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Supporting Information

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Enantioselective Total Synthesis of (–)-Acylfulvene and (–)-Irofulven

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General Procedures. All reactions were performed in oven-dried or flame-dried round bottomed flasks or modified Schlenk (Kjeldahl shape) flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 μm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (Anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer^{TM}) and were purified by the method of Grubbs et al. under positive argon pressure.[2] Triethylamine, diisopropylamine, *N*-methyl morpholine, 1-methyl-2-pyrrolidinone, and chlorotrimethylsilane were distilled from calcium hydride immediately before use. Methanol was

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[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

distilled from anhydrous magnesium methoxide. Lithium hexamethyldisilazane was purchased from Aldrich and was stored in a glove box. Sodium hydride was purchased from Aldrich Chemicals as dispersion (60%) in oil and washed four times with hexanes and stored in a glove box. Methanolic sodium methoxide solution (1.0 N) was prepared by addition of sodium hydride to anhydrous methanol at –78 °C. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).[3]

Instrumentation. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer with a Magnex Scientific superconducting magnet, a Bruker Avance-400 (400 MHz) spectrometer with a SpectroSpin superconducting magnet at 23˚C, or a Varian 500 INOVA (500 MHz) as noted. Proton nuclear magnetic resonance (^{1}H NMR) spectra are reported in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, C_6HD_5: δ 7.16, CHD_2CN: δ 1.94). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, st = sextet, sp = septet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra are reported in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.2, C_6D_6: δ 128.0, CD_3CN: δ 118.7 and δ 1.39). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Gas chromatography was performed on an Agilent Technologies 6890N Network GC System with a HP-5 5% Phenyl Methyl Siloxane column (100 °C, 1 min; 30 °C/min to 250 °C; 250 °C, 2 min). The structure of **S12** was obtained at the X-ray crystallography laboratory of the Department of Chemistry, Massachusetts Institute of Technology, with the assistance of Dr. Peter Mueller and Mr. Michael A. Schmidt. Gas chromatography low-resolution mass spectra (GC-LRMS) were recorded on an Agilent Technologies 6890N Network GC System with a Restek Rtx-1 100% dimethyl polysiloxane column (100 °C, 5 min; 20 °C/min to 250 °C; 250 °C, 5 min; 30 °C/min to 320 °C; 320 °C, 5 min) with a Agilent 5973*Network* mass selective detector using electron impact ion source (EI). Optical Rotation was recorded on a Jasco P-1010 Polarimeter (Chloroform, Aldrich, Chromosolv Plus 99.9%; Ethanol, Aldrich, Absolute, 200 Proof 99.5%). We are grateful to Dr. Li Li for obtaining the mass spectroscopic data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High-resolution mass spectra (HRMS) were recorded on a Bruker APEX 4.7 Tesler FTMS spectrometer using electronspray ion source (ESI), unless otherwise noted.

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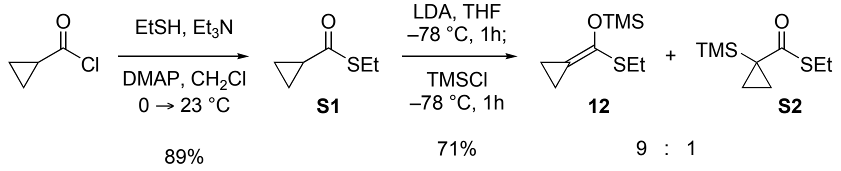
[3] Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.



(Cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane (12):

Ethanethiol (16.3 mL, 220 mmol, 1.10 equiv) was added slowly to a solution of cyclopropanecarbonyl chloride (18.3 mL, 200 mmol, 1 equiv), triethylamine (33.5 mL, 240 mmol, 1.20 equiv), and 4-dimethylaminopyridine (2.40 g, 20.0 mmol, 0.100 equiv) in dichloromethane (500 mL) at 0 °C and the resulting mixture was allowed to warm to 23 °C. After 3 h, the reaction mixture was concentrated under reduced pressure and the residue was partitioned between diethyl ether (400 mL) and water (300 mL). The organic phase was separated and washed with brine (300 mL), was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The residue was purified by vacuum distillation (50 °C, 5 mmHg) to afford *S*-ethyl cyclopropanecarbothioate (**S1**, 23.1 g, 89%) as a clear colorless liquid.

n-Butyllithium (2.50 M, 33.8 mL, 1.10 equiv) was added to a solution of diisopropylamine (12.9 mL, 92.3 mmol, 1.20 equiv) in THF (192 mL) at 0 °C under argon. The mixture was cooled to –78 °C, and *S*-ethyl cyclopropanecarbothioate (**S1**, 10.0 g, 76.9 mmol, 1 equiv) was added drop-wise via syringe. After 1 h, freshly distilled chlorotrimethylsilane (11.7 mL, 92.3 mmol, 1.20 equiv) was added drop-wise. After an additional 1h, the reaction mixture was diluted with pentane (500 mL), was washed with water (300 mL), phosphate buffer (pH 7, 300 mL), and brine (300 mL). The organic layer was dried over anhydrous sodium sulfate, and was concentrated under reduced pressure. The residue was purified by vacuum distillation (60 °C, 1 mmHg) to afford a mixture (9:1) of (cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane (**12**) and 1-(trimethyl-silanyl)-cyclopropanecarbothioic acid *S*-ethyl ester (**S2**), as clear colorless oil (11.0 g, 71%).

***S*-Ethyl cyclopropanecarbothioate (S1):**

^{1}H NMR (500 MHz, $CDCl_3$) δ:	2.87 (q, *J* = 7.3 Hz, 2H, SC**H**$_2$), 1.98 (tt, *J* = 7.7 Hz, 4.6 Hz, 1H, C**H**), 1.23 (t, *J* = 7.3, 3H, C**H**$_3$), 1.15-1.11 (m, 2H, C**H**$_2$), 0.93-0.89 (m, 2H, C**H**$_2$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	199.5, 23.4, 22.7, 15.0, 10.7.
FTIR (neat) cm^{-1}:	2970 (m, C–H), 1681 (s, C=O), 1451 (m), 1419 (m), 1368 (s), 1039 (s), 993 (s).
GC-LRMS:	calcd for $C_6H_{10}OS$ $[M]^+$: 130, found: 130 (7.3 min)
GC, t_R:	1.494 min
TLC (20% EtOAc in hexanes) R*f*:	0.55 (UV)

(Cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane (12; containing ≤10% S2):

^{1}H NMR (500 MHz, $CDCl_3$) δ:	2.78 (q, *J* = 7.3 Hz, 2H, SC**H**$_2$), 1.33-1.24 (m, 4H, C**H**$_2$C**H**$_2$), 1.27 (t, *J* = 7.3 Hz, 3H, C**H**$_3$), 0.24 (s, 9H, Si(C**H**$_3$)$_3$).

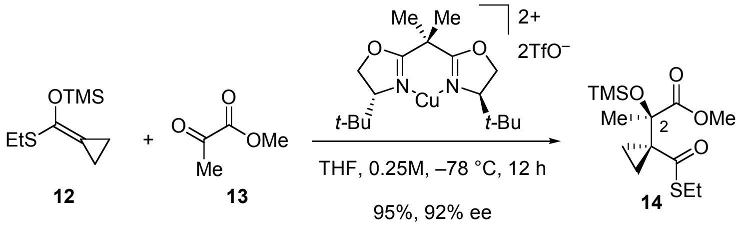
^{13}C NMR (125.8 MHz, CDCl$_3$) δ: 135.8, 100.5, 25.5, 15.4, 7.2, 5.1, 0.7.

FTIR (neat) cm^{-1}: 2965 (s), 1751 (s), 1449 (w), 1252 (s), 1189 (s), 1071 (m).

