Supporting Information:

Exploiting orthogonally reactive functionality: synthesis and stereochemical assignment of (-)-ushikulide A

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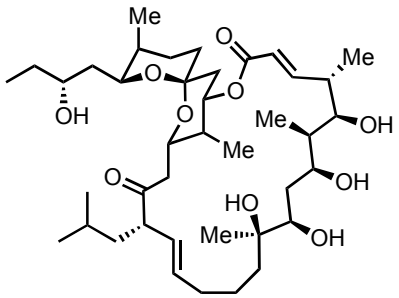


Ushikulide A

General: All reactions were run under an atmosphere of nitrogen unless otherwise indicated. Anhydrous solvents were transferred via oven-dried syringe or cannula. Flasks were flame-dried under vacuum and cooled under a stream of nitrogen or argon. Tetrahydrofuran (THF), and dimethoxyethane (DME), benzene, pyridine, diisopropylamine, triethylamine, diisopropylethylamine, and dimethylsulfoxide, acetonitrile, hexane, toluene, diethyl ether, and dichloromethane were purified with a Solv-Tek solvent purification system by passing through a column of activated alumina. Acetone was distilled from calcium sulfate. Methanol was distilled from magnesium methoxide.

Where indicted, solvents are degassed via freezing in liquid nitrogen and thawing under high vacuum. The above cycle is repeated three times, unless otherwise indicated.

Analytical thin layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (DC-Fertigplatten Krieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still. Solvents for chromatography are listed as volume:volume ratios.

Melting points were determined on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Elemental analyses were performed by M-H-W Laboratories, Phoenix, Arizona. High resolution mass spectra (HRMS) were obtained from the Mass Spectrometry Regional Center of the University of California-San Francisco on a Kratos MS-90 mass spectrometer with an ionizing current of 98 A and an ionizing voltage of 79 eV and reported as m/e (relative intensity). Accurate masses are reported for the molecular ion (M^+) or a suitable fragment ion. Low resolution CI mass spectral data was obtained using an AX-505H mass spectrometer (JEOL, USA, Inc.).

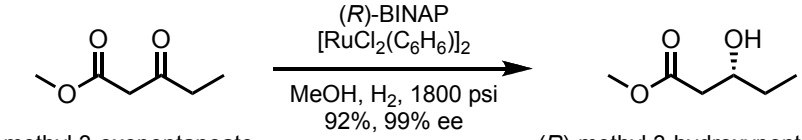
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Varian UI-600 (600 MHz), UI-500 (500 MHz) or Varian MERC-400 (400 MHz). Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from tetramethylsilane (TMS) relative to the singlet at 7.27 ppm for deuterochloroform. Coupling constants are reported in Hertz (Hz). The following abbreviations are used: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet.

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Varian UI-600 (150 MHz), Varian UI-500 (125 MHz) or Varian MERC-400 (100 MHz). Chemical shifts are reported in

delta (δ) units, part per million (ppm) relative to the center line of the triplet at 77.0 ppm for deuterochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

Other refences used: C_6D_6 [7.16 ppm, 128.0 ppm], d^6 Acetone [2.10 ppm, 206.3 ppm], CD_3OD [3.30 ppm, 55.0 ppm].

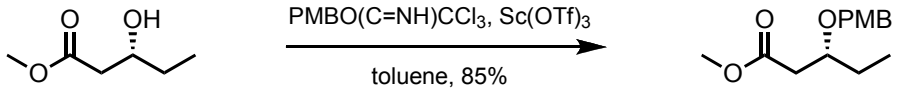
Optical rotation data was obtained with a Jasco DIP-360 digital polarimeter at the sodium D line (589 nm) in the solvent and concentration indicated.



methyl 3-oxopentanoate (*R*)-methyl 3-hydroxypentanoate

Methyl (3*R*)-3-hydroxypentanoate: Reaction is carried out according to a known procedure.[1] A flask is charged with (*R*)-BINAP (21.0mg) and $[RuCl_2(C_6H_6)]_2$ (7.6mg). Degassed DMF is injected and the red homogenous solution is heated to 100 °C in an oil bath for 15 minutes. DMF is removed under reduced pressure and this catalyst is used directly. In a separate flask methyl 3-oxopentanoate (5.02mL) and methanol (5mL) are degassed by freeze-pump-thaw method and transferred into the catalyst mixture. With some heating, a homogenous mixture is formed and this is transferred into a high pressure bomb-reactor. The reactor is pressurized to ~1800 psi and excess pressure is bleed off. This is repeated 3 times and on the third cycle the reactor is sealed and heated to 60 °C for 16 hours. The reactor is allowed to cool and then gas is released. The homogenous solution is purified by distillation: first methanol is distilled off, and then the product at reduced pressure (bp: 82-85 °C, 20 mmHg). Methyl (3*R*)-3-hydroxypentanoate distills as a clear liquid (4.690g, 92%, 99% ee), which corresponds to the known compound in all respects.

IR (neat): 3445 (broad), 2960, 1737 (sharp) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.01-3.85 (m, 1H), 3.70 (s, 3H), 2.92 (d, *J*=3.7 Hz, 1H), 2.57-2.47 (m, 1H), 2.40 (ddd, *J*=16.4, 9.2, 1.5 Hz, 1H), 1.69-1.31 (m, 2H), 0.95 (t, *J*=7.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.45, 69.28, 51.69, 40.64, 29.35, 9.77 ppm.



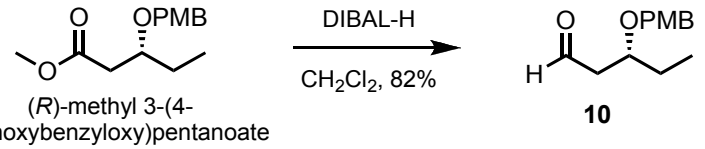
(*R*)-methyl 3-hydroxypentanoate (*R*)-methyl 3-(4-methoxybenzyloxy)pentanoate

Methyl (3*R*)-3-[(4-methoxybenzyl)oxy]pentanoate: Scandium (III) triflate is weighed out in the glovebox (206.0mg, 0.42mmoles) and dissolved in a minimum amount acetonitrile (~1mL). A solution of methyl (3*R*)-3-hydroxypentanoate (5.53g, 41.81mmoles) and PMB imidate (17.72g, 62.72mmoles) are dissolved in toluene (400mL) and cooled to 0 °C. The scandium triflate solution is injected and the reaction is stirred for 3 hours before saturated sodium bicarbonate (100mL) is used to quench the reaction. The organic phase is washed with brine, dried and concentrated onto silica gel. Flash chromatography (7:1 Hexane/EtOAc) gives the product as a yellow oil (9.064g, 85%).

r_f=0.19 (7:1 Hexane/EtOAc); $[\alpha]_D$ = -5.7° (c=0.95, $CHCl_3$); IR (neat): 2960, 1734 (sharp) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J*=8.7Hz, 2H), 6.86 (d, *J*=8.6Hz, 2H), 4.47 (s, 2H), 3.95-3.71 (m, 4H), 3.67 (s, 3H), 2.59 (dd, *J*=15.1, 7.5Hz, 1H), 2.46 (dd, *J*=15.1, 5.3Hz, 1H), 1.73-1.49 (m, 2H), 0.93 (t, *J*=7.4Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.28, 159.08, 130.61, 129.28, 113.67, 76.73,

[1] Kitamura, M., Tokunaga, M., Ohkuma, T., Noyori, R.; *Organic Syntheses,* **1993**, *71*, 1.

71.10, 55.21, 51.55, 39.28, 26.93, 9.38 ppm; HRMS (EI+) calc'd for $C_{14}H_{20}O_4$ $(M)^+$ 252.1362, found 252.1360.

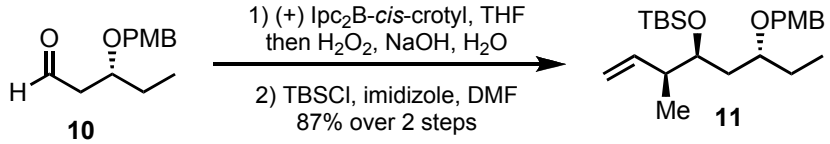


(*R*)-methyl 3-(4-methoxybenzyloxy)pentanoate

10

(3R)-3-[(4-methoxybenzyl)oxy]pentanal (10): A flask containing methyl (3*R*)-3-[(4-methoxybenzyl)oxy]pentanoate (1.532g, 6.07mmoles) is flushed with nitrogen and methylene chloride (15mL) is injected. The solution is cooled in an acetone/dry ice bath and DIBAL-H (8mL, 1.0M in toluene) is injected dropwise. The reaction is stirred at -78 ˚C for 3 hours and then quenched with methanol. After warming, a saturated sodium potassium tartrate solution is added (~5mL) and the biphasic mixture is stirred vigorously for two hours. The organic phase is diluted with diethyl ether and washed with brine, then dried over sodium sulfate, filtered and concentrated. Flash chromatography (7:1 Hexane/EtOAc) gives aldehyde **10** as a clear yellow oil (1.256g, 82%).

r_f=0.22 (8:1 Hexane/EtOAc); $[\alpha]_D$ = +20° (c=0.54, $CHCl_3$); IR (neat): 2965, 2837, 1718 (sharp), 1515, 1247, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.79 (dd, *J*=2.6, 1.9Hz, 1H), 7.24 (d, *J*=8.3Hz, 2H), 6.87 (d, *J*=8.7Hz, 2H), 3.92-3.84 (m, 3H), 3.80 (s, 3H), 2.66 (ddd, *J*=16.3, 7.5, 2.6Hz, 1H), 2.53 (ddd, *J*=16.3, 4.6, 1.9Hz, 1H), 1.79-1.54 (m, 2H), 0.94 (t, *J*=7.4Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.83, 159.19, 130.28, 129.33, 113.77, 74.95, 70.77, 55.23, 47.81, 26.72, 9.28 ppm; HRMS (EI+) calc'd for $C_{13}H_{18}O_3$ $(M)^+$ 222.1256, found 222.1259.



10 **11**

Alkene (11): First a solution of the crotyl borane is prepared via the procedure of Brown.[2] Potassium *tert*-Butoxide (604.8mg, 5.39mmoles) is weighed into a dry flask in the glovebox and dry THF (40mL) is injected to give a slurry of the salt. The reaction is cooled to -78 °C and a solution of *cis*-2-butene (1.07g, 26.3mmoles) in THF (10mL) is injected, followed by *n*-BuLi (15.1mmoles, 6.3mmoles). The reaction is warmed to -45 °C for 15 minutes and then cooled back to -78 °C. In a separate flask (+)Ipc_2BOMe (4.973g, 15.72mmoles) is dissolved in THF (10mL) and transferred into the reaction flask. After 30 minutes $BF_3{\cdot}OEt_2$ is injected (1.57mL, 17.03mmoles). Finally, the aldehyde **10** (2.9105g, 13.10mmoles) is dissolved in THF (10mL) and transferred into the crotyl borane solution after cooling to -90 °C. After 2 hours the reaction is warmed to -78 °C for 2 more hours and then quenched with 1N NaOH (50mL) and 30% peroxide (5mL) and allowed to warm to 0 °C. After 30 minutes the reaction is diluted with $Na_2S_2O_3$ (100mL) and EtOAc (200mL) and transferred to a separatory funnel. The organics are washed with water and brine, dried over sodium sulfate, filtered and concentrated. The material thus obtained is of sufficient purity and is used in the subsequent step without further purification.

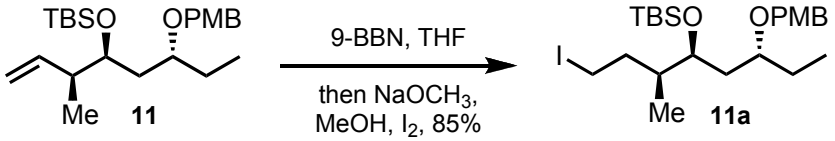
r_f=0.19 (3:1 PE/DCM); $[\alpha]_D$ = -44.3° (c=0.420, $CHCl_3$); IR (neat): 3478 (broad), 2965, 2876, 1613, 1514, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J=8.5Hz, 2H), 6.88 (d, J=8.5Hz, 2H), 5.76 (ddd, J=7.5, 10.0, 17.5Hz, 1H), 5.07-5.00 (m, 2H), 4.52 (d, J=11.0Hz, 1H), 4.45 (d, J=11.0Hz, 1H), 3.81 (s, 3H), 3.73-3.62 (m, 2H), 2.80 (d, J=3.9Hz, 1H), 2.22 (q, 1H, J=7.0Hz), 1.75-1.56 (m, 4H), 1.06 (t, J=7.6Hz, 3H), 0.91 (t, J=7.5Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 141.4, 130.8, 129.8,

[2] Brown, H.C. and Bhat, K.S.; *J. Am. Chem. Soc.* **108**, *119,* 5919-5923.

115.2, 114.1, 78.3, 71.8, 71.1, 55.6, 44.3, 36.5, 26.3, 15.6, 10.1 ppm; HRMS (EI+) calculated for $C_{17}H_{26}O_3Si$ $(M)^+$ 278.1882 found 278.1888.

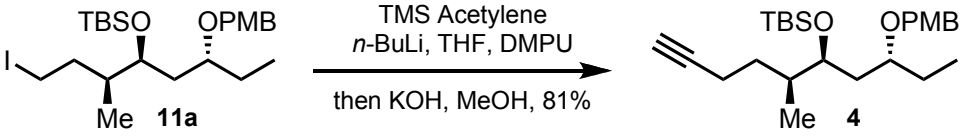
The crude alcohol is dissolved in DMF (10mL). Imidazole (2.01g, 29.5mmoles) and TBSCl (3.70g, 24.6mmoles) are added. After 6 hours the reaction is quenched with 1N sodium bisulfate solution (100mL) and washed with diethyl ether (3x50mL). The combined organics are dried over magnesium sulfate, filtered and concentrated. Flash chromatography (4% EtOAc/hexane) gives the product **(11)** as a yellow oil (3.3519, 70% over 2 steps), which is greater than 20:1 ratio of diastereomers by NMR analysis.

r_f=0.35 (2:1 PE/DCM); $[\alpha]_D$ = -30° (c=0.18, CH_2Cl_2); IR (neat): 2957, 1514 cm^{-1}; ^1H NMR (500 MHz, C_6D_6): δ 7.28 (d, J=8.5Hz, 2H), 6.88 (d, J=8.5Hz, 2H), 5.97 (ddd, J=7.5, 10.0, 17.5Hz, 1H), 5.06-4.98 (m, 2H), 4.51 (d, J=11.0Hz, 1H), 4.36 (d, J=11.0Hz, 1H), 3.86-3.81 (m, 4H), 3.52-3.46 (m, 1H), 2.38-2.33 (m, 1H), 1.67-1.56 (m, 3H), 1.41 (dddd, J=3.2, 8.6, 14.2, 18.7Hz, 1H), 1.00-0.85 (m, 15H), 0.06 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 158.9, 140.8, 131.3, 129.0, 114.0, 113.7, 76.9, 73.2, 69.8, 55.3, 43.0, 37.8, 26.3, 26.0,18.1, 14.2, 9.1, -4.0, -4.4 ppm; HRMS (EI+) calculated for $C_{23}H_{40}O_3NaSi$ $(M+Na)^+$ 415.2644 found 415.2639.



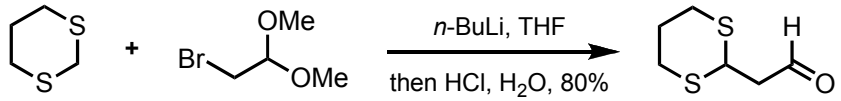
Primary Iodide (11a): 9-BBN (490.9mg, 4.02mmoles) is added to a cooled (0 °C) solution of alkene **11** (1.317g, 3.35mmoles) in THF (10mL). After 30 minutes the solution is allowed to warm to room temperature and stirring is continued for 6 hours. After recooling to 0 °C a solution of sodium methoxide in dry methanol (2M, 6mL, 12.0mmoles) is injected followed by solid iodine (2.989g, 11.73mmoles). After 30 minutes the reaction is quenched with an aqueous solution of saturated sodium thiosulfate (50mL). After vigorous stirring (~10min), the biphasic solution is diluted with ethyl acetate (100mL). The organics are washed with water and brine (50mL portions) and the organic phase is dried over sodium sulfate filtered and concentrated. The crude product is purified by flash chromatography (4% EtOAc/hexane) yielding the primary iodide **11a** (1.409g, 85%).

r_f=0.19 (40:1 PE/EtOAc); $[\alpha]_D$ = +16° (c=0.41, CH_2Cl_2); IR (neat): 2930, 2856, 1508 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ7.26 (d, *J*=8.7Hz, 2H), 6.87 (d, *J*=8.7Hz, 2H), 4.45 (d, *J*=11.2Hz, 1H), 4.39 (d, *J*=11.2Hz, 1H), 3.81 (s, 3H), 3.68 (dt, *J*=6.5, 2.2Hz, 1H), 3.38-3.31 (m, 1H), 3.24 (ddd, *J*=9.5, 8.5, 4.9Hz, 1H), 3.09 (td, *J*=9.5, 7.7Hz, 1H), 2.05-1.91 (m, 2H), 1.74-1.46 (m, 12H), 0.92 (t, *J*=7.4Hz, 3H), 0.87 (s, 9H), 0.80 (d, *J*=6.4Hz, 3H), 0.04 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ159.02, 131.07, 129.31, 113.68, 76.90, 71.93, 70.34, 55.30, 38.38, 37.76, 36.83, 26.31, 25.90, 25.19, 18.03, 12.94, 9.34, 5.92, -4.24, -4.37 ppm; HRMS (EI+) calculated for $C_{23}H_{39}IO_3Si$ $(M-H)^+$ 519.1760, found 519.1771.



Alkyne (4): A solution of TMS Acetylene (4.8 mL, 33.8 mmoles) in THF (40 mL) is treated with *n*-BuLi (12.8 mL, 30.0 mmoles) at -78 °C and the solution is allowed to warm to ambient temperature. This solution is then transferred into a DMPU solution (20 mL) of the iodide **11a** (8.786 g, 16.88 mmoles) at ambient temperature. After 18 hours the reaction is quenched with a solution of potassium hydroxide in methanol (47 mL, 2M solution). After 2 hours the reaction is diluted with water and diethyl ether. The organics are washed with brine and dried over magnesium sulfate, filtered and concentrated. Flash chromatography (3% EtOAc/PE) gives alkyne **4** as a clear oil (5.701 g, 81%).

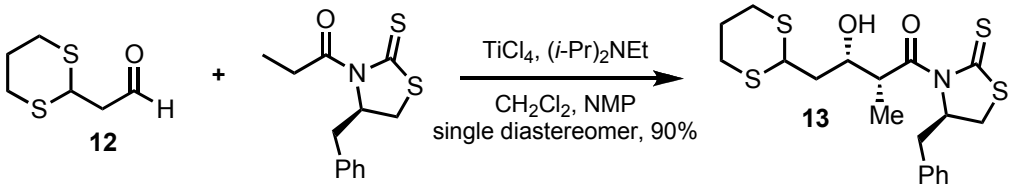
r_f=0.22 (2:1 Hexane/Benzene); $[\alpha]_D$ = -32.5° (c=1.13, CH_2Cl_2); IR (neat): 3312, 2957, 2858, 1613, 1514, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, *J*=8.7Hz, 2H), 6.87 (d, *J*=8.7Hz, 2H), 4.44 (d, *J*=11.2Hz, 1H), 4.40 (d, *J*=11.2Hz, 1H), 3.81 (s, 3H), 3.69 (dt, *J*=6.8, 2.6Hz, 1H), 3.40-3.33 (m, 1H), 2.23 (dddd, *J*=16.6, 8.3, 5.7, 2.6Hz, 1H), 2.12 (dtd, *J*=10.6, 7.9, 2.7Hz, 1H), 1.92 (t, *J*=2.6Hz, 1H), 1.80-1.63 (m, 1H), 1.63-1.43 (m, 1H), 1.40-1.28 (m, 1H), 0.93 (t, *J*=7.4Hz, 3H), 0.88 (s, 9H), 0.82 (d, *J*=6.8Hz, 3H), 0.04 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.99, 131.12, 129.28, 113.66, 84.72, 77.04, 72.38, 70.33, 68.18, 55.25, 37.49, 36.56, 31.17, 26.33, 25.91, 18.05, 16.52, 13.51, 9.39, -4.29, -4.37 ppm; HRMS (EI+) calculated for $C_{21}H_{33}O_3Si$ $(M–t\text{-}Bu)^+$ 361.2199, found 361.2206.



12

1,3-dithian-2-ylacetaldehyde (12): A dry 100 mL flask is charged with 1,3 dithiane (2.0106g, 16.7mmoles) and dry THF (40 mL). After cooling to -78 °C, *n*-BuLi is injected (7mL, 16.7mmoles). The cooling bath is removed and the reaction is allowed to warm to ambient temperature for 1 hour. After recooling (-78 °C) 1-bromo-2,2'-dimethoxy ethane is injected (1.64mL, 13.91mmoles) and the reaction is stirred at room temperature for 3 hours. The reaction is then quenched with a 50% aqueous HCl solution (10mL), followed by 18 hours of stirring at ambient temperature. The mixture is transferred to a separatory funnel and diluted with water (100mL) and ethyl acetate (150mL). The organic phase is dried over magnesium sulfate, filtered and concentrated to yield the crude product, which is further purified by flash chromatography (4:1 Hexane/EtOAc) to yield 1.802g (80%) of aldehyde **12** as a yellow oil.

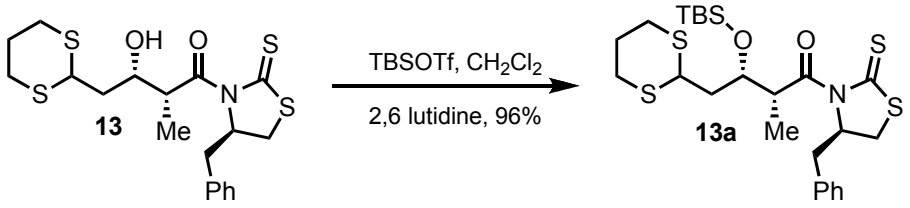
r_f=0.25 (4:1 Hexane/EtOAc); IR (neat): 2900, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.74 (t, *J*=1.8Hz, 1H), 4.51 (t, *J*=6.9Hz, 1H), 3.00-2.83 (m, 4H), 2.80 (dd, *J*=6.9, 1.8Hz, 2H), 2.17-2.07 (m, 1H), 1.95-1.81 (m, 1H), 1.56 (d, *J*=0.8Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.01, 48.19, 40.09, 30.01, 24.92 ppm.



Aldol Adduct (13): The chiral auxiliary (809.4mg, 3.05mmoles) is dissolved in dry dichloromethane (15mL) and cooled to 0 °C. Titanium tetrachloride is injected (335µL, 3.05mmoles) and the reaction is stirred for 15 minutes. DIPEA (0.7mL, 3.05mmoles) is injected and the reaction is stirred for an additional 20 minutes at 0 °C and then cooled to -78 °C. NMP (0.3mL, 3.05mmoles) is injected followed immediately by the aldehyde **12** (449.5mg, 2.77mmoles) in dichloromethane (5mL). The reaction is stirred for 2 hours at -78 °C and 30 minutes at 0 °C. After this time TLC indicates consumption of starting material and the reaction is poured into a saturated ammonium chloride solution (25mL). After dilution with ethyl acetate (50mL) the biphasic mixture is transferred to a separatory funnel and the aqueous phase is separated. The organic phase is washed with 1N HCl (10mL) and saturated sodium bicarbonate (10mL). The organic phase is dried over magnesium sulfate, filtered and concentrated under reduced pressure. Flash chromatography (2:1 EtOAc/Hexane) provides aldol adduct **13** as a yellow foam (1.174g, 90%).

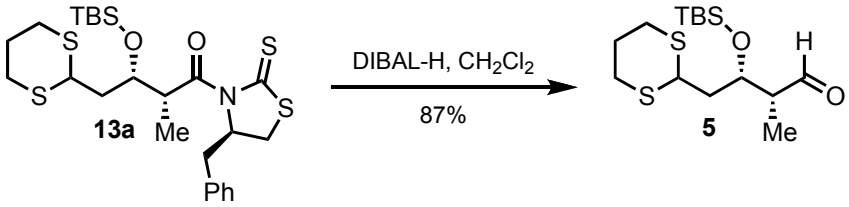
r_f=0.28 (7:3 Hexane/EtOAc); $[\alpha]_D$ = -120° (c=1.67 $CHCl_3$); IR (neat): 3456, 2900, 1691 (sharp) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.36-7.33 (m, 2H), 7.30-7.20 (m, 3H), 5.36 (ddd, J=4.0, 6.8, 15.2Hz, 1H), 4.47 (ddd, J=3.3, 6.9, 13.8Hz, 1H), 4.28-4.22 (m, 2H), 3.43 (ddd, J=0.6, 7.1, 12.5Hz, 1H), 3.19 (dd,

J=3.9, 13.2Hz, 1H), 3.06-3.01 (m, 2H), 2.95-2.82 (m, 5H), 2.14-2.10 (m, 1H), 2.01 (ddd, J=4.7, 9.7, 19.0Hz, 1H), 1.91-1.88 (m, 1H), 1.78 (ddd, J=6.6, 9.8, 11.1Hz, 1H), 1.28 (t, J=9.0Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.6, 177.9, 136.5, 129.7, 129.2, 127.5, 69.3, 68.9, 44.1, 43.5, 39.9, 37.0, 32.3, 30.5, 30.1, 26.1, 11.2 ppm; HRMS (ESI+) calculated for $C_{19}H_{25}O_2S_4Na$ $(M+Na)^+$ 450.0666, found 450.0663.



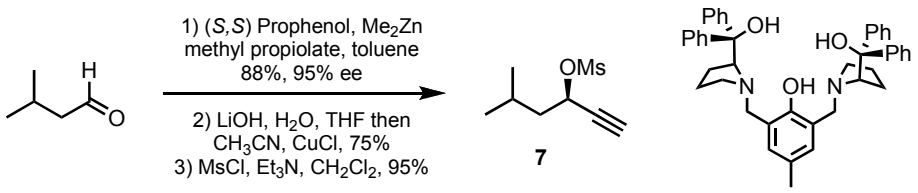
Silyl Ether (13a): A solution of the Aldol product **13** (1.1742g, 2.75mmoles) and 2,6-lutidine (0.96mL, 8.25mmoles) in dry dichloromethane (15mL) is cooled to -78 °C and treated with TBSOTf (0.95mL, 4.11mmoles). The reaction is transferred to a dry ice/acetonitrile bath (-45 °C) and stirring is continued for 2 hours. TLC shows consumption of the starting material and the reaction is quenched with several drops of methanol and allowed to warm. The solvent is removed under reduced pressure and the residue is purified by flash chromatography (10% EtOAc/Hexane) to yield silyl ether **13a** as a yellow oil (1.556g, 96%).

IR (neat): 2931, 1699 (sharp) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.24 (m, 5H), 5.20 (ddd, *J*=10.6, 6.7, 3.7Hz, 1H), 4.61 (dq, *J*=6.8, 4.9Hz, 1H), 4.23 (dd, *J*=10.9, 5.1Hz, 1H), 4.07 (t, *J*=6.9Hz, 1H), 3.35 (ddd, *J*=11.5, 6.9, 0.8Hz, 1H), 3.27 (dd, *J*=13.2, 3.6Hz, 1H), 3.03 (dd, *J*=13.1, 10.7Hz, 1H), 2.97-2.80 (m, 5H), 2.18-2.05 (m, 1H), 2.02-1.97 (m, 2H), 1.93-1.78, 1.23 (d, *J*=6.8Hz, 3H), 0.89 (s, 9H), 0.12 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 176.0, 136.4, 129.4, 128.8, 127.0, 71.2, 69.2, 44.2, 43.4, 40.4, 36.4, 31.9, 30.6, 30.1, 25.7, 17.9, 12.5, -4.5, -4.8 ppm.



Aldehyde (5): A round bottomed flask is charged with thiazolidine thione **13a** (2.221g, 4.09mmoles) and dichloromethane is injected (40mL). After cooling to -78 °C, diisobutylaluminum hydride (8.2mL, 8.2mmoles) is injected via syringe pump (10mL/hour) and the reaction is stirred for 3 hours after the addition is complete. After this time methanol is added slowly and once hydrogen evolution has ceased the solution is poured into a solution of aqueous HCl (25mL, 2M). The organic phase is diluted with ethyl acetate and washed with brine. It is then separated, dried over sodium sulfate and concentrated under reduced pressure. Flash chromatography (4:6 DCM/PE to pure DCM) gives the aldehyde **5** as a low melting yellow solid (1.186g, 87%).

r_f=0.22 (8:1 Hexane/EtOAc); $[\alpha]_D$ = -69° (c=0.11, CH_2Cl_2); IR (neat): 2930, 1726 (sharp) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 4.56 (ddd, J=3.4, 6.7, 11.1Hz, 1H), 4.04 (t, J=8.4Hz, 1H), 2.92-2.80 (m, 4H), 2.53 (ddd, J=3.2, 7.0, 10.4Hz, 1H), 2.15-2.09 (m, 1H), 1.91-1.89 (m, 3H), 1.07 (d, J=7.1Hz, 3H), 0.87 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.47, 68.57, 51.30, 43.58, 39.84, 30.40, 30.01, 25.85, 25.74, 18.01, 7.68, -4.34, -4.62 ppm; HRMS (EI+) calculated for $C_{11}H_{21}O_2S_2Si$ $(M\text{-}t\text{-}Bu)^+$ 277.0752, found 277.0738.



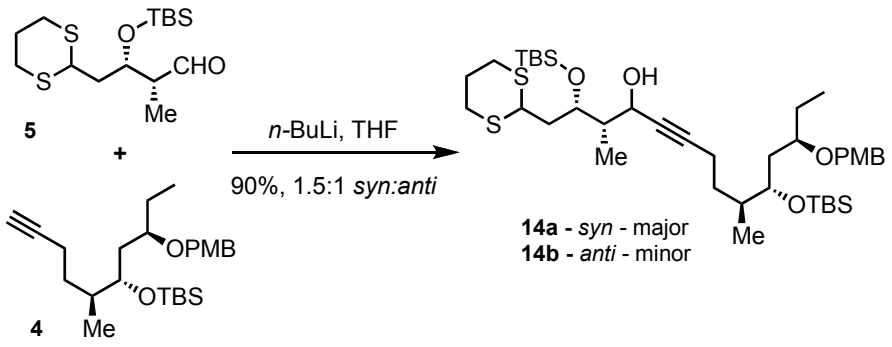
Propargyl Mesylate (7): A flask containing *(S,S)* Prophenol (479.1mg, 0.75mmoles) dissolved in dry toluene (50mL) is treated with methyl propiolate (1.87mL, 21.0mmoles) and dimethyl zinc (1.2M in hexane, 17.5mL, 21.0mmoles). After 30 minutes isovaleraldehyde is injected (804µL, 7.5mmoles). The reaction is transferred to the cold room (ca 5 ºC) and stirred for a period of 60 hours. Concentrated aqueous ammonium chloride (50mL) and diethyl ether (50mL) are added and the reaction is transferred to a separatory funnel. The organic phase is dried over magnesium sulfate, filtered and concentrated under reduced pressure (ca 100 torr). The resulting solution is purified by flash chromatography (4:1 PE/Et_2O) to yield the propargylic alcohol as a clear oil (1.1193g, 88%).

Enantiomeric excess is determined to be 95% on Chiracel OD column. 98:2 heptane/isopropanol. Flowrate=0.8mL/min. Detector set to 220nm. R_t(major S): 21.6min, R_t(minor R): 23.67min.

A solution of the resulting methyl ester (198.2mg, 1.17mmoles) is dissolved in THF (5mL) and treated with an aqueous lithium hydroxide solution (1M, 5mL). The methyl ester is consumed within 2 hours and the reaction is poured into a 1M solution of sodium bisulfate (pH=1). The resulting emulsion is diluted with ethyl acetate and the organic phase is separated and concentrated under reduced pressure. The oily residue is dissolved in acetonitrile (6mL) and copper (I) choride is added in a single portion (150.6mg, 1.52mmoles). After 3 hours the reaction is diluted with diethyl ether and brine. The organic phase is dried over magnesium sulfate, filtered and concentrated under reduced pressure. Flash chromatography (2:1 PE/Et_2O) gives the alkyne as a clear oil (98.2mg, 75%).

The alkyne (387.0mg, 2.95mmoles) is dissolved in dichloromethane (30mL) and cooled to -78 °C. Triethylamine (0.65mL, 5.90mmoles) and mesyl chloride (0.34mL, 4.43mmoles) are injected and the reaction is stirred for 1 hour and poured into water. Organics are separated and filtered though sodium sulfate. Concentration gives the crude propargyl mesylate **(7)**, which requires no further purification (533.2mg, 95%).

r_f=0.12 (9:1 Hexane/EtOAc); $[\alpha]_D$ = +102° (c=1.26, $CHCl_3$); IR (neat): 3270, 2961, 1362, 1177 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.20 (t, J=7.2Hz, 1H), 3.15 (s, 3H), 2.85 (s, 1H), 1.92-1.85 (m, 2H), 1.75-1.69 (m, 2H), 1.00-0.95 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 79.6, 76.8, 70.1, 44.2, 39.2, 24.4, 22.3, 21.9 ppm; HRMS (ESI+) calc'd for $C_8H_{14}NaO_3S$ $(M+Na)^+$ 213.0561, found 213.0558.

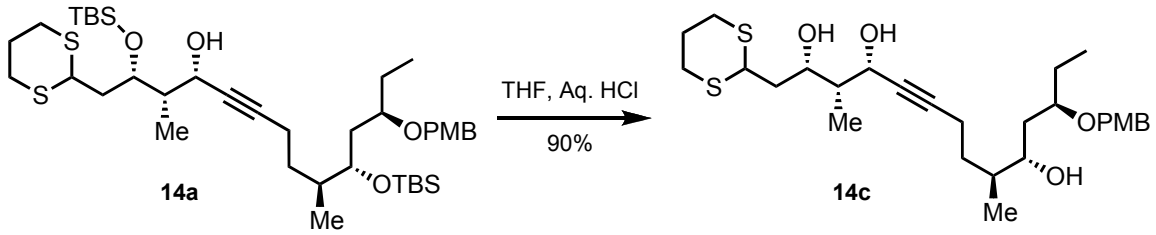


Propargyl Alcohols (14a - *syn* and 14b - *anti*): Separate round bottom flasks are charged with the alkyne **4** (465.6mg, 1.11mmoles) and the aldehyde **5** (375.2mg, 1.12mmoles). The flask containing the alkyne is charged with THF under an atmosphere of nitrogen (5mL). After cooling to -78 °C, *n*-BuLi (0.51mL, 1.22mmoles) is injected. After 1 hour the aldehyde solution in THF (5mL) is precooled

to -78 °C and transferred quickly into the reaction flask. After 2 hours the reaction is complete by TLC and it is quenched with ammonium chloride and allowed to warm to room temperature. Once warm, it is diluted with brine (25mL) and ethyl acetate (100mL). The organic phase is dried over sodium sulfate, filtered and concentrated. Flask chromatography (10:1:1 Hexane/DCM/EtOAc; 100:1 silica loading) gives minor diastereomer **(14b)** (epimeric at propagyl position, 294.4mg, 35%) followed by the major diastereomer **(14a)** (451.9mg, 55%).

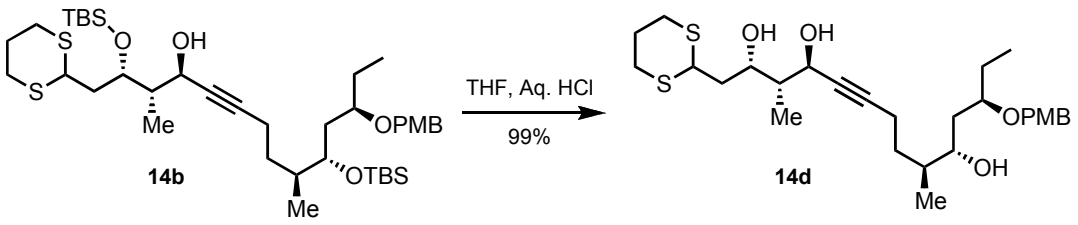
Major Diastereomer (14a): r_f=0.31 (8:1:1 Hexane/DCM/EtOAc); $[\alpha]_D$ = -19° (c=0.83, $CHCl_3$); IR (neat): 3463 (broad), 2930, 2857, 1612, 1514 cm^{-1}; ^1H NMR (500 MHz, d^6 Acetone): δ 7.28 (d, J=8.8Hz, 2H), 6.90 (d, J=8.6Hz, 2H), 4.53 (d, J=11.4Hz, 1H), 4.38-4.35 (m, 2H), 4.25 (dddd, J=2.8, 5.9, 6.8, 8.6Hz, 1H), 4.10-4.05 (m, 2H), 3.88-3.85 (m, 1H), 3.78 (s, 3H), 3.52 (ddd, 1H, J=1.6, 5.5, 7.3Hz), 2.96-2.70 (m, 6H), 2.27-2.06 (m, 3H), 1.87-1.50 (m, 10H), 1.41-1.36 (m, 1H), 1.00 (d, 3H, J=6.9Hz), 0.91 (s, 9H), 0.90 (s, 9H), 0.84 (d, 3H, J=6.7Hz), 0.16 (s, 3H), 0.14 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, d^6Acetone): δ 160.6, 132.9, 130.5, 130.2, 114.9, 86.2, 83.3, 78.0, 74.1, 74.4, 71.4, 70.6, 64.8, 56.0, 46.5, 45.1, 42.2, 39.5, 38.8, 32.4, 31.4, 31.2, 27.4, 27.4, 27.0, 26.9, 26.9, 19.3, 19.2, 18.2, 15.5, 10.1 9.9, -3.2, -3.4, -3.5, -3.6 ppm; HRMS (EI+) calculated for $C_{40}H_{73}O_5S_2Si_2$ $(M+H)^+$ 753.4438, found 753.4432.

