S10
(crude)


4-184-1H
Archive directory: /i400/dob/vnmrsys/data
File: mjw4_184_1H_B
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw4_184_1H_B
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137400 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec
R =
29
9
8
7
6
5
4
3
2
1
-0
ppm


4-184-13C
Archive directory: /i400/dob/vnmrsys/data
File: mjw4_184_B_13C
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw4_184_B_13C
INOVA-400 "nmrsun3"
Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
5120 repetitions
OBSERVE C13, 100.6086795 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 3 hr, 4 min, 19 sec
R =
29
180
160
140
120
100
80
60
40
20
0 ppm

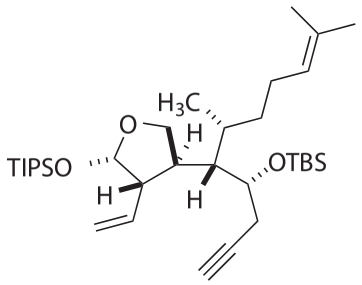
4-240-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137400 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




S11

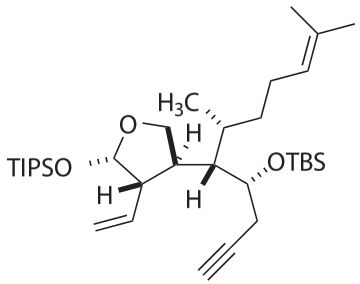
4-240-13C

Archive directory: /i400/dob/vnmrsys/data
File:

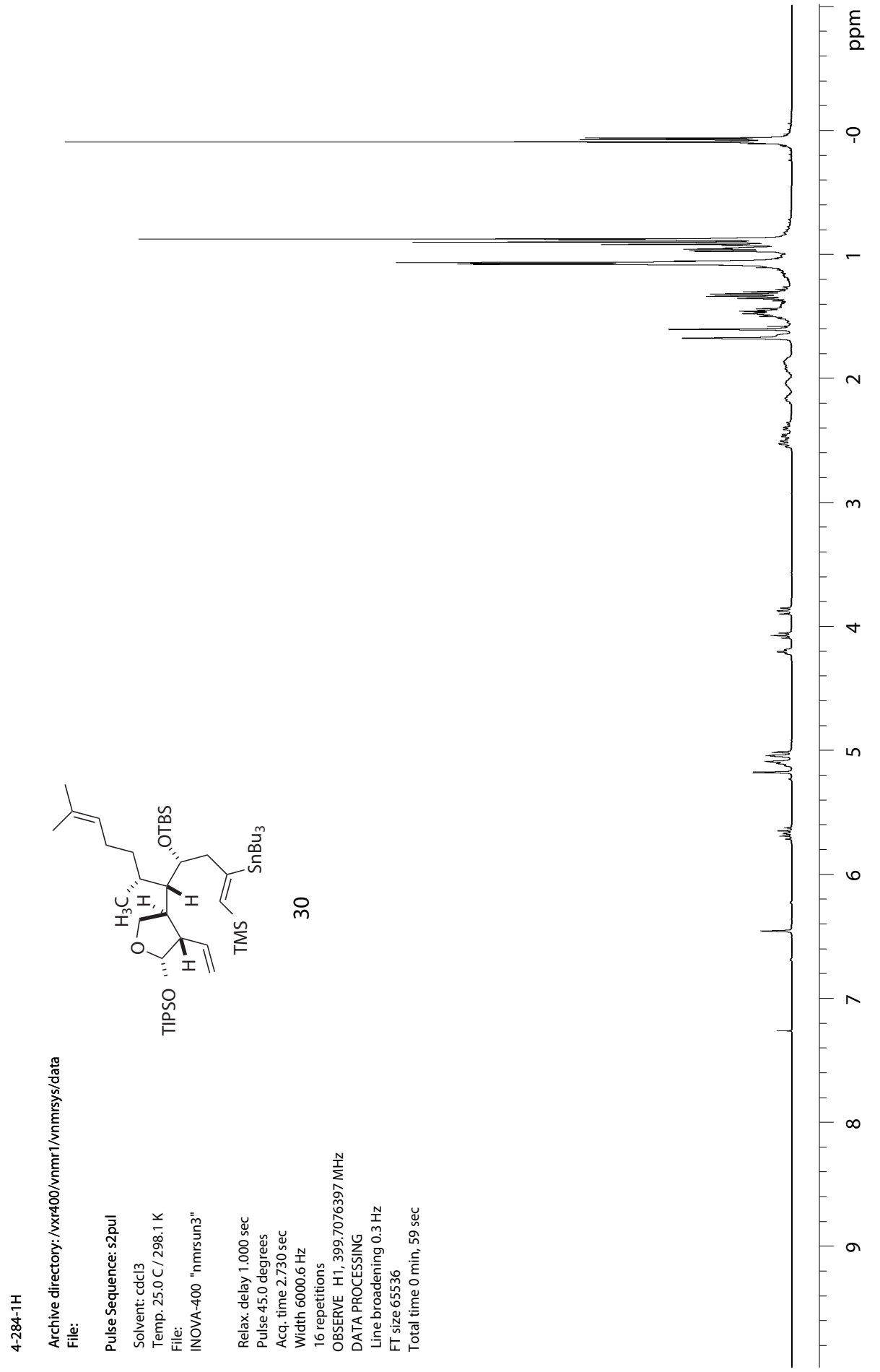
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
512 repetitions
OBSERVE C13, 100.6086795 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 18 min, 25 sec