HRMS (ESI): calcd for $C_9H_{19}OSSi$ $[M+H]^+$: 203.0920, found: 203.0926.

GC, t_R: 2.499 min

TLC (10% EtOAc in hexanes) R*f*: 0.5 (UV)



(+)-(2*R*)-2-(1-Ethylsulfanylcarbonyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (14): A flame-dried flask was charged with (*R*,*R*)-2,2'-isopropylidene-bis(4-*tert*-butyl-2-oxazoline) (982 mg, 3.33 mmol, 0.10 equiv)[4] and copper (II) triflate (1.21 g, 3.33 mmol, 0.10 equiv) in a glove-box under a dinitrogen atmosphere. The flask was sealed with a rubber septum and removed from the glove-box. The flask containing the solids was charged with THF (133 mL), and the resulting mixture was stirred at 23 °C under an argon atmosphere. After 1h, the resulting bright green solution was cooled to –78 °C, and methyl pyruvate (3.43 g, 1.00 mmol, 1 equiv) was added followed by (cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane (**12** [mixture of **12**:**S2** = 9:1], 8.22 g, 36.6 mmol, 1.10 equiv) and the resulting mixture was maintained at –78 °C. After 12 h, the reaction mixture was diluted with diethyl ether (100 mL), and filtered through a plug of silica gel (5 × 4 cm, eluent: 1% triethyamine in diethyl ether). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatrography (silica gel: diam. 8 cm, ht. 15 cm; eluent: hexanes–EtOAc–TEA [97:2:1] to hexanes–EtOAc–TEA [79:20:1]) to afford the desired (2*R*)-2-(1-ethylsulfanylcarbonyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (**14**, 11.5 g, 95%, $[\alpha]^{20}_{D}$ = +30.2 (*c* 2.22, $CHCl_3$)) as a colorless liquid. Protodesilyaltion of the C2-trimethylsilyloxy group of **14** afforded samples of the corresponding C2-alcohol that were found to be of 92% ee by chiral HPLC analysis [Chirapak AD-H; 1.5 mL/min; 10% ^{i}PrOH in hexanes; t_R(major) = 4.59 min, t_R(minor) = 5.03 min]. The (*R*,*R*)-2,2'-isopropylidene-bis(4-*tert*-butyl-2-oxazoline) ligand was recovered from the reaction mixture (~85%) and purified by flash column chromatography (silica gel: diam. 2.5 cm, ht. 10 cm; eluent: CH_2Cl_2–EtOAc [4:1]).

^{1}H NMR (500 MHz, $CDCl_3$) δ:	3.72 (s, 3H, OC**H**$_3$), 2.79 (q, *J* = 7.3 Hz, 2H, SC**H**$_2$), 1.58-1.54 (m, 1H, C**H**$_2$), 1.53 (s, 3H, C**H**$_3$), 1.27-1.19 (m, 2H, C**H**$_2$), 1.19 (t, *J* = 7.3 Hz, 3H, CH_2C**H**$_3$), 1.12-1.08 (m, 1H, C**H**$_2$), 0.07 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	200.9, 173.4, 75.4, 52.1, 41.8, 24.2, 23.0, 15.3, 14.8, 11.6, 1.5.
FTIR (neat) cm^{-1}:	2954 (m, C–H), 1747 (s, CO_2Me), 1666 (s, COSEt) 1456 (m), 1413 (m), 1372 (m), 1289 (m), 1263 (s).
HRMS (ESI):	calcd for $C_{13}H_{24}NaO_4SSi$ [M+Na]$^+$: 327.1057, found: 327.1066.
GC, t_R:	4.450 min
TLC (10% EtOAc in hexanes) R*f*:	0.4 (UV, CAM)

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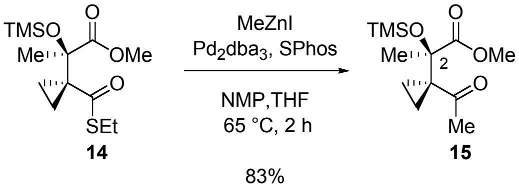
[4] For the preparation of (*R*,*R*)-2,2'-isopropylidene-bis(4-^{t}butyl-2-oxazoline), see: Evans, D. A.; Peterson, G. S.; Johnson, J. S.; Barnes, D. M.; Campos, K. R.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 4541-4544.