Minor Diastereomer (14b): r_f=0.40 (8:1:1 Hexane/DCM/EtOAc); $[\alpha]_D$ = -16.5° (c=0.753, $CHCl_3$); ^1H NMR (500 MHz, d^6 Acetone): δ 7.28 (d, J=8.5Hz, 2H), 6.90 (d, J=8.4Hz, 2H), 4.52 (d, J=11.4Hz, 1H), 4.43-4.36 (m, 2H), 4.20-4.17 (m, 1H), 4.12-4.06 (m, 2H), 3.88-3.87 (m, 1H), 3-79-3.78 (m, 4H), 3.51 (ddd, 1H, J=5.4, 10.9, 12.7Hz), 2.24 (d, J=5.6Hz, 1H), 2.96-2.78 (m, 6H), 2.28-2.12 (m, 3H), 1.93-1.54 (m, 10H), 1.42-1.38 (m, 1H), 0.99 (d, 3H, J=6.9Hz), 0.94 (s, 9H), 0.93 (s, 9H), 0.87 (d, 3H, J=6.7Hz), 0.18 (s, 3H), 0.15 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, d^6Acetone): δ 160.5, 132.9, 130.2, 114.9, 86.1, 83.3, 79.0, 74.3, 70.6, 69.1, 64.2, 56.0, 46.0, 44.9, 42.1, 39.0, 38.8, 32.0, 31.4, 31.2, 27.3, 27.3, 26.9, 26.9, 26.8, 19.3, 19.2, 17.8, 15.1, 10.9, 10.1, 9.9, -3.4, -3.5, -3.6, -3.7 ppm; HRMS (EI+) calculated for $C_{40}H_{73}O_5S_2Si_2$ $(M+H)^+$ 753.4438, found 753.4452.



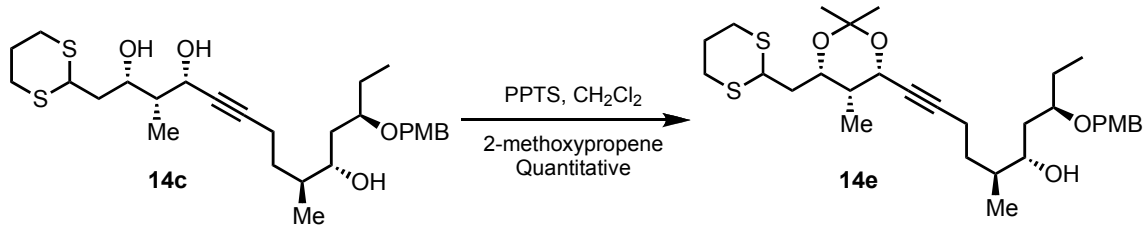
Triol (14c): The propargyl alcohol **14a** (557.2,g 0.74mmoles) is dissolved in methanol (12.5mL) and 1N HCl (7.5mL). THF (3mL) is added to give a homogenous solution which is stirred at ambient temperature for 28 hours. The reaction is quenched with sodium bicarbonate (25mL) and washed three times with EtOAc (25mL portions). The combined organic portions are dried over sodium sulfate, filtered and concentrated. Flash chromatography (1:1 EtOAc/Hexane) gives the triol **14c** as a clear oil (350.7mg, 90%).

r_f=0.25 (1:1 Hexane/EtOAc); $[\alpha]_D$ = -40.3° (c=3.79, CH_2Cl_2); IR (neat): 3432 (broad), 2936, 1612, 1514, 1249 cm^{-1}; ^1H NMR (500 MHz, d^6 Acetone): δ 7.28 (d, 2H, J=8.4Hz), 6.90 (d, 2H, J=8.5Hz), 4.52 (d, 1H, J=11.1Hz), 4.44-4.38 (m, 2H), 4.32 (d, 1H, J=5.2Hz), 4.28-4.18 (m, 2H), 3.78 (s, 3H), 3.70-3.58 (m, 3H), 3.55 (d, 1H, J=3.4Hz), 2.90-2.78 (m, 4H), 2.30-2.17 (m, 2H), 1.89-1.52 (m, 10H), 1.41-1.35 (m, 1H), 1.03 (d, 3H, J=6.9Hz), 1.02 (t, 3H, J=6.5Hz), 0.85 (J=6.7Hz); ^{13}C NMR (100 MHz, d^6Acetone): δ 160.4, 132.2, 114.8, 86.1, 82.4, 80.5, 73.3, 70.9, 70.2, 69.3, 55.9, 45.7., 44.9, 42.3, 38.8, 38.7, 33.3, 31.1, 30.8, 29.7, 27.3, 26.9, 17.5, 14.2, 9.7, 9.3 ppm.



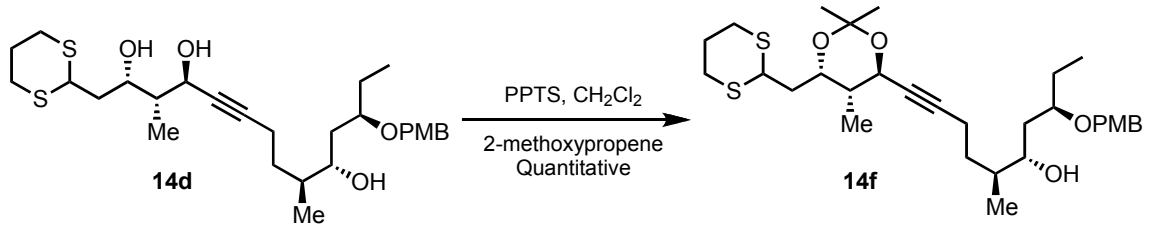
Triol (14d): The propargyl alcohol **14b** (95.3mg, 0.126mmoles) is dissolved in methanol (6mL) and 1N HCl (3mL). THF (3mL) is added to give a homogenous solution which is stirred at ambient temperature for 28 hours. The reaction is quenched with sodium bicarbonate (25mL) and washed three times with EtOAc (25mL portions). The combined organic portions are dried over sodium sulfate, filtered and concentrated. Flash chromatography (1:1 EtOAc/Hexane) gives triol **14d** as a clear oil (66.0mg, 99%)

r_f=0.25 (1:1 Hexane/EtOAc); $[\alpha]_D$ = -39° (c=0.28, CH_2Cl_2); IR (neat): 3418 (broad), 2936, 1612, 1514, 1249 cm^{-1}; ^1H NMR (500 MHz, d^6 Acetone): δ 7.30 (d, J=8.4Hz, 2H), 6.89 (d, J=8.5Hz, 2H), 4.52 (d, J=11.1Hz, 1H), 4.46-4.38 (m, 2H), 4.36-4.31 (m, 2H), 4.26 (dd, J=4.3, 10.1Hz, 1H), 3.82-3.76 (m, 4H), 3.74 (d, J=5.2Hz, 1H), 3.68-3.64 (m, 1H), 3.41 (d, J=5.2Hz, 1H), 2.98-2.76 (m, 5H), 2.32-2.08 (m, 3H), 1.88-1.50 (m, 10H), 1.41-1.38 (m, 1H), 0.99 (d, J=6.9Hz, 3H), 0.91 (t, J=6.5Hz, 3H), 0.88 (d, J=6.7Hz, 3H); ^{13}C NMR (100 MHz, d^6Acetone): δ 160.5, 132.4, 130.6, 114.9, 86.2, 82.7, 80.6, 73.2, 71.1, 68.2, 65.9, 55.9, 45.8, 45.1, 42.0, 39.0, 38.8, 33.6, 31.2, 27.4, 27.1, 17.6, 14.2, 11.2, 9.8 ppm.



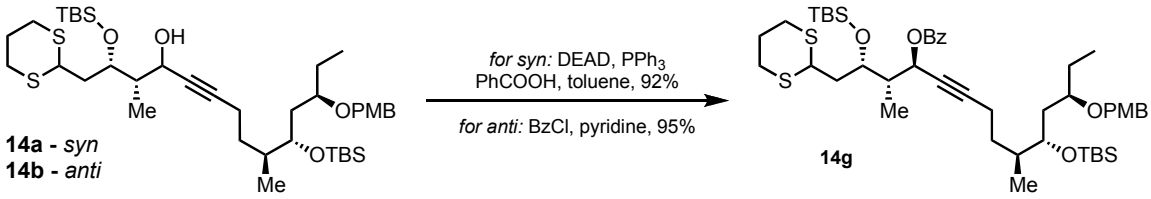
Acetonide (14e): The triol **14c** (35.7mg, 68µmoles) and PPTS (3.2mg, 13.6µmoles) are dissolved in dry dichloromethane (1.5mL) and cooled to 0 °C. 2-methoxypropene (8µL, 82µmoles) is injected. After 3 hours the reaction is quenched with 1 drop of triethylamine and solvent is removed *in vacuo*. Flash chromatography of the residue (4:1 Hexane/EtOAc) affords the acetonide **14e** as a clear oil (38mg, Quant.).

r_f=0.29 (4:1 Hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, J=8.8Hz, 2H), 6.87 (d, J=8.6Hz, 2H), 4.78 (s, 1H), 4.59 (d, J=10.8Hz, 1H), 4.36 (d, J=10.9Hz, 1H), 4.22 (dt, J=1.0, 8.5Hz, 1H), 4.12 (dd, J=5.0, 9.8Hz, 1H), 3.80 (s, 3H), 3.71-3.62 (m, 3H), 2.93-2.82 (m, 4H), 2.34-2.22 (m, 2H), 2.12 (dt, J=1.0, 14.2Hz, 1H), 1.99 (ddd, J=5.1, 9.0, 14.2Hz, 1H), 1.92-1.87 (m, 1H), 1.76-1.52 (m, 10H), 1.46 (s, 3H), 1.42 (s, 3H), 1.08 (d, J=6.8Hz, 3H), 0.92 (t, J=7.4Hz, 3H), 0.87 (d, J=6.9Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 130.3, 129.8, 114.2, 99.9, 86.9, 81.5, 78.0, 74.9, 70.5, 68.5, 66.1, 55.6, 43.4, 39.0, 38.2, 37.4, 36.6, 31.9, 30.4, 30.2, 30.1, 26.3, 26.1, 19.6, 17.1, 13.9, 9.0, 6.8 ppm; gHSQC confirms the acetonide carbons are 99.9, 30.2 and 19.6, indicative of a *cis* 1,3 diol.



Acetonide (14f): The triol **14d** (26.0mg, 49.8µmoles) and PPTS (3.2mg, 13.6µmoles) are dissolved in dry dichloromethane (1.5mL) and cooled to 0 °C. 2-methoxypropene (8µL, 82µmoles) is injected. After 3 hours the reaction is quenched with 1 drop of triethylamine and solvent is removed *in vacuo*. Flash chromatography of the residue (4:1 Hexane/EtOAc) affords the acetonide **14f** as a clear oil (28mg, Quant.).

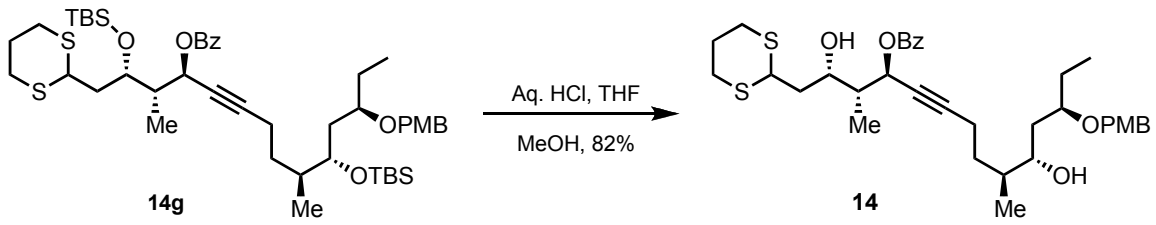
r_f=0.29 (4:1 Hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, J=8.7Hz, 2H), 6.87 (d, J=8.7Hz, 2H), 4.59 (d, J=10.8Hz, 1H), 4.44 (td, J=3.1, 14.4Hz, 1H), 4.38 (d, J=10.7Hz, 1H), 4.19 (td, J=1.9, 5.8Hz, 1H), 4.13 (dd, J=8.5, 12.6Hz, 1H), 3.80 (s, 3H), 3.70 (td, J=3.6, 9.8Hz, 1H), 3.65-3.60 (m, 2H), 2.95-2.80 (m, 4H), 2.34-2.22 (m, 2H), 2.12-2.08 (m, 1H), 1.96-1.85 (m, 3H), 1.75-1.60 (m, 8H), 1.53 (s, 3H), 1.36 (s, 3H), 0.98 (d, J=6.8Hz, 3H), 0.93 (t, J=7.4Hz, 3H), 0.87 (d, J=6.9Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 129.8, 114.2, 101.2, 86.6, 81.5, 74.8, 70.5, 66.9, 64.9, 55.5, 55.2, 43.7, 40.1, 38.2, 37.7, 37.5, 31.9, 30.6, 30.0, 27.1, 26.4, 26.1, 24.3, 17.1, 13.9, 11.9, 9.0 ppm; gHSQC confirms the acetonide carbons are 101.2, 27.1 and 24.3, indicative of a *trans* 1,3 diol.



Benzoate (14g): A solution of propargyl alcohol **14a** (1.278g, 1.69mmoles) in toluene (10mL) is cooled to -30 °C and treated with a solution of benzoic acid (310.8mg, 2.54mmoles) and triphenyl phosphine (666.2mg, 2.54mmoles) in toluene (10mL). Next, DEAD (400µL, 2.54mmoles) is injected. The reaction is allowed to warm to room temperature over 2 hours and is stirred for an additional 3 hours and then quenched with sodium bicarbonate and diluted with ethyl acetate. The organic phase is washed with water and brine, dried over magnesium sulfate and concentrated onto silica gel. Flash chromatography (9:1 Hexane/EtOAc) gives the benzoate **14g** as a yellow oil (1.337g, 92%).

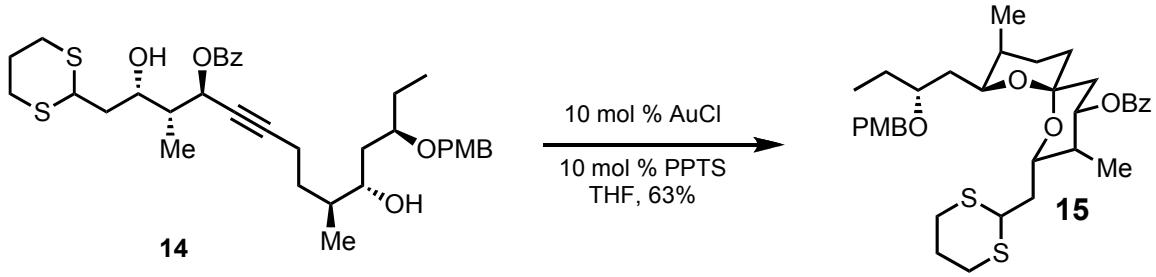
Alternatively, a solution of the epimeric propagryl alcohol **(14b)** (504.1mg, 0.67mmoles) is dissolved in pyridine (2mL) and treated with benzoyl chloride (233µL, 2.00mmoles). After 2 hours the reaction is diluted with sodium bicarbonate and ethyl acetate. The organic phase is filtered though sodium sulfate and concentrated. Flash chromatography (9:1 Hexane/EtOAc) gives the benzoate **14g** as a yellow oil (573.8mg, 95%).

r_f=0.20 (9:1 Hexane/EtOAc); IR (neat): 2954, 1790, 1726, 1513, 1466 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13-8.10 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.34 (m, 2H), 7.27 (d, J=8.5Hz, 2H), 6.88 (d, J=8.5Hz, 2H), 5.42 (td, J=1.8,3.7Hz), 4.49 (d, J=11.0Hz, 1H), 4.35 (d, J=11.0Hz, 1H), 4.29 (dt, J=2.6, 6.7Hz, 1H), 4.08 (t, J=7.3Hz, 1H0, 3.82 (s, 3H), 3.81-3.76 (m, 1H), 3.45-3.43 (m, 1H), 2.30-2.16 (m, 4H), 2.00-1.22 (m, 10H), 1.14 (d, J=7.5Hz, 3H), 0.91 (t, J=6.9Hz, 3H), 0.90-0.88 (m, 18H), 0.83 (d, J=7.5Hz, 3H), 0.09-0.02 (m, 9H), -0.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 159.2, 133.2, 131.6, 130.6, 130.1, 129.2, 128.6, 114.0, 87.7, 73.2, 70.1, 67.8, 66.6, 55.6, 44.4, 42.5, 40.4, 38.2, 37.7, 30.7, 30.6, 26.6, 26.3, 26.2, 18.4, 18.3, 17.4, 14.6, 10.2, 9.4, -3.8, -3.9, -4.1, -4.6 ppm.



Diol 14: A solution of silyl ether **14g** (1.9095g, 2.22mmoles) is dissolved in methanol (5mL) and THF (15mL). 6N HCl (4mL) is added and the reaction is stirred at room temperature for 25 hours and then poured into aqueous sodium bicarbonate (50mL). The aqueous phase is washed three times with ethyl acetate (50mL portions). The combined organic portions are dried over sodium sulfate filtered and concentrated. Flash chromatography (2:1 Hexane/EtOAc) gives the diol **14** as a yellow oil (1.1492g, 82%).

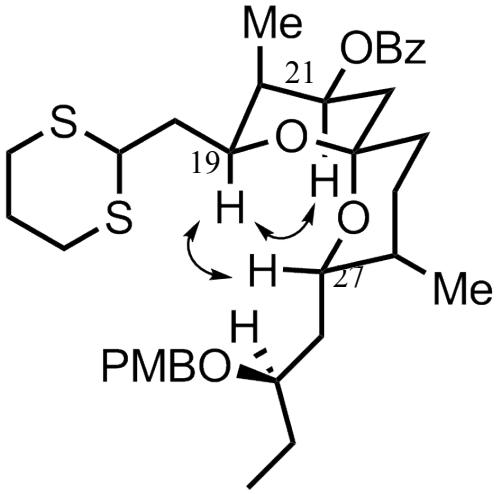
r_f=0.19 (2:1 Hexane/EtOAc); $[\alpha]_D$=-12° (c=0.071, CH_2Cl_2); IR (neat): 3456 (broad), 2934, 1720 (sharp), 1514, 1269 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.08-8.04 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 7.26 (d, J=11.2Hz, 2H), 6.87 (d, J=11.2Hz, 2H), 5.64 (dt, J=2.0, 6.9Hz, 1H), 4.50 (d, J=10.7Hz, 1H), 4.44 (d, J=10.7Hz, 1H), 4.24 (dd, J=4.8, 9.6Hz, 1H), 4.21-4.18 (m, 1H), 3.82-3.79 (m, 4H), 3.61-3.59 (m, 1H), 2.93-2.80 (m, 4H), 2.60 (s, broad, 1H), 2.46 (s, broad, 1H), 2.38-2.19 (m, 2H), 2.17-1.98 (m, 3H), 1.93-1.79 (m, 2H), 1.78-1.58 (m, 6H), 1.40-1.37 (m, 1H), 1.14 (d, J=6.5Hz, 1H), 1.13 (d, J=7.0Hz, 3H) 0.91 (t, J=7.5Hz, 3H), 0.89 (d, J=6.6Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 159.5, 133.5, 130.8, 130.1, 129.7, 128.7, 114.1, 88.4, 78.3, 76.3, 71.1, 71.0, 67.7, 67.6, 55.6, 44.6, 43.2, 40.6, 38.1, 36.3, 31.9, 30.6, 30.3, 26.3, 26.3, 26.2, 17.1, 14.1, 10.2, 9.7 ppm; HRMS (ESI+) calc'd for $C_{35}H_{48}NaO_6S_2$ $(M+Na)^+$ 651.2790, found 651.3694.

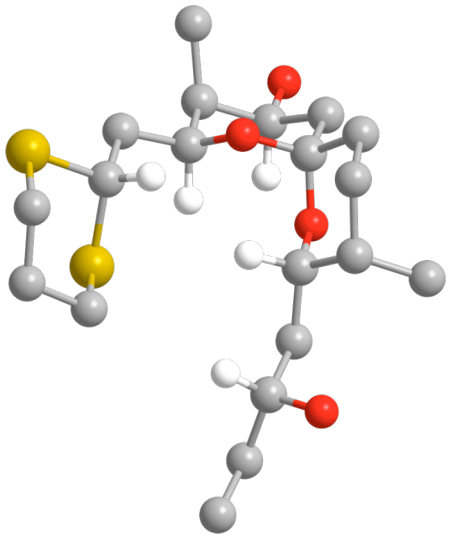


Spiroketal (15): A solution of diol **14** (1.1492g, 1.82mmoles) in dry THF (0.05M, 36mL) is degassed (2x freeze/pump/thaw) and allowed to warm under argon. Gold (I) chloride (42.3mg, 0.18mmoles) and PPTS (45.7mg, 0.18mmoles) are added and degassing is repeated for 2 additional cycles. The reaction is then warmed to 50 ˚C for a period of 22 hours. After this time the solvent is removed under reduced pressure and the residue is purified by flash chromatography (9:1 hexane/THF) yielding spiroketal **15** (729.6mg, 63%).

r_f=0.23 (9:1 Hexane/THF); $[\alpha]_D$ = -5.2° (c=0.71, $CHCl_3$); IR (neat): 2936, 1719 (sharp) cm^{-1}; ^1H NMR (500 MHz, C_6D_6): δ 8.17-8.16 (m, 2H), 7.39 (d, J=8.5Hz, 2H), 7.16-7.07 (m, 3H), 6.85 (d, J=8.5Hz, 2H), 5.56 (dt, 1H, J=4.7, 12.1Hz), 4.56 (d, J=11.4Hz, 1H), 4.50 (d, J=11.4Hz, 1H), 4.34 (ddd, 1H, J=3.4, 3.6, 11.4Hz), 4.26 (dd, 1H, J=5.9, 8.5Hz), 4.19 (dt, J=2.4, 6.8Hz, 1H), 3.71-3.68 (m, 1H), 2.43-2.24 (m, 4H), 2.09 (t, J=7.0Hz, 1H), 1.92-1.84 (m, 3H), 1.73-1.58 (m, 4H), 1.14 (t, J=7.4Hz, 3H), 0.98 (d, J=6.9Hz, 3H), 0.87 (d, J=6.9Hz); ^{13}C NMR (125 MHz, C_6D_6): δ 165.2, 159.4, 132.7, 132.0, 131.3, 129.7, 129.1, 128.5, 125.7, 113.9, 97.7, 78.3, 71.0, 69.9, 67.4, 54.7, 44.4, 39.3, 37.5, 36.0, 35.8, 30.5, 30.3, 30.2, 29.9, 29.9, 27.4, 26.8, 25.9, 11.4, 9.6, 5.4 ppm; HRMS (ESI+) calc'd for $C_{35}H_{48}NaO_6S_2$ $(M+Na)^+$ 651.2790, found 651.3694.

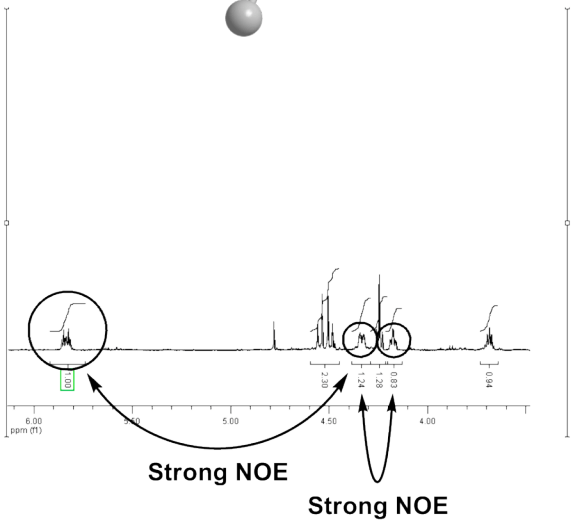
Further NMR studies on this intermediate confirmed the desired relative configuration of the seven stereogenic centers.

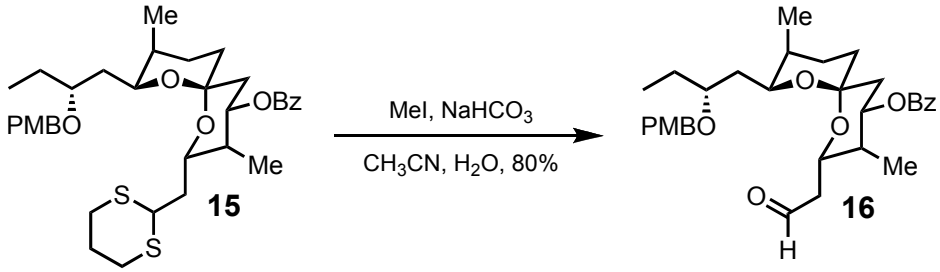




C-19 4.26 (dd, 1H, J=5.9, 8.5Hz)
C-21 5.56 (dt, 1H, J=4.7, 12.1Hz)
C-27 4.34 (ddd, 1H, J=3.4, 3.6, 11.4Hz)

The relative configuration of the 1,3 diol (C-19 relative to C-21) is known to be *anti* by conversion to the corresponding acetonide (see above). The spiroketal (C-23) is confirmed to have the configuration shown above based on strong NOE correlations between the C-19 and C-21 hydrogens (7.1%) and the C-19 and C-27 hydrogens (4.9%). Furthermore, the configurations at C-20 and C-26 are confirmed to have axial methyl groups based on the coupling patterns above (both show equatorial-axial coupling [*J* = 4-5 Hz] for C-19 to C-20, C-21 to C-20 and C-27 to C-26).





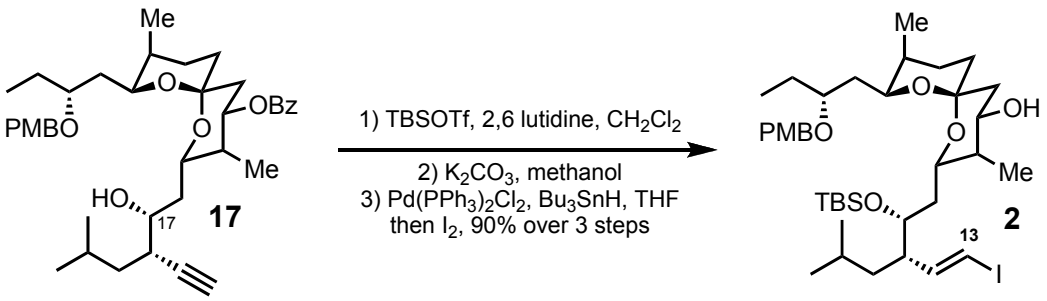
Aldehyde (16): The thioacetal **15** (19.9mg, 31.6μmoles) is dissolved in a mixture of acetonitrile and water (3:1, 0.8mL). Sodium bicarbonate (53.2mg, 0.63mmoles) is added followed by methyl iodide (40μL, 0.63mmoles). The reaction is warmed to 50 °C for 2 hours and then allowed to cool and poured into ethyl acetate and brine. The organic phase is separated and filtered though sodium sulfate. Flash chromatography (10% EtOAc/hexanes) gives the aldehyde **16** as a clear yellow oil (13.7mg, 80%).

IR (neat): 2966, 1723 (sharp) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 9.52 (dd, *J*=3.7, 1.1Hz, 1H), 8.08-8.03 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.45 (m, 1H), 7.30 (d, *J*=8.7Hz, 2H), 6.88 (d, *J*=8.7Hz, 2H), 5.61 (td, *J*=12.0, 4.8Hz, 1H), 4.60 (d, *J*=11.2Hz, 1H), 4.43 (ddd, *J*=10.2, 3.7, 2.3Hz, 1H), 4.40-4.35 (m, 1H), 3.94 (td, *J*=6.0, 3.3Hz, 1H), 3.80 (s, 3H), 3.78-3.71 (m, 1H), 2.58-2.47 (m, 1H), 2.43 (ddd, *J*=8.0, 7.3, 2.7Hz, 1H), 2.26-2.16 (m, 1H), 2.10-1.98 (m, 2H), 1.95 (dd, *J*=12.6, 4.8Hz, 1H), 1.82-1.54 (m, 10H), 1.52-1.44 (m, 2H), 1.43-1.36 (m, 1H), 1.01-0.91 (m, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.20, 165.68, 158.94, 132.96, 131.24, 130.40, 129.47, 128.72, 128.37, 113.72, 113.65, 97.73, 76.39, 70.74, 69.19, 67.85, 65.28, 55.27, 46.10, 37.00, 35.38, 34.90, 30.33, 29.42, 26.25, 25.85, 11.32, 8.74, 5.46 ppm.

Homo-propargyl Alcohol (17): The aldehyde **16** (132.9mg, 0.25mmoles) and propargyl mesylate **7** (71.5mg, 0.38mmoles) are dissolved in dry THF (1.7mL) and cooled to -78 °C. A solution of palladium acetate (5.6mg, 25.1μmoles) and triphenylphosphine (6.6mg, 25.1μmoles) in THF (1mL) is transferred into the reaction flask via syringe, followed by a solution of diethyl zinc in hexanes (0.75mL, 1M, 0.75mmoles). The reaction is allowed to warm to -20 °C for a period of 14hrs, after which time it is poured into a saturated solution of ammonium chloride. The organic phase is diluted with ethyl acetate, separated and dried over sodium sulfate. Following filtration and concentration the crude residue is purified by flash chromatography (19:1 toluene/EtOAc) yielding the product **17** (113.2 mg, 71%) followed by its C-17 epimer (30.0mg, 19%).

Major Diastereomer (17): r_f=0.20 (19:1 Toluene/EtOAc); $[\alpha]_D$ = -69° (c=0.93, $CHCl_3$); IR (neat): 3505 (broad), 3305, 2955, 1718 (sharp), 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J*=7.2Hz, 2H), 7.57 (t, *J*=7.4Hz, 1H), 7.45 (t, *J*=7.6Hz, 2H), 7.29 (d, *J*=8.5Hz, 2H), 6.85 (d, *J*=8.6Hz, 2H), 5.54 (td, *J*=12.0, 4.8Hz, 1H), 4.50 (d, *J*=11.4Hz, 1H), 4.45 (d, *J*=11.2Hz, 1H), 4.17 (m, 1H), 4.02-3.95 (m, 1H), 3.87 (s, 1H), 3.78 (s, 3H), 3.73 (dd, *J*=9.7, 3.0Hz, 1H), 3.64 (dt, *J*=10.0, 5.4Hz, 1H), 2.34-2.22 (m, 1H), 2.17-2.10 (m, 1H), 2.04 (d, *J*=2.3Hz, 1H), 1.99-1.90 (m, 3H), 1.84-1.73 (m, 2H), 1.73-1.41 (m, 10H), 1.38 (dd, *J* = 14.36, 1.78 Hz, 1H), 1.17-1.05 (m, 1H), 0.97 (d, *J*=6.9Hz, 3H), 0.96 (d, *J*=7.3Hz, 3H), 0.95-0.90 (m, 6H), 0.84 (d, *J*=6.6Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.67, 158.80, 132.94, 131.28, 129.48, 128.68, 128.37, 113.66, 98.19, 84.58, 76.87, 73.03, 71.62, 70.63, 69.29, 68.24, 55.18, 38.95, 37.03, 36.61, 36.23, 35.66, 30.14, 29.12, 26.56, 26.21, 25.76, 23.59, 21.14, 11.22, 9.20, 5.55 ppm; HRMS (ESI+) calculated for $C_{39}H_{54}O_7Na$ $(M+Na)^+$ 657.3766 found 657.3767.

Minor Diastereomer: r_f=0.17 (19:1 Toluene/EtOAc); IR (neat): 3450 (broad), 3306, 2957, 1717 (sharp), 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.10-7.99 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.42 (m, 2H), 7.29 (d, *J*=8.7Hz, 2H), 6.87 (d, *J*=8.7Hz, 2H), 5.55 (td, *J*=12.1, 5.0Hz, 1H), 4.45 (d, *J*=11.2Hz, 1H), 4.36 (d, *J*=11.2Hz, 1H), 4.20-4.12 (m, 1H), 4.05-3.99 (m, 1H), 3.83-3.73 (m, 4H), 3.63 (td, *J*=10.3, 5.9Hz, 1H), 3.49, 2.37-2.30 (m, 1H), 2.16-2.06 (m, 2H), 2.05 (d, *J*=2.4Hz, 1H), 1.95 (dd, *J*=12.6, 4.6Hz, 1H), 1.90-1.78 (m, 2H), 1.79-1.48 (m, 8H), 1.47-1.39 (m, 1H), 1.36 (ddd, *J*=14.0, 10.7, 1.1Hz, 1H), 1.29-1.24 (m, 1H), 1.14-1.06 (m, 1H), 1.02-0.93 (m, 9H), 0.91 (d, *J*=6.7Hz, 3H), 0.86 (d, *J*=6.6Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ165.54, 158.98, 132.73, 130.57, 130.36, 129.39, 128.23, 116.78, 113.69, 97.33, 85.15, 76.87, 71.18, 70.80, 69.50, 67.70, 66.53, 65.39, 55.05, 39.47, 37.60, 37.35, 36.34, 36.14, 35.75, 31.23, 29.65, 26.57, 26.02, 25.86, 23.57, 21.19, 10.85, 10.11, 5.34 ppm.

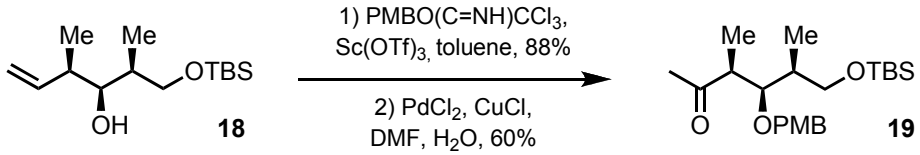


Spiroketal Fragment (2): A solution of alcohol **17** (307.3mg, 0.48mmoles) in dry methylene chloride (5mL) is cooled to 0 °C and 2,6-lutidine (175 µL, 1.5mmoles) is injected followed by TBSOTf (330µL, 1.45mmoles). The reaction is stirred for 2 hours and quenched several drops of methanol. Solvent is removed under reduced pressure and flash chromatography (5% EtOAc/hexanes gives the silyl ether (338.8mg, quantitative).

The silyl ether prepared above is suspended in a methonolic solution of saturated potassium carbonate (6mL) and stirred at ambient temperature for 24 hours. The reaction is transferred to a separatory funnel and diluted with saturated ammonium chloride and ethyl acetate. The organic phase is dried over sodium sulfate, filtered and concentrated *in vacuo*.

The alcohol prepared above and palladium-dichloro-bis-triphenylphosphine (16.8mg, 24µmoles) are dissolved in dry THF (5 mL) and tributyltinhydride (1.27mL, 4.8mmoles) is injected via slow addition over a period of 8 hours. Stirring is continued for 2 additional hours and the reaction is treated with a solution of iodine in THF (1.28g, 5.0 mmoles in 3 mL THF). The reaction is poured into a mixture of ethyl acetate and ammonium chloride and the organic phase is concentrated under reduced pressure. Flash chromatography (20% EtOAc/toluene) gives the spiroketal fragment **2** as a yellow oil (338.8mg, 90% over 3 steps).

r_f=0.23 (4:1 hexanes/ethyl acetate); $[\alpha]_D$ = -43° (c=0.91, benzene); IR (neat): 3435 (broad), 2955, 1613, 1513 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, *J*=8.7Hz, 2H), 6.87 (d, *J*=8.7Hz, 2H), 6.36 (dd, *J*=14.5, 9.7Hz, 1H), 5.98 (d, *J*=14.5Hz, 1H), 4.51-4.37 (m, 2H), 4.18 (td, *J*=11.8, 4.8Hz, 1H), 3.85-3.74 (m, 5H), 3.73-3.66 (m, 1H), 3.54-3.29 (m, 1H), 2.26 (tt, *J*=11.4, 3.5Hz, 1H), 2.12-2.01 (m, 2H), 1.87-1.81 (m, 1H), 1.80-1.30 (m, 12H), 1.30-1.24 (m, 1H), 1.14 (ddd, *J*=13.4, 9.7, 3.6Hz, 1H), 0.98-0.91 (m, 6H), 0.90 (s, 9H), 0.85 (d, *J*=6.6Hz, 3H), 0.81 (d, *J* = 6.9Hz, 3H), 0.79 (d, *J* = 6.6Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.97, 147.48, 131.07, 129.06, 113.71, 97.50, 77.86, 75.70, 72.25, 70.39, 69.66, 67.87, 67.10, 55.24, 50.72, 39.34, 38.00, 37.23, 36.98, 36.45, 29.98, 29.83, 29.12, 27.00, 26.41, 25.97, 25.46, 23.98, 21.47, 18.09, 10.98, 9.27, 3.87, -4.07, -4.48 ppm; HRMS (ESI+) calculated for $C_{38}H_{65}O_6NaSiI$ $(M+Na)^+$ 795.3493 found 795.3488.



Methyl Ketone (19): A solution of alkene **18** (15.41g, 59.60mmoles, prepared according to the procedures of Schreiber[3] and Keck[4]) in toluene (500mL) is cooled in an ice bath to 0 °C. Scandium triflate (320.0mg, 0.65mmoles) is dissolved in a minimum amount of acetonitrile and transferred into

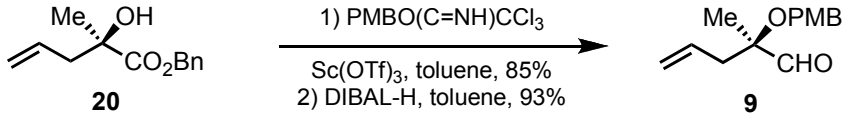
[3] M. Nakatsuka, J.A. Ragan, T. Sammakia, D.B. Smith, D.E. Uehling, S.L. Schreiber; *J. Am. Chem. Soc.,* **1990**, *112,* 5583-5601.

[4] G.C. Keck, D.E. Abbott, E.P. Boden, E.J. Enholm, *Tetrahedron Lett.,* **1984**, *25,* 3927-3930.
See also White's reference, which contained more specific experimental data… J.D. White, R. Hanselmann, R.W. Jacksonm W.J. Porter, Y. Ohba, T. Tiller, S. Wang, *J. Org. Chem.,* **2001**, *66,* 5217-5231.

the reaction flask. Finally, PMBTCl (33.44g, 119.2mmoles) is dissolved in toluene (3mL/g) and transferred via syringe into the reaction flask over a period of 3 hours. After an additional 2 hours of stirring, the reaction is quenched with a 1:1 mixture of sodium bicarbonate and ammonium chloride (200mL). The organic phase is washed with water and brine (100mL portions). The organic phase is dried over sodium sulfate, filtered and concentrated onto 50g of silica gel. Flash chromatography (19:1 petrol ether/diethyl ether) gives the *p*-methoxylbenzyl ether as a yellow oil (19.98g, 88%).