S11


4-284-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.7076397 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
TIPSO
OTBS
TMS
SnBu3
30
ppm
9
8
7
6
5
4
3
2
1
-0

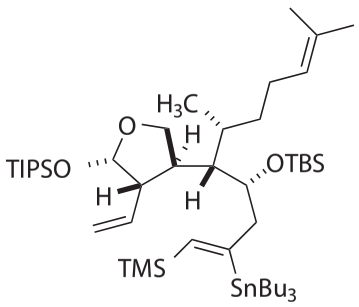
4-284-13C

Archive directory: /vxr400/maw/vnmrsys/data
File:

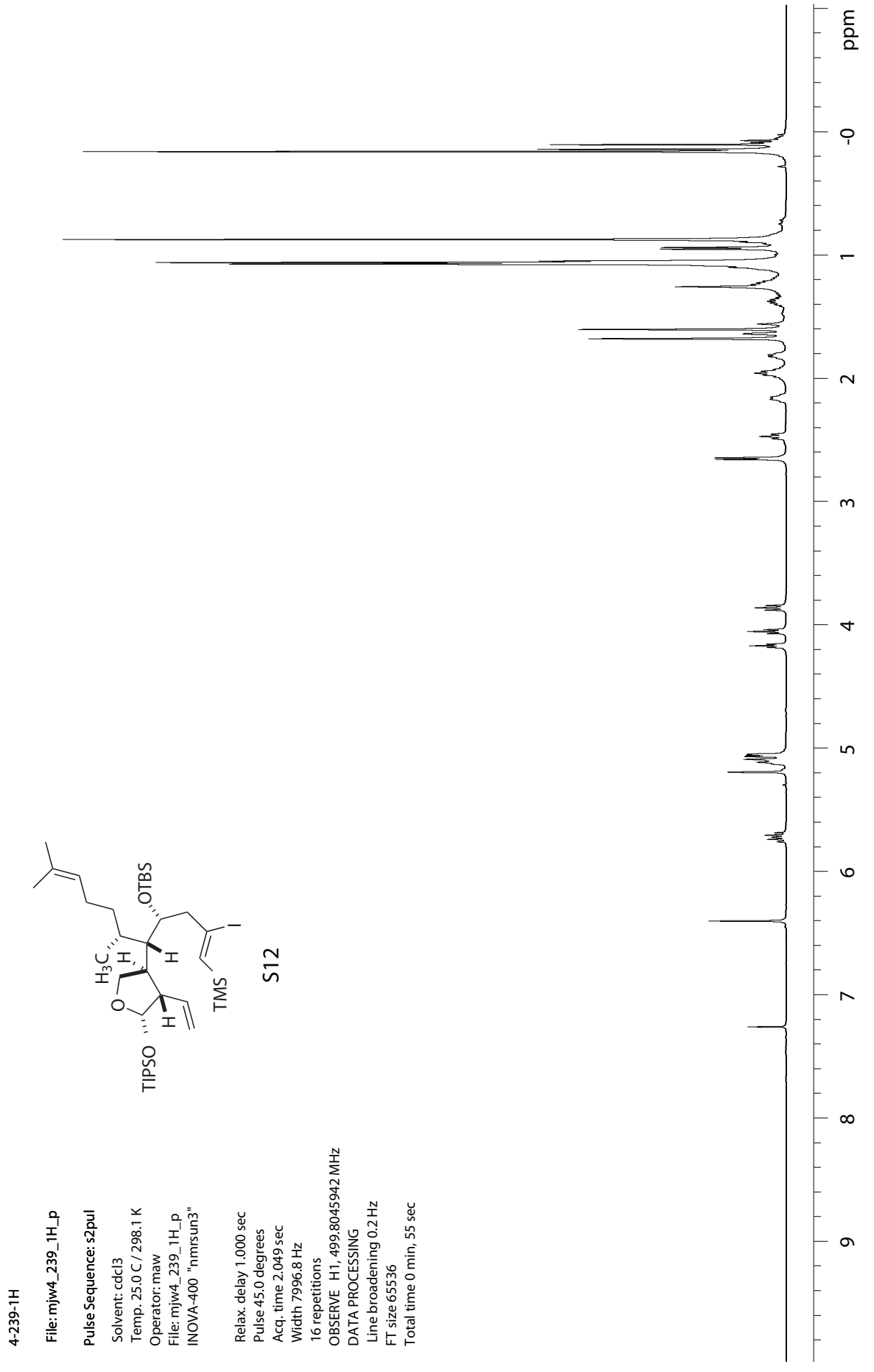
Pulse Sequence: s2pul

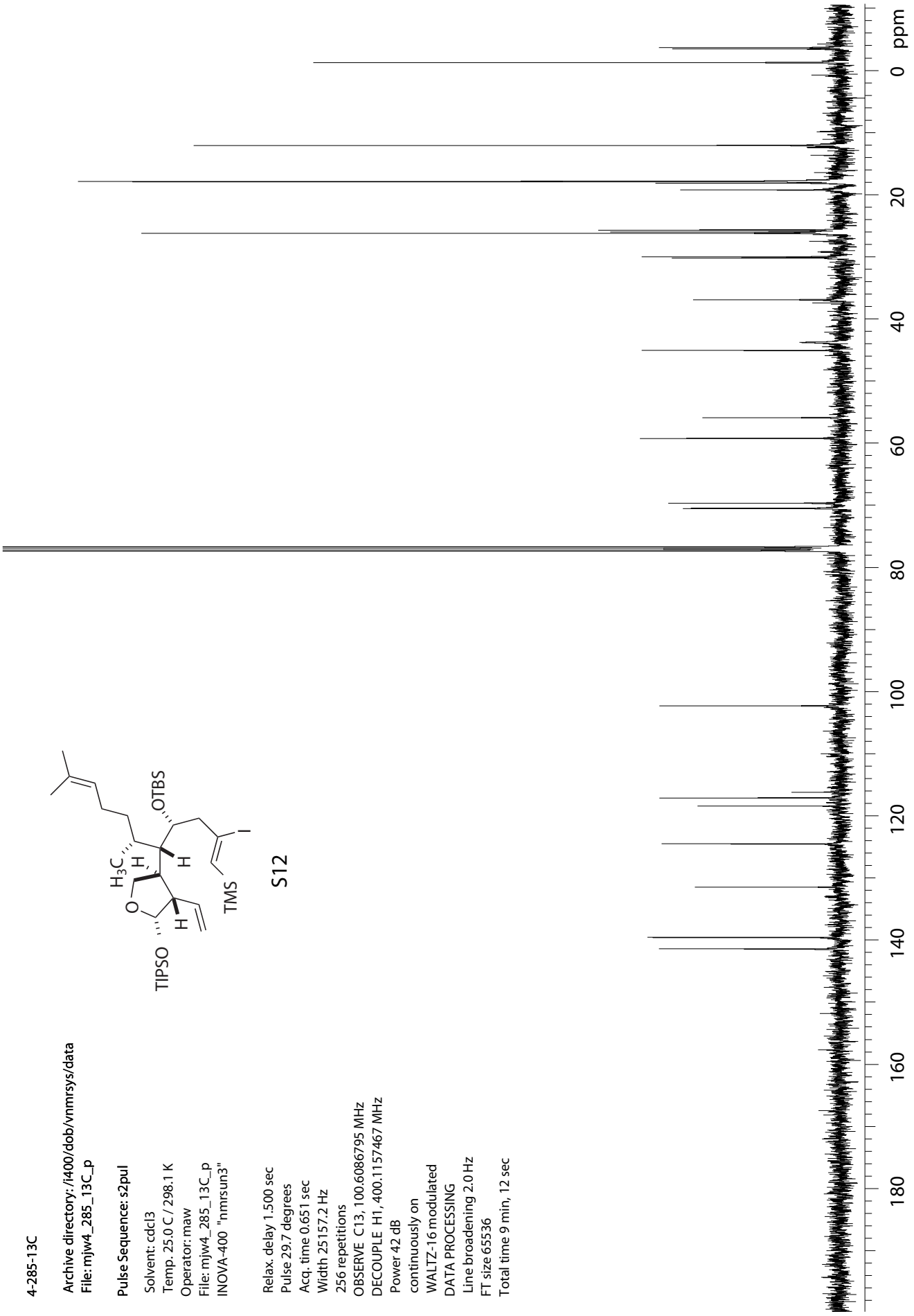
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.6 degrees
Acq. time 0.655 sec
Width 25000.0 Hz
469 repetitions
OBSERVE C13, 100.5065640 MHz
DECOUPLE H1, 399.7096465 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 18 min, 28 sec




30


4-239-1H
File: mjw4_239_1H_p
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw4_239_1H_p
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 7996.8 Hz
16 repetitions
OBSERVE H1, 499.8045942 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 55 sec
TIPSO
OTBS
TMS
S12
ppm


4-285-13C
Archive directory: /i400/dob/vnmrsys/data
File: mjw4_285_13C_p
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw4_285_13C_p
INOVA-400 "nmrsun3"
Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
256 repetitions
OBSERVE C13, 100.6086795 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 9 min, 12 sec
OTBS
TIPSO
TMS
S12
ppm
0
20
40
60
80
100
120
140
160
180