(+)-(2*R*)-2-(1-Acetyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (15):

A Schlenk flask was charged with activated Zn dust (981 mg, 15.0 mmol, 1.50 equiv)[5], placed under reduced pressure (1 Torr), and heated to 65 °C. After 30 min, the flask was backfilled with argon and cooled to 23 °C. Anhydrous *N*-methyl pyrrolidin-2-one (NMP, 10 ml) and iodine (127 mg, 0.500 mmol, 0.050 equiv) were added and the reaction mixture was stirred vigorously for 25 min at which time the red color disappeared. Methyliodide (619 µL, 10.0 mmol, 1 equiv) was added and the reaction mixture was stirred at 23 °C for 14 h to provide a solution of iodomethylzinc in NMP (~1 M).

A solution of iodomethylzinc (~1 M, 8.22 mL, 8.22 mmol, 5.00 equiv), prepared as described above, was added via syringe to a solution of thioester **14** (500 mg, 1.64 mmol, 1 equiv), tris(dibenzylideneacetone)dipalladium (75.3 mg, 0.08 mmol, 0.05 equiv), and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 135 mg, 0.33 mmol, 0.20 equiv) in THF (5.5 mL) at 23 °C. The reaction mixture was heated to 65 °C and stirred under an argon atmosphere. After 2 h, the reaction mixture was cooled to 23 °C, diluted with diethyl ether (200 mL), and filtered through a plug of silica gel (diam. 5 cm, ht. 10 cm) to remove most of the NMP. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 12 cm; hexane-EtOAc [95:5]) to afford the desired ketoester **15** as a light yellow oil (353 mg, 83%, $[\alpha]^{20}_{D} = +41.8$ (*c* 2.14, $CHCl_3$)).

^{1}H NMR (500 MHz, $CDCl_3$) δ:	3.69 (s, 3H, OC**H**$_3$), 1.84 (s, 3H, COC**H**$_3$), 1.60-1.54 (m, 1H, C**H**$_2$), 1.49 (s, 3H, C**H**$_3$), 1.19-1.09 (m, 2H, C**H**$_2$), 1.08-1.03 (m, 1H, C**H**$_2$), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	207.7, 173.4, 75.1, 52.1, 41.1, 24.4, 24.2, 13.3, 10.7, 1.6.
FTIR (neat) cm^{-1}:	2953 (m, C–H), 1745 (s, CO_2Me), 1685 (s, C=O), 1458 (m), 1434 (m), 1369 (s), 1327 (m), 1253 (s).
HRMS (ESI):	calcd for $C_{12}H_{22}NaO_4Si$ $[M+Na]^+$: 281.1180, found: 281.1181.
GC, t_R:	3.425 min
TLC (20% EtOAc in hexanes) R*f*:	0.33 (Anis)

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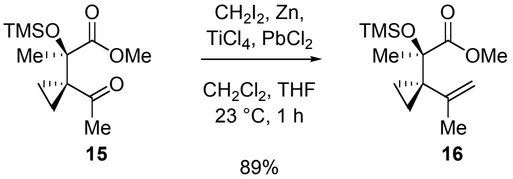
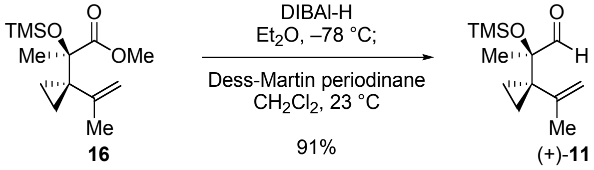
[5] Activated zinc dust was prepared by sequential washing of Zn dust with 1.2N HCl in H_2O, H_2O, methanol, and diethyl ether, and drying under vacuum; see: Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967, Vol. 1, p. 1267.