The product obtained above (3.00g, 7.90mmoles) is dissolved in DMF/H_2O (80mL, 7:1 mixture). Copper (I) chloride (0.78g, 7.91mmoles) and palladium (II) chloride (140.0mg, 0.79mmoles) are added to the solution and the reaction is put under an atmosphere of oxygen and warmed to 40 °C in an oil bath. After 8 hours the solution is poured into 0.2N HCl (150mL) and washed with Et_2O (3x150mL portions). The combined organics are washed with water and brine (150mL portions) and dried over magnesium sulfate. After filtration and concentration, flash chromatography (7% EtOAc/Hexane) gives the methyl ketone **19** as a yellow oil (1.850g, 60%).

r_f=0.28 (7% EtOAc/Hexane); $[\alpha]_D$ = +17° (c=0.94, $CHCl_3$); IR (neat): 2931, 1711 (sharp), 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, J=7.8Hz, 2H), 6.87 (d, J=7.7Hz, 1H), 4.50 (s, 2H), 3.88 (dd, J=4.0, 6.9Hz, 1H), 3.81 (s, 3H), 3.55-3.46 (m, 2H), 2.88-2.83 (m, 1H), 2.18 (s, 3H), 1.75-1.68 (m, 1H), 1.18 (d, J=7.0Hz, 3H), 0.91 (s, 9H), 0.51 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.6, 159.1, 130.8, 129.3, 133.7, 79.6, 74.2, 65.5, 55.2, 50.5, 39.3, 28.8, 25.9, 18.2, 12.8, 11.5, -5.4, -5.5 ppm; HRMS (ESI+) calculated for $C_{22}H_{38}O_4NaSi$ $(M+Na)^+$ 417.2437 found 417.2443.



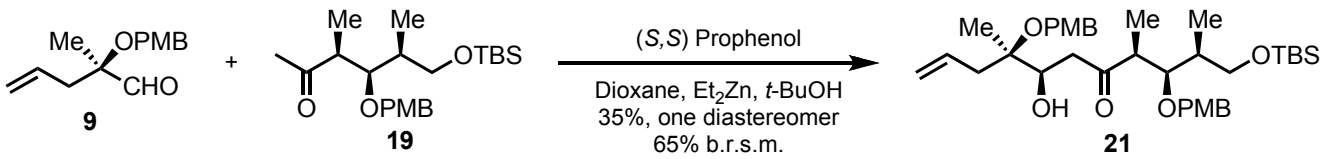
20 **9**

(*R*)-2-(4-methoxybenzyloxy)-2-methylpent-4-enal (9): The tertiary alcohol **20** (46.9mg, 0.21mmoles, prepared according to the procedure of Mukaiyama[5]) and PMB imidate (95.0mg, 0.32mmoles) are dissolved in toluene (2mL) and cooled to 0 °C. Scandium triflate (1.0mg) is dissolved in acetonitrile (100µL) and transferred into the reaction. After 2 hours the reaction is quenched with sodium bicarbonate and diluted with ethyl acetate. The organic phase is separated, dried and concentrated. The product (61.2mg, 85%) is obtained by flash chromatography (25:4:1 Hexane/DCM/EtOAc).

The substrate above (595.7mg, 1.75moles) is dissolved in dichloromethane (9mL) and cooled to -78 °C. DIBAL-H is injected (3.5mL, 3.5mmoles). The reaction is stirred for 90 minutes and quenched with methanol, followed by saturated sodium potassium tartrate. The organics are separated, dried and purified by flash chromatography (9:1 Hexane/EtOAc) to yield the aldehyde **9** as a clear oil (384.1mg, 93%).

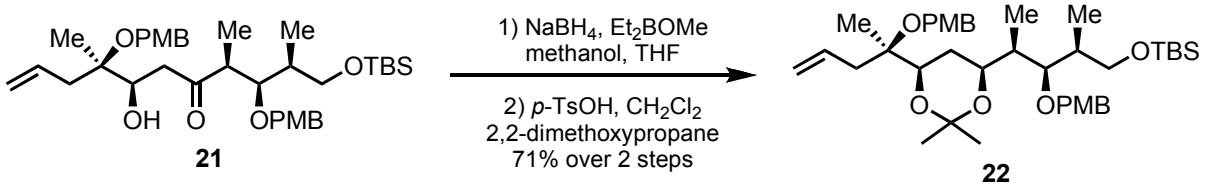
r_f=0.13 (25:4:1 Hexane/DCM/EtOAc); $[\alpha]_D$ = -23° (c=0.51, $CHCl_3$); IR (neat): 2936, 1734, 1515, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.28 (d, J=10.6Hz, 2H), 6.89 (d, J=10.6Hz, 2H), 5.88-5.78 (m, 1H), 5.20-5.10 (m, 2H), 4.45 (d, J=10.6Hz, 1H), 4.40 (d, J=10.6Hz, 1H), 2.54 (ddt, J=0.7, 6.9, 13.1Hz, 1H), 2.46 (ddt, J=0.8, 6.9, 13.1Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 205.0, 159.6, 131.9, 130.4, 129.5, 119.4, 114.1, 82.4, 66.4, 55.6, 39.6, 18.6 ppm; HRMS (ESI+) calculated for $C_{14}H_{18}O_3Na$ $(M+Na)^+$ 257.1154 found 257.1156.

[5] K. Yamada, T. Tozawa, M. Nishida, T. Mukaiyama, *Bull. Chem. Soc. Jpn.,* **1997**, *70*, 2301-2308.



Aldol Adduct (21): A solution of (*S,S*) Prophenol (590.2mg, 0.92mmoles) in dioxane (8mL) is treated with diethyl zinc (1M in hexanes, 1.84mL) at ambient temperature. A separate flask is charged with ketone **19** (913.6mg, 2.31mmoles), aldehyde **9** (759.5mg, 3.24mmoles) and activated 4Å powdered molecular sieves (500mg). After 30 minutes the catalyst solution is transferred into the reaction flask at ambient temperature. The reaction is stirred for 45 hours and quenched with 0.1N HCl (50mL) and diluted with ethyl acetate (100mL). The solution is filtered and the organic phase is washed with an addition portion of 0.1N HCl followed by sodium bicarbonate (25mL portions). The organics are dried over sodium sulfate, filtered and concentrated. Flash chromatography (85:15 Hexane/EtOAc) gives aldol adduct **21** (518.5mg, 35%) as a single diastereomer along with a 1.4:1 mixture of the aldehyde and ketone (1.026g, 60%). Repetition of the procedure above 2 additional times (identical relative stoichiometry) with recovered starting material gives a total of 65% yield based on recovered starting material.

r_f=0.33 (4:1 Hexane/EtOAc); $[\alpha]_D$ = +28° (c=0.28, CH_2Cl_2); IR (neat): 3525 (broad), 2931, 1703 (sharp), 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, J=9.3Hz, 2H), 6.84 (d, J=8.7Hz, 2H), 5.94-5.82 (m, 1H), 5.20-5.05 (m, 2H), 4.43 (dd, J=11.3, 16.7Hz, 2H), 4.19-4.06 (m, 1H), 3.88-3.71 (m, 4H), 3.54-3.40 (m, 2H), 3.04-2.82 (m, 2H), 2.63-2.48 (m, 2H), 2.45-2.32 (m, 1H), 1.73-1.69 (m, 1H), 1.21 (s, 3H), 1.14 (d, J=6.7Hz, 3H), 0.85 (d, J=6.8Hz, 3H), 0.90 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.87, 159.10, 158.92, 133.72, 131.16, 130.77, 129.33, 128.76, 117.89, 113.76, 113.73, 113.70, 79.72, 78.49, 73.91, 71.66, 65.52, 63.75, 55.26, 55.24, 49.99, 43.48, 39.02, 38.83, 29.69, 25.91, 19.58, 18.21, 12.63, 11.54, -5.37, -5.46; HRMS (ESI+) calculated for $C_{14}H_{18}O_3Na$ $(M+Na)^+$ 651.3693 found 651.3694.

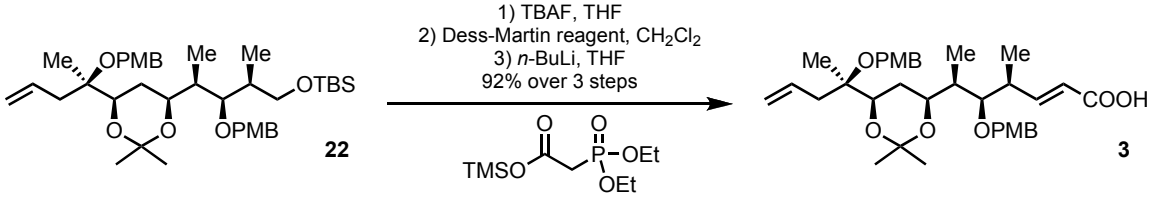


Acetonide (22): A flask containing the aldol product **21** (82.5mg, 0.13mmoles) is charged with THF (2mL) and methanol (0.6mL). After cooling to -78 ºC Et_2BOCH_3 is injected (35µL, 0.26mmoles) and sodium borohydride is added (9.9mg, 0.26mmoles). After 6 hours the reaction is warmed to 0 ºC and stirred for 20 minutes before quenching with a solution of 30% peroxide and 1N sodium hydroxide (1:5, 1.2mL). After 30 minutes the reaction is diluted with additional water (10mL) and washed with dichloromethane (3x10mL). The combined organic portions are dried over sodium sulfate, filtered and concentrated.

The crude diol is dissolved in dichloromethane (4mL) and 2,2 dimethoxypropane (1mL). *p*-TsOH is added (1mg) and the reaction is stirred for 30 minutes and quenched with 1 drop of triethylamine. After concentration, flash chromatography (gradient 19:1 to 9:1 hexane/EtOAc) gives the acetonide **22** as a clear oil (62.3mg, 71%).

r_f=0.15 (19:1 Hexane/EtOAc); $[\alpha]_D$ = +3.2° (c=0.32, CH_2Cl_2); IR (neat): 2932, 1613 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 4H), 7.06-6.75 (m, 4H), 5.92 (tdd, J=17.2, 10.1, 7.2Hz, 1H), 5.22-5.04 (m, 1H), 4.68 (d, J=11.0Hz, 1H), 4.56 (d, J=11.0Hz, 1H), 4.53-4.44 (m, 2H), 3.82-3.80 (m, 6H), 3.78 (dd, J=11.6, 2.0Hz, 1H), 3.65-3.56 (m, 2H), 3.50 (dd, J=9.8, 5.8Hz, 1H), 2.46 (d, J=7.1Hz, 2H), 1.99-1.89 (m, 1H), 1.79-1.69 (m, 1H), 1.62 (d, J=11.9Hz, 1H), 1.57 (d, J=11.8Hz, 1H), 1.42 (s, 3H), 1.38 (s, 3H), 1.17 (s, 3H), 1.06 (d, J=6.8Hz, 3H), 0.97-0.90 (m, 12H), 0.07 (s, 6H) ppm; ^{13}C NMR (125 MHz,

$CDCl_3$): δ 158.88, 158.69, 134.51, 132.07, 131.59, 129.06, 128.82, 117.40, 113.62, 113.59, 98.31, 79.37, 77.71, 74.06, 73.96, 69.93, 65.53, 64.64, 55.20, 53.39, 41.09, 39.08, 38.67, 30.21, 28.48, 25.89, 20.94, 19.23, 18.17, 11.69, 10.15, -5.38, -5.43 ppm; HRMS (ESI+) calculated for $C_{39}H_{62}O_7NaSi$ $(M+Na)^+$ 693.4163, found 693.4156.

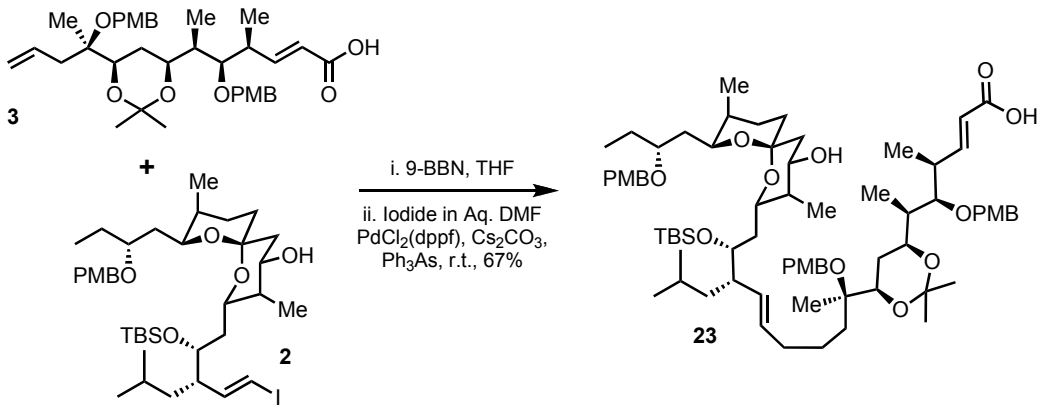


Carboxylic Acid (3): A solution of the silyl ether **22** (191.2mg, 0.28mmoles) in THF (2mL) is treated with a solution of TBAF in THF (1M, 0.85mL). After 3.5 hours the reaction is judged to be complete and silica gel (~500mg) is added. The solvent is removed under reduced pressure and flash chromatography (2:1 hexane/EtOAc) gives the product as a clear oil (161.9mg, quantitative).

The alcohol prepared above is dissolved in dichloromethane (3mL) and Dess Martin reagent is added (367.4mg, 0.87mmoles). After 2 hours the reaction is diluted with sodium thiosulfate (5mL) and diethyl ether (10mL). The organic phase is washed with sodium bicabonate (2x3mL) and then dried over magnesium sulfate. After filtration and concentration the crude aldehyde is carried on directly to the next step.

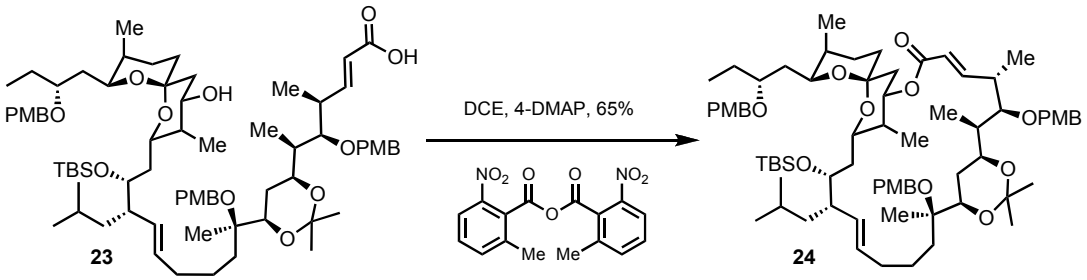
A flask containing THF (3mL) is charged with trimethylsilyl diethylphosphonoacetate (0.28mL, 1.01mmoles). After cooling to -78 ºC, *n*-BuLi is injected (0.44mL, 0.99mmoles). The resulting solution is allowed to warm to ambient temperature for 30 minutes and is then transferred via canula into a flask containing the aldehyde prepared above in THF (2mL). After 5 hours the reaction is poured into a 0.1M sodium bisulfate solution (25mL, resulting pH~2). The aqueous phase is washed with ethyl acetate (50mL) and the resulting organic portion is dried over sodium sulfate, filtered and concentrated. Flash chromatography (2:1 chloroform/EtOAc) gives the carboxylic acid **3** as a clear oil (158.9mg, 92% over 2 steps).

r_f=0.20 (1:1 EtOAc/Hexanes); $[\alpha]_D$ = -0.10 ° (c=1.1); IR (neat): 2934, 1695, 1613, 1513, 1249 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31-7.24 (m, 4H), 7.18 (dd, *J*=15.7, 7.7Hz, 1H), 6.90-6.85 (m, 4H), 5.98-5.82 (m, 2H), 5.19-5.08 (m, 2H), 4.68 (d, *J*=11.0Hz, 1H), 4.56-4.48 (m, 2H), 4.44 (d, *J*=11.0 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.80-3.74 (m, 2H), 3.47 (dd, *J*=5.5, 4.5Hz, 1H), 2.84-2.72 (m, 1H), 2.53-2.41 (m, 2H), 1.75-1.64 (m, 1H), 1.55 (dd, *J*=24.0, 11.8Hz, 1H), 1.43 (s, 3H), 1.39 (s, 3H), 1.17 (s, 3H), 1.16 (d, *J*=6.8Hz, 3H), 1.01 (d, *J*=6.9Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.59, 159.07, 158.73, 154.84, 134.44, 131.97, 130.71, 129.17, 128.82, 119.84, 117.51, 113.72, 113.64, 98.43, 82.32, 77.71, 74.01, 73.59, 70.59, 64.71, 55.24, 55.23, 40.94, 39.73, 39.02, 30.24, 28.01, 21.10, 19.26, 14.72, 9.96 ppm; HRMS (ESI+) calculated for $C_{35}H_{48}NaO_8$ $(M)^+$ 619.3247, found 619.3239.



***Seco*-Acid (23):** The carboxylic acid **3** (64.8mg, 0.109mmoles) and 9-BBN (33.1mg, 0.271mmoles) are dissolved in THF (1mL) and stirred under a nitrogen atmosphere for a period of 14 hours. The solvent is removed under reduced pressure and water is injected (60µL). In a separate flask the vinyl iodide **2** (109.5mg, 0.141mmoles) is dissolved in DMF (2mL) and the solvent is degassed (2 x freeze/pump/thaw). $PdCl_2$(dppf) (7.9mg, 10.9µmoles), cesium carbonate (106.5mg, 0.327mmoles) and triphenyl arsine (3.3mg, 11.0µmoles) are added to the flask containing **3**. The DMF solution of **2** is transferred into the reaction flask and the reaction is stirred at ambient temperature under argon for 21 hours. The reaction is then cooled in an ice bath and 30% peroxide (2mL) is injected and the reaction is allowed to warm for 30 minutes. The reaction is then poured into sodium thiosulfate (5mL) acidified with 1M sodium bisulfate (pH=2, ~15mL) and further diluted with water (30mL). The aqueous solution is washed with ethyl acetate (3x25mL) and the combined organics are dried over sodium sulfate, filtered and concentrated. Flash chromatography (gradient 10% to 20% to 35% chloroform/EtOAc) gives *seco*-acid **23** as a white foam (89.1mg, 67%).

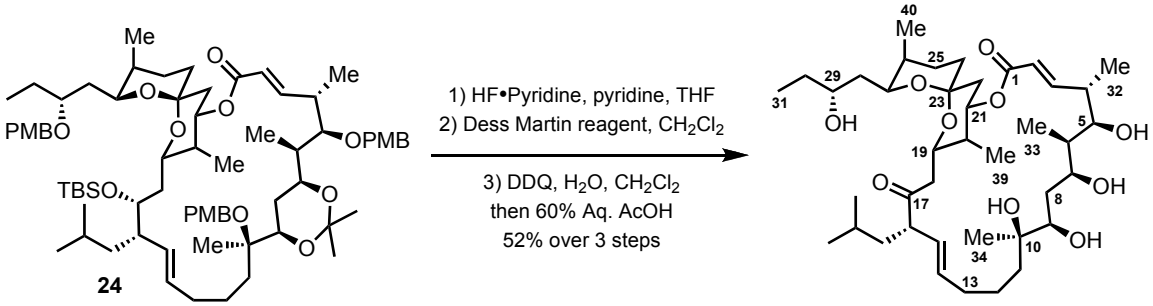
r_f=0.35 (2:1 chloroform/EtOAc with ~1% methanol); $[\alpha]_D$ = -16° (c=0.26, benzene); IR (neat): 3419 (broad), 2956, 1697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.18 (m, 6H), 7.10 (dd, J=15.7, 7.9Hz, 1H), 6.91-6.85 (m, 6H), 5.83 (d, J=15.8Hz, 1H), 5.40 (dd, J=14.3, 7.5Hz, 1H), 5.19 (dd, J=15.2, 8.9Hz, 1H), 4.63-4.34 (m, 6H), 4.25-4.13 (m, 1H), 3.88-3.76 (m, 10H), 3.71-3.63 (m, 1H), 3.51-3.38 (m, 2H), 2.82-2.68 (m, 1H), 2.27-2.15 (m, 1H), 2.12-2.00 (m, 2H), 1.95-1.81 (m, 1H), 1.82-1.44 (m, 16H), 1.39 (s, 1H), 1.36 (s, 3H), 1.14 (s, 3H), 1.12 (d, J=6.8Hz, 3H), 0.98 (d, J=6.9Hz, 3H), 0.98-0.93 (m, 6H), 0.88 (s, 9H), 0.82 (d, J=6.6Hz, 3H), 0.81-0.77 (m, 6H), 0.07 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.17, 159.08, 158.96, 158.71, 154.40, 132.44, 132.04, 131.11, 130.75, 129.18, 129.15, 128.77, 128.27, 119.85, 113.73, 113.69, 113.65, 98.40, 97.49, 82.54, 77.92, 74.07, 73.73, 73.66, 73.54, 70.67, 69.63, 68.20, 67.28, 64.32, 55.24 (3C), 47.09, 41.14, 39.99, 39.36, 37.44, 36.43, 34.64, 30.25, 30.05, 29.83, 28.31, 27.82, 27.38, 27.01, 26.84, 26.45, 26.03, 25.59, 24.31, 22.61, 20.60, 19.30, 18.13, 17.50, 14.94, 13.60, 10.88, 9.82, 9.26, -4.14, -4.34 ppm; HRMS (ESI+) calculated for $C_{73}H_{114}O_{14}NaSi$ $(M+Na)^+$ 1265.7876 found 1265.7885.



Macrocycle (24): A solution of *seco*-acid **23** (84.3mg, 68.8µmoles) in dry DCE (5mL) is transferred to a gastight syringe and injected into a flask containing MNDA (38.6mg, 0.105mmoles) and 4-DMAP (18.0mg, 0.126mmoles) in additional DCE (55mL) over a period of 18 hours. After 2 additional hours

the reaction is poured into a separatory funnel containing saturated sodium bicarbonate (30mL) and ethyl acetate (90mL). The aqueous phase is separated and the organic phase is washed with ammonium chloride and sodium bicarbonate (30mL portions). The organic phase is then dried over sodium sulfate, filtered and concentrated. Flash chromatography (95:5 toluene/ethyl acetate) gives the macrocycle as a white foam (55.4mg, 65%).

r_f=0.54 (9:1 toluene/EtOAc); $[\alpha]_D$ = -20° (c=0.10, chloroform); IR (neat): 2926, 1718, 1514 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.29-7.21 (m, 6H), 7.10 (dd, J=15.6, 7.9Hz, 1H), 6.88-6.82 (m, 6H), 5.83 (d, J=15.8Hz, 1H), 5.54-5.28 (m, 2H), 5.19 (dd, J=15.2, 9.3Hz, 1H), 4.58-4.35 (m, 6H), 4.18 (td, J=11.9, 4.9Hz, 1H), 3.82-3.75 (m, 10H), 3.67-3.61 (m, 1H), 3.48-3.34 (m, 2H), 2.78-2.61 (m, 1H), 2.12-1.91 (m, 2H), 1.90-1.77 (m, 1H), 1.79-1.42 (m, 19H), 1.39 (s, 3H), 1.36 (s, 3H), 1.28-1.22 (m, 2H), 1.14 (s, 3H), 1.12 (d, J=6.8Hz, 3H), 0.98 (d, J=6.9Hz, 3H), 0.96-0.90 (m, 6H), 0.88 (s, 9H), 0.85-0.79 (m, 6H), 0.78-0.74 (m, 6H), 0.07 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.5, 159.1, 158.9, 158.7, 150.6, 132.5, 132.1, 131.9, 131.2, 130.9, 129.4, 129.2, 129.0, 128.6, 128.2, 125.3, 122.2, 113.7, 113.7, 113.6, 98.4, 97.4, 84.4, 78.2, 77.9, 74.2, 73.9, 73.4, 70.7, 69.7, 67.4, 63.7, 55.2 (3C), 47.1, 42.2, 37.5, 36.0, 34.3, 33.7, 33.0, 30.2, 30.1, 29.9, 29.7, 26.9, 26.4, 26.0, 25.5, 24.3, 22.6, 21.3, 20.3, 19.5, 18.1, 17.7, 10.9, 9.1, 7.8, 4.7, -4.2, -4.4 ppm; HRMS (ESI+) calculated for $C_{73}H_{112}O_{13}NaSi$ $(M+Na)^+$ 1247.7770 found 1247.7766.



Ushikulide A (1): A plastic vial is charged with THF (10mL), pyridine (5.7mL) and HF·pyridine (Aldrich, 3.0mL). To a second plastic vial containing the macrocycle **(24)** (10.6mg, 8.7µmoles) is added the stock solution prepared above (5mL). The reaction is stirred under nitrogen for 26 hours and diluted with ethyl acetate (100mL), diluted with water (25mL) and neutralized with saturated sodium bicarbonate (~20mL). The organic phase is washed with copper sulfate (30mL) water (30mL) and brine (30mL). Then the organic phase is dried over sodium sulfate, filtered and concentrated. Flash chromagraphy (9:1 toluene/EtOAc) gives the alcohol as a white foam.

The substrate prepared above is immediately dissolved in dichloromethane (1mL) and Dess-Martin reagent is added (15.0mg). The milky white solution is stirred for 4 hours and quenched with sodium thiosulfate (5mL) and diluted with diethyl ether (40mL). The organic phase is washed with sodium bicarbonate (2x15mL) dried over sodium sulfate, concentrated and used directly in the next step without further purification.

The crude ketone is dissolved in dichloromethane (3mL) and water (0.5mL). DDQ (10.2mg) is added at ambient temperature and the red solution is stirred vigorously for 45 minutes. Silica gel (300mg) is added along with additional dichloromethane (10mL). The solution is concentrated to dryness and the remaining silica gel loaded onto a short column of silica gel. The product elutes (single fraction collected, 9:1 DCM/EtOAc) separating easily from the red catechol byproduct. After concentration the crude triol is suspended in a 3:2 mixture of glacial acetic acid and water (3mL) and the reaction is stirred vigorously under nitrogen for 5 hours. The solvent is removed *in vacuo,* and the residue is dissolved three times in toluene and concentrated to dryness (for the first cycle a minimum amount of methanol is added to give a homogeneous solution). The resulting oil is purified by flash

chromatography (10:1 chloroform/methanol) yielding the natural product as a white powder (3.3mg, 52% over 3 steps).

Ushikulide A – Synthetic Material:

r_f=0.30 (9:1 chloroform/methanol); $[\alpha]_D$ = -12° (c=0.28, CH_3OH); IR (neat): 3440 (broad), 1711 (sharp), 1463, 1276, 985 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ 6.76 (dd, *J*=15.7, 10.1Hz, 1H), 5.81 (d, *J*=15.7Hz, 1H), 5.60 (ddd, *J*=15.0, 9.4, 4.2Hz, 1H), 5.44 (dd, *J*=15.4, 8.8Hz, 1H), 5.30 (ddd, *J*=11.6, 5.0, 5.0Hz, 1H), 4.33 (t, broad, *J*=8.2Hz, 1H), 4.09 (m, 1H), 4.02 (m, 1H), 3.78 (m, 1H), 3.62 (*J*=dd, 9.5, 1.5Hz, 1H), 3.18 (*J*=dd, 11.0, 2.0Hz, 1H), 3.07 (ddd, *J*=15.1, 9.0, 8.0Hz, 1H), 2.78 (dd, *J*=17.6, 6.6Hz, 1H), 2.73 (*J*=dd, 17.4, 8.1Hz, 1H), 2.46 (m, 1H), 2.23 (m, 1H), 2.15-2.00 (m, 3H), 1.80-1.40 (m, 18H), 1.14 (d, *J*=6.6Hz, 3H), 1.06 (s, 3H), 0.98 (t, *J*=7.3Hz, 3H), 0.94 (d, *J*=7.1Hz, 3H), 0.91 (d, *J*=6.8Hz, 3H), 0.87 (d, *J*=7.1Hz, 3H), 0.85 (d, *J*=7.0Hz, 3H), 0.79 (d, *J*=7.0Hz, 3H) ppm; ^{13}C NMR (125 MHz): δ 212.5, 166.5, 152.1, 136.6, 129.5, 122.7, 98.8, 81.3, 75.9, 75.4, 74.9, 71.2, 70.5, 69.0, 67.1, 57.8, 42.9, 41.6, 41.9, 41.3, 39.7, 38.4, 36.3, 36.3, 34.6, 34.5, 33.0, 32.0, 30.6, 27.5, 26.6, 24.1, 23.2, 22.7, 22.3, 17.9, 11.4, 10.2, 6.1, 4.2 ppm; HRMS (ESI+) calculated for $C_{40}H_{68}NaO_{10}$ $(M+Na)^+$ 731.4710, found 731.4700.

Ushikulide A – Authentic Material:*

r_f = 0.30 (9:1 chloroform/methanol); $[\alpha]_D$ = -13° (c=0.50, CH_3OH); IR (neat): 3443 (broad), 1710 (sharp), 1460, 1276, 986 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ 6.76 (dd, *J*=15.7, 10.0Hz, 1H), 5.81 (d, *J*=15.7Hz, 1H), 5.60 (ddd, *J*=15.0, 9.4, 4.2Hz, 1H), 5.44 (dd, *J*=15.4, 9.0Hz, 1H), 5.29 (ddd, *J*=11.1, 5.4, 5.4Hz, 1H), 4.33 (t, broad, *J*=7.2Hz, 1H), 4.09 (m, 1H), 4.02 (m, 1H), 3.78 (m, 1H), 3.62 (dd, *J*=9.9, 1.5Hz, 1H), 3.18 (dd, *J*=10.8, 1.7Hz, 1H), 3.07 (ddd, *J*=12.6, 8.5, 7.5Hz, 1H), 2.77 (dd, *J*=17.6, 6.6Hz, 1H), 2.73 (dd, *J*=17.4, 8.0Hz, 1H), 2.46 (m, 1H), 2.23 (m, 1H), 2.15-2.00 (m, 3H), 1.80-1.40 (m, 18H), 1.14 (d, *J*=6.6Hz, 3H), 1.06 (s), 0.98 (t, *J*=7.0Hz, 3H), 0.94 (d, *J*=7.1Hz, 3H), 0.91 (d, *J*=6.8Hz, 3H), 0.87 (d, *J*=7.1Hz, 3H), 0.85 (d, *J*=7.0Hz, 3H), 0.79 (d, *J*=7.0Hz, 3H) ppm; ^{13}C NMR (150 MHz, CD_3OD): δ 212.5, 166.5, 152.2, 136.7, 129.6, 122.7, 98.9, 81.3, 76.0, 75.5, 75.0, 71.3, 70.6, 69.1, 67.2, 57.8, 42.9, 42.0, 41.7, 41.3, 39.8, 38.6, 36.4, 36.4, 34.7, 34.6, 32.1, 33.0, 31.9, 30.6, 27.5, 26.7, 24.1, 23.2, 22.7, 22.4, 18.0, 11.5, 10.2, 6.2, 4.2 ppm.

* The ^1H NMR and IR specta shown above (and in the table below) for authentic Ushikulide A are from an authentic sample generously provided by K. Takahashi. The spectrum was obtained on the same instrument (600 Mhz) and at the same concentration (~2 mg/mL) as our synthetic sample. All protons are within 0.01 ppm, and the coupling constants for all peaks also match. The ^{13}C spectra is taken from the literature[6] and is in excellent agreement (within 0.1 ppm) with our synthetic sample.

The optical rotation measured in our laboratory, matches the literature value measured by Takahashi, confirming that the synthetic sample is of the same enantiomer as the natural product.

[6] Takahashi, K.; Yoshihara, T.; Kurosawa, K. *J. Antibiot.* **2005**, *58*, 420.

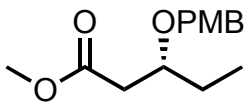
Carbon #	^{1}H Natural (600 Mhz)	^{1}H Synthetic (Same Instrument)	^{13}C Natural	^{13}C Synthetic
1	--	--	166.5	166.5
2	5.81 (d, 15.7)	5.81 (d, 15.7)	122.7	122.7
3	6.76 (dd, 15.7, 10.0)	6.76 (dd, 15.6, 10.1)	152.2	152.1
4	2.45 (m)	2.46 (m)	42.9	42.9
5	3.62 (dd, 9.9, 1.5)	3.62 (dd, 9.5, 1.5)	81.3	81.3
6	1.56 (m)	1.56 (m)	38.6	38.4
7	4.09 (m)	4.09 (m)	76.0	75.9
8	1.69 (m)	1.69 (m)	36.4	36.3
	1.73 (m)	1.73 (m)		
9	3.17 (dd, 10.8, 1.7)	3.18 (dd, 11.0, 2.0)	75.0	74.9
10	--	--	75.5	75.4
11	1.52 (m)	1.52 (m)	39.8	39.7
	1.54 (m)	1.54 (m)		
12	1.43 (m)	1.43 (m)	24.1	24.1
	1.52 (m)	1.52 (m)		
13	2.04 (m)	2.04 (m)	34.6	34.6
	2.23 (m)	2.23 (m)		
14	5.60 (ddd, 15.0, 9.4, 4.2)	5.60 (ddd, 15.0, 9.4, 4.2)	136.7	136.6
15	5.44 (dd, 15.0, 9.0)	5.44 (dd, 15.4, 8.8)	129.6	129.5
16	3.07 (ddd, 12.6, 8.0, 7.5)	3.07 (ddd, 15.1, 9.0, 8.0)	57.8	57.8
17	--	--	212.5	212.5
18	2.77 (dd, 17.6, 6.6)	2.78 (dd, 17.6, 6.6)	42.0	41.9
	2.73 (dd, 17.4, 8.0)	2.73 (dd, 17.4, 8.1)		
19	4.33 (t, broad, 7.2)	4.33 (t, broad, 8.2)	67.2	67.1
20	2.05 (m)	2.05 (m)	34.7	34.6
21	5.29 (ddd, 11.1, 5.4, 5.4)	5.30 (ddd, 11.6, 5.0, 5.0)	71.3	71.2
22	1.68 (m)	1.68 (m)	36.4	36.3
	1.72 (m)	1.72 (m)		
23	--	--	98.9	98.8
24	1.40 (m)	1.40 (m)	30.6	30.6
	1.65 (m)	1.65 (m)		
25	1.40 (m)	1.40 (m)	27.5	27.5
	2.19 (m)	2.19 (m)		
26	1.48 (m)	1.48 (m)	32.1	32.0
27	4.02 (m)	4.02 (m)	69.1	69.0
28	1.28 (m)	1.28 (m)	41.7	41.6
	1.63 (m)	1.63 (m)		
29	3.77 (m)	3.78 (m)	70.6	70.5
30	1.47 (m)	1.47 (m)	31.9	32.0
	1.53 (m)	1.53 (m)		
31	0.97 (t, 7.4)	0.98 (t, 7,3)	10.2	10.2
32	1.14 (d, 6.4)	1.14 (d, 6.6)	18.0	17.9
33	0.85 (d, 6.9)	0.85 (d, 7.0)	4.2	4.2
34	1.06 (s)	1.06 (s)	22.7	22.7
35	1.41 (m)	1.41 (m)	41.3	41.3
	1.53 (m)	1.53 (m)		
36	1.53 (m)	1.53 (m)	26.7	26.6
37	0.91 (d, 5.9)	0.91 (d, 6.8)	23.2	23.3
38	0.87 (d, 6.2)	0.87 (d, 7.1)	22.4	22.3
39	0.79 (d, 6.9)	0.79 (d, 7.0)	6.2	6.1
40	0.94 (d, 6.9)	0.94 (d, 7.1)	11.5	11.4

BMO-22-XV-product

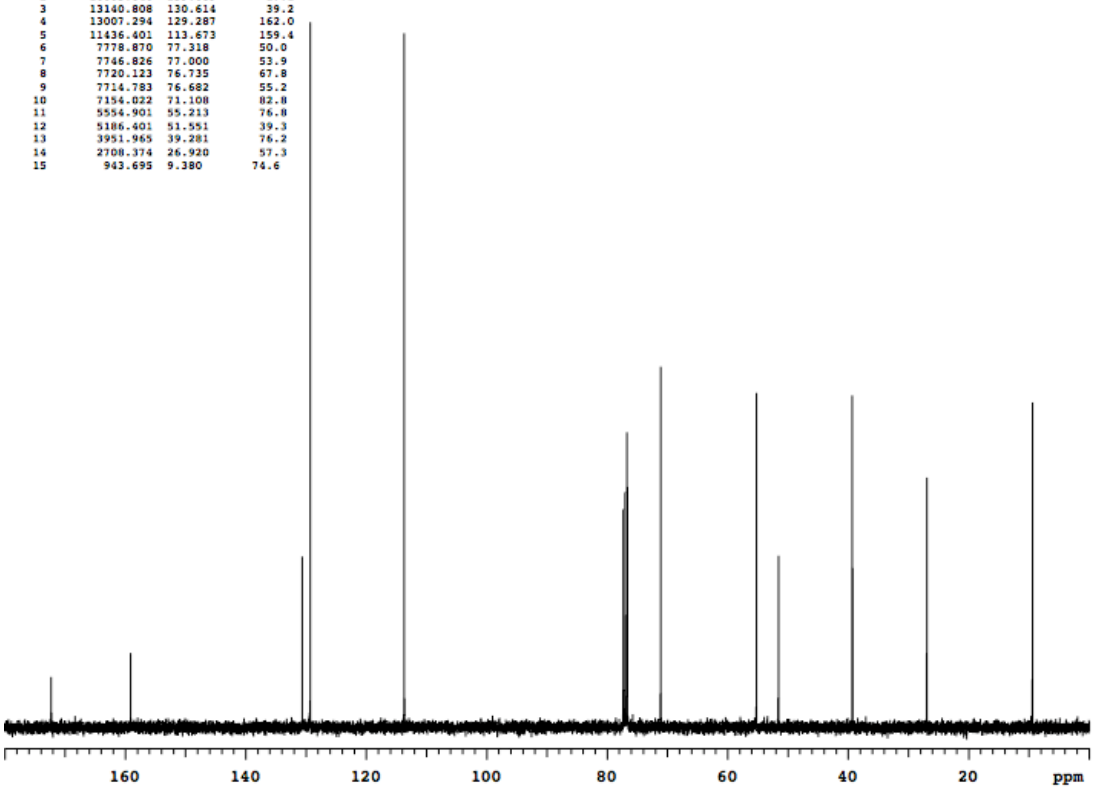
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