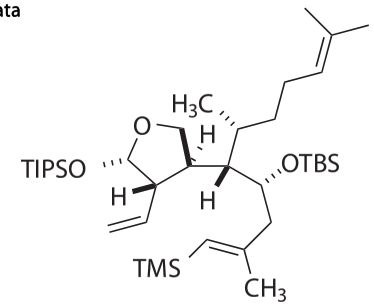
4-238-1H

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.003 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.1137400 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 48 sec




S13

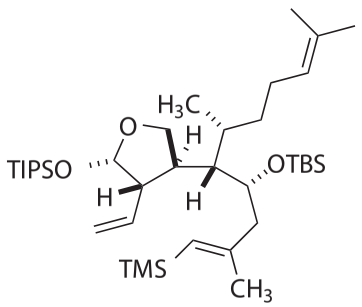
4-238-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
1024 repetitions
OBSERVE C13, 100.6082852 MHz
DECOUPLE H1, 400.1157467 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 36 min, 51 sec




S13

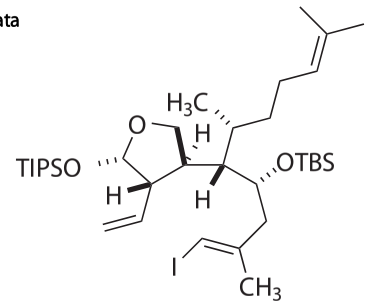
5-24-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 399.7076397 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




31

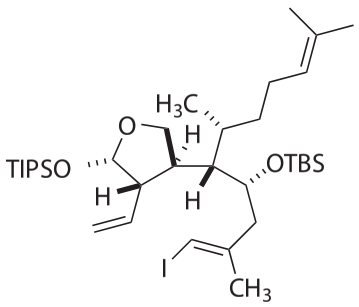
4-278-13C

Archive directory: /vxr400/maw/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.6 degrees
Acq. time 0.655 sec
Width 25000.0 Hz
393 repetitions
OBSERVE C13, 100.5065655 MHz
DECOUPLE H1, 399.7096465 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 36 min, 56 sec




31

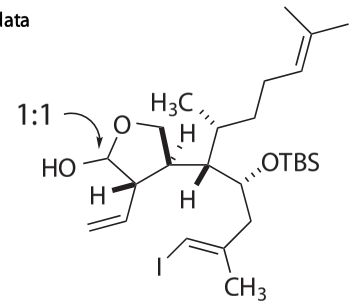
5-163-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1085059 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




S18

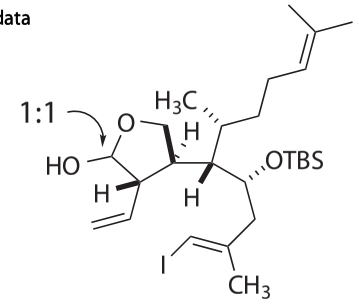
5-163-13C

Archive directory: /i400/dob/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
274 repetitions
OBSERVE C13, 100.6073671 MHz
DECOUPLE H1, 400.1105092 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 18 min, 25 sec




S18

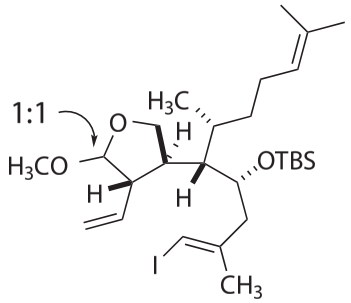
5-210-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1084593 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec



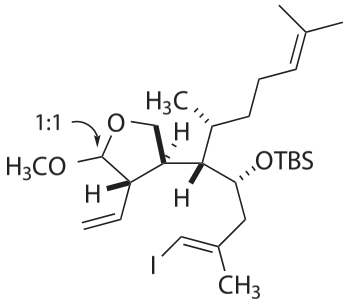

39

5-162-13C

**Pulse Sequence: s2pul**

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: mjw5_162_13C_p
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.6 degrees
Acq. time 0.868 sec
Width 18864.9 Hz
16287 repetitions
OBSERVE C13, 75.4519967 MHz
DECOUPLE H1, 300.0688577 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 16 hr, 54 min, 19 sec




39

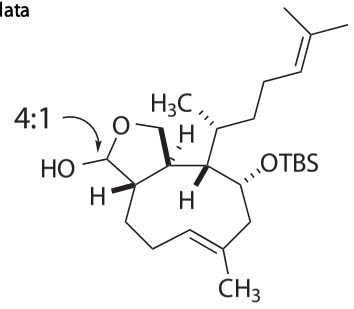
6-17-1H

Archive directory: /vxr400/vnmr1/vnmrsys/data
File:

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083663 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec




38

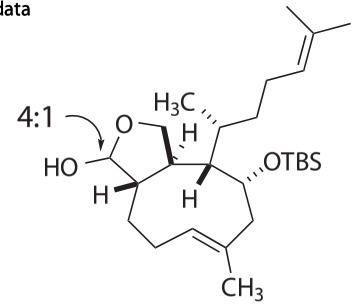
6-17-13C

Archive directory: /i400/dob/vnmrsys/data
File:

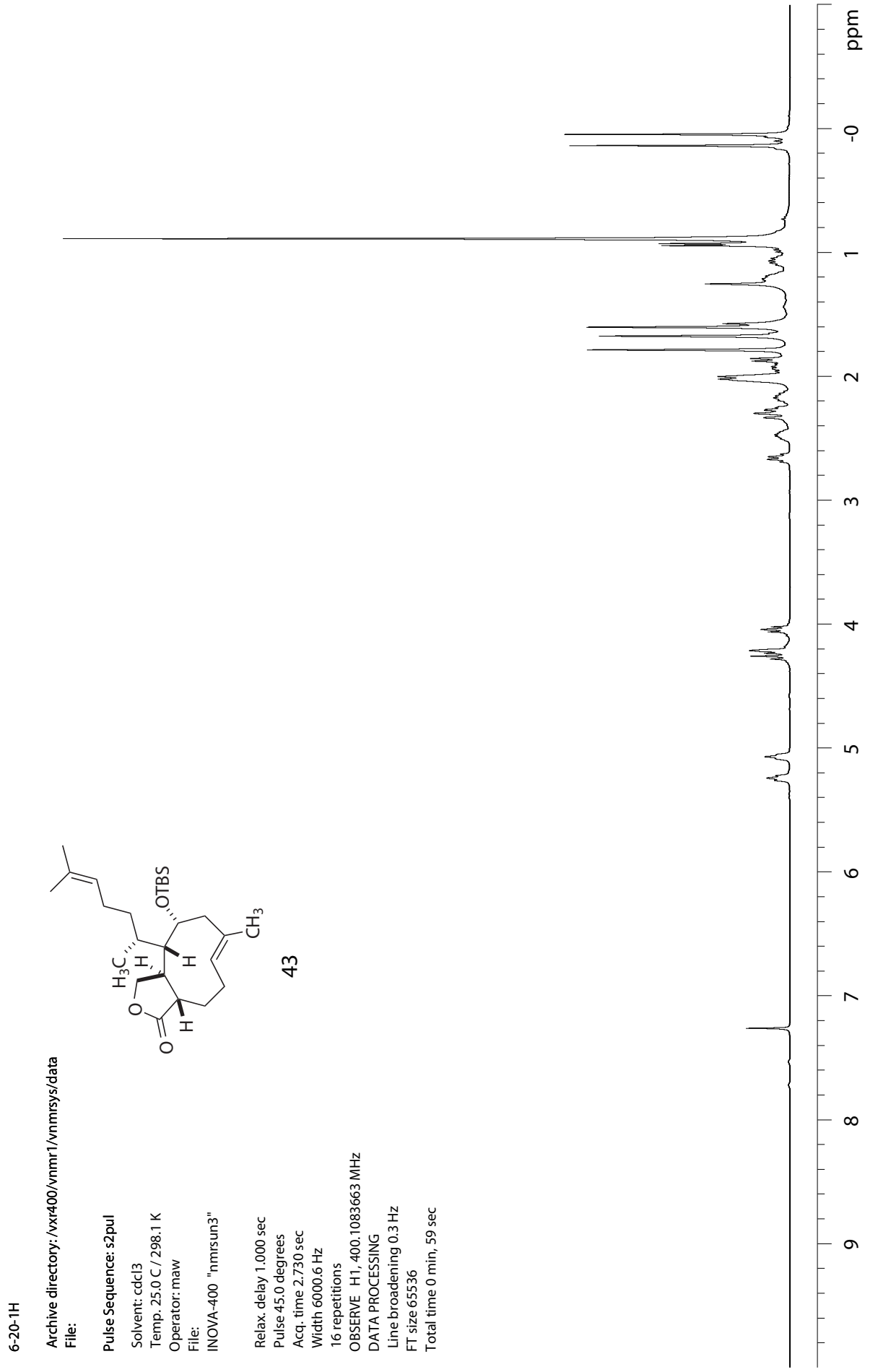
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
1334 repetitions
OBSERVE C13, 100.6073289 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec




38


6-20-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083663 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
OTBS
$H_3C$
$CH_3$
O
O
H
H
H
43
9
8
7
6
5
4
3
2
1
-0
ppm

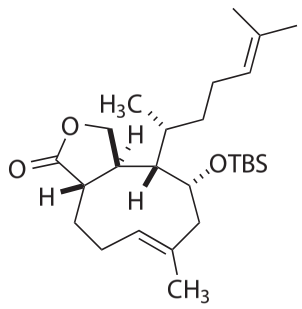
6-20-13C

Archive directory: /i400/dob/vnmrsys/data
File:

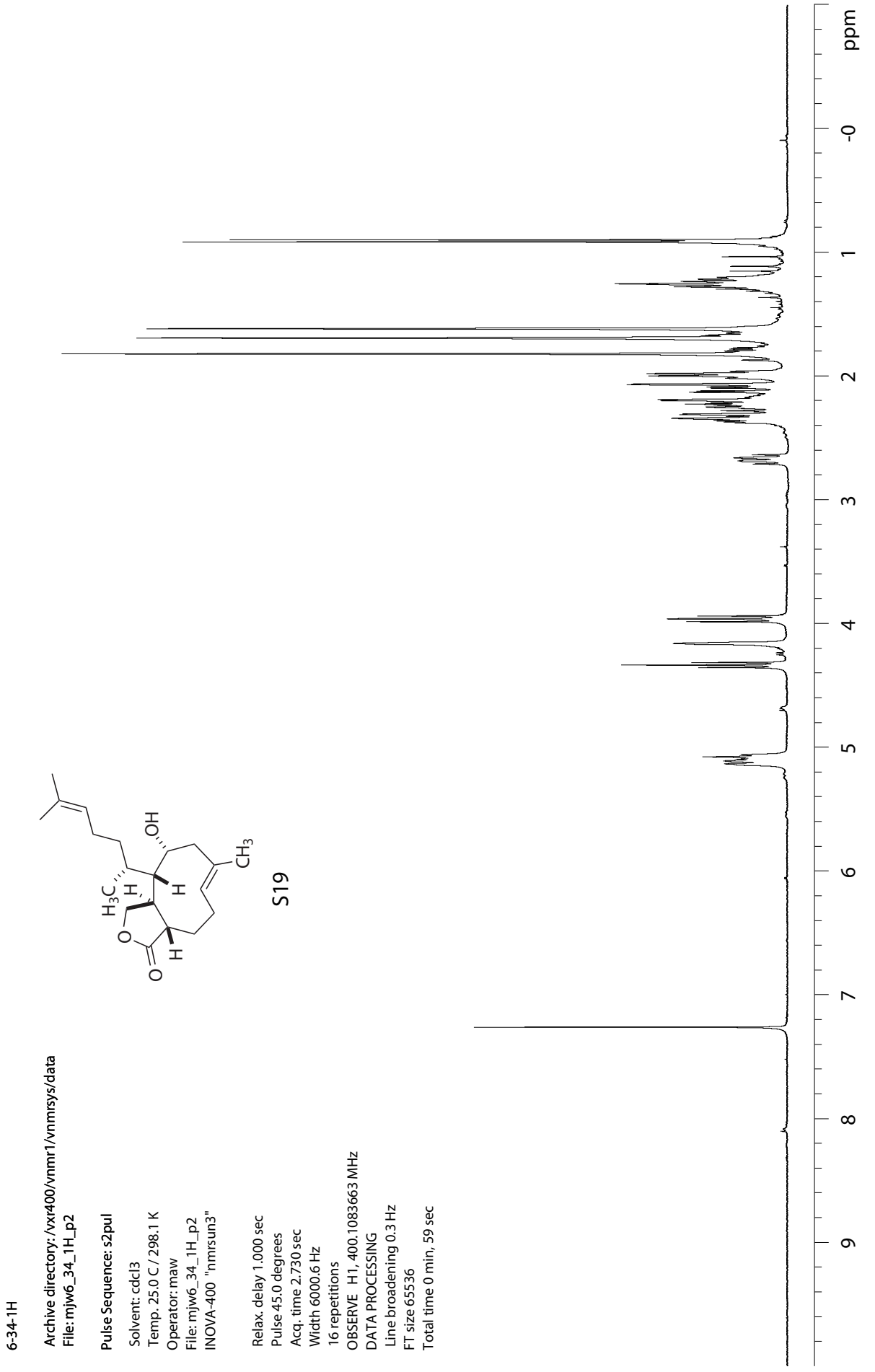
Pulse Sequence: s2pul

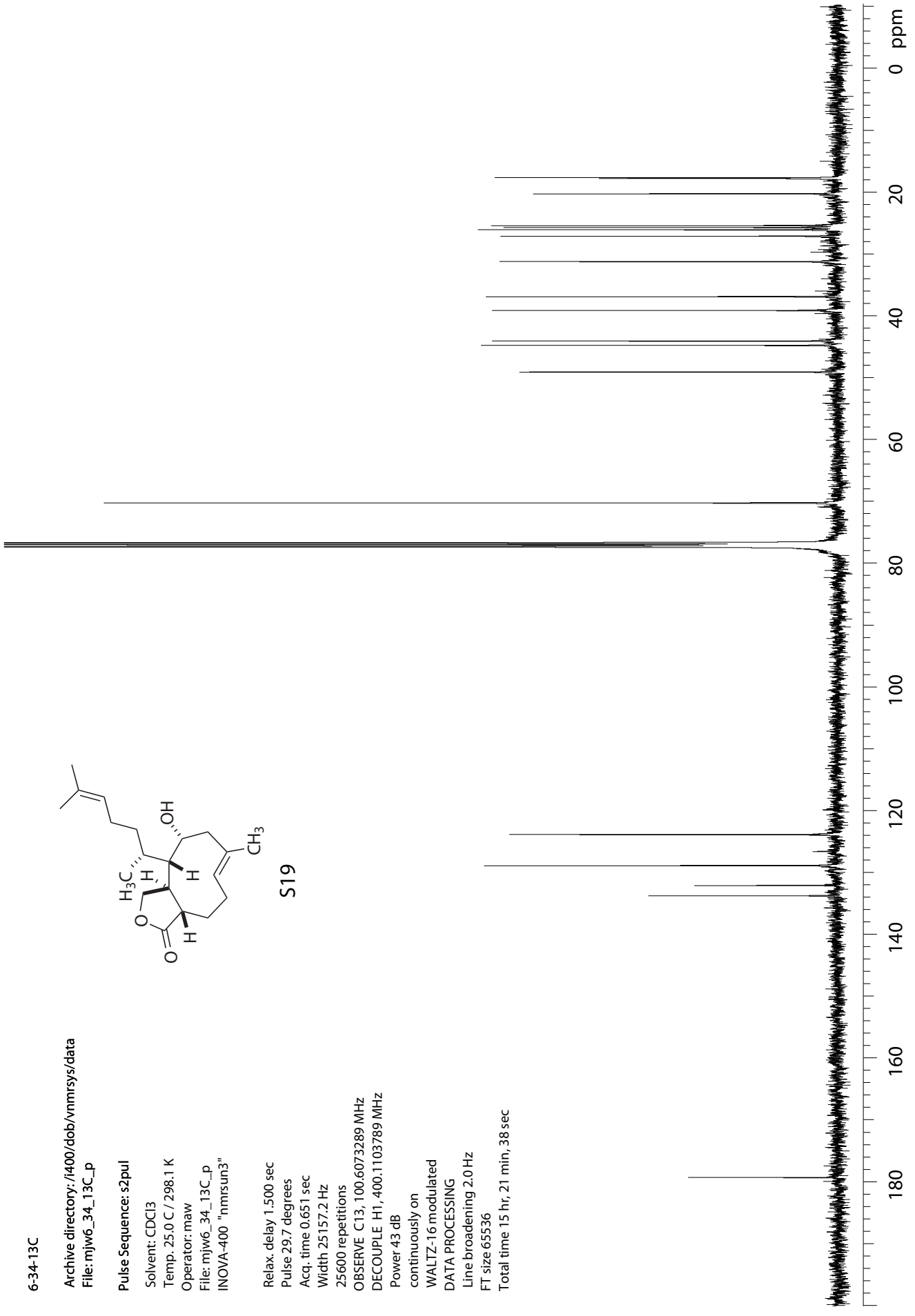
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: maw
File:
INOVA-400 "nmrsun3"