(+)-(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (16):

Diiodomethane (3.93 mL, 48.8 mmol, 6.00 equiv) was added to a vigorously stirred suspension of activated zinc dust (5.30 g, 81.0 mmol, 10.8 equiv)[5] and lead (II) chloride (114 mg, 0.410 mmol, 0.05 equiv) in THF (60.0 mL) at 23 °C under an argon atmosphere. After 30 min, the reaction mixture was cooled to 0 °C, and titanium tetrachloride (1M in dichloromethane, 9.72 mL, 9.72 mmol, 1.20 equiv) was added drop-wise via syringe. The resulting brown reaction mixture was warmed to 23 °C with continued stirring. After 30 min, the reaction mixture was cooled to 0 °C and a solution of ketoester **15** (2.10 g, 8.10 mmol, 1 equiv) in THF (20.0 mL) was added via cannula. After 1 h, the excess reagent was quenched by the addition of saturated aqueous sodium bicarbonate solution (200 mL). The mixture was extracted with diethyl ether (3 × 200 mL), and the combined organic layers were dried over sodium sulfate, and were concentrated under reduced pressure. Purification by flash column chromatography (silica gel: diam. 4 cm, ht. 8 cm; pentane-diethyl ether [9:1]) afforded the desired (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (**16**, 1.86 g, 89%, $[\alpha]^{20}_{D} = +25.4$ (*c* 0.763, $CHCl_3$)) as a clear colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ:	4.92 (s, 1H, C=C**H**$_2$), 4.87 (s, 1H, C=C**H**$_2$), 3.68 (s, 3H, OC**H**$_3$), 1.71 (s, 3H, C=CCH$_3$), 1.42 (s, 3H, C**H**$_3$), 1.05 (ddd, *J* = 3.9, 5.9, 9.7 Hz, 1H, C**H**$_2$), 0.83 (ddd, *J* = 3.9, 5.9, 9.7 Hz, 1H, C**H**$_2$), 0.47 (ddd, *J* = 3.9, 5.9, 9.7 Hz, 1H, C**H**$_2$), 0.38 (ddd, *J* = 3.9, 5.9, 9.7 Hz, 1H, C**H**$_2$), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	175.6, 146.5, 117.3, 78.0, 51.7, 35.0, 24.6, 22.5, 9.7, 9.5, 1.7.
FTIR (neat) cm^{-1}:	2954 (m, C–H), 1743 (s, CO_2Me), 1639 (w), 1450 (m), 1373 (m), 1252 (s), 1154 (s), 1126 (s), 1019 (m).
HRMS (ESI):	calcd for $C_{13}H_{24}NaO_3Si$ $[M+Na]^+$: 279.1387, found: 279.1384.
GC, t_R:	2.933 min
TLC (20% EtOAc in hexanes) R*f*:	0.60 (Anis)



(+)-(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde (11):