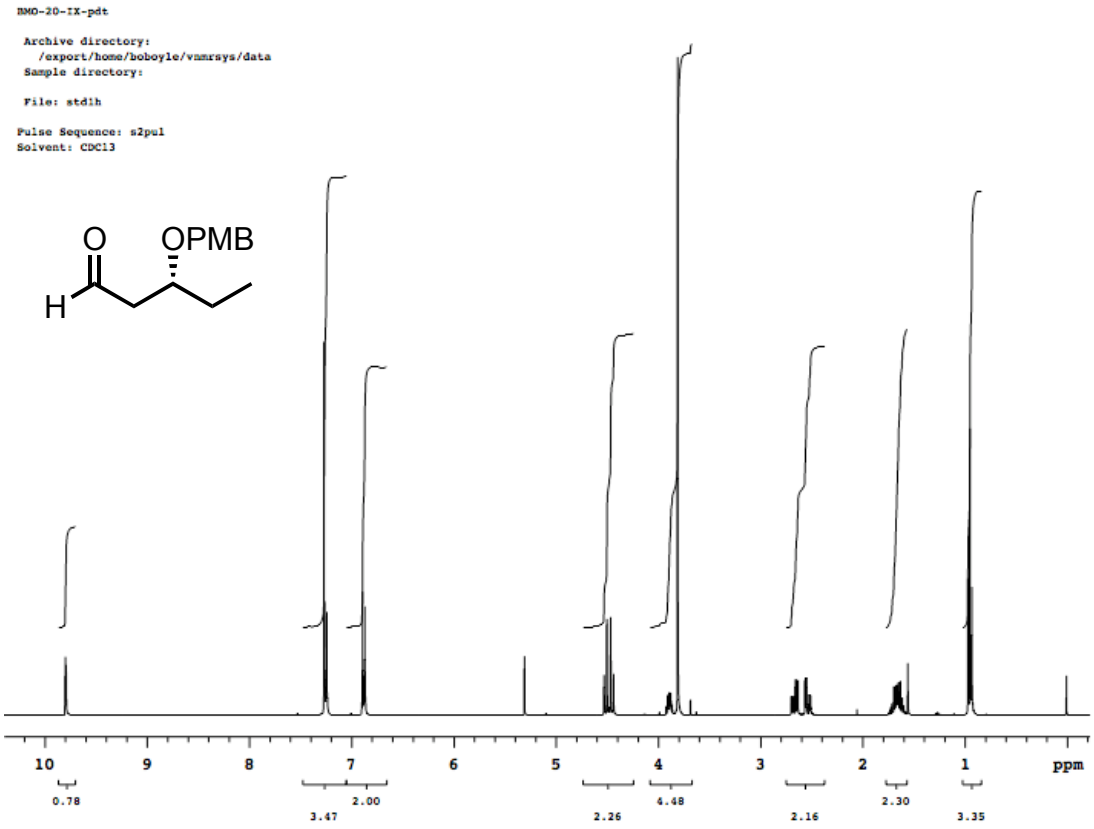
File: bmo-22-XV-pdt

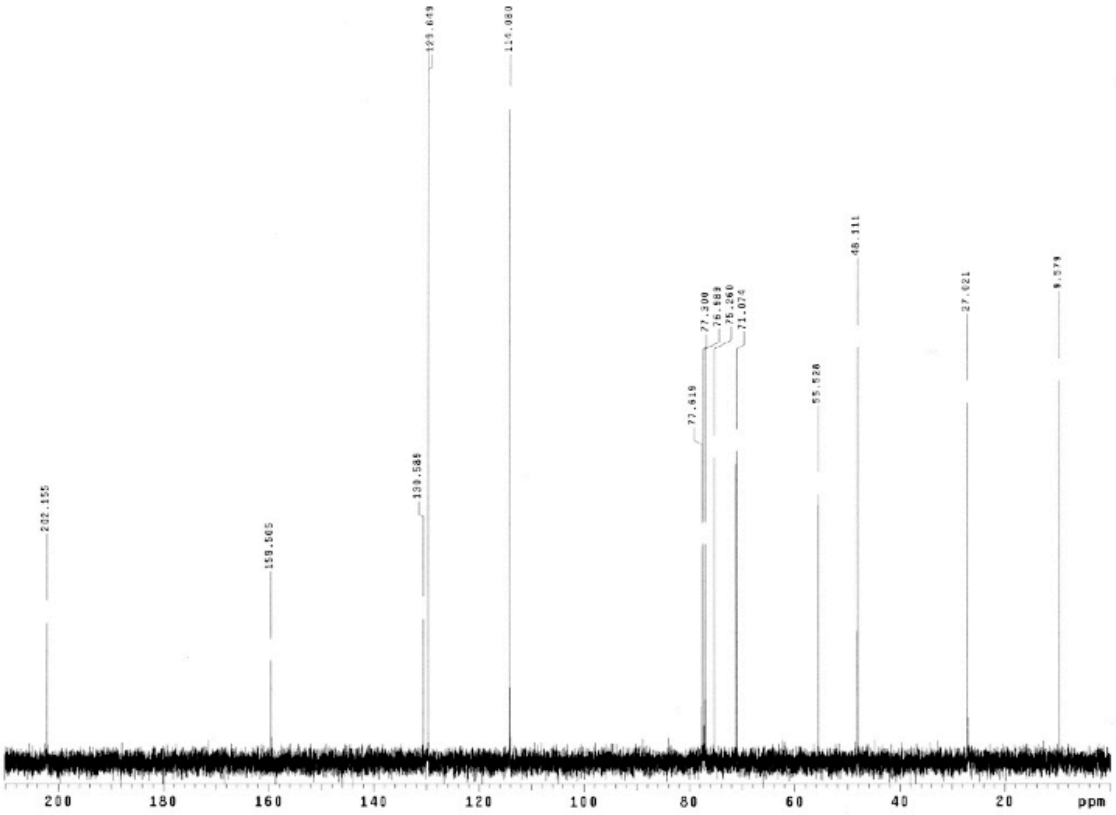
Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	17333.160	172.284	11.5
2	16005.646	159.089	17.1
3	13140.808	130.614	39.2
4	13007.294	129.287	162.0
5	11436.401	113.673	159.4
6	7778.870	77.318	50.0
7	7746.826	77.000	53.9
8	7720.123	76.735	67.8
9	7714.783	76.682	55.2
10	7154.022	71.108	82.8
11	5554.901	55.213	76.8
12	5186.401	51.551	39.3
13	3951.965	39.281	76.2
14	2708.374	26.920	57.3
15	943.695	9.380	74.6




BMO-20-IX-pdt
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:
File: std1h
Pulse Sequence: s2pul
Solvent: CDCl3
O
OPMB
H
10
9
8
7
6
5
4
3
2
1
ppm
0.78
3.47
2.00
2.26
4.48
2.16
2.30
3.35

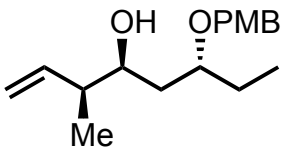

202.155
159.665
139.585
129.659
114.089
77.619
77.300
76.980
76.660
76.260
71.074
55.526
48.111
37.621
9.579
200
180
160
140
120
100
80
60
40
20
ppm

BMO-29-XV-product

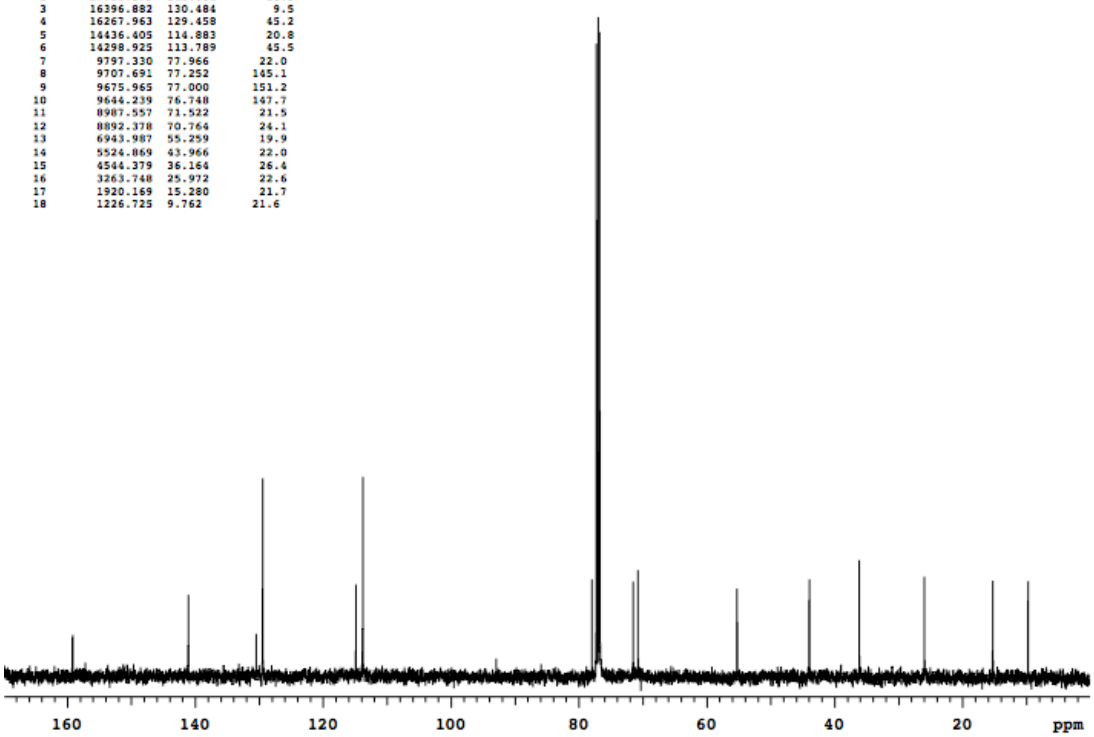
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-29-XV-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	20002.590	159.178	9.2
2	17728.879	141.084	18.5
3	16396.882	130.484	9.5
4	16267.963	129.458	45.2
5	14436.405	114.883	20.8
6	14298.925	113.789	45.5
7	9797.330	77.966	22.0
8	9707.691	77.252	145.1
9	9675.965	77.000	151.2
10	9644.239	76.748	147.7
11	8987.557	71.522	21.5
12	8892.378	70.764	24.1
13	6943.987	55.259	19.9
14	5524.869	43.966	22.0
15	4544.379	36.164	26.4
16	3263.748	25.972	22.6
17	1920.169	15.280	21.7
18	1226.725	9.762	21.6

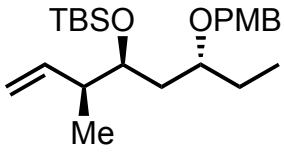


BMO-37-XVII-product

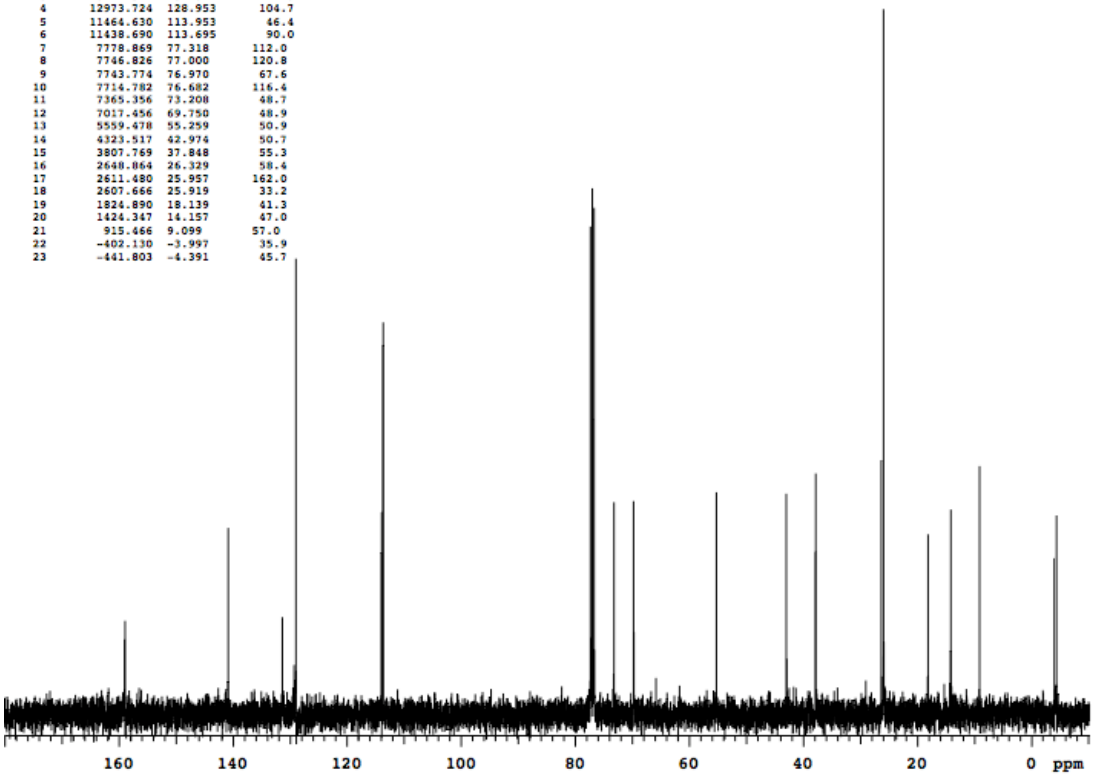
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-37-XVII-fraction1

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	15991.150	158.945	21.4
2	14170.013	140.844	42.8
3	13212.524	131.327	22.3
4	12973.724	128.953	104.7
5	11464.630	113.953	46.4
6	11438.690	113.695	90.0
7	7778.869	77.318	112.0
8	7746.826	77.000	120.8
9	7743.774	76.970	67.6
10	7714.782	76.682	116.4
11	7365.356	73.208	48.7
12	7017.456	69.750	48.9
13	5559.478	55.259	50.9
14	4323.517	42.974	50.7
15	3807.769	37.848	55.3
16	2648.864	26.329	58.4
17	2611.480	25.957	162.0
18	2607.666	25.919	33.2
19	1824.890	18.139	41.3
20	1424.347	14.157	47.0
21	915.466	9.099	57.0
22	-402.130	-3.997	35.9
23	-441.803	-4.391	45.7

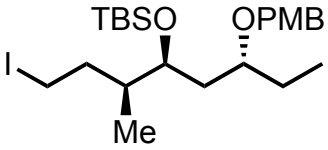


BMO-11-XIII-product

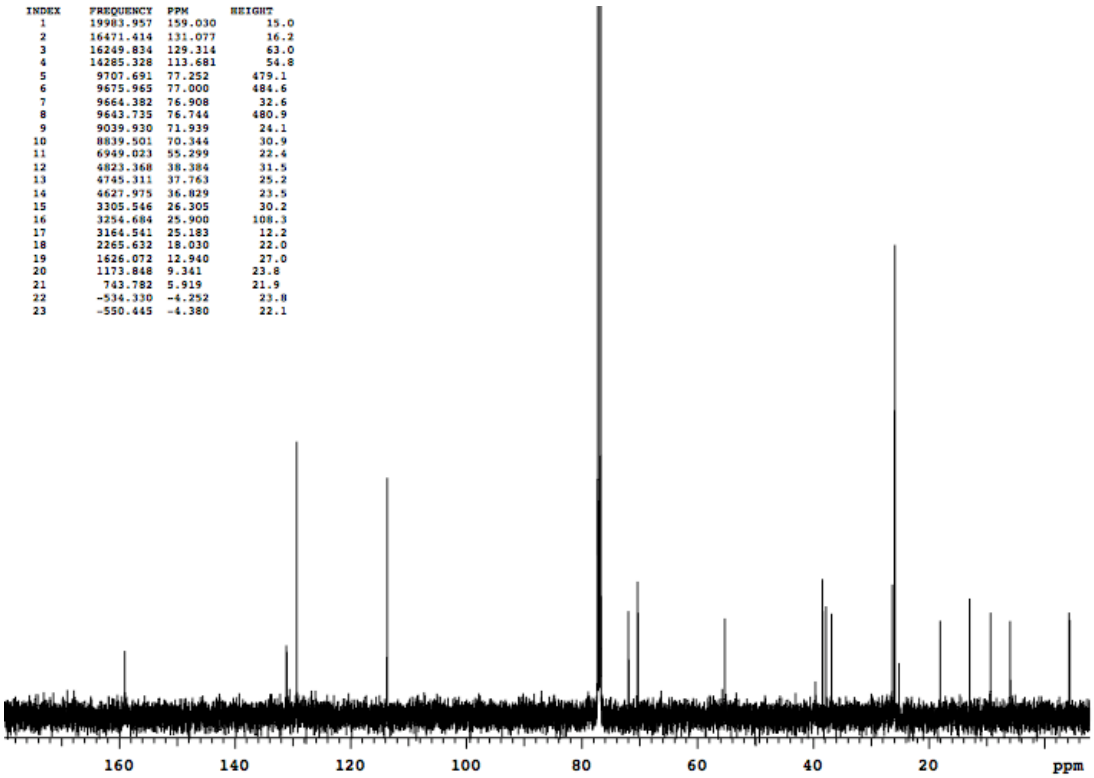
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-11-XIII-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	19983.957	159.030	15.0
2	16471.414	131.077	16.2
3	16249.834	129.314	63.0
4	14285.328	113.681	54.8
5	9707.691	77.252	479.1
6	9675.965	77.000	484.6
7	9664.382	76.908	32.6
8	9643.735	76.744	480.9
9	9039.930	71.939	24.1
10	8839.501	70.344	30.9
11	6949.023	55.299	22.4
12	4823.368	38.384	31.5
13	4745.311	37.763	25.2
14	4627.975	36.829	23.5
15	3305.546	26.305	30.2
16	3254.684	25.900	108.3
17	3164.541	25.183	12.2
18	2265.632	18.030	22.0
19	1626.072	12.940	27.0
20	1173.848	9.341	23.8
21	743.782	5.919	21.9
22	-534.330	-4.252	23.8
23	-550.445	-4.380	22.1

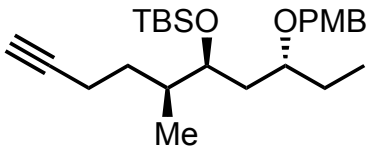


BMO-36-XV-product

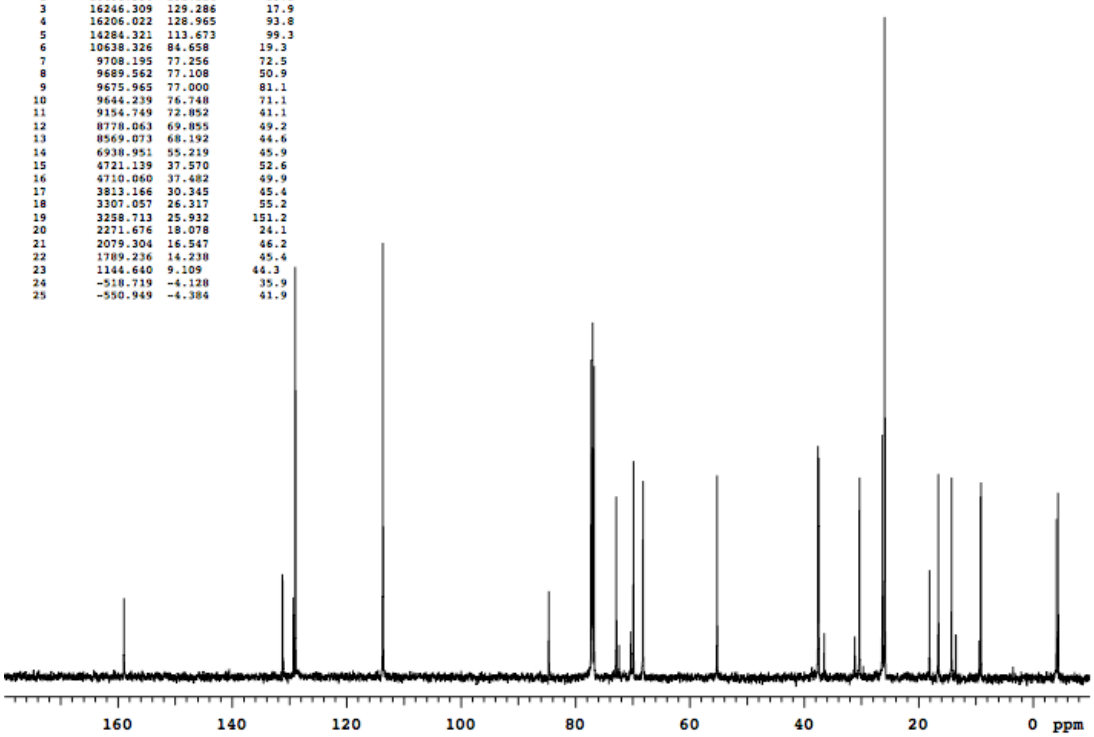
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

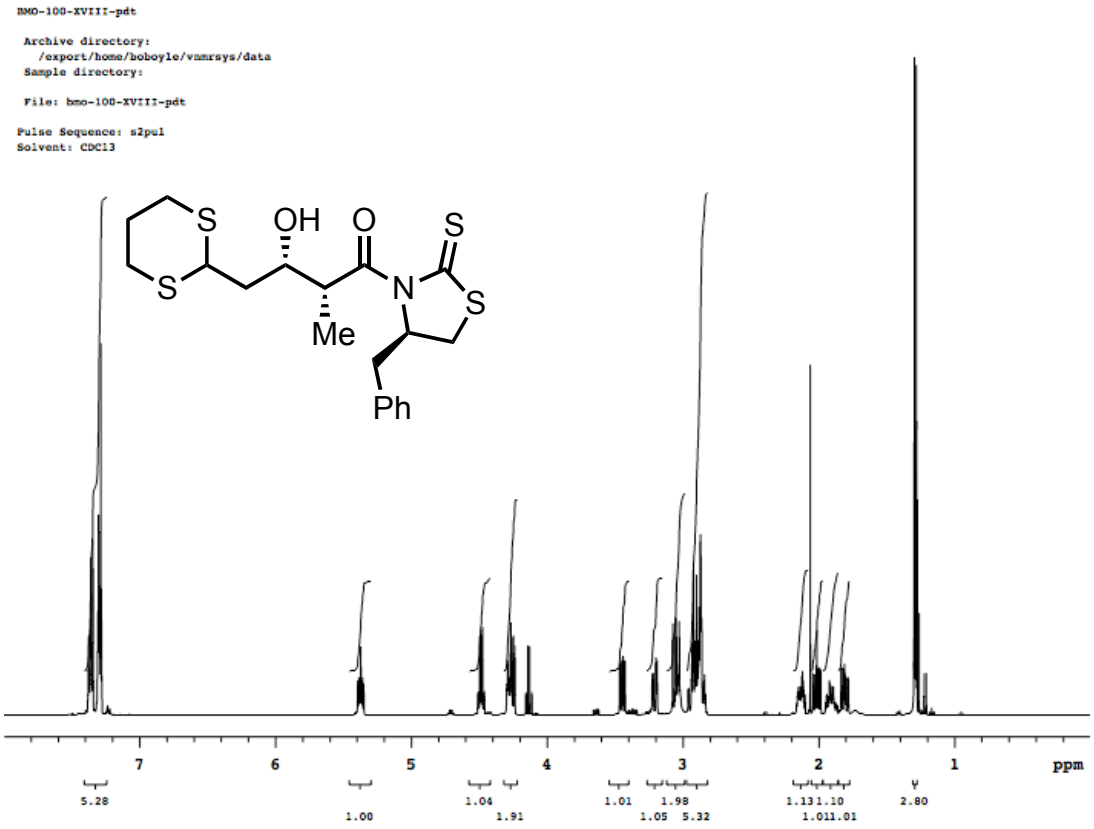
File: bmo-36-XV-pdt

Pulse Sequence: s2pul
Solvent: CDCl3

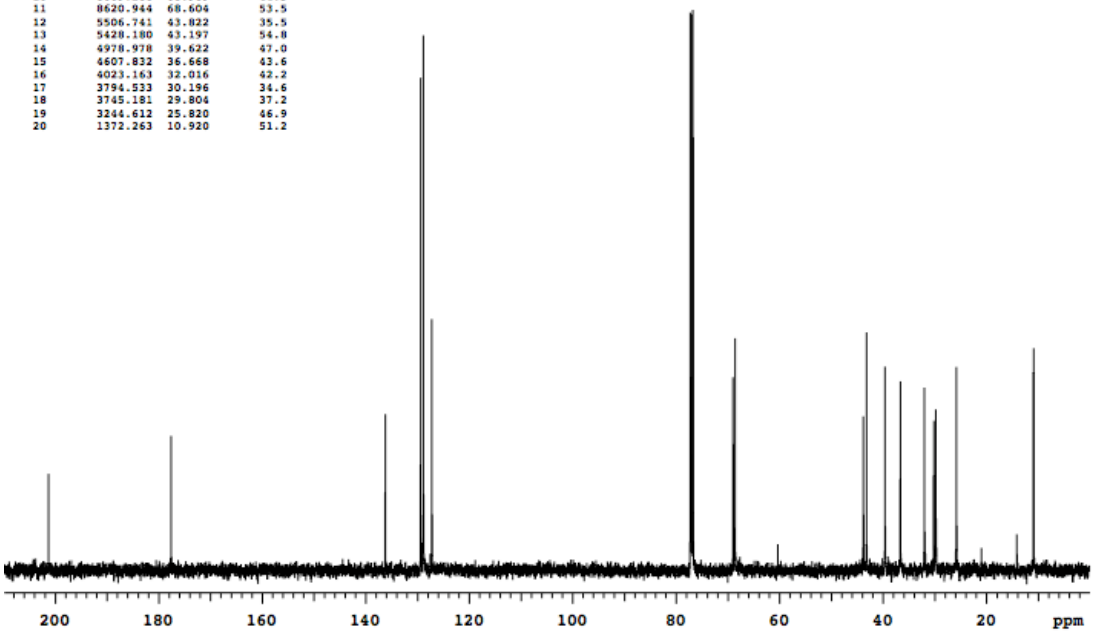


INDEX	FREQUENCY	PPM	HEIGHT
1	19970.864	158.925	17.7
2	16488.536	131.214	23.2
3	16246.309	129.286	17.9
4	16206.022	128.965	93.8
5	14284.321	113.673	99.3
6	10638.326	84.658	19.3
7	9708.195	77.256	72.5
8	9689.562	77.108	50.9
9	9675.965	77.000	81.1
10	9644.239	76.748	71.1
11	9154.749	72.852	41.1
12	8778.063	69.855	49.2
13	8569.073	68.192	44.6
14	6938.951	55.219	45.9
15	4721.139	37.570	52.6
16	4710.060	37.482	49.9
17	3813.166	30.345	45.4
18	3307.057	26.317	55.2
19	3258.713	25.932	151.2
20	2271.676	18.078	24.1
21	2079.304	16.547	46.2
22	1789.236	14.238	45.4
23	1144.640	9.109	44.3
24	-518.719	-4.128	35.9
25	-550.949	-4.384	41.9





INDEX	FREQUENCY	PPM	HEIGHT
1	25296.836	201.309	22.4
2	22317.092	177.596	31.1
3	17117.521	136.219	36.1
4	16256.885	129.370	113.4
5	16191.922	128.853	123.1
6	15985.450	127.210	58.0
7	9708.195	77.256	128.3
8	9675.965	77.000	127.9
9	9644.239	76.748	128.9
10	8669.288	68.989	44.5
11	8620.944	68.604	53.5
12	5506.741	43.822	35.5
13	5428.180	43.197	54.8
14	4978.978	39.622	47.0
15	4607.832	36.668	43.6
16	4023.163	32.016	42.2
17	3794.533	30.196	34.6
18	3745.181	29.804	37.2
19	3244.612	25.820	46.9
20	1372.263	10.920	51.2

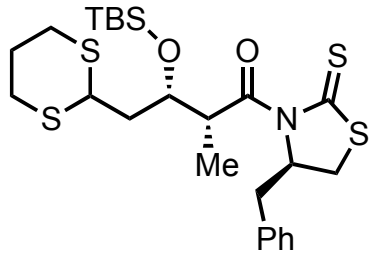


BMO-01-XIX-pdt

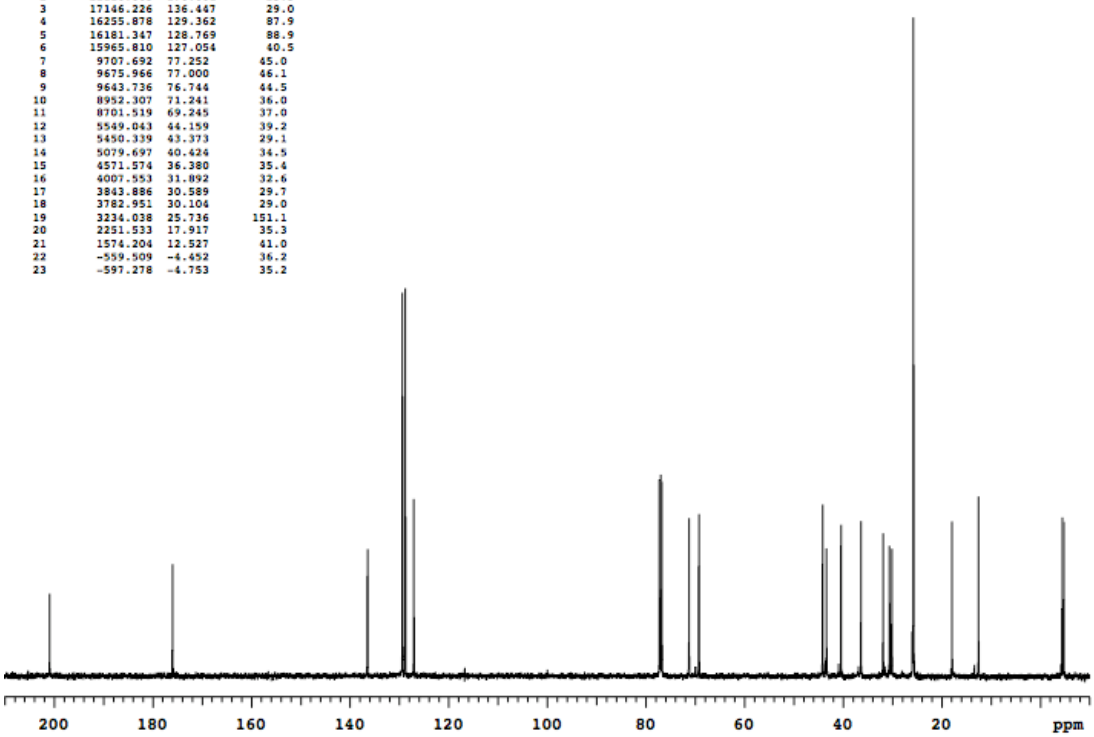
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-01-XIX-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	25250.003	200.936	18.7
2	22116.663	176.001	25.5
3	17146.226	136.447	29.0
4	16255.878	129.362	87.9
5	16181.347	128.769	88.9
6	15965.810	127.054	40.5
7	9707.692	77.252	45.0
8	9675.966	77.000	46.1
9	9643.736	76.744	44.5
10	8952.307	71.241	36.0
11	8701.519	69.245	37.0
12	5549.043	44.159	39.2
13	5450.339	43.373	29.1
14	5079.697	40.424	34.5
15	4571.574	36.380	35.4
16	4007.553	31.892	32.6
17	3843.886	30.589	29.7
18	3782.951	30.104	29.0
19	3234.038	25.736	151.1
20	2251.533	17.917	35.3
21	1574.204	12.527	41.0
22	-559.509	-4.452	36.2
23	-597.278	-4.753	35.2

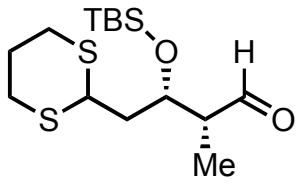


BMO-57-XIII-product

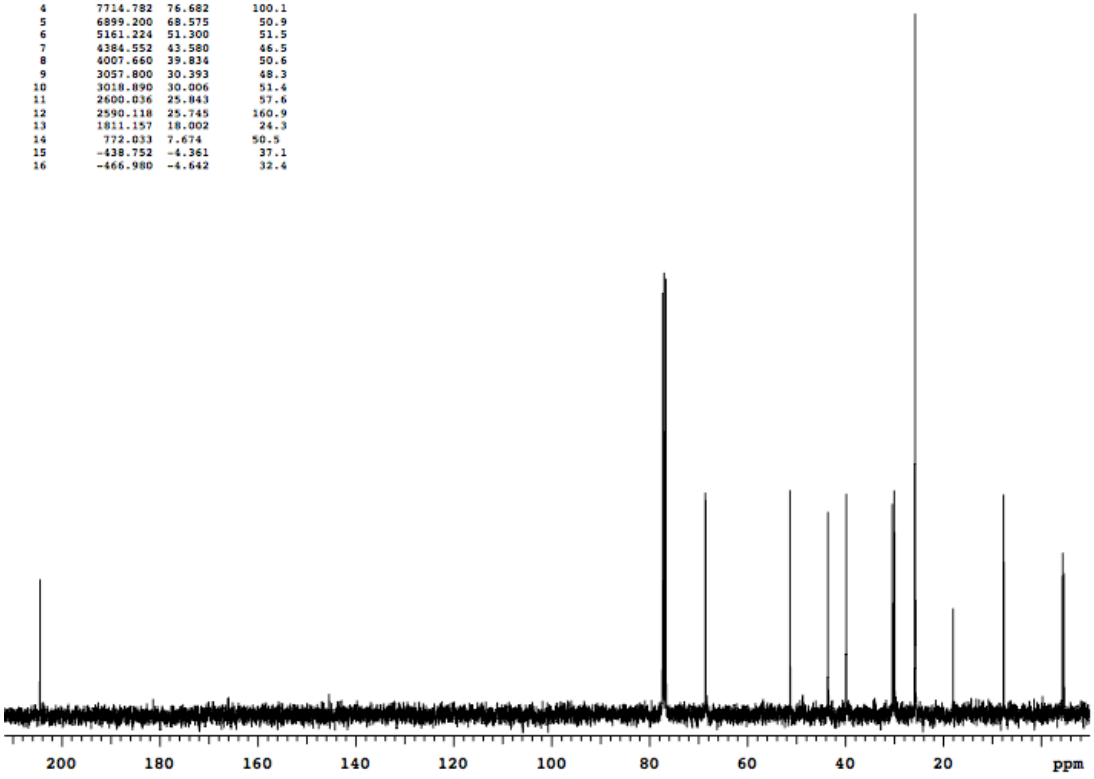
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-57-XIII-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	20572.601	204.482	31.0
2	7778.869	77.318	96.8
3	7746.826	77.000	101.4
4	7714.782	76.682	100.1
5	6899.200	68.575	50.9
6	5161.224	51.300	51.5
7	4384.552	43.580	46.5
8	4007.660	39.834	50.6
9	3057.800	30.393	48.3
10	3018.890	30.006	51.4
11	2600.036	25.843	57.6
12	2590.118	25.745	160.9
13	1811.157	18.002	24.3
14	772.033	7.674	50.5
15	-438.752	-4.361	37.1
16	-466.980	-4.642	32.4

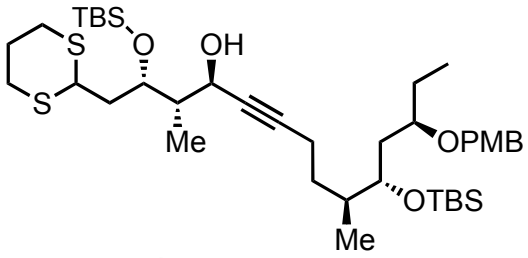


BMO-37-XIV--minor diastereomer

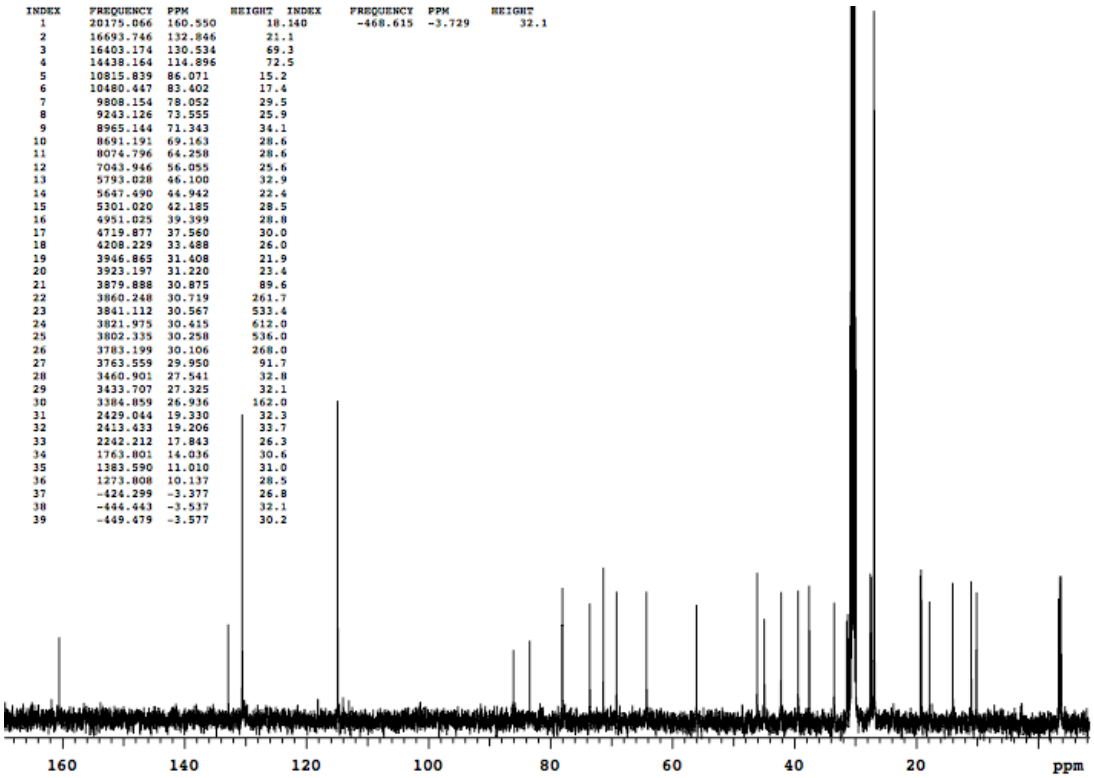
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-37-XIV-Fractio1-minor