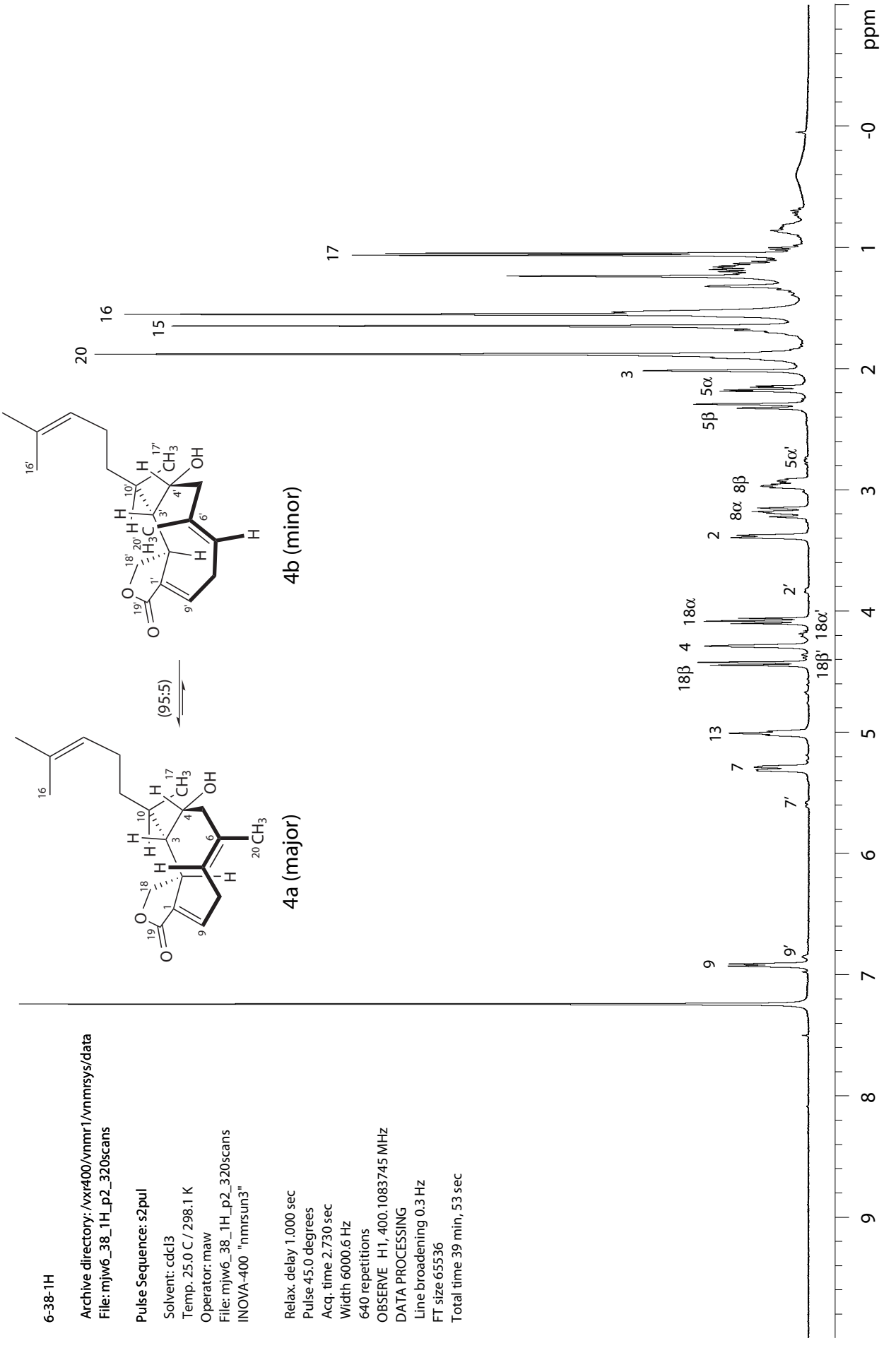
Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
2161 repetitions
OBSERVE C13, 100.6073289 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 32 min, 9 sec




43


6-34-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File: mjw6_34_1H_p2
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw6_34_1H_p2
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
16 repetitions
OBSERVE H1, 400.1083663 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 59 sec
OH
CH3
H3C
H
O
O
H
H
S19
ppm
9
8
7
6
5
4
3
2
1
-0


6-34-13C
Archive directory: /i400/dob/vnmrsys/data
File: mjw6_34_13C_p
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw6_34_13C_p
INOVA-400 "nmrsun3"
Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 0.651 sec
Width 25157.2 Hz
25600 repetitions
OBSERVE C13, 100.6073289 MHz
DECOUPLE H1, 400.1103789 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 15 hr, 21 min, 38 sec
OH
CH3
H3C
H
H
H
O
O
S19
180
160
140
120
100
80
60
40
20
0 ppm


6-38-1H
Archive directory: /vxr400/vnmr1/vnmrsys/data
File: mjw6_38_1H_p2_320scans
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: maw
File: mjw6_38_1H_p2_320scans
INOVA-400 "nmrsun3"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.730 sec
Width 6000.6 Hz
640 repetitions
OBSERVE H1, 400.1083745 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 39 min, 53 sec
4a (major)
(95:5)
4b (minor)
ppm

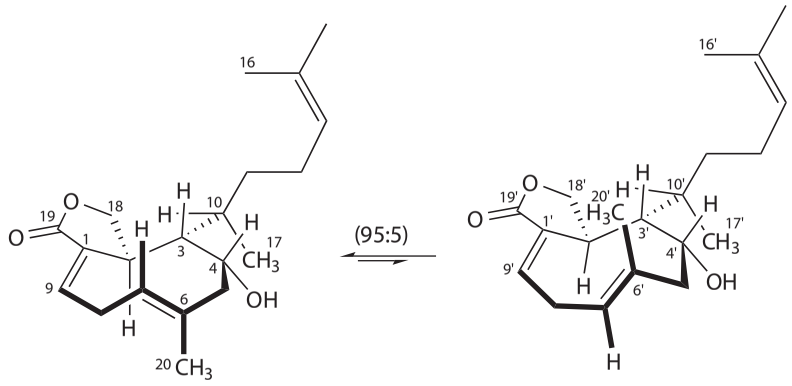
6-38-13C

File: mjw6_38_13C_p

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: majwalsh
File: mjw6_38_13C_p
INOVA-400 "nmrsun3"

Relax. delay 1.500 sec
Pulse 29.7 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
85867 repetitions
OBSERVE C13, 125.6759644 MHz
DECOUPLE H1, 499.8070831 MHz
Power 46 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 780382 hr, 34 min, -8 sec




4a (major) 4b (minor)