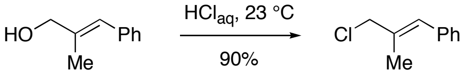
Diisobutylaluminum hydride (DIBAl-H, 1.5M in Toluene, 11.7 mL, 17.6 mmol, 3.00 equiv) was added drop-wise down the side of the flask into a solution of (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (**16,** 1.5 g, 5.80 mmol, 1 equiv) in diethyl ether (29 mL) at –78 °C under argon. The reaction mixture was stirred and maintained at –78 °C. After 1 h, excess hydride was quenched by the slow addition of methanol (17.6 mmol, 713 μL, 3.00 equiv). The mixture was diluted first with diethyl ether (300 mL), and then with a saturated aqueous solution of Rochelle's salt (200 mL). The mixture was allowed to warm to 23 °C, and the layers were separated. The organic layer was washed with brine (200 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford a mixture of (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propan-1-ol (**S3**) and (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde (**11**) as a colorless oil (**S3**:**11**, 2.5:1). Dess-Martin periodinane (2.71 g, 6.38 mmol, 1.10 equiv) was added to the mixture of (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propan-1-ol (**S3**) and (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde (**11**) in dichloromethane (29 mL) at 23 °C under argon. After 1 h, the reaction mixture was filtered through a plug of silica gel (diam. 3 cm, ht. 3 cm; eluent: pentane), and was concentrated to afford (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde (**11**, 1.22 g, 91%, $[\alpha]^{20}_{D}$ = +63.0 (*c* 0.564, $CHCl_3$)) as a colorless oil.

(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propan-1-ol (S3):

^1H NMR (500 MHz, $CDCl_3$) δ:	4.99 (m, 2H, C=C**H**$_2$), 3.57 (dd, *J* = 7.5, 11.0 Hz, 1H, C**H**$_2$OH), 3.46 (dd, *J* = 5.3, 11.0 Hz, 1H, C**H**$_2$OH), 1.83 (t, *J* = 1.0 Hz, 3H, C**H**$_3$C=CH$_2$), 1.81 (dd, *J* = 5.3, 7.5 Hz, 1H, O**H**), 1.27 (s, 3H, C**H**$_3$), 0.91-0.88 (m, 1H, CH$_2$C**H**$_2$), 0.65-0.60 (m, 1H, CH$_2$C**H**$_2$), 0.43-0.35 (m, 2H, C**H**$_2$), 0.14 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	147.7, 117.6, 69.9, 46.4, 33.2, 23.5, 23.2, 9.2, 8.4, 2.6.
FTIR (neat) cm^{-1}:	3465 (br, O–H), 3078 (w, C–H), 2956 (s, C–H), 1637 (w), 1450 (m), 1413 (m), 1374 (m), 1252 (s).
HRMS (ESI):	calcd for $C_{12}H_{24}NaO_2Si$ $[M+Na]^+$: 251.1438, found: 251.1442.
GC, t_R:	3.013 min
TLC (5% EtOAc in hexanes) R*f*:	Prod. **S3**: 0.19 (Anis)

(+)-(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde (11):

^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ:	9.50 (s, 1H, $\mathrm{C\mathbf{H}O}$), 4.95 (br-s, 1H, $\mathrm{C{=}C\mathbf{H}_2}$), 4.87 (br-s, 1H, $\mathrm{C{=}C\mathbf{H}_2}$), 1.71 (br-s, 3H, $\mathrm{C\mathbf{H}_3C{=}CH_2}$), 1.29 (s, 3H, $\mathrm{C\mathbf{H}_3COTMS}$), 0.97 (ddd, *J* = 3.8, 5.8, 9.6 Hz, 1H, $\mathrm{C\mathbf{H}_2CH_2}$), 0.78 (ddd, *J* = 3.9, 5.8, 9.6 Hz, 1H, $\mathrm{C\mathbf{H}_2CH_2}$), 0.48 (ddd, *J* = 4.0, 5.8, 9.6 Hz, 1H, $\mathrm{CH_2C\mathbf{H}_2}$), 0.41 (ddd, *J* = 3.8, 5.8, 9.6 Hz, 1H, $\mathrm{CH_2C\mathbf{H}_2}$), 0.09 (s, 9H, $\mathrm{Si(C\mathbf{H}_3)_3}$).
^{13}C NMR (125.8 MHz, $\mathrm{CDCl_3}$) δ:	203.0, 145.6, 118.0, 79.7, 32.6, 23.2, 20.8, 8.5, 7.5, 2.2.
FTIR (neat) cm^{-1}:	2958 (m, C–H), 1735 (s, C=O), 1639 (w), 1448 (w), 1377 (w), 1252 (s).
HRMS (ESI):	calcd for $\mathrm{C_{12}H_{22}NaO_2Si}$ $[\mathrm{M{+}Na}]^+$: 249.1281, found: 249.1293.
TLC (100% hexanes) R*f*:	Prod. **11**: 0.17 (Anis)