Pulse Sequence: s2pul
Solvent: Acetone



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20175.066	160.550	18.140		-468.615	-3.729	32.1
2	16693.746	132.846	21.1				
3	16403.174	130.534	69.3				
4	14438.164	114.896	72.5				
5	10815.839	86.071	15.2				
6	10480.447	83.402	17.4				
7	9808.154	78.052	29.5				
8	9243.126	73.555	25.9				
9	8965.144	71.343	34.1				
10	8691.191	69.163	28.6				
11	8074.796	64.258	28.6				
12	7043.946	56.055	25.6				
13	5793.028	46.100	32.9				
14	5647.490	44.942	22.4				
15	5301.020	42.185	28.5				
16	4951.025	39.399	28.8				
17	4719.877	37.560	30.0				
18	4208.229	33.488	26.0				
19	3946.865	31.408	21.9				
20	3923.197	31.220	23.4				
21	3879.888	30.875	89.6				
22	3860.248	30.719	261.7				
23	3841.112	30.567	533.4				
24	3821.975	30.415	612.0				
25	3802.335	30.258	536.0				
26	3783.199	30.106	268.0				
27	3763.559	29.950	91.7				
28	3460.901	27.541	32.8				
29	3433.707	27.325	32.1				
30	3384.859	26.936	162.0				
31	2429.044	19.330	32.3				
32	2413.433	19.206	33.7				
33	2242.212	17.843	26.3				
34	1763.801	14.036	30.6				
35	1383.590	11.010	31.0				
36	1273.808	10.137	28.5				
37	-424.299	-3.377	26.8				
38	-444.443	-3.537	32.1				
39	-449.479	-3.577	30.2				

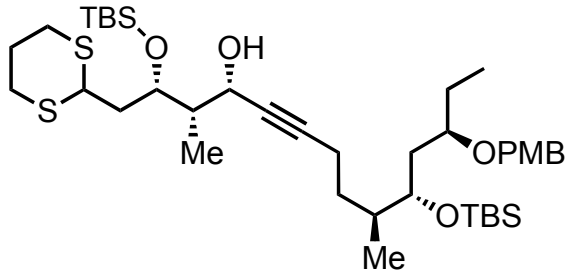


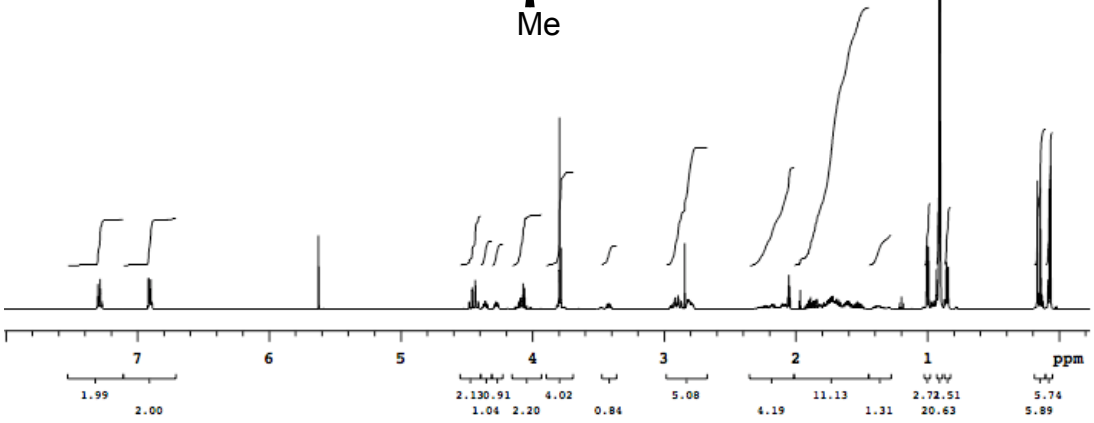
BMO-37-XIV-major diastereomer

Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

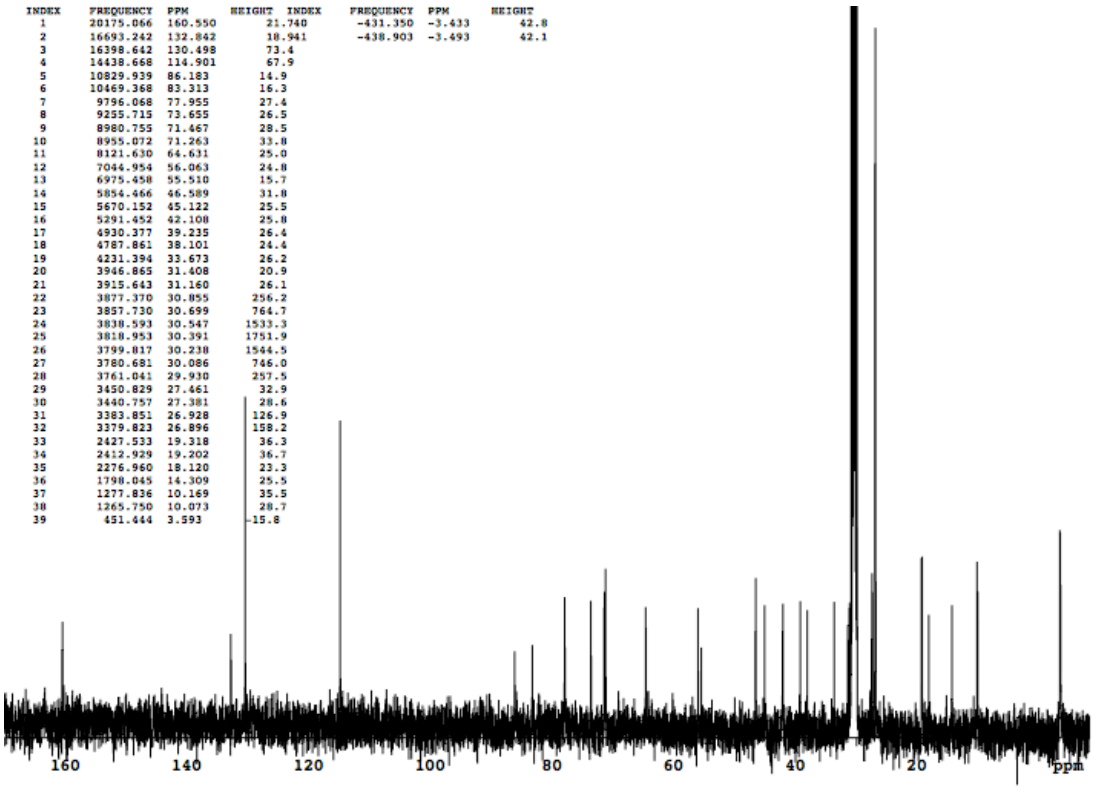
File: bmo-37-XIV-fraction1-major

Pulse Sequence: s2pul
Solvent: Acetone





INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20175.066	160.550	21.740		-431.350	-3.433	42.8
2	16693.242	132.842	18.941		-438.903	-3.493	42.1
3	16398.642	130.498	73.4				
4	14438.668	114.901	67.9				
5	10829.939	86.183	14.9				
6	10469.368	83.313	16.3				
7	9796.068	77.955	27.4				
8	9255.715	73.655	26.5				
9	8980.755	71.467	28.5				
10	8955.072	71.263	33.8				
11	8121.630	64.631	25.0				
12	7044.954	56.063	24.8				
13	6975.458	55.510	15.7				
14	5854.466	46.589	31.8				
15	5670.152	45.122	25.5				
16	5291.452	42.108	25.8				
17	4930.377	39.235	26.4				
18	4787.861	38.101	24.4				
19	4231.394	33.673	26.2				
20	3946.865	31.408	20.9				
21	3915.643	31.160	26.1				
22	3877.370	30.855	256.2				
23	3857.730	30.699	764.7				
24	3838.593	30.547	1533.3				
25	3818.953	30.391	1751.9				
26	3799.817	30.238	1544.5				
27	3780.681	30.086	746.0				
28	3761.041	29.930	257.5				
29	3450.829	27.461	32.9				
30	3440.757	27.381	28.6				
31	3383.851	26.928	126.9				
32	3379.823	26.896	158.2				
33	2427.533	19.318	36.3				
34	2412.929	19.202	36.7				
35	2276.960	18.120	23.3				
36	1798.045	14.309	25.5				
37	1277.836	10.169	35.5				
38	1265.750	10.073	28.7				
39	451.444	3.593	15.8				



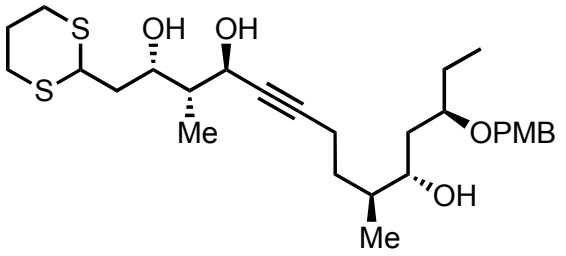
BMO-38-XIV-product

Archive directory:

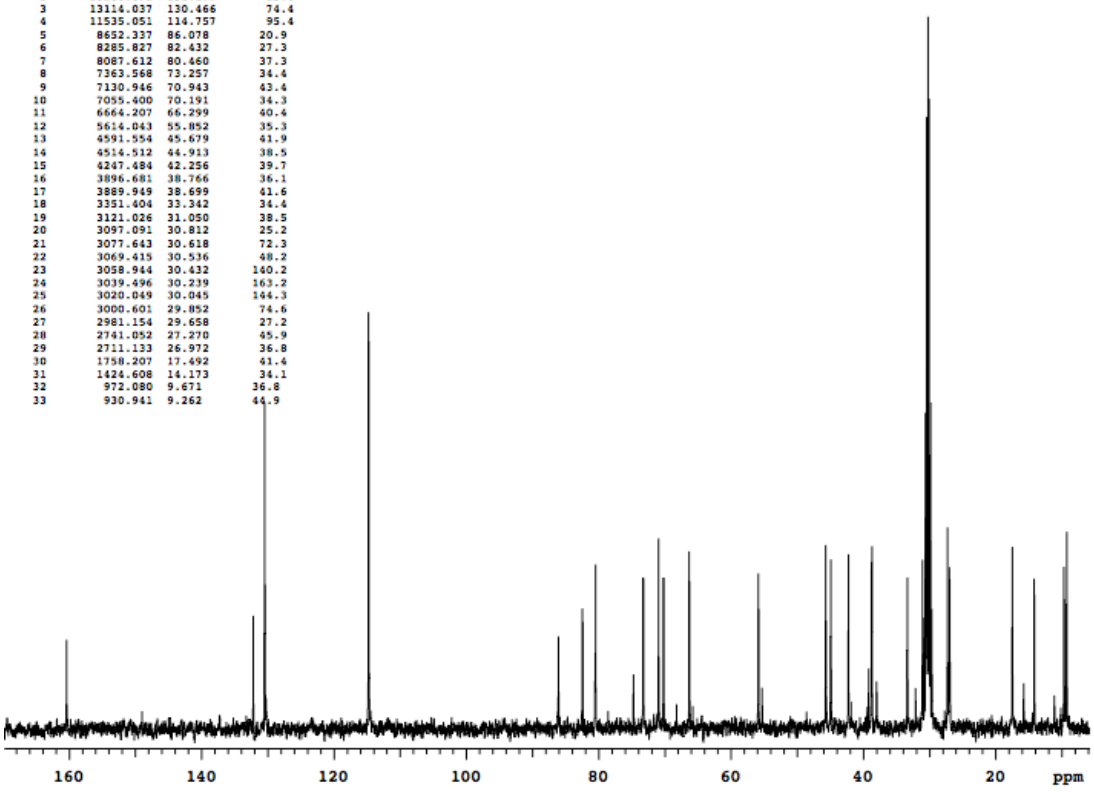
Sample directory:

File: bmo-38-XIV-pdt

Pulse Sequence: s2pul
Solvent: acetone



INDEX	FREQUENCY	PPM	HEIGHT
1	16122.412	160.395	20.0
2	13286.072	132.177	25.6
3	13114.037	130.466	74.4
4	11535.051	114.757	95.4
5	8652.337	86.078	20.9
6	8285.827	82.432	27.3
7	8087.612	80.460	37.3
8	7363.568	73.257	34.4
9	7130.946	70.943	43.4
10	7055.400	70.191	34.3
11	6664.207	66.299	40.4
12	5614.043	55.852	35.3
13	4591.554	45.679	41.9
14	4514.512	44.913	38.5
15	4247.484	42.256	39.7
16	3896.681	38.766	36.1
17	3889.949	38.699	41.6
18	3351.404	33.342	34.4
19	3121.026	31.050	38.5
20	3097.091	30.812	25.2
21	3077.643	30.618	72.3
22	3069.415	30.536	48.2
23	3058.944	30.432	140.2
24	3039.496	30.239	163.2
25	3020.049	30.045	144.3
26	3000.601	29.852	74.6
27	2981.154	29.658	27.2
28	2741.052	27.270	45.9
29	2711.133	26.972	36.8
30	1758.207	17.492	41.4
31	1424.608	14.173	34.1
32	972.080	9.671	36.8
33	930.941	9.262	44.9



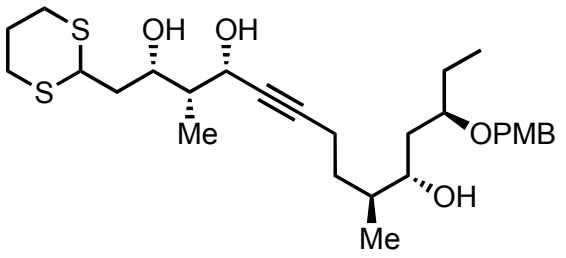
BMO-39-XIV-product

Archive directory:

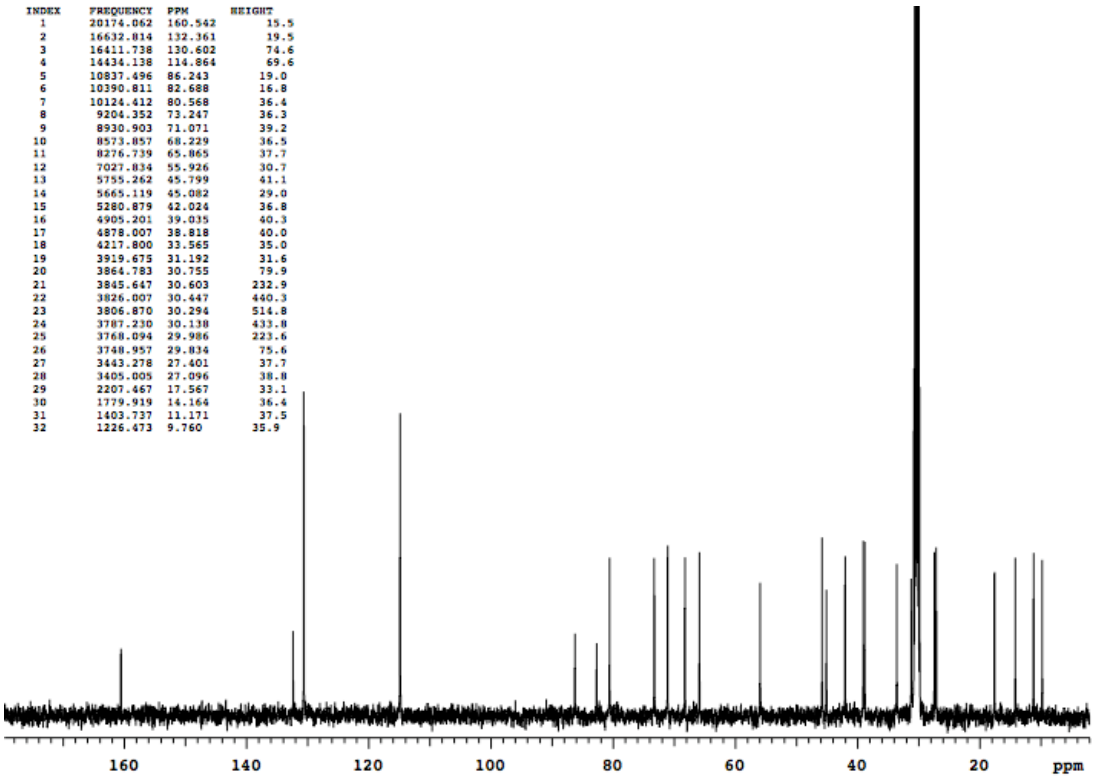
Sample directory:

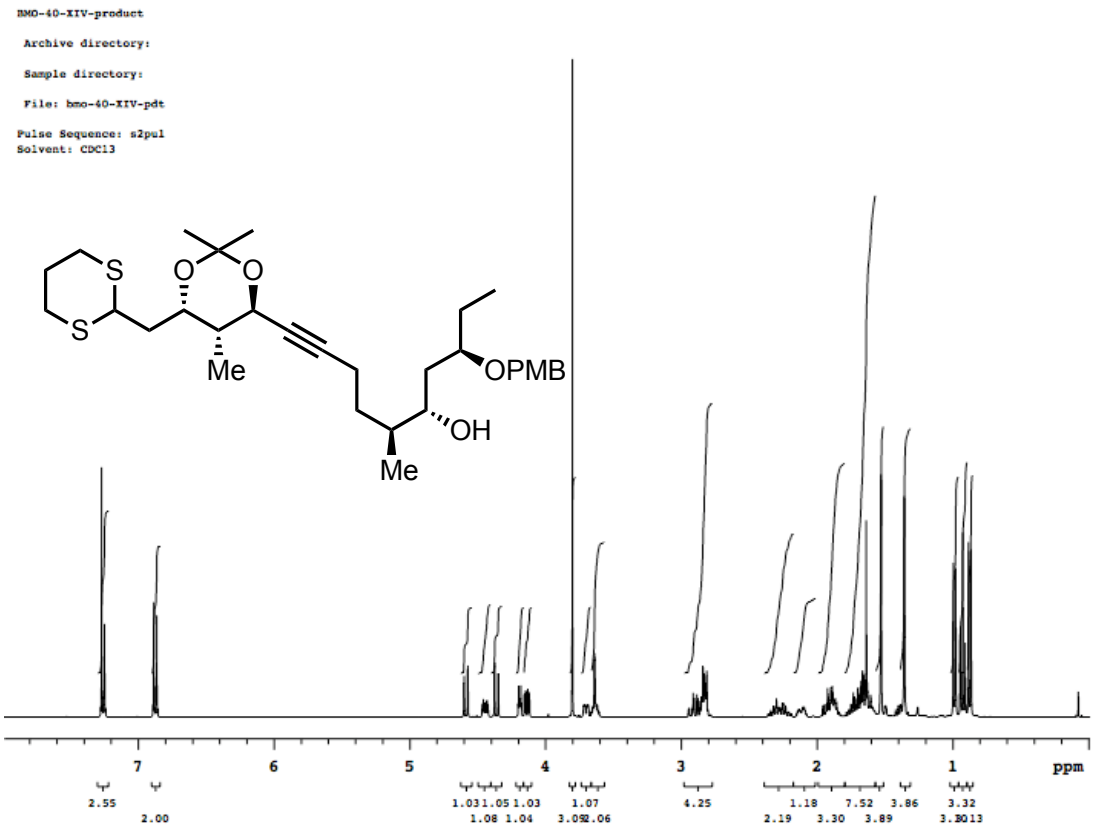
File: bmo-38-XIV-pdt

Pulse Sequence: s2pul
Solvent: acetone

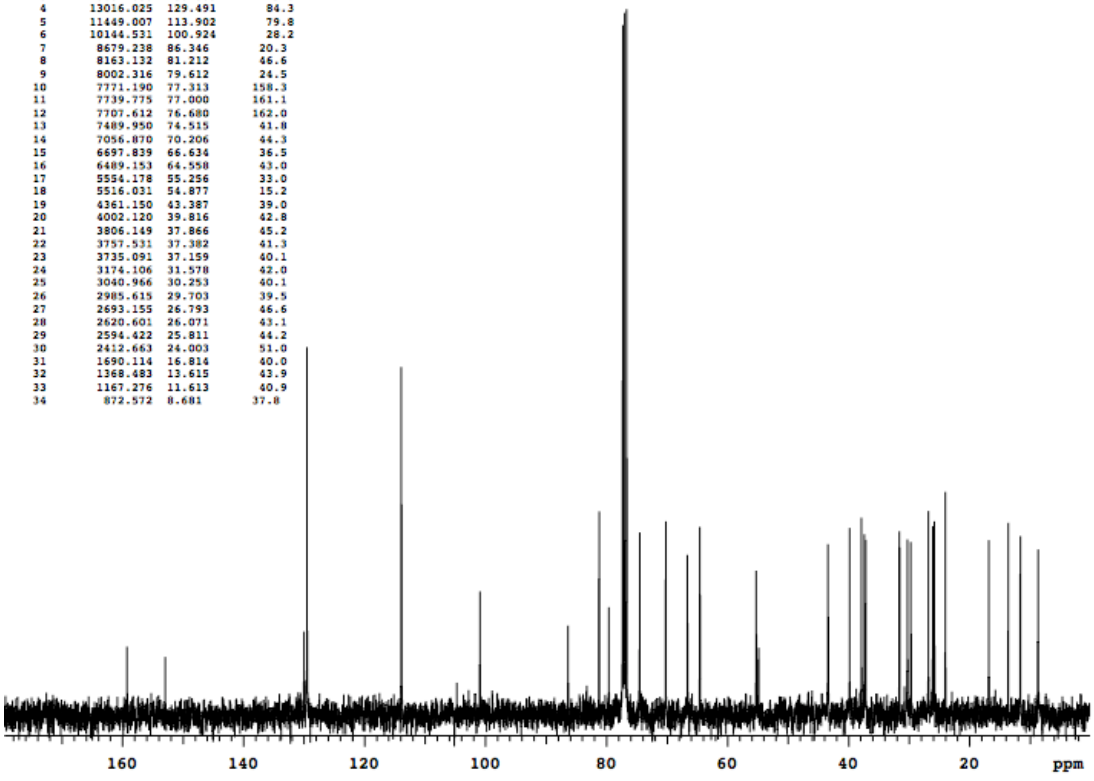


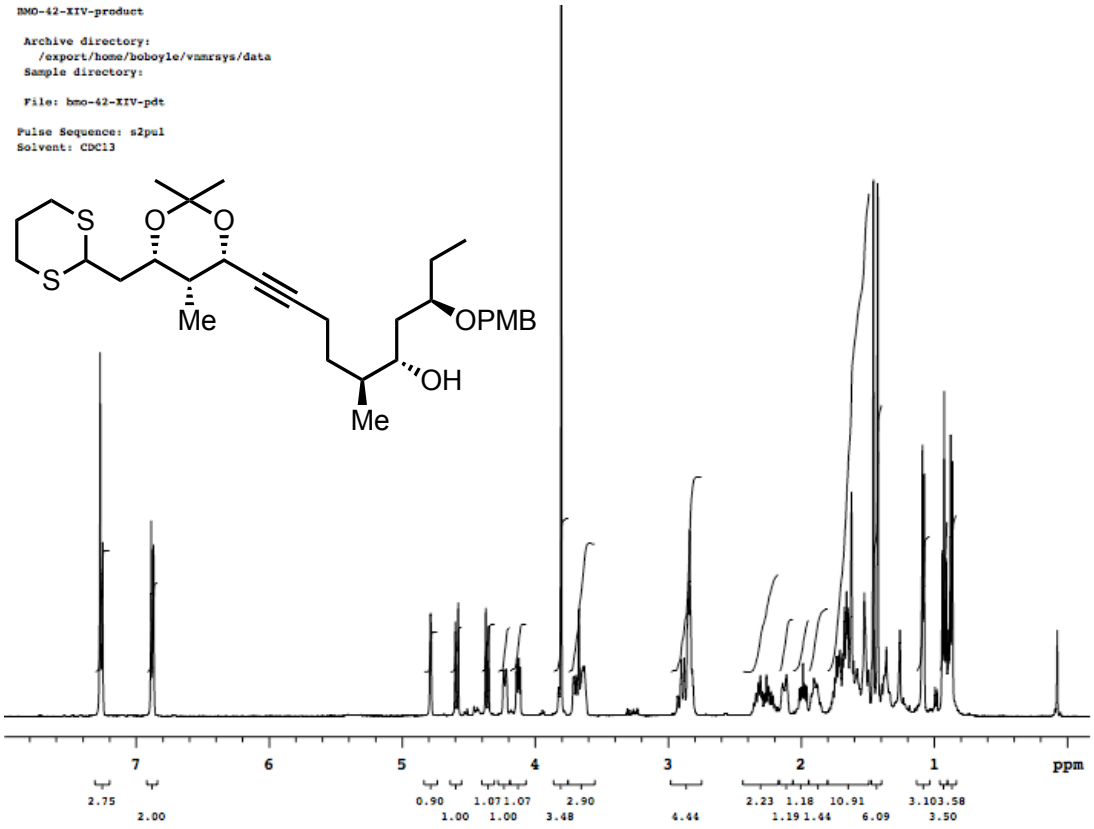
INDEX	FREQUENCY	PPM	HEIGHT
1	20174.062	160.542	15.5
2	16632.814	132.361	19.5
3	16411.738	130.602	74.6
4	14434.138	114.864	69.6
5	10837.496	86.243	19.0
6	10390.811	82.688	16.8
7	10124.412	80.568	36.4
8	9204.352	73.247	36.3
9	8930.903	71.071	39.2
10	8573.857	68.229	36.5
11	8276.739	65.865	37.7
12	7027.834	55.926	30.7
13	5755.262	45.799	41.1
14	5665.119	45.082	29.0
15	5280.879	42.024	36.8
16	4905.201	39.035	40.3
17	4878.007	38.818	40.0
18	4217.800	33.565	35.0
19	3919.675	31.192	31.6
20	3864.783	30.755	79.9
21	3845.647	30.603	232.9
22	3826.007	30.447	440.3
23	3806.870	30.294	514.8
24	3787.230	30.138	433.8
25	3768.094	29.986	223.6
26	3748.957	29.834	75.6
27	3443.278	27.401	37.7
28	3405.005	27.096	38.8
29	2207.467	17.567	33.1
30	1779.919	14.164	36.4
31	1403.737	11.171	37.5
32	1226.473	9.760	35.9



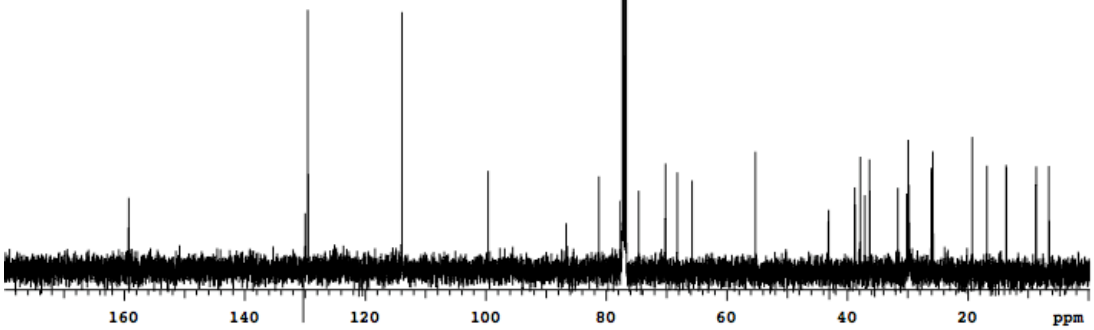


INDEX	FREQUENCY	PPM	HEIGHT
1	16007.945	159.257	15.5
2	15370.666	152.917	13.1
3	13067.636	130.005	19.0
4	13016.025	129.491	84.3
5	11449.007	113.902	79.8
6	10144.531	100.924	28.2
7	8679.238	86.346	20.3
8	8163.132	81.212	46.6
9	8002.316	79.612	24.5
10	7771.190	77.313	158.3
11	7739.775	77.000	161.1
12	7707.612	76.680	162.0
13	7489.950	74.515	41.8
14	7056.870	70.206	44.3
15	6697.839	66.634	36.5
16	6489.153	64.558	43.0
17	5554.178	55.256	33.0
18	5516.031	54.877	15.2
19	4361.150	43.387	39.0
20	4002.120	39.816	42.8
21	3806.149	37.866	45.2
22	3757.531	37.382	41.3
23	3735.091	37.159	40.1
24	3174.106	31.578	42.0
25	3040.966	30.253	40.1
26	2985.615	29.703	39.5
27	2693.155	26.793	46.6
28	2620.601	26.071	43.1
29	2594.422	25.811	44.2
30	2412.663	24.003	51.0
31	1690.114	16.814	40.0
32	1368.483	13.615	43.9
33	1167.276	11.613	40.9
34	872.572	8.681	37.8





INDEX	FREQUENCY	PPM	HEIGHT
1	20012.158	159.254	16.1
2	16372.710	130.292	-12.5
3	16334.437	129.987	12.6
4	16275.013	129.514	59.4
5	14314.032	113.909	58.9
6	12515.711	99.598	22.3
7	10886.093	86.630	10.3
8	10205.742	81.216	21.1
9	9763.590	77.697	15.5
10	9708.195	77.256	498.0
11	9675.965	77.000	506.4
12	9644.239	76.748	498.7
13	9375.321	74.608	17.8
14	8819.861	70.187	24.0
15	8572.598	68.220	22.0
16	8263.897	65.763	20.2
17	6943.987	55.259	26.7
18	5419.619	43.129	13.4
19	4867.684	38.736	18.6
20	4757.901	37.863	25.5
21	4662.722	37.105	16.8
22	4559.990	36.288	25.0
23	3972.804	31.615	18.5
24	3787.482	30.140	17.1
25	3757.770	29.904	29.5
26	3740.145	29.764	19.2
27	3270.295	26.025	23.0
28	3240.583	25.788	26.8
29	2421.745	19.272	30.1
30	2116.066	16.839	23.5
31	1712.186	13.625	23.7
32	1089.749	8.672	23.4
33	822.846	6.548	23.4

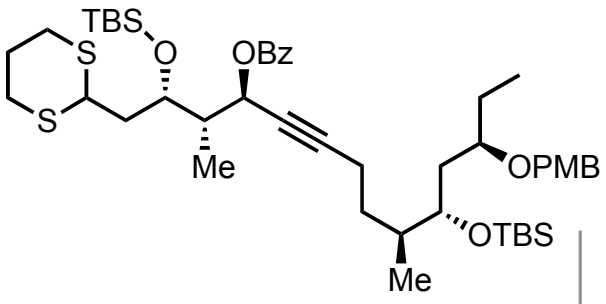


BMO-45-XV-product

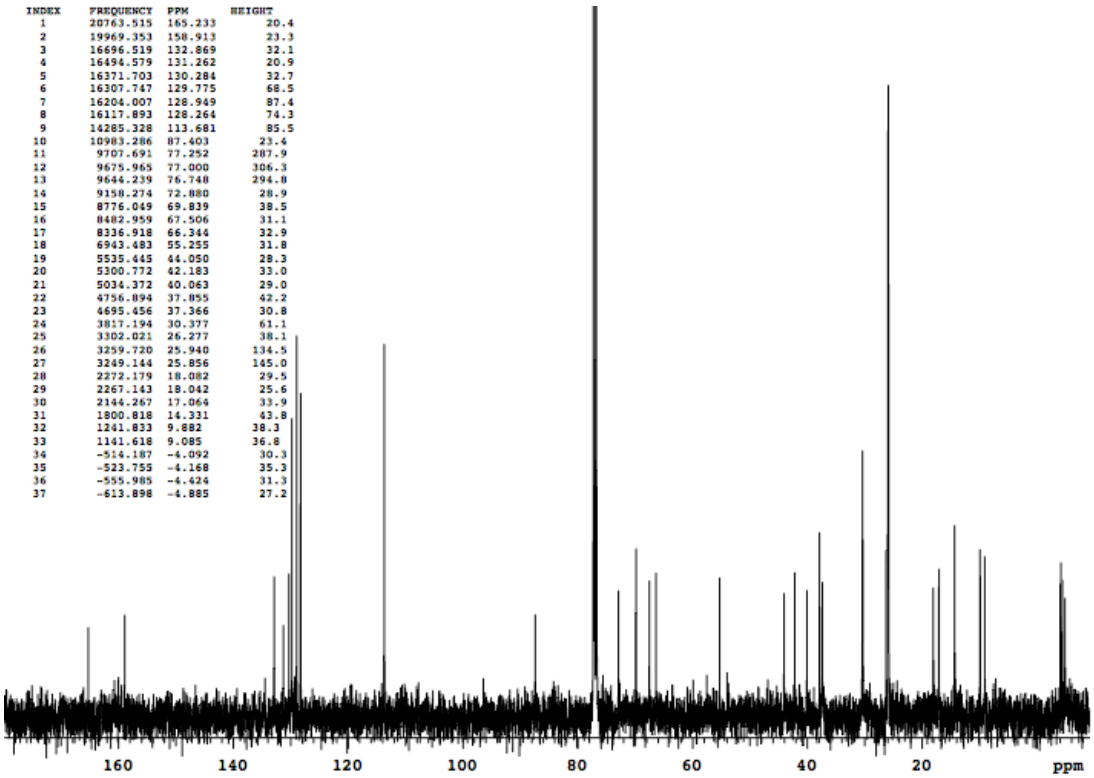
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-45-XV-fraction2-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	20763.515	165.233	20.4
2	19969.353	158.913	23.3
3	16696.519	132.869	32.1
4	16494.579	131.262	20.9
5	16371.703	130.284	32.7
6	16307.747	129.775	68.5
7	16204.007	128.949	87.4
8	16117.893	128.264	74.3
9	14285.328	113.681	85.5
10	10983.286	87.403	23.4
11	9707.691	77.252	287.9
12	9675.965	77.000	306.3
13	9644.239	76.748	294.8
14	9158.274	72.880	28.9
15	8776.049	69.839	38.5
16	8482.959	67.506	31.1
17	8336.918	66.344	32.9
18	6943.483	55.255	31.8
19	5535.445	44.050	28.3
20	5300.772	42.183	33.0
21	5034.372	40.063	29.0
22	4756.894	37.855	42.2
23	4695.456	37.366	30.8
24	3817.194	30.377	61.1
25	3302.021	26.277	38.1
26	3259.720	25.940	134.5
27	3249.144	25.856	145.0
28	2272.179	18.082	29.5
29	2267.143	18.042	25.6
30	2144.267	17.064	33.9
31	1800.818	14.331	43.8
32	1241.833	9.882	38.3
33	1141.618	9.085	36.8
34	-514.187	-4.092	30.3
35	-523.755	-4.168	35.3
36	-555.985	-4.424	31.3
37	-613.898	-4.885	27.2

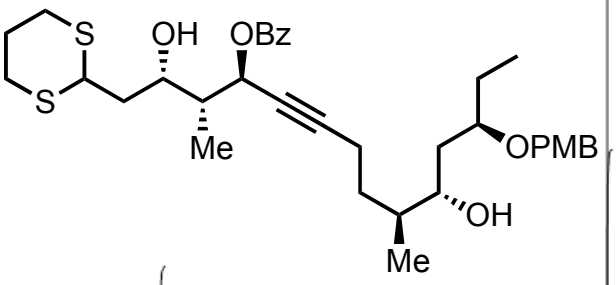


BMO-39-XV-product

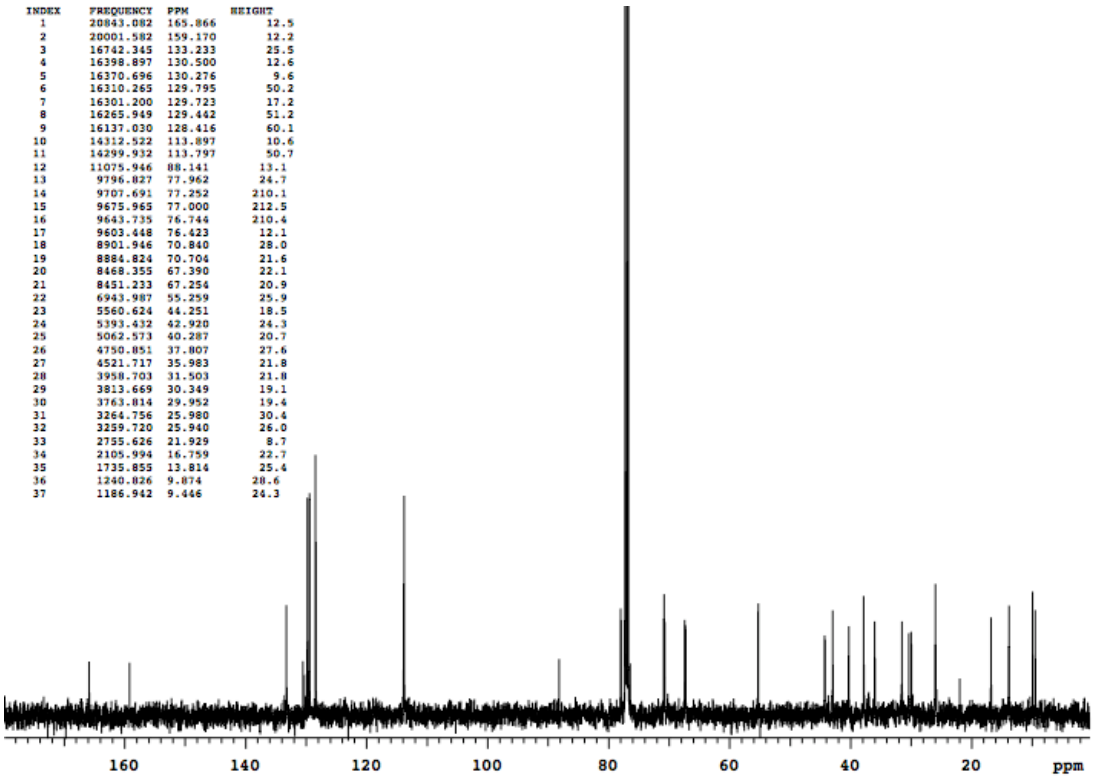
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-39-XV-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	20843.082	165.866	12.5
2	20001.582	159.170	12.2
3	16742.345	133.233	25.5
4	16398.897	130.500	12.6
5	16370.696	130.276	9.6
6	16310.265	129.795	50.2
7	16301.200	129.723	17.2
8	16265.949	129.442	51.2
9	16137.030	128.416	60.1
10	14312.522	113.897	10.6
11	14299.932	113.797	50.7
12	11075.946	88.141	13.1
13	9796.827	77.962	24.7
14	9707.691	77.252	210.1
15	9675.965	77.000	212.5
16	9643.735	76.744	210.4
17	9603.448	76.423	12.1
18	8901.946	70.840	28.0
19	8884.824	70.704	21.6
20	8468.355	67.390	22.1
21	8451.233	67.254	20.9
22	6943.987	55.259	25.9
23	5560.624	44.251	18.5
24	5393.432	42.920	24.3
25	5062.573	40.287	20.7
26	4750.851	37.807	27.6
27	4521.717	35.983	21.8
28	3958.703	31.503	21.8
29	3813.669	30.349	19.1
30	3763.814	29.952	19.4
31	3264.756	25.980	30.4
32	3259.720	25.940	26.0
33	2755.626	21.929	8.7
34	2105.994	16.759	22.7
35	1735.855	13.814	25.4
36	1240.826	9.874	28.6
37	1186.942	9.446	24.3