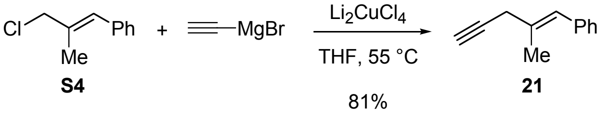


S4

_E_-(3-chloro-2-methylprop-1-enyl)benzene (S4):

Aqueous hydrochloric acid solution (12 N, 51.7 mL, 620 mmol, 3.00 equiv) was slowly added to 2-methyl-3-phenyl-prop-2-en-1-ol (30.6 g, 207 mmol, 1 equiv), and the reaction mixture was stirred and maintained at 23 °C. After 12 h, the reaction mixture was diluted with diethyl ether (50 mL), the layers were separated, and the aqueous layer was further extracted with additional diethyl ether (2 × 50 mL). The combined organic layers were washed with brine (100 mL), were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure (30 °C, 100 mmHg). The residue was purified by vacuum distillation (120 °C, 12 mmHg) to afford *E*-(3-chloro-2-methylprop-1-enyl)benzene (**S4**, 31.0 g, 90%) as a clear colorless oil.

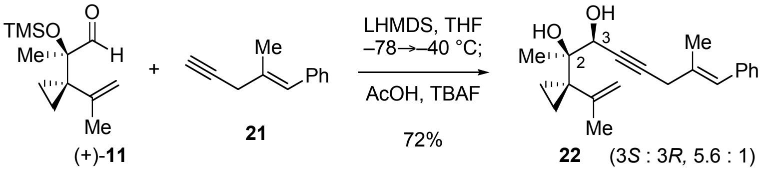
^{1}H NMR (500 MHz, $CDCl_3$) δ:	8.05-8.0 (m, 2H, Ar**H**), 7.98-7.90 (m, 3H, Ar**H**), 7.27 (br-s, 1H, C=C**H**), 4.87 (s, 2H, C**H**$_2$Cl), 2.67 (d, *J* = 1.5 Hz, 3H, C**H**$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	136.9, 134.3, 130.0, 129.1, 128.4, 127.2, 53.1, 16.1.
FTIR (neat) cm^{-1}:	2985 (m, C–H), 1950 (w), 1885 (w), 1808 (w), 1599 (m), 1492 (s), 1442 (s), 1261 (s).
HRMS (ESI):	calcd for $C_{10}H_{11}Cl$ $[M]^+$: 166.0544, found: 166.0538.
TLC (20% EtOAc in hexane) R*f*:	0.70 ($KMnO_4$)