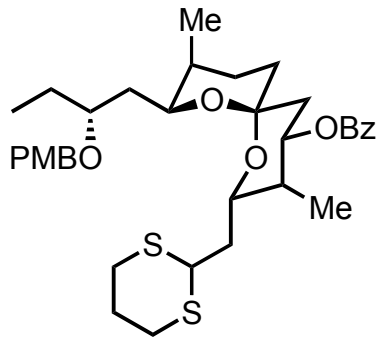


BMO-61-XV-product

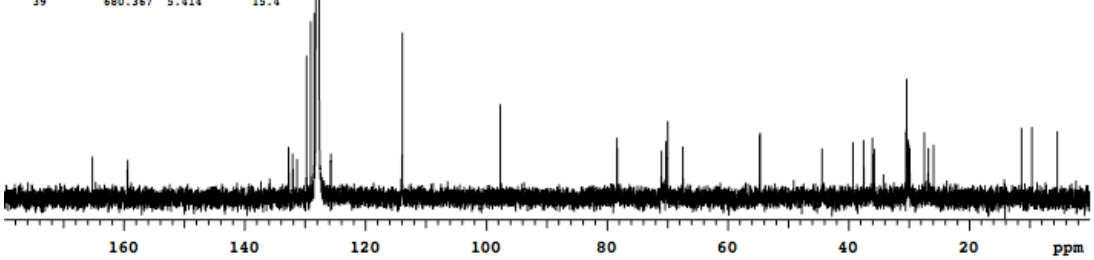
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-61-XV-pdt

Pulse Sequence: s2pul
Solvent: Benzene



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20764.559	165.242	9.6				
2	20032.338	159.415	8.8				
3	16677.419	132.717	11.8				
4	16592.312	132.039	10.3				
5	16502.673	131.326	9.0				
6	16306.273	129.763	32.8				
7	16218.648	129.066	40.6				
8	16143.110	128.465	42.6				
9	16113.901	128.232	110.9				
10	16101.312	128.132	2297.5				
11	16090.233	128.044	82.3				
12	16077.139	127.940	2341.3				
13	16065.557	127.848	98.0				
14	16052.967	127.747	2327.5				
15	15802.683	125.756	10.2				
16	14315.580	113.921	38.1				
17	12275.535	97.687	21.6				
18	9842.690	78.327	13.9				
19	8922.127	71.001	10.9				
20	8823.927	70.220	13.1				
21	8789.683	69.947	17.7				
22	8473.932	67.434	11.8				
23	6869.493	54.666	15.1				
24	5577.280	44.383	11.4				
25	4937.216	39.290	12.8				
26	4710.097	37.482	13.4				
27	4525.783	36.016	13.9				
28	4492.546	35.751	11.3				
29	3827.303	30.457	15.8				
30	3813.202	30.345	27.5				
31	3789.534	30.157	13.5				
32	3766.872	29.976	12.3				
33	3752.268	29.860	11.6				
34	3446.589	27.427	15.2				
35	3367.021	26.794	11.5				
36	3258.749	25.933	12.2				
37	1427.695	11.361	16.2				
38	1210.647	9.634	16.3				
39	680.367	5.414	15.4				



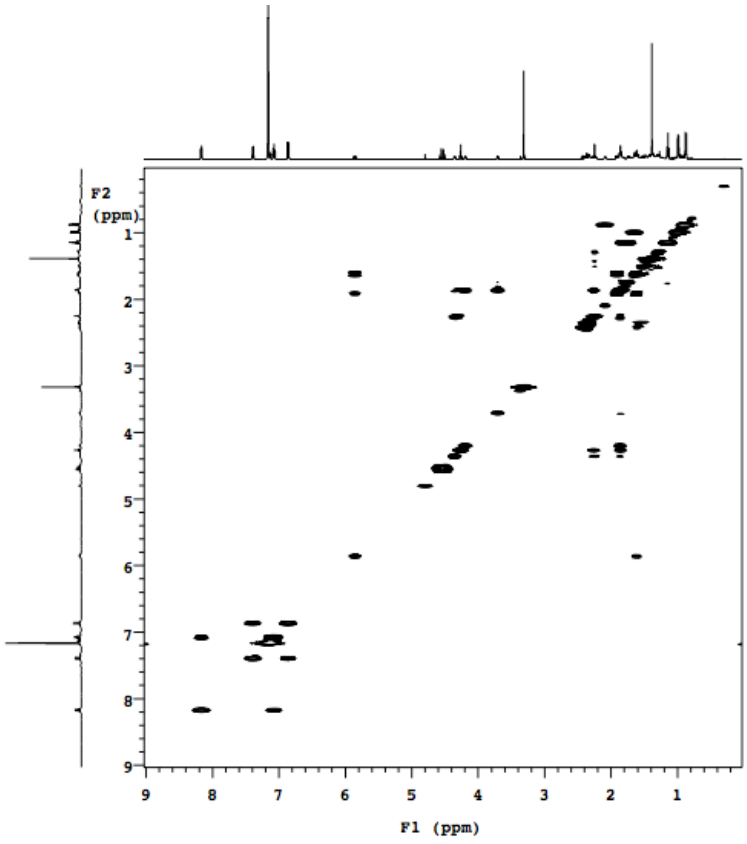
BMO-61-XV-fraction2-product

Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-61-XV-gcosy

Pulse Sequence: gCOSY
Solvent: Benzene

Relax. delay 1.500 sec
Acq. time 0.228 sec
Width 4499.2 Hz
2D Width 4499.2 Hz
4 repetitions
256 increments
OBSERVE H1, 499.7485961 MHz
DATA PROCESSING
Sq. sine bell 0.114 sec
F1 DATA PROCESSING
Sq. sine bell 0.014 sec
FT size 2048 x 2048
Total time 30 min



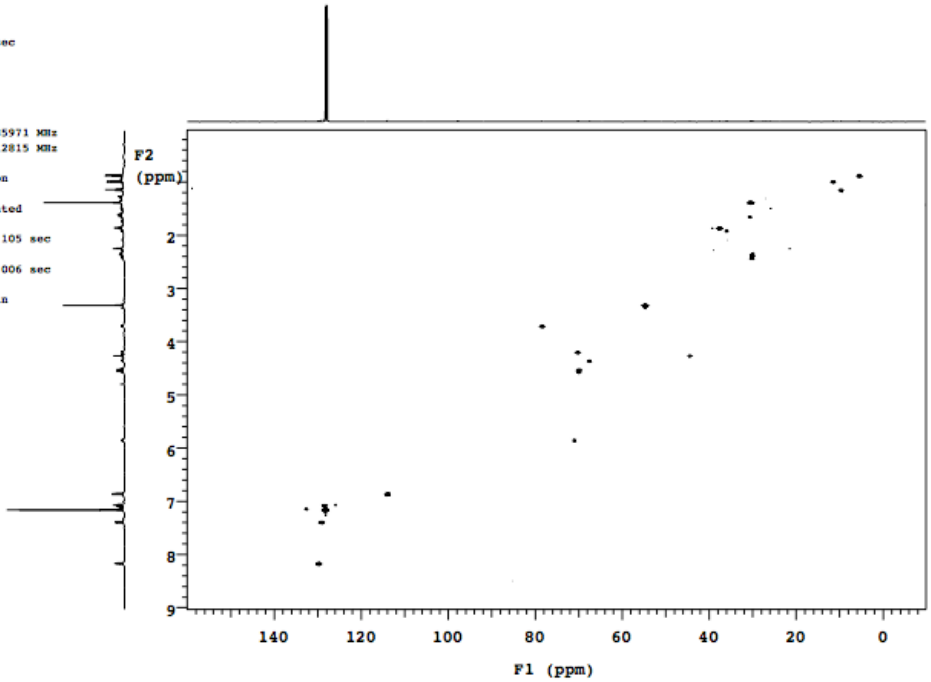
BMO-61-XV-fraction2-product

Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-61-XV-gHSQC

Pulse Sequence: gHSQC
Solvent: Benzene
User: 1-15-87

Relax. delay 1.700 sec
Acq. time 0.228 sec
Width 4499.2 Hz
2D Width 21361.8 Hz
4 repetitions
2 x 256 increments
OBSERVE H1, 499.7485971 MHz
DECOUPLE C13, 125.6712815 MHz
Power 35 dB
on during acquisition
off during delay
W40_testprobe modulated
DATA PROCESSING
Gauss apodization 0.105 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 2048 x 2048
Total time 1 hr, 9 min



BMO-61-XV-fraction2-product

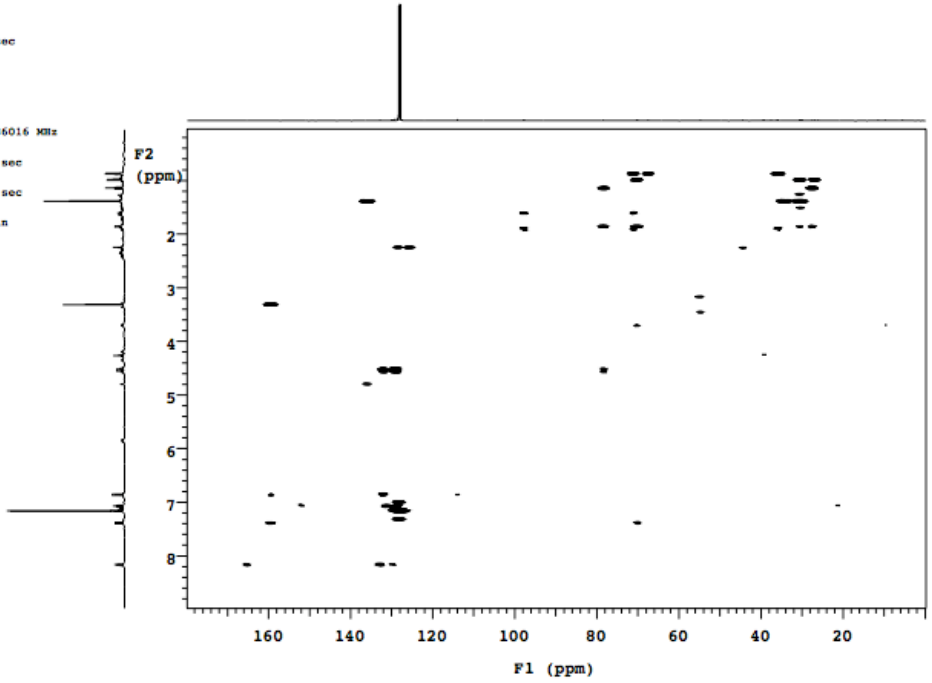
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-61-XV-gHMBC

Pulse Sequence: gHMBC
Solvent: Benzene

User: 1-15-87

Relax. delay 1.700 sec
Acq. time 0.228 sec
Width 4499.2 Hz
2D Width 30154.5 Hz
8 repetitions
256 increments
OBSERVE H1, 499.7486016 MHz
DATA PROCESSING
Sq. sine bell 0.114 sec
F1 DATA PROCESSING
Sq. sine bell 0.004 sec
FT size 2048 x 2048
Total time 1 hr, 9 min



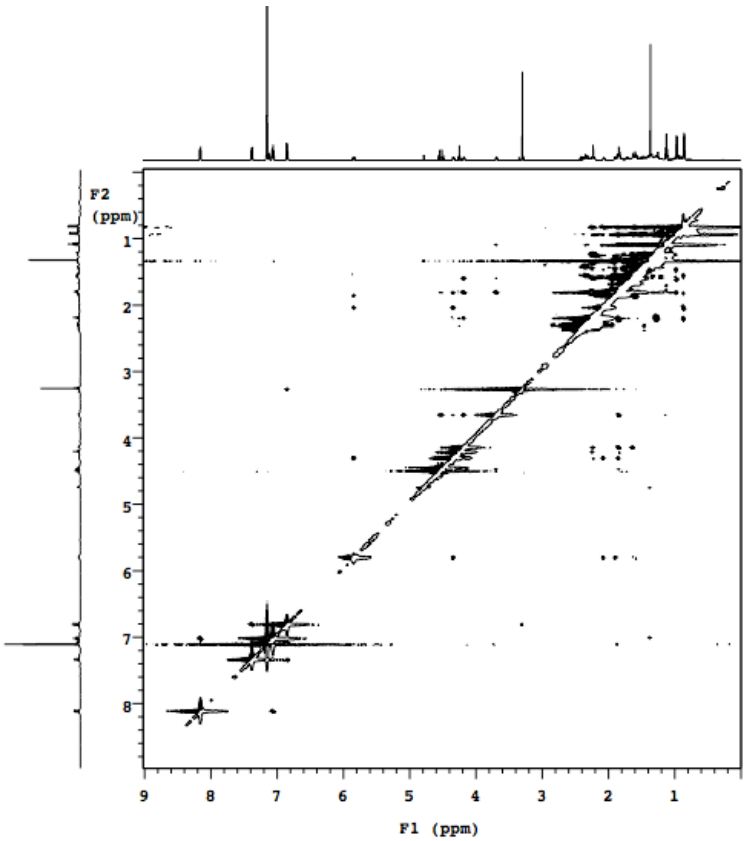
STANDARD PROTON PARAMETERS

Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-61-XV-pdt-ROESY

Pulse Sequence: ROESY
Solvent: Benzene

Relax. delay 1.000 sec
Mixing 0.200 sec
Acq. time 0.227 sec
Width 4509.8 Hz
2D Width 4509.8 Hz
32 repetitions
2 x 350 increments
OBSERVE H1, 499.7486240 MHz
DATA PROCESSING
Gauss apodization 0.105 sec
F1 DATA PROCESSING
Gauss apodization 0.041 sec
FT size 2048 x 2048
Total time 9 hr, 10 min

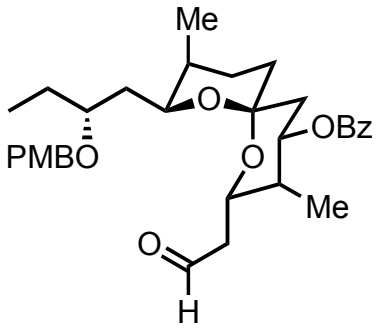


BMO-20-XVIII-pdt

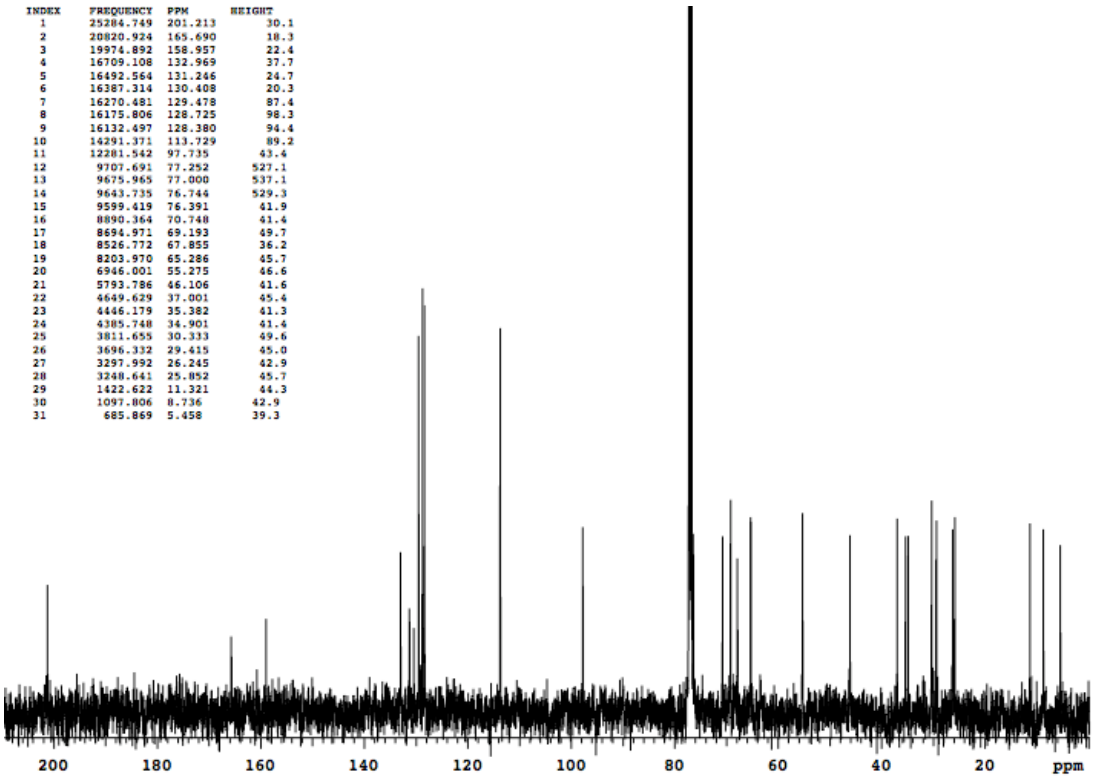
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

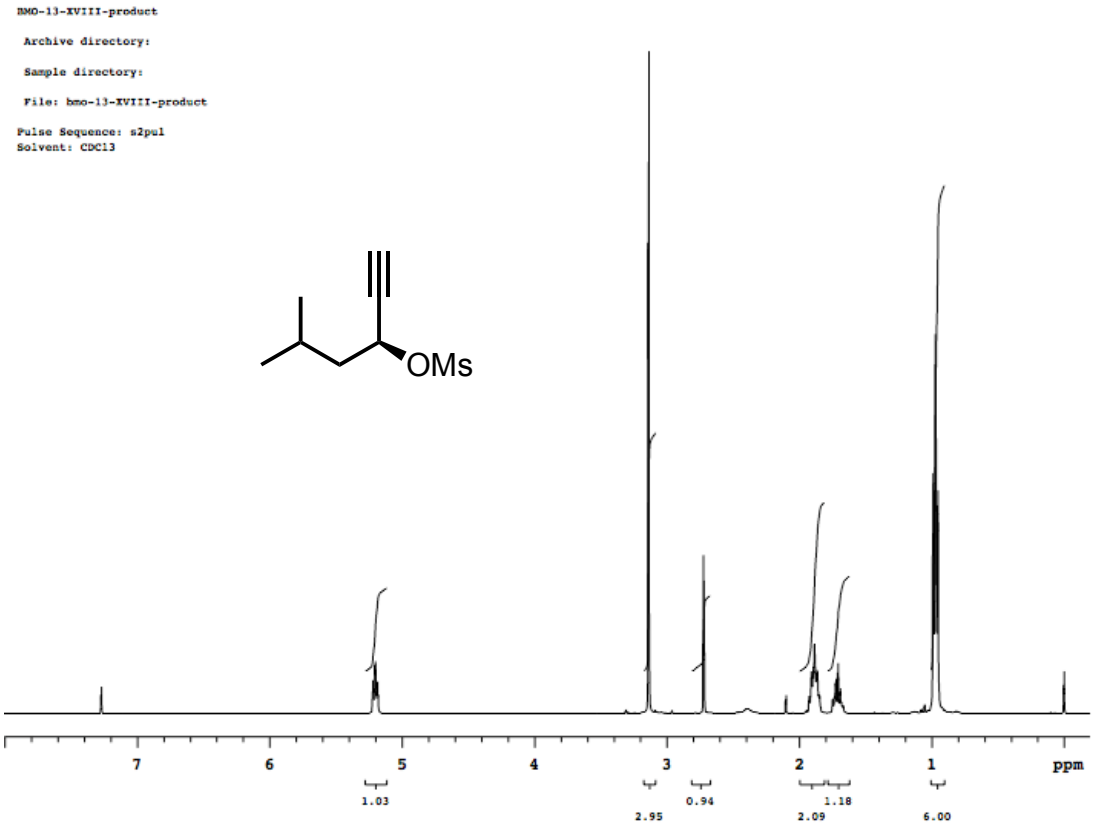
File: bmo-20-XVIII-product

Pulse Sequence: s2pul
Solvent: CDCl3

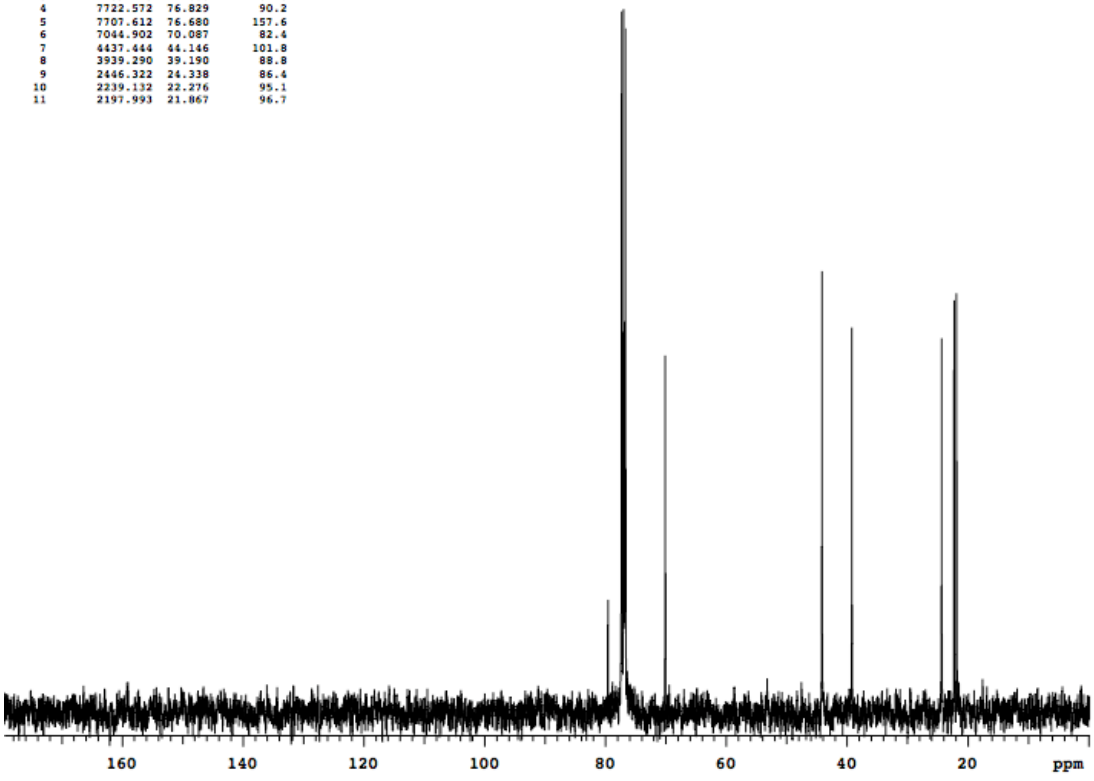


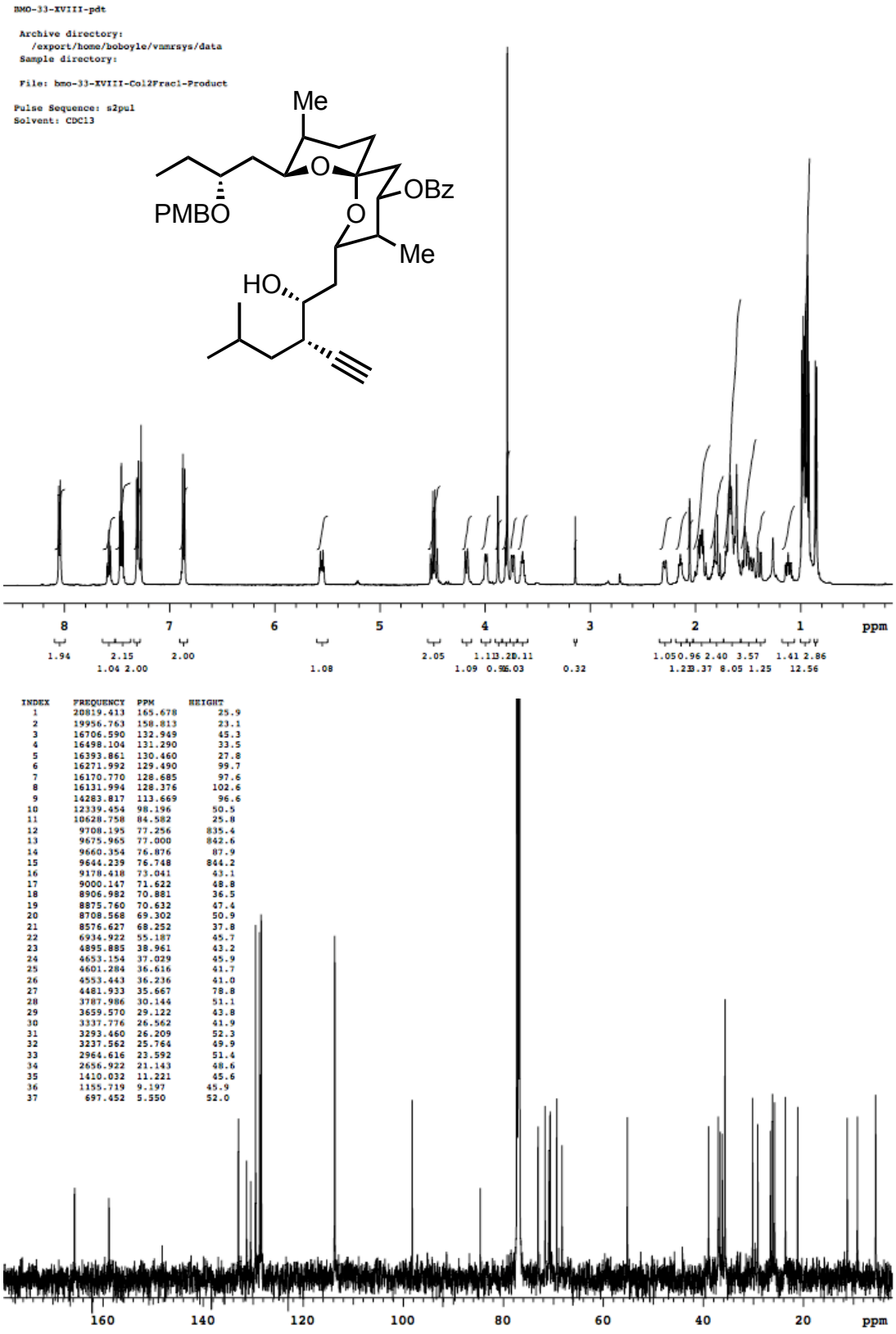
INDEX	FREQUENCY	PPM	HEIGHT
1	25284.749	201.213	30.1
2	20820.924	165.690	18.3
3	19974.892	158.957	22.4
4	16709.108	132.969	37.7
5	16492.564	131.246	24.7
6	16387.314	130.408	20.3
7	16270.481	129.478	87.4
8	16175.806	128.725	98.3
9	16132.497	128.380	94.4
10	14291.371	113.729	89.2
11	12281.542	97.735	43.4
12	9707.691	77.252	527.1
13	9675.965	77.000	537.1
14	9643.735	76.744	529.3
15	9599.419	76.391	41.9
16	8890.364	70.748	41.4
17	8694.971	69.193	49.7
18	8526.772	67.855	36.2
19	8203.970	65.286	45.7
20	6946.001	55.275	46.6
21	5793.786	46.106	41.6
22	4649.629	37.001	45.4
23	4446.179	35.382	41.3
24	4385.748	34.901	41.4
25	3811.655	30.333	49.6
26	3696.332	29.415	45.0
27	3297.992	26.245	42.9
28	3248.641	25.852	45.7
29	1422.622	11.321	44.3
30	1097.806	8.736	42.9
31	685.869	5.458	39.3





INDEX	FREQUENCY	PPM	HEIGHT
1	7998.576	79.575	26.2
2	7771.939	77.320	161.4
3	7739.775	77.000	162.0
4	7722.572	76.829	90.2
5	7707.612	76.680	157.6
6	7044.902	70.087	82.4
7	4437.444	44.146	101.8
8	3939.290	39.190	88.8
9	2446.322	24.338	86.4
10	2239.132	22.276	95.1
11	2197.993	21.867	96.7





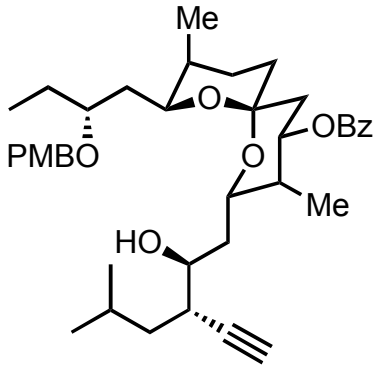
INDEX	FREQUENCY	PPM	HEIGHT
1	20819.413	165.678	25.9
2	19956.763	158.813	23.1
3	16706.590	132.949	45.3
4	16498.104	131.290	33.5
5	16393.861	130.460	27.8
6	16271.992	129.490	99.7
7	16170.770	128.685	97.6
8	16131.994	128.376	102.6
9	14283.817	113.669	96.6
10	12339.454	98.196	50.5
11	10628.758	84.582	25.8
12	9708.195	77.256	835.4
13	9675.965	77.000	842.6
14	9660.354	76.876	87.9
15	9644.239	76.748	844.2
16	9178.418	73.041	43.1
17	9000.147	71.622	48.8
18	8906.982	70.881	36.5
19	8875.760	70.632	47.4
20	8708.568	69.302	50.9
21	8576.627	68.252	37.8
22	6934.922	55.187	45.7
23	4895.885	38.961	43.2
24	4653.154	37.029	45.9
25	4601.284	36.616	41.7
26	4553.443	36.236	41.0
27	4481.933	35.667	78.8
28	3787.986	30.144	51.1
29	3659.570	29.122	43.8
30	3337.776	26.562	41.9
31	3293.460	26.209	52.3
32	3237.562	25.764	49.9
33	2964.616	23.592	51.4
34	2656.922	21.143	48.6
35	1410.032	11.221	45.6
36	1155.719	9.197	45.9
37	697.452	5.550	52.0

BMO-18-XIX-minor

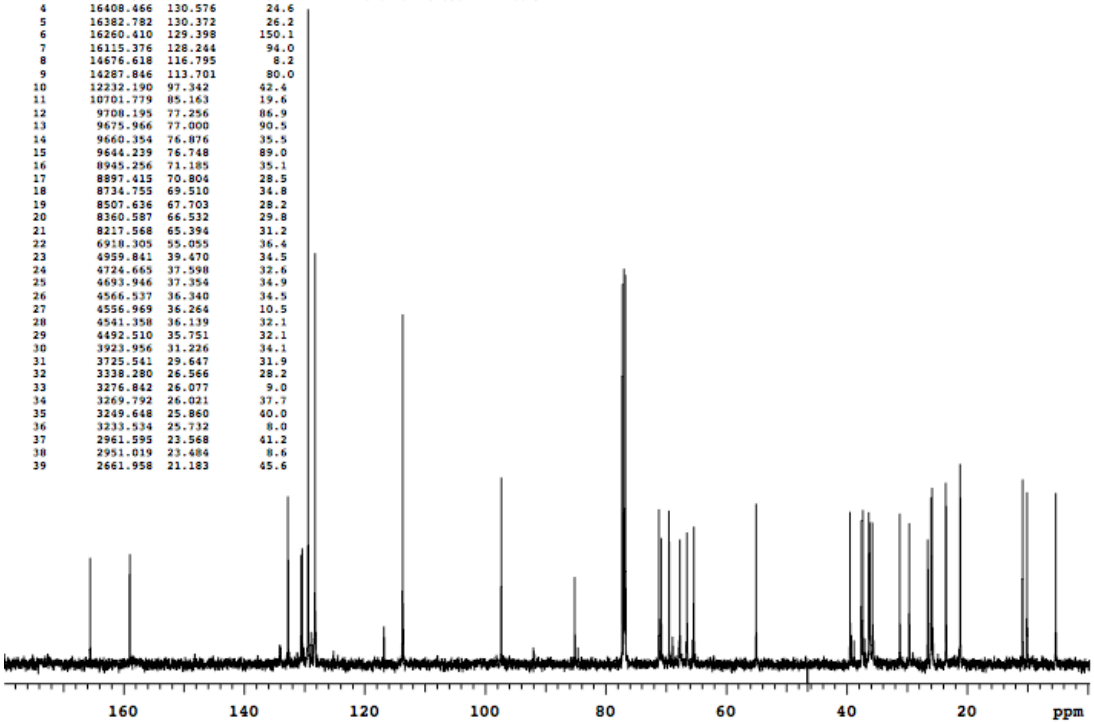
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-18-XIX-fraction2-minor

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20803.803	165.554	24.040		1362.695	10.844	42.0
2	19979.929	158.998	24.841		1270.538	10.111	39.0
3	16680.908	132.744	38.142		670.762	5.338	38.9
4	16408.466	130.576	24.6				
5	16382.782	130.372	26.2				
6	16260.410	129.398	150.1				
7	16115.376	128.244	94.0				
8	14676.618	116.795	8.2				
9	14287.846	113.701	80.0				
10	12232.190	97.342	42.4				
11	10701.779	85.163	19.6				
12	9708.195	77.256	86.9				
13	9675.966	77.000	90.5				
14	9660.354	76.876	35.5				
15	9644.239	76.748	89.0				
16	8945.256	71.185	35.1				
17	8897.415	70.804	28.5				
18	8734.755	69.510	34.8				
19	8507.636	67.703	28.2				
20	8360.587	66.532	29.8				
21	8217.568	65.394	31.2				
22	6918.305	55.055	36.4				
23	4959.841	39.470	34.5				
24	4724.665	37.598	32.6				
25	4693.946	37.354	34.9				
26	4566.537	36.340	34.5				
27	4556.969	36.264	10.5				
28	4541.358	36.139	32.1				
29	4492.510	35.751	32.1				
30	3923.956	31.226	34.1				
31	3725.541	29.647	31.9				
32	3338.280	26.566	28.2				
33	3276.842	26.077	9.0				
34	3269.792	26.021	37.7				
35	3249.648	25.860	40.0				
36	3233.534	25.732	8.0				
37	2961.595	23.568	41.2				
38	2951.019	23.484	8.6				
39	2661.958	21.183	45.6				

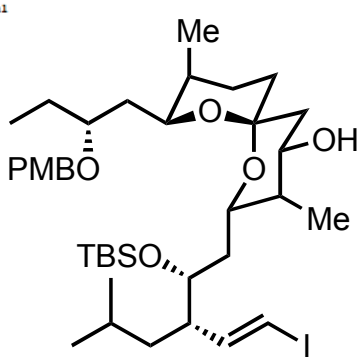


BMO-87-XVIII-product

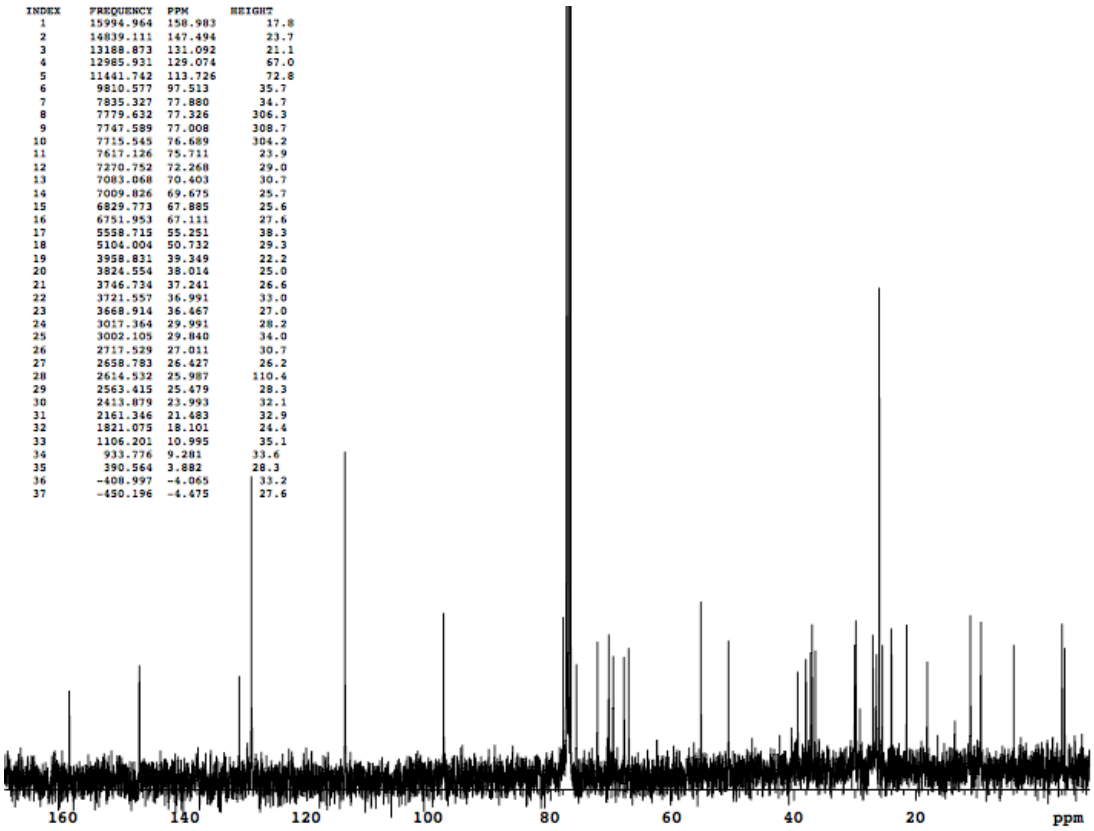
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: std1h

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	15994.964	158.983	17.8
2	14839.111	147.494	23.7
3	13188.873	131.092	21.1
4	12985.931	129.074	67.0
5	11441.742	113.726	72.8
6	9810.577	97.513	35.7
7	7835.327	77.880	34.7
8	7779.632	77.326	306.3
9	7747.589	77.008	308.7
10	7715.545	76.689	304.2
11	7617.126	75.711	23.9
12	7270.752	72.268	29.0
13	7083.068	70.403	30.7
14	7009.826	69.675	25.7
15	6829.773	67.885	25.6
16	6751.953	67.111	27.6
17	5558.715	55.251	38.3
18	5104.004	50.732	29.3
19	3958.831	39.349	22.2
20	3824.554	38.014	25.0
21	3746.734	37.241	26.6
22	3721.557	36.991	33.0
23	3668.914	36.467	27.0
24	3017.364	29.991	28.2
25	3002.105	29.840	34.0
26	2717.529	27.011	30.7
27	2658.783	26.427	26.2
28	2614.532	25.987	110.4
29	2563.415	25.479	28.3
30	2413.879	23.993	32.1
31	2161.346	21.483	32.9
32	1821.075	18.101	24.4
33	1106.201	10.995	35.1
34	933.776	9.281	33.6
35	390.564	3.882	28.3
36	-408.997	-4.065	33.2
37	-450.196	-4.475	27.6

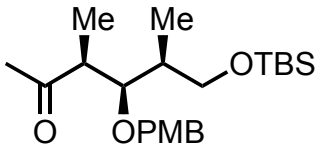


BMO-24-XVI-product

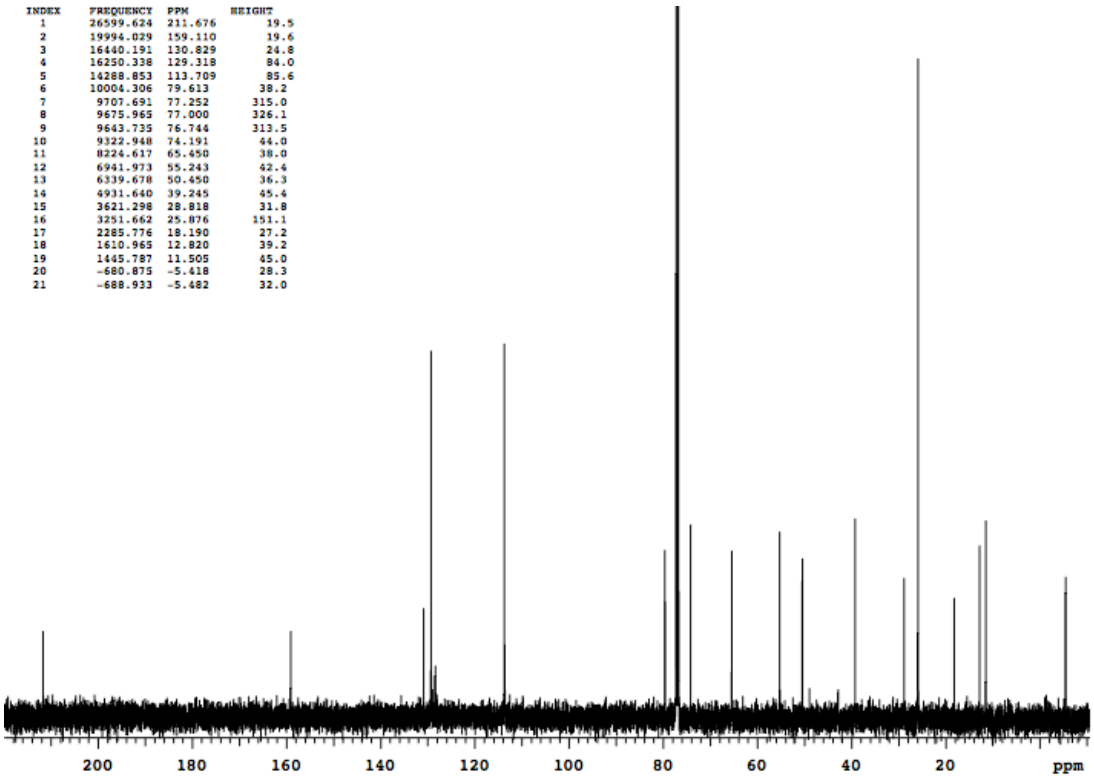
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-24-XVI-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	26599.624	211.676	19.5
2	19994.029	159.110	19.6
3	16440.191	130.829	24.8
4	16250.338	129.318	84.0
5	14288.853	113.709	85.6
6	10004.306	79.613	38.2
7	9707.691	77.252	315.0
8	9675.965	77.000	326.1
9	9643.735	76.744	313.5
10	9322.948	74.191	44.0
11	8224.617	65.450	38.0
12	6941.973	55.243	42.4
13	6339.678	50.450	36.3
14	4931.640	39.245	45.4
15	3621.298	28.818	31.8
16	3251.662	25.876	151.1
17	2285.776	18.190	27.2
18	1610.965	12.820	39.2
19	1445.787	11.505	45.0
20	-680.875	-5.418	28.3
21	-688.933	-5.482	32.0

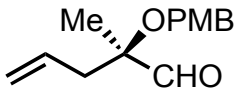


BMO-72-XIV-product

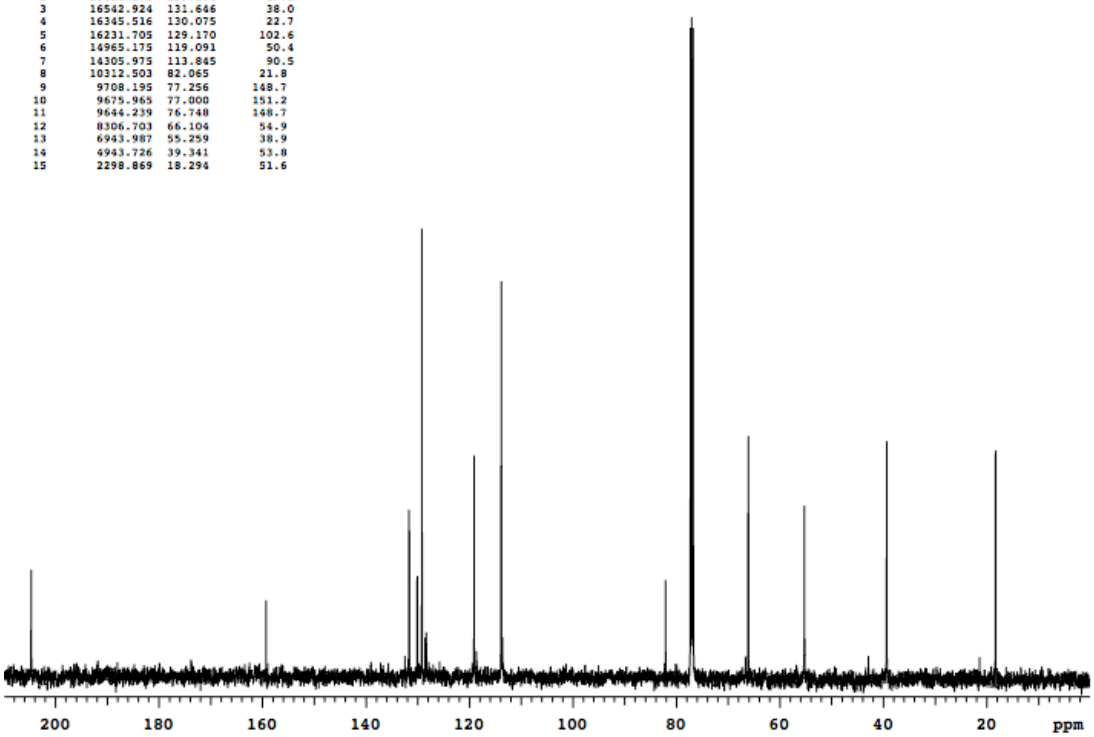
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-73-XIV-pdt

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	25721.866	204.691	24.2
2	20014.172	159.270	17.2
3	16542.924	131.646	38.0
4	16345.516	130.075	22.7
5	16231.705	129.170	102.6
6	14965.175	119.091	50.4
7	14305.975	113.845	90.5
8	10312.503	82.065	21.8
9	9708.195	77.256	148.7
10	9675.965	77.000	151.2
11	9644.239	76.748	148.7
12	8306.703	66.104	54.9
13	6943.987	55.259	38.9
14	4943.726	39.341	53.8
15	2298.869	18.294	51.6

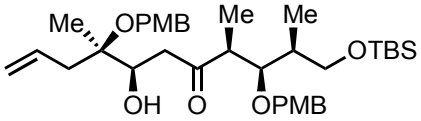


BMO-43-XVII-product

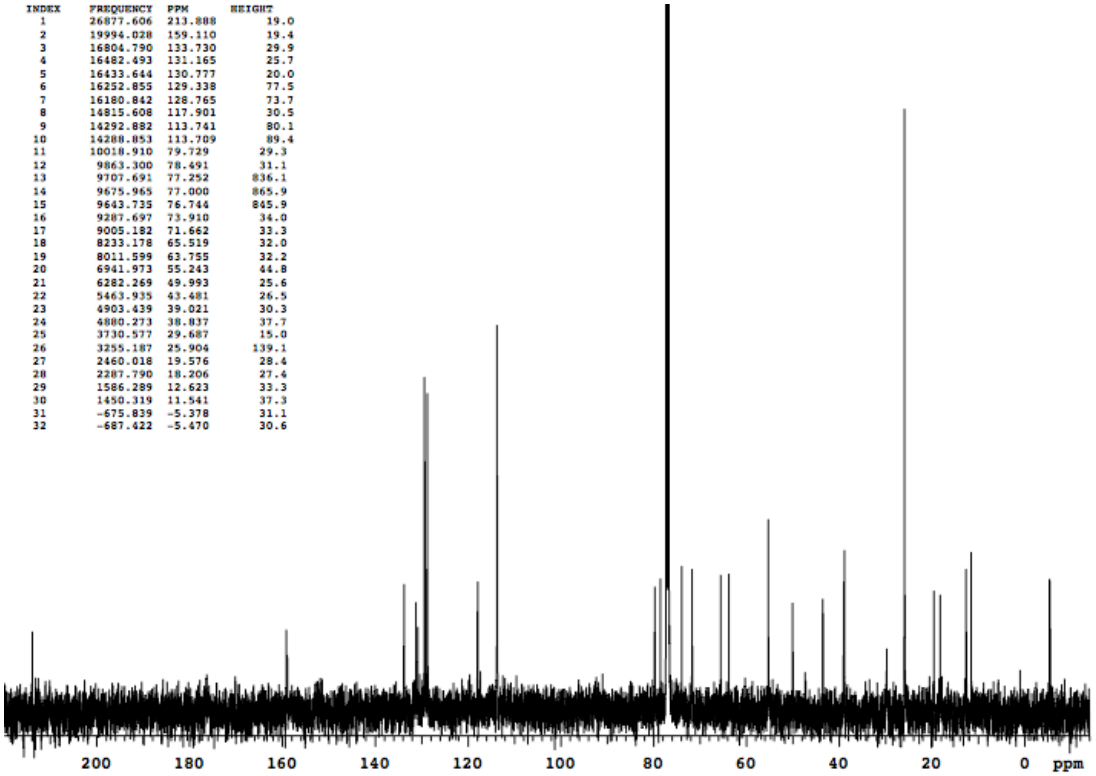
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-43-XVII-fraction2-product

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	26877.606	213.888	19.0
2	19994.028	159.110	19.4
3	16804.790	133.730	29.9
4	16482.493	131.165	25.7
5	16433.644	130.777	20.0
6	16252.855	129.338	77.5
7	16180.842	128.765	73.7
8	14815.608	117.901	30.5
9	14292.882	113.741	80.1
10	14288.853	113.709	89.4
11	10018.910	79.729	29.3
12	9863.300	78.491	31.1
13	9707.691	77.252	836.1
14	9675.965	77.000	865.9
15	9643.735	76.744	845.9
16	9287.697	73.910	34.0
17	9005.182	71.662	33.3
18	8233.178	65.519	32.0
19	8011.599	63.755	32.2
20	6941.973	55.243	44.8
21	6282.269	49.993	25.6
22	5463.935	43.481	26.5
23	4903.439	39.021	30.3
24	4880.273	38.837	37.7
25	3730.577	29.687	15.0
26	3255.187	25.904	139.1
27	2460.018	19.576	28.4
28	2287.790	18.206	27.4
29	1586.289	12.623	33.3
30	1450.319	11.541	37.3
31	-675.839	-5.378	31.1
32	-687.422	-5.470	30.6

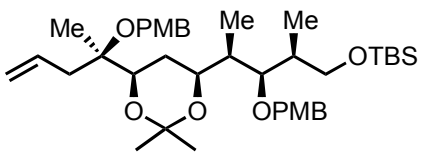


BMO-90-XVIII-product

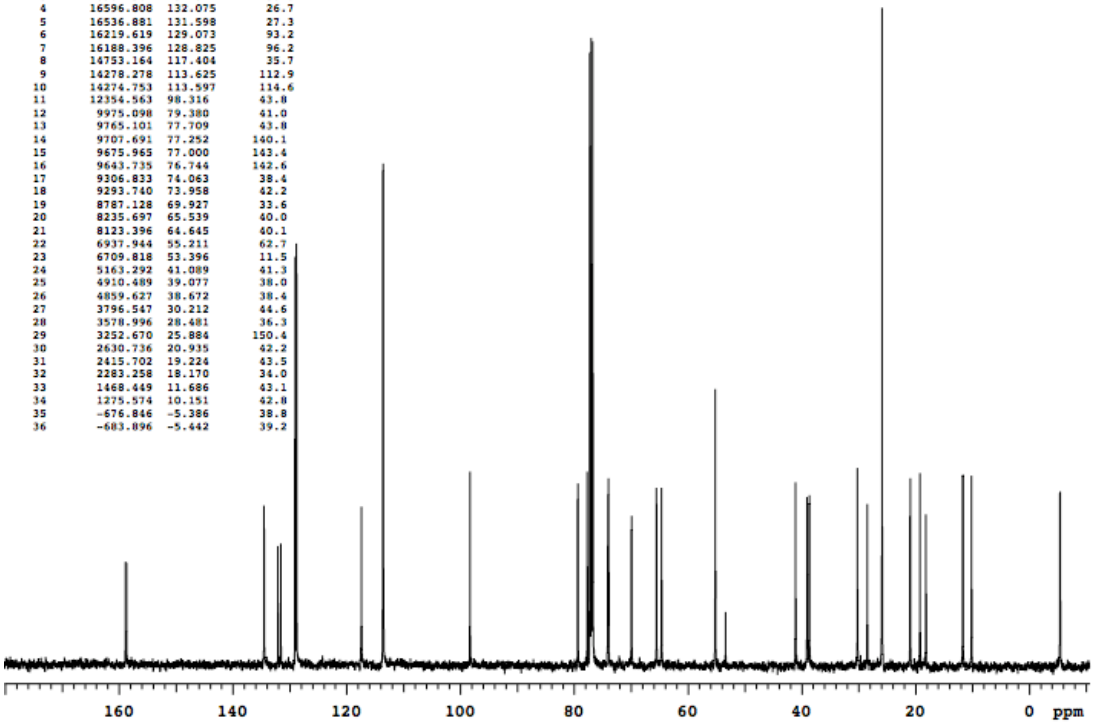
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

File: bmo-90-XVIII-product

Pulse Sequence: s2pul
Solvent: CDCl3



INDEX	FREQUENCY	PPM	HEIGHT
1	19966.835	158.893	23.1
2	19943.166	158.705	22.9
3	16904.502	134.524	36.0
4	16596.808	132.075	26.7
5	16536.881	131.598	27.3
6	16219.619	129.073	93.2
7	16188.396	128.825	96.2
8	14753.164	117.404	35.7
9	14278.278	113.625	112.9
10	14274.753	113.597	114.6
11	12354.563	98.316	43.8
12	9975.098	79.380	41.0
13	9765.101	77.709	43.8
14	9707.691	77.252	140.1
15	9675.965	77.000	143.4
16	9643.735	76.744	142.6
17	9306.833	74.063	38.4
18	9293.740	73.958	42.2
19	8787.128	69.927	33.6
20	8235.697	65.539	40.0
21	8123.396	64.645	40.1
22	6937.944	55.211	62.7
23	6709.818	53.396	11.5
24	5163.292	41.089	41.3
25	4910.489	39.077	38.0
26	4859.627	38.672	38.4
27	3796.547	30.212	44.6
28	3578.996	28.481	36.3
29	3252.670	25.884	150.4
30	2630.736	20.935	42.2
31	2415.702	19.224	43.5
32	2283.258	18.170	34.0
33	1468.449	11.686	43.1
34	1275.574	10.151	42.8
35	-676.846	-5.386	38.8
36	-683.896	-5.442	39.2

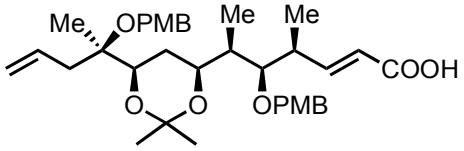


BMO-52-XVIII-product

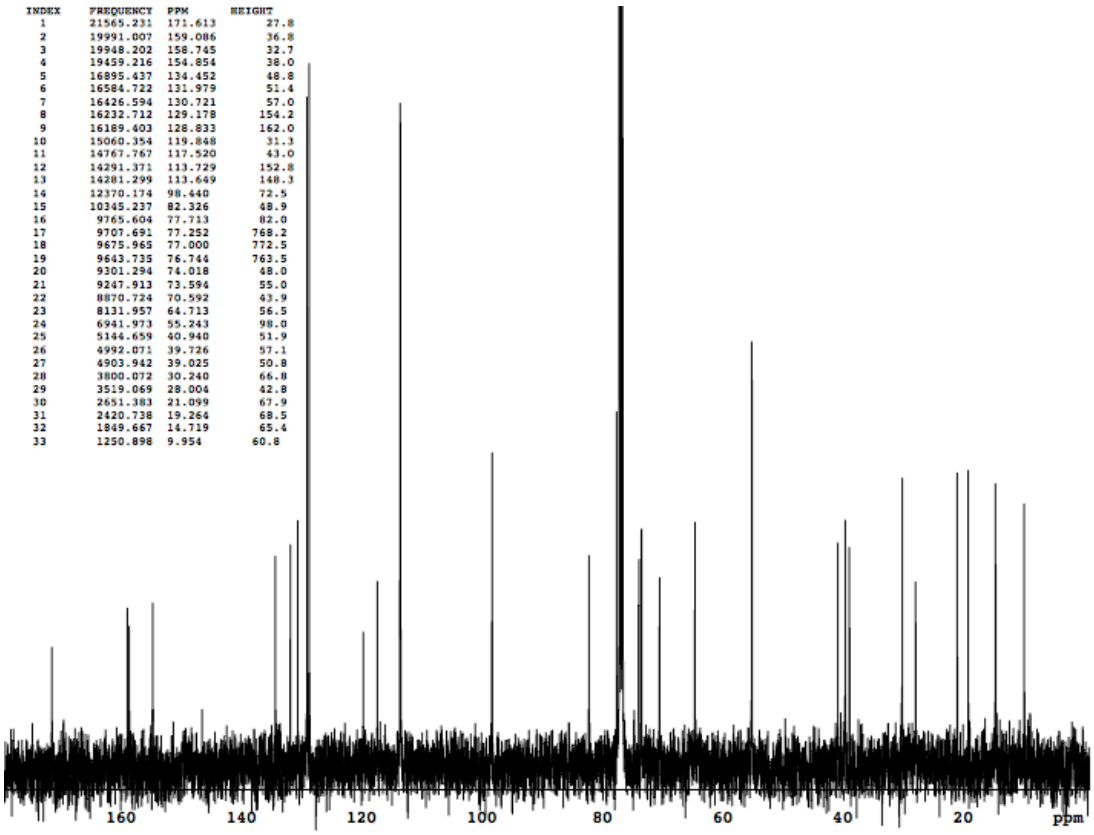
Archive directory:
/export/home/boboyle/vnmrsys/data
Sample directory:

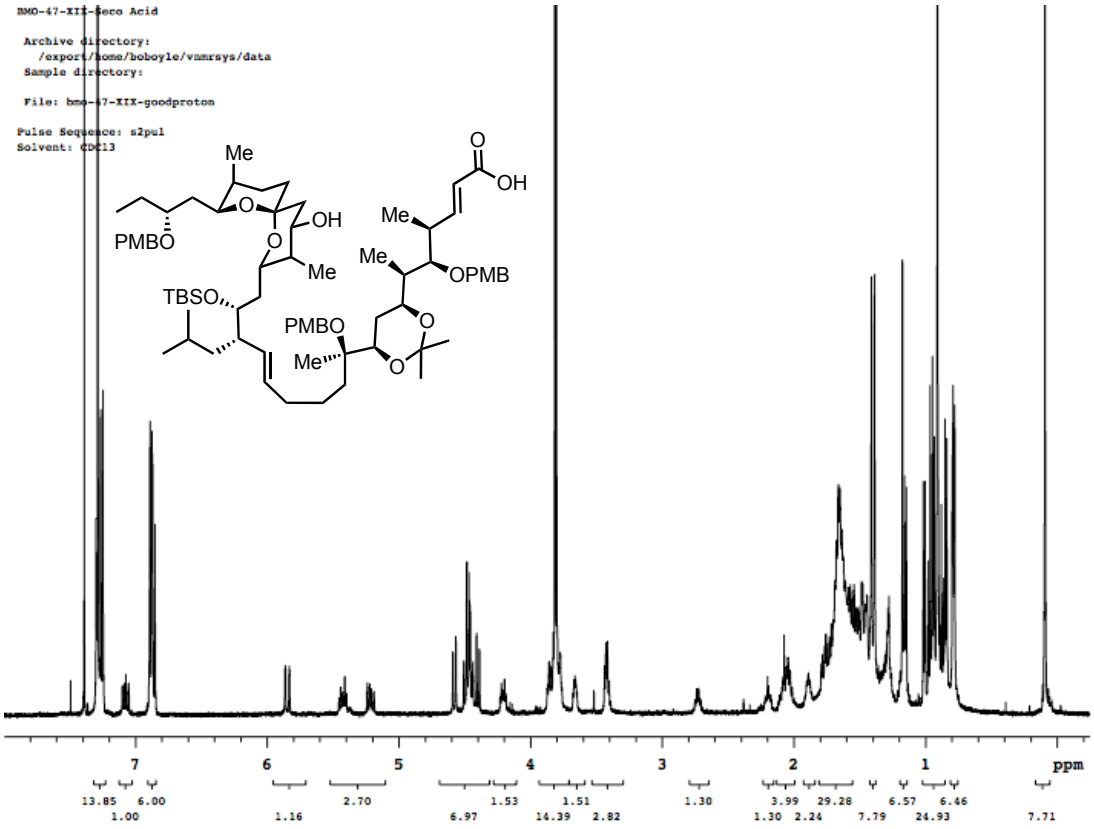
File: bmo-52-XVIII-fraction2-pdt

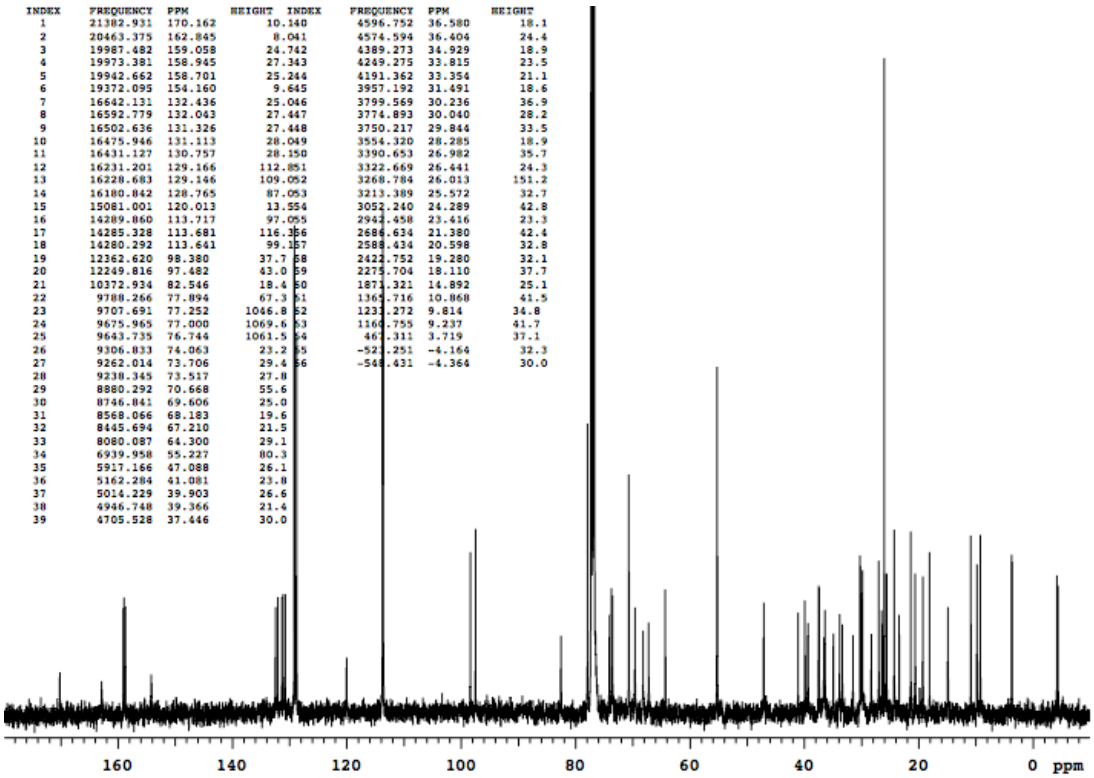
Pulse Sequence: s2pul
Solvent: CDCl3



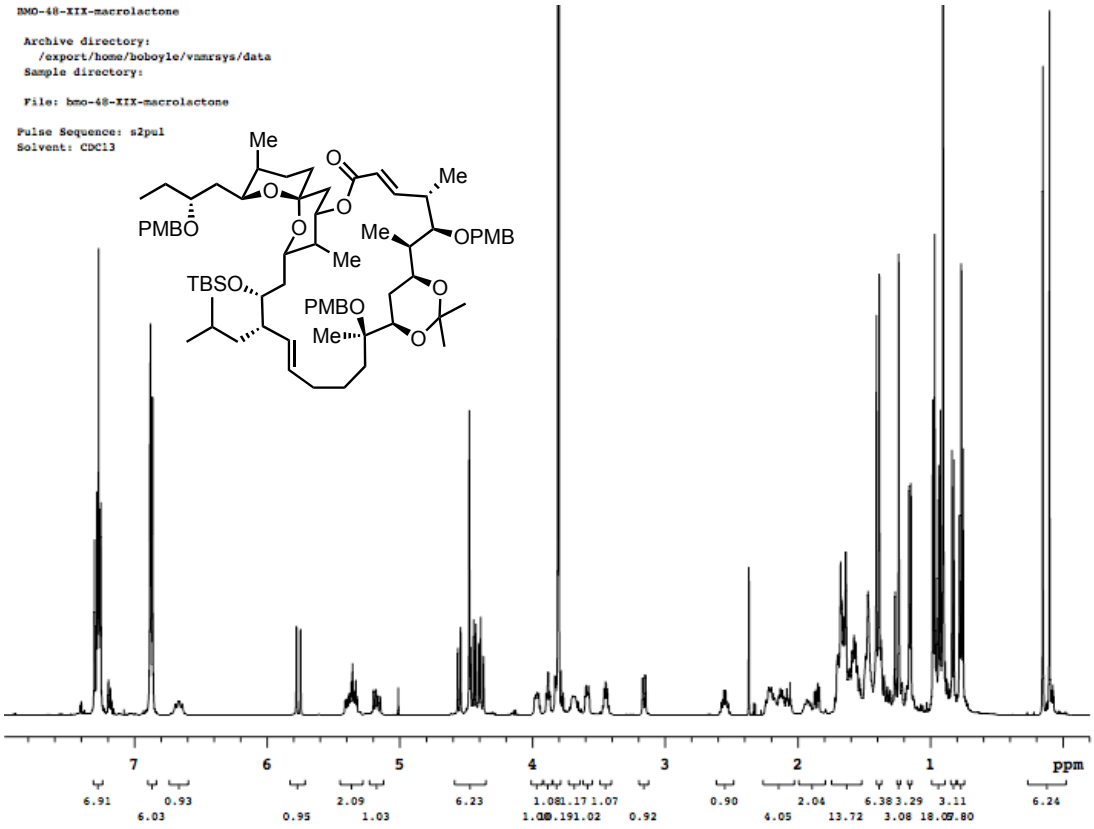
INDEX	FREQUENCY	PPM	HEIGHT
1	21565.231	171.613	27.8
2	19991.007	159.086	36.8
3	19948.202	158.745	32.7
4	19459.216	154.854	38.0
5	16895.437	134.452	48.8
6	16584.722	131.979	51.4
7	16426.594	130.721	57.0
8	16232.712	129.178	154.2
9	16189.403	128.833	162.0
10	15060.354	119.848	31.3
11	14767.767	117.520	43.0
12	14291.371	113.729	152.8
13	14281.299	113.649	148.3
14	12370.174	98.440	72.5
15	10345.237	82.326	48.9
16	9765.604	77.713	82.0
17	9707.691	77.252	768.2
18	9675.965	77.000	772.5
19	9643.735	76.744	763.5
20	9301.294	74.018	48.0
21	9247.913	73.594	55.0
22	8870.724	70.592	43.9
23	8131.957	64.713	56.5
24	6941.973	55.243	98.0
25	5144.659	40.940	51.9
26	4992.071	39.726	57.1
27	4903.942	39.025	50.8
28	3800.072	30.240	66.8
29	3519.069	28.004	42.8
30	2651.383	21.099	67.9
31	2420.738	19.264	68.5
32	1849.667	14.719	65.4
33	1250.898	9.954	60.8



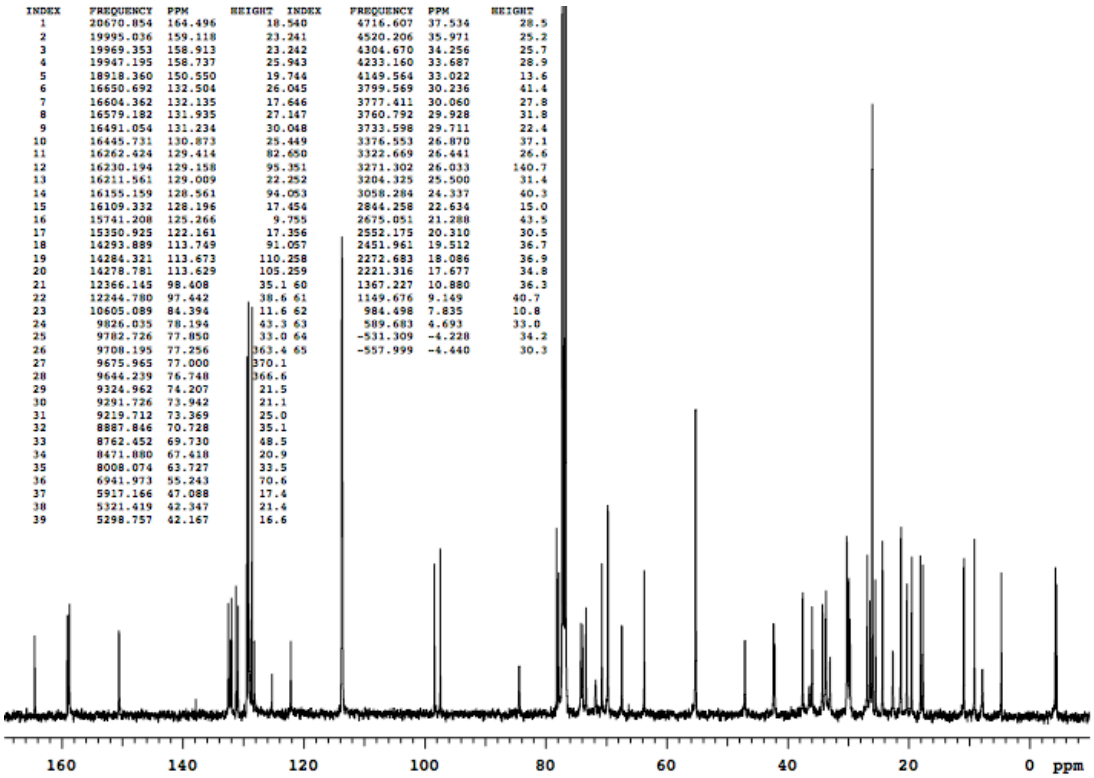


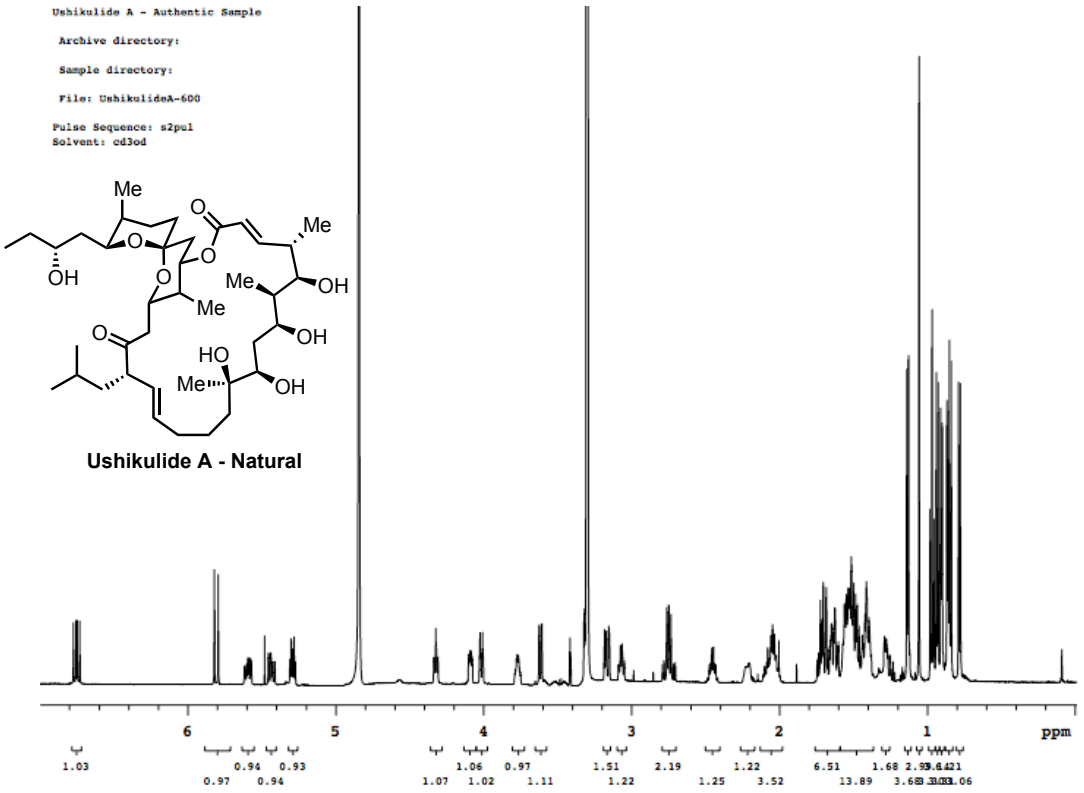


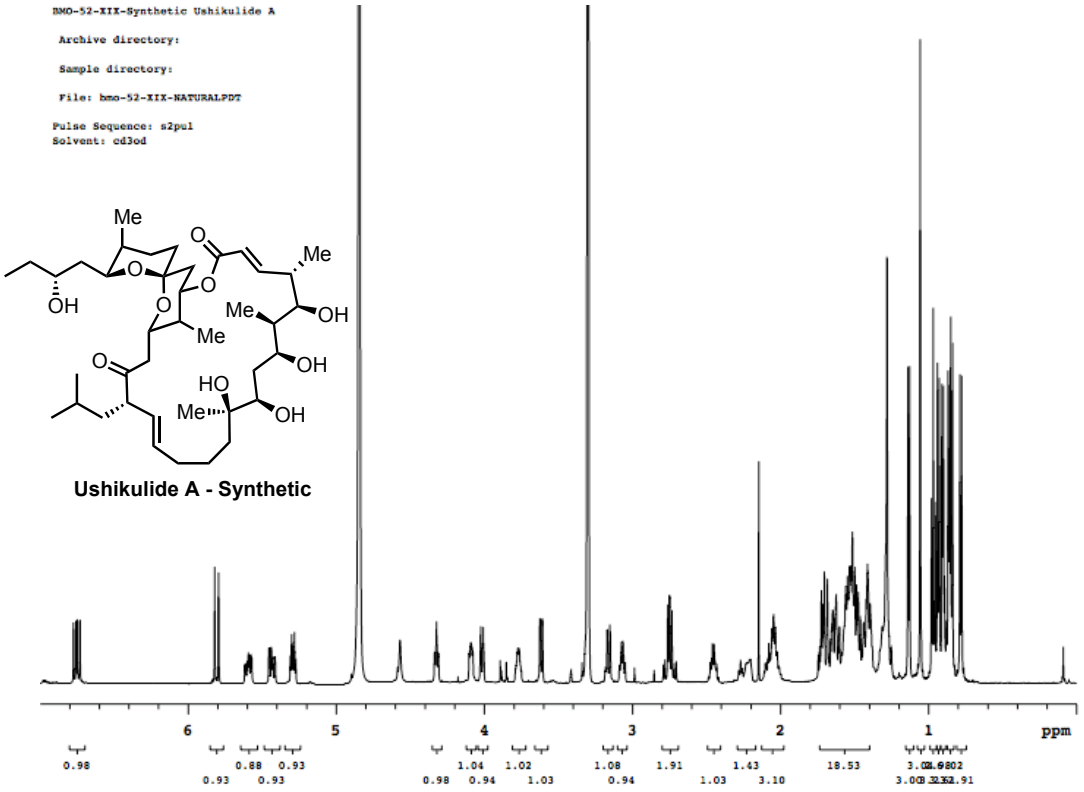
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	21382.931	170.162	10.140		4596.752	36.580	18.1
2	20463.375	162.845	8.041		4574.594	36.404	24.4
3	19987.482	159.058	24.742		4389.273	34.929	18.9
4	19973.381	158.945	27.343		4249.275	33.815	23.5
5	19942.662	158.701	25.244		4191.362	33.354	21.1
6	19372.095	154.160	9.645		3957.192	31.491	18.6
7	16642.131	132.436	25.046		3799.569	30.236	36.9
8	16592.779	132.043	27.447		3774.893	30.040	28.2
9	16502.636	131.326	27.448		3750.217	29.844	33.5
10	16475.946	131.113	28.049		3554.320	28.285	18.9
11	16431.127	130.757	28.150		3390.653	26.982	35.7
12	16231.201	129.166	112.851		3322.669	26.441	24.3
13	16228.683	129.146	109.052		3268.784	26.013	151.2
14	16180.842	128.765	87.053		3213.389	25.572	32.7
15	15081.001	120.013	13.554		3052.240	24.289	42.8
16	14289.860	113.717	97.055		2942.458	23.416	23.3
17	14285.328	113.681	116.356		2686.634	21.380	42.4
18	14280.292	113.641	99.157		2588.434	20.598	32.8
19	12362.620	98.380	37.7	58	2422.752	19.280	32.1
20	12249.816	97.482	43.0	59	2275.704	18.110	37.7
21	10372.934	82.546	18.4	60	1871.321	14.892	25.1
22	9788.266	77.894	67.3	61	1365.716	10.868	41.5
23	9707.691	77.252	1046.8	62	1231.272	9.814	34.8
24	9675.965	77.000	1069.6	63	1166.755	9.237	41.7
25	9643.735	76.744	1061.5	64	467.311	3.719	37.1
26	9306.833	74.063	23.2	65	-521.251	-4.164	32.3
27	9262.014	73.706	29.4	66	-548.431	-4.364	30.0
28	9238.345	73.517	27.8				
29	8880.292	70.668	55.6				
30	8746.841	69.606	25.0				
31	8568.066	68.183	19.6				
32	8445.694	67.210	21.5				
33	8080.087	64.300	29.1				
34	6939.958	55.227	80.3				
35	5917.166	47.088	26.1				
36	5162.284	41.081	23.8				
37	5014.229	39.903	26.6				
38	4946.748	39.366	21.4				
39	4705.528	37.446	30.0				

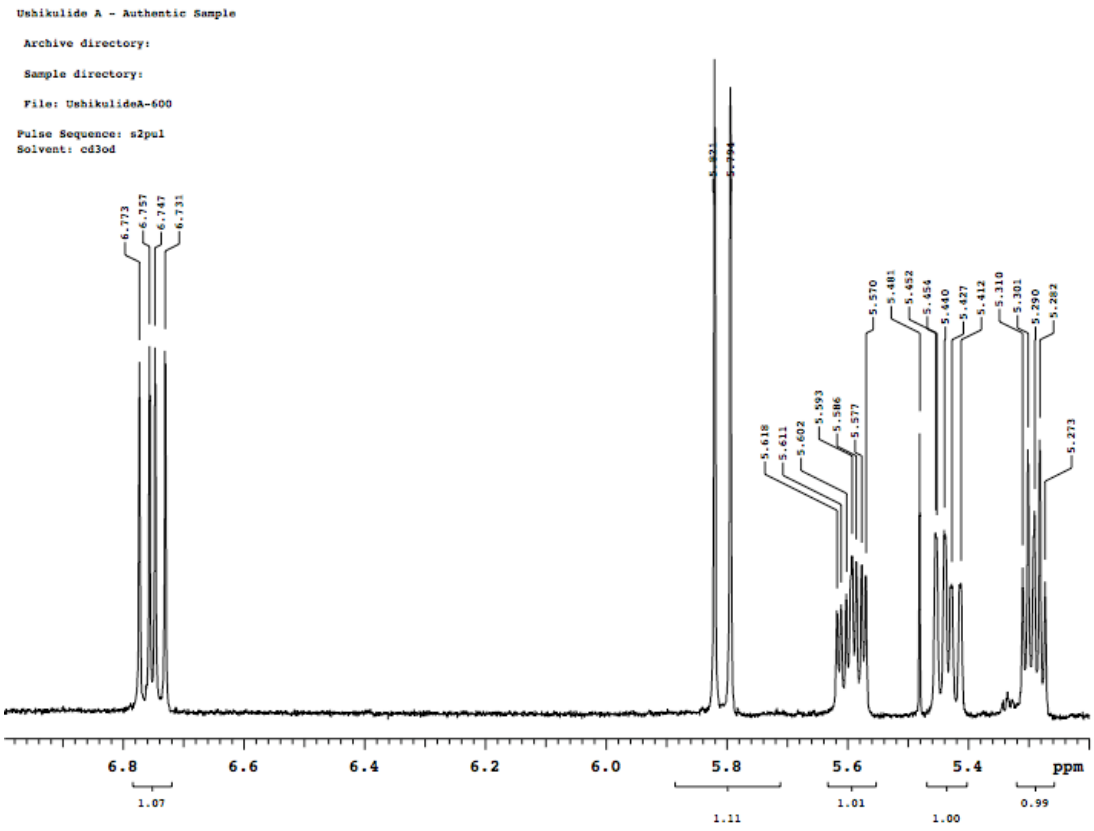


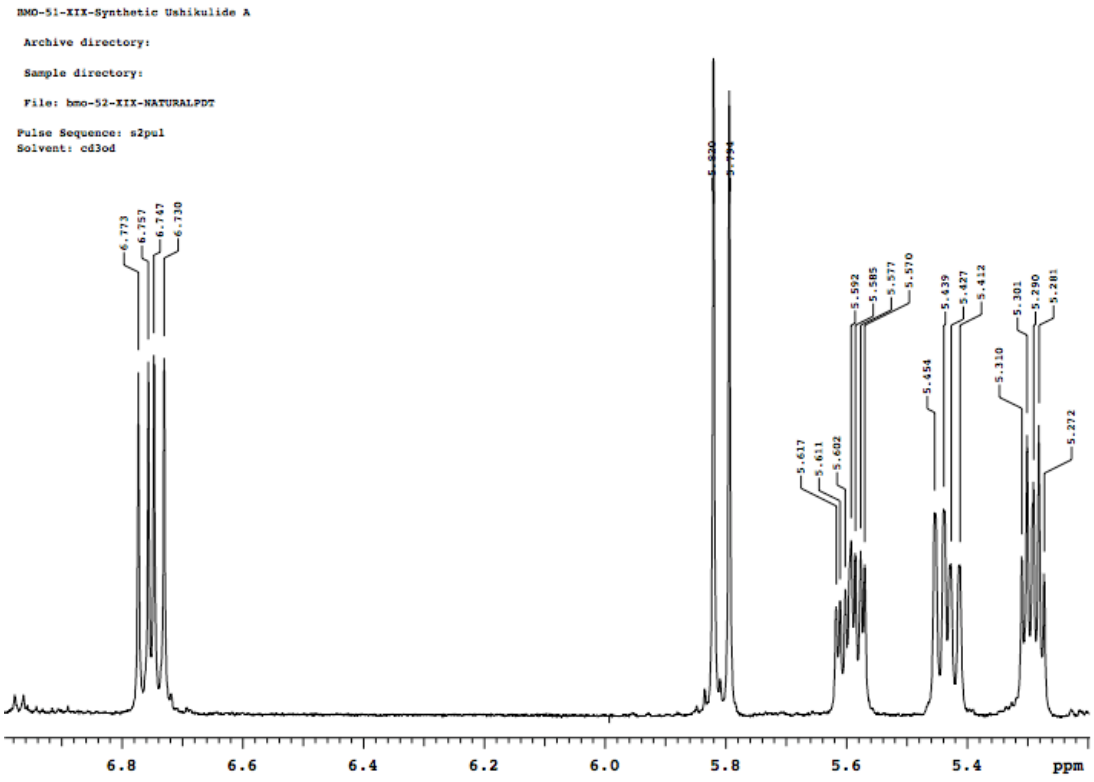
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20670.854	164.496	18.540		4716.607	37.534	28.5
2	19995.036	159.118	23.241		4520.206	35.971	25.2
3	19969.353	158.913	23.242		4304.670	34.256	25.7
4	19947.195	158.737	25.943		4233.160	33.687	28.9
5	18918.360	150.550	19.744		4149.564	33.022	13.6
6	16650.692	132.504	26.045		3799.569	30.236	41.4
7	16604.362	132.135	17.646		3777.411	30.060	27.8
8	16579.182	131.935	27.147		3760.792	29.928	31.8
9	16491.054	131.234	30.048		3733.598	29.711	22.4
10	16445.731	130.873	25.449		3376.553	26.870	37.1
11	16262.424	129.414	82.650		3322.669	26.441	26.6
12	16230.194	129.158	95.351		3271.302	26.033	140.7
13	16211.561	129.009	22.252		3204.325	25.500	31.4
14	16155.159	128.561	94.053		3058.284	24.337	40.3
15	16109.332	128.196	17.454		2844.258	22.634	15.0
16	15741.208	125.266	9.755		2675.051	21.288	43.5
17	15350.925	122.161	17.356		2552.175	20.310	30.5
18	14293.889	113.749	91.057		2451.961	19.512	36.7
19	14284.321	113.673	110.258		2272.683	18.086	36.9
20	14278.781	113.629	105.259		2221.316	17.677	34.8
21	12366.145	98.408	35.1	60	1367.227	10.880	36.3
22	12244.780	97.442	38.6	61	1149.676	9.149	40.7
23	10605.089	84.394	11.6	62	984.498	7.835	10.8
24	9826.035	78.194	43.3	63	589.683	4.693	33.0
25	9782.726	77.850	33.0	64	-531.309	-4.228	34.2
26	9708.195	77.256	363.4	65	-557.999	-4.440	30.3
27	9675.965	77.000	370.1				
28	9644.239	76.748	366.6				
29	9324.962	74.207	21.5				
30	9291.726	73.942	21.1				
31	9219.712	73.369	25.0				
32	8887.846	70.728	35.1				
33	8762.452	69.730	48.5				
34	8471.880	67.418	20.9				
35	8008.074	63.727	33.5				
36	6941.973	55.243	70.6				
37	5917.166	47.088	17.4				
38	5321.419	42.347	21.4				
39	5298.757	42.167	16.6				

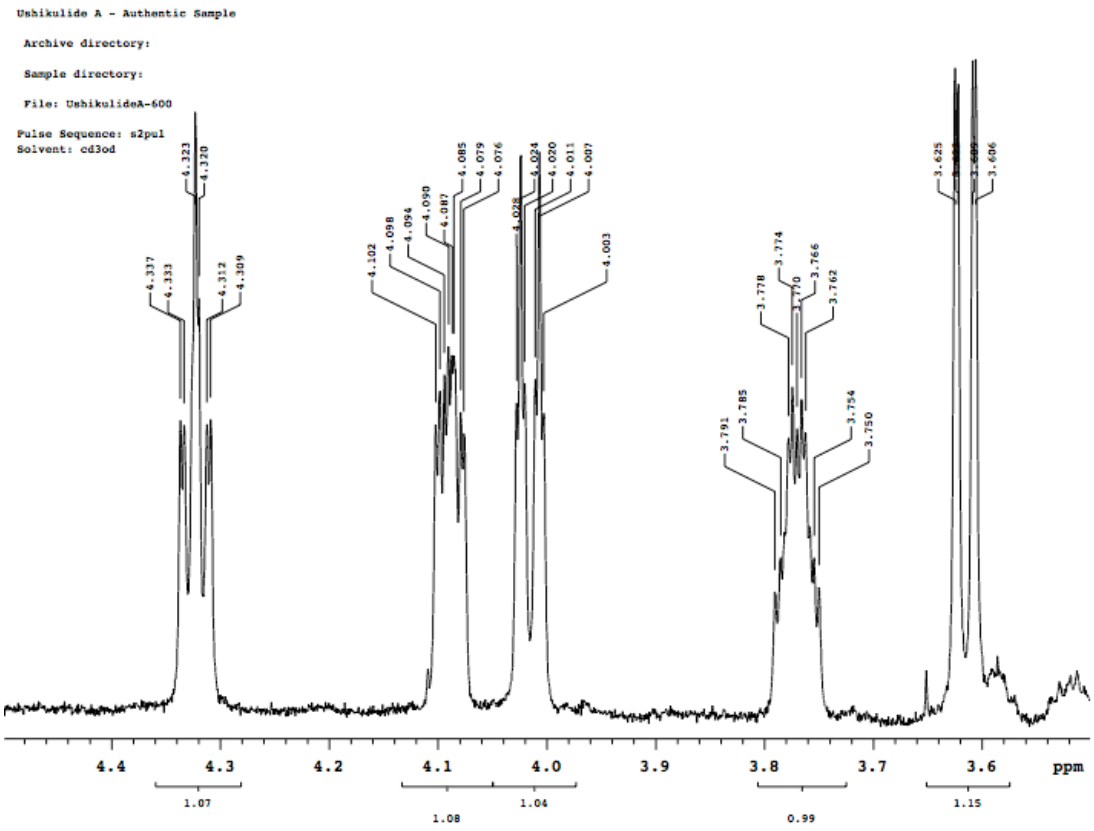


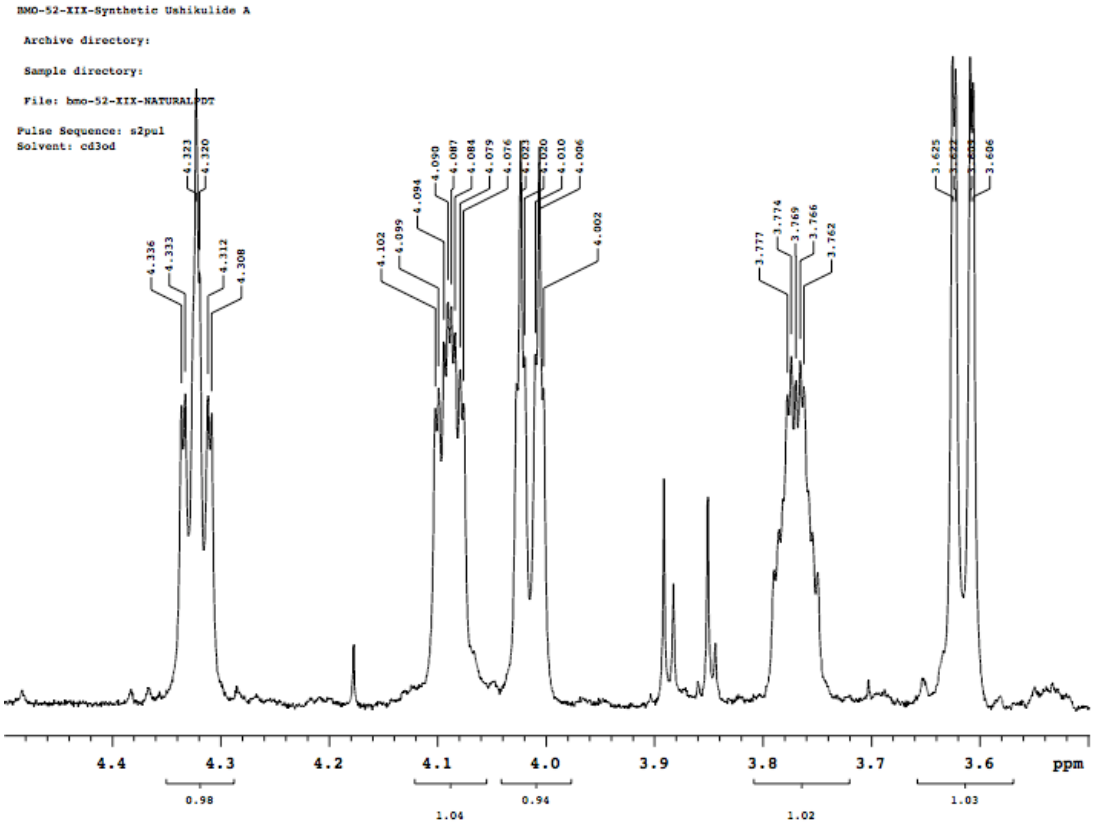

Ushikulide A - Authentic Sample
Archive directory:
Sample directory:
File: UshikulideA-600
Pulse Sequence: s2pul
Solvent: cd3od
Me
O
Me
OH
O
O
Me
Me
OH
O
OH
HO
Me
OH
Ushikulide A - Natural
ppm

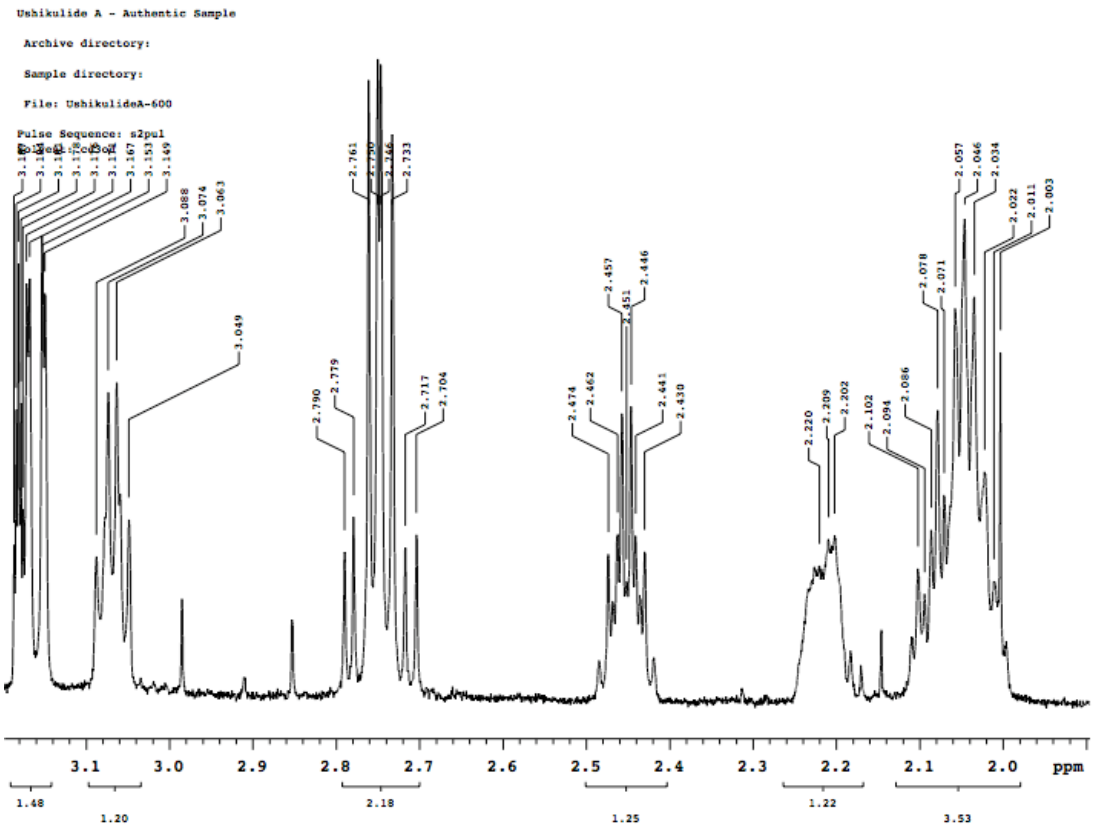

BMO-52-XIX-Synthetic Ushikulide A
Archive directory:
Sample directory:
File: bmo-52-XIX-NATURALPDT
Pulse Sequence: s2pul
Solvent: cd3od
Me
O
Me
OH
O
O
Me
Me
OH
O
OH
HO
Me
OH
Ushikulide A - Synthetic
ppm

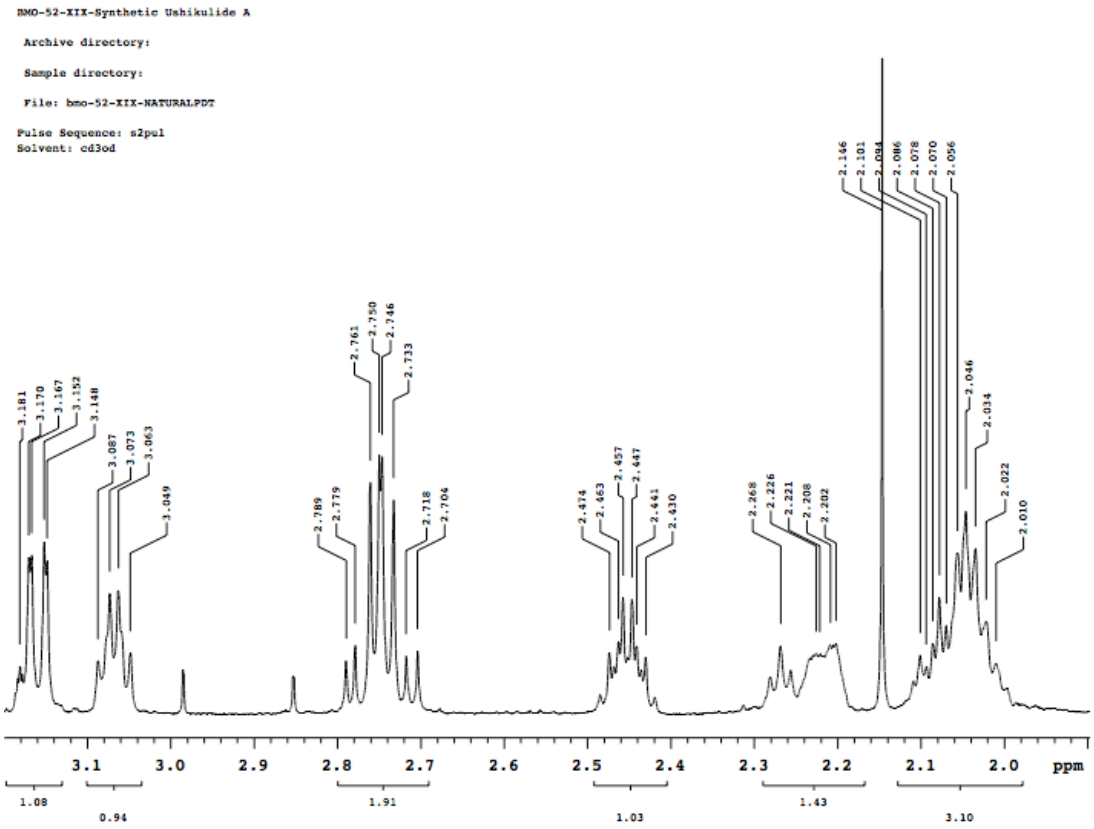

Ushikulide A - Authentic Sample
Archive directory:
Sample directory:
File: UshikulideA-600
Pulse Sequence: s2pul
Solvent: cd3od
6.773
6.757
6.747
6.731
5.821
5.794
5.618
5.611
5.602
5.593
5.586
5.577
5.570
5.481
5.452
5.454
5.440
5.427
5.412
5.310
5.301
5.290
5.282
5.273
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm
1.07
1.11
1.01
1.00
0.99

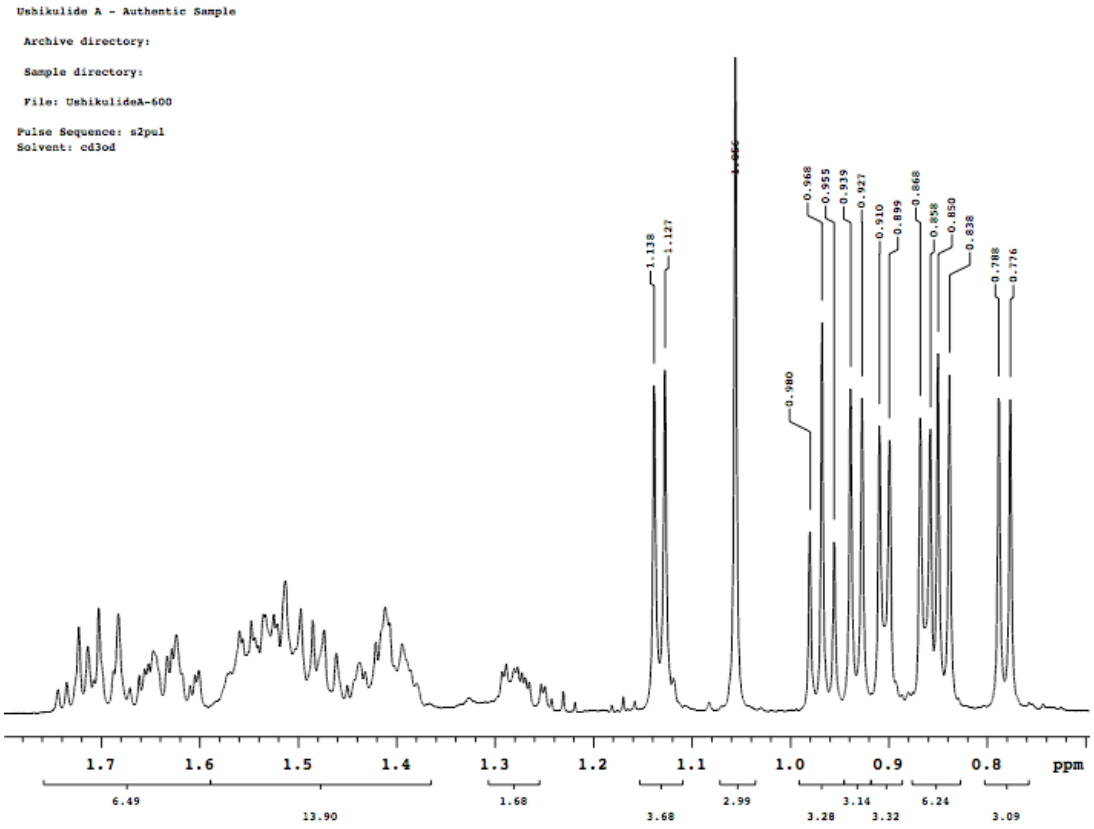

BMO-51-XIX-Synthetic Ushikulide A
Archive directory:
Sample directory:
File: bmo-52-XIX-NATURALPDT
Pulse Sequence: s2pul
Solvent: cd3od
6.773
6.757
6.747
6.730
5.820
5.794
5.617
5.611
5.602
5.592
5.585
5.577
5.570
5.454
5.439
5.427
5.412
5.310
5.301
5.290
5.281
5.272
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm

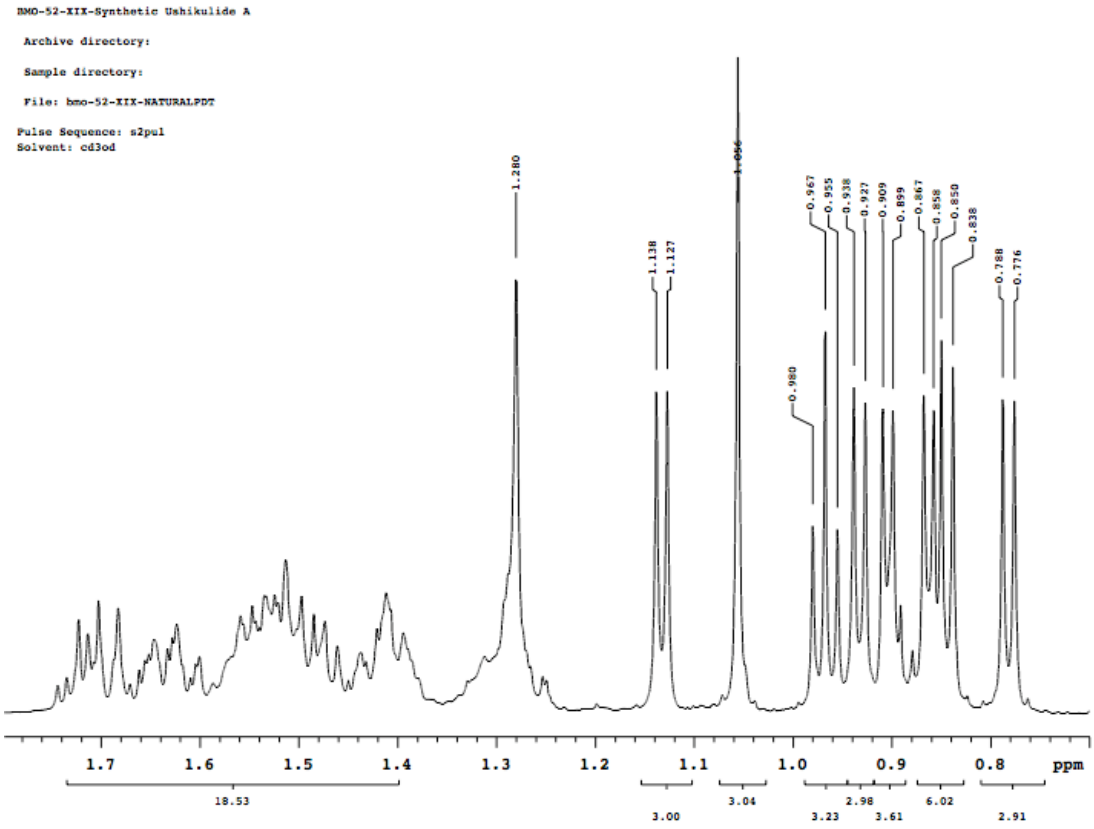

Ushikulide A - Authentic Sample
Archive directory:
Sample directory:
File: UshikulideA-600
Pulse Sequence: s2pul
Solvent: cd3od
4.337
4.333
4.323
4.320
4.312
4.309
4.102
4.098
4.094
4.090
4.087
4.085
4.079
4.076
4.028
4.024
4.020
4.011
4.007
4.003
3.791
3.785
3.778
3.774
3.770
3.766
3.762
3.754
3.750
3.625
3.622
3.606
3.602
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
ppm
1.07
1.08
1.04
0.99
1.15

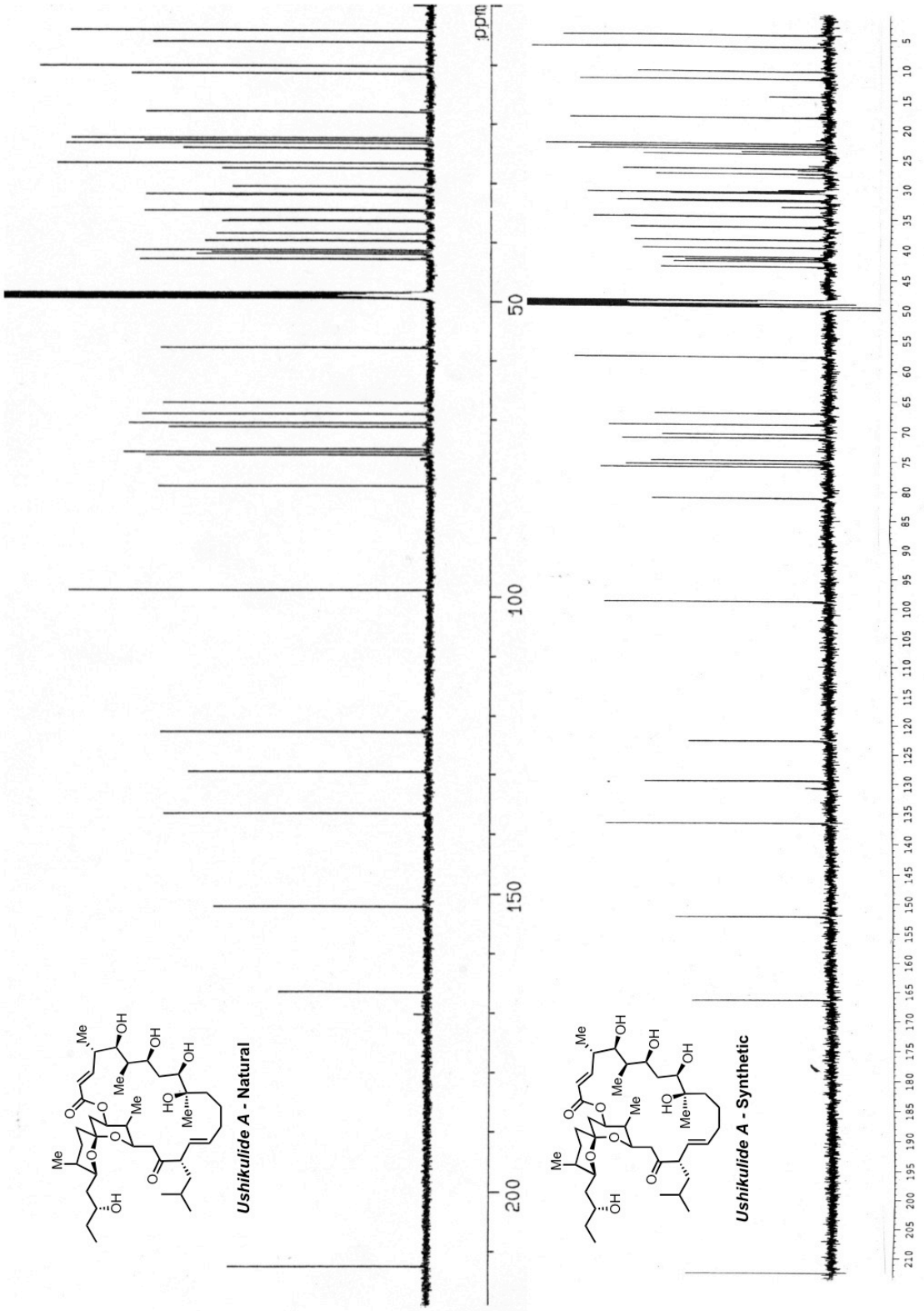

BMO-52-XIX-Synthetic Ushikulide A
Archive directory:
Sample directory:
File: bmo-52-XIX-NATURAL.FDT
Pulse Sequence: s2pul
Solvent: cd3od
4.336
4.333
4.323
4.320
4.312
4.308
4.102
4.099
4.094
4.090
4.087
4.084
4.079
4.076
4.023
4.020
4.010
4.006
4.002
3.777
3.774
3.769
3.766
3.762
3.625
3.622
3.606
3.602
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
ppm
0.98
1.04
0.94
1.02
1.03

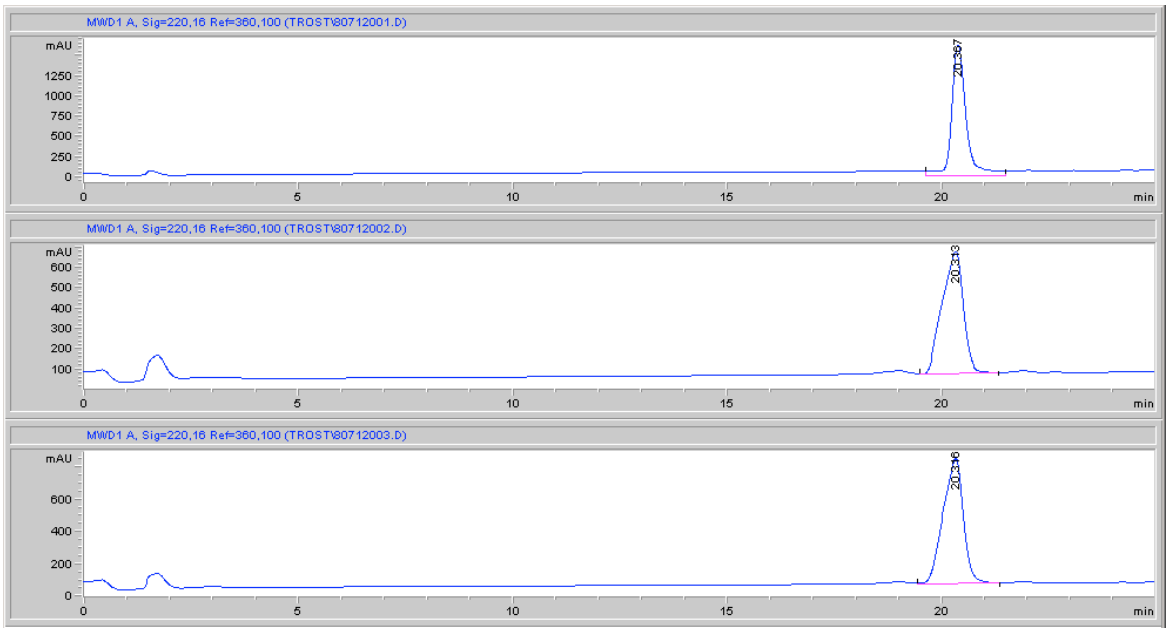

Ushikulide A - Authentic Sample
Archive directory:
Sample directory:
File: UshikulideA-600
Pulse Sequence: s2pul
Solvent: cd3od
3.181
3.170
3.167
3.153
3.149
3.088
3.074
3.063
3.049
2.790
2.779
2.761
2.750
2.746
2.733
2.717
2.704
2.474
2.463
2.457
2.451
2.446
2.441
2.430
2.220
2.209
2.202
2.102
2.094
2.086
2.078
2.071
2.057
2.046
2.034
2.022
2.011
2.003
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
ppm
1.48
1.20
2.18
1.25
1.22
3.53


BMO-52-XIX-Synthetic Ushikulide A
Archive directory:
Sample directory:
File: bmo-52-XIX-NATURALPDT
Pulse Sequence: s2pul
Solvent: cd3od
3.181
3.170
3.167
3.152
3.148
3.087
3.073
3.063
3.049
2.789
2.779
2.761
2.750
2.746
2.733
2.718
2.704
2.474
2.463
2.457
2.447
2.441
2.430
2.268
2.226
2.221
2.208
2.202
2.146
2.101
2.084
2.086
2.078
2.070
2.056
2.046
2.034
2.022
2.010
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
ppm
1.08
0.94
1.91
1.03
1.43
3.10


Ushikulide A - Authentic Sample
Archive directory:
Sample directory:
File: UshikulideA-600
Pulse Sequence: s2pul
Solvent: cd3od
1.138
1.127
1.066
0.980
0.968
0.955
0.939
0.927
0.910
0.899
0.868
0.858
0.850
0.838
0.788
0.776
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
ppm
6.49
13.90
1.68
3.68
2.99
3.28
3.14
3.32
6.24
3.09


BMO-52-XIX-Synthetic Ushikulide A
Archive directory:
Sample directory:
File: bmo-52-XIX-NATURALPDT
Pulse Sequence: s2pul
Solvent: cd3od
1.280
1.138
1.127
1.066
0.980
0.967
0.955
0.938
0.927
0.909
0.899
0.867
0.858
0.850
0.838
0.788
0.776
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
ppm
18.53
3.00
3.04
3.23
2.98
3.61
6.02
2.91


Ushikulide A - Natural
Ushikulide A - Synthetic
ppm
50
100
150
200



The HPLC traces above were obtained using a C-18 reversed phase analytical column and a gradient of 30%-70% of acetonitrile to water (flow rate = 1mL/min, gradient over 20 minutes, lamp set to 220 nm).

The top trace is an authentic sample of ushikulide A, the middle is of synthetic ushikulide A, and the third is a coinjection of a 50:50 mixture of the two samples.