<u>*E*-(2-Methyl-pent-1-en-4-ynyl)-benzene (21):</u>

A flame-dried 200-mL round-bottom flask was sequentially charged with a solution of ethynyl magnesium bromide (0.5M in THF, 448 mL, 224 mmol, 2.60 equiv) and a solution of dilithium tetrachlorocuprate (0.1 M in THF, 86.2 mL, 8.62 mmol, 0.10 equiv) and the resulting mixture was stirred at 23 °C. After 15 min, a solution of the allylic chloride **S4** (14.4 g, 86.2 mmol, 1 equiv) in THF (20 mL) was added via cannula and the resulting brown solution was heated to 55 ºC. After 50 h, the reaction mixture was cooled to 23 ºC and partitioned between diethyl ether (300 mL) and saturated aqueous ammonium chloride solution (150 mL). The aqueous layer was extracted with diethyl ether (2 × 300 mL) and the combined organic layers were washed with brine (150 mL), were dried over anhydrous magnesium sulfate, and were filtered. The dark solution of the crude alkyne **21** was concentrated (to approximately 300 mL) under reduced pressure (~350 Torr, 28 ºC) and was passed through silica gel (diam. 7.5 cm, ht. 30.0 cm; eluent: ^{n}pentane) to give the crude alkyne **21** as a dark yellow oil after removal of volatiles under reduced pressure. Purification of the residue by flash column chromatography (silica gel: diam. 7.5 cm, ht. 32 cm; ^{n}pentane:CH_2Cl_2, [20:1]) afforded the alkyne **21** (10.9 g, 81%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ:	7.38-7.33 (m, 2H, Ar**H**), 7.30-7.21 (m, 3H, Ar**H**), 6.61 (br-s, 1H, C=C**H**Ph), 3.10 (br-s, 2H, C**H**$_2$), 2.21 (t, *J* = 2.4 Hz, 1H, C≡C–**H**), 1.94 (br-s, 3H, C**H**$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	138.0, 133.1, 129.0, 128.3, 126.5, 81.6, 71.2, 65.7, 29.5, 17.4.
FTIR (neat) cm^{-1}:	3298 (s, C≡C–H), 2984 (m, C–H), 2117 (w, C≡C), 1658 (w), 1599 (w), 1490 (m), 1442 (m), 1294 (w), 1155 (w).
HRMS (ESI):	calcd for $C_{12}H_{12}Na$ $[M+Na]^+$: 156.0939, found: 156.0937.
TLC (5% CH_2Cl_2 in hexane) R*f*:	0.22 ($KMnO_4$)



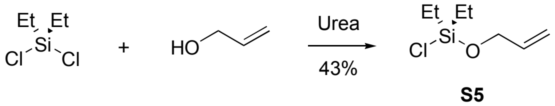
*E*-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-7-methyl-8-phenyl-oct-7-en-4-yne-2,3-diol (22):

A solution of the alkyne **21** (1.47 g, 9.40 mmol, 1.25 equiv) in THF (50 mL) was added dropwise to a solution of lithium bis(trimethylsilyl)amide (LHMDS, 1.68 g, 9.77 mmol, 1.30 equiv) in THF (50 mL) at –78 ºC. After 5 min, a solution of the aldehyde **11** (1.70 g, 7.52 mmol, 1 equiv) in THF (12 mL) was added slowly via cannula, and the mixture was warmed to –40 ºC. After 40 min, the excess base was quenched by the addition of a saturated aqueous ammonium chloride solution (5 mL) and the resulting mixture was warmed to 23 ºC. The reaction mixture was diluted with H_2O (150 mL) and was extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried over anhydrous sodium sulfate and were partially concentrated under reduced pressure (to ~10 mL). The flask was charged with additional THF (40 mL) and a mixture of tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 15.0 mL, 15.0 mmol, 2.00 equiv) and acetic acid (0.430 mL, 7.52 mmol, 1.00 equiv) was added to this crude mixture. After 40 min, a saturated aqueous ammonium chloride solution (150 mL) was added, and the mixture was extracted with ethyl acetate (3 × 150 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and the volatiles were removed under reduced pressure. The resulting yellow oil was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 30 cm; eluent: hexanes:EtOAc, [4:1]) to give the propargylic alcohol **22** (1.80 g, 72%) as a mixture of C3-diastereomers favoring the *anti*-isomer (3*S*:3*R*, 5.6:1). The C3-stereochemistry of the major diastereomer of **22** was secured using nOe data for a more advanced intermediate (alcohol **27**, see page S20).

^{1}H NMR (500 MHz, C_6D_6, 5.6:1 mixture of (3*S*)- and (3*R*)-diastereomers; minor (3*R*)-isomer denoted by *) δ: 7.40-7.00 (m, 5H, Ar**H***), 7.24-7.14 (m, 4H, Ar**H**), 7.08-7.03 (m, 1H, Ar**H**), 6.65 (br-s, 1H, C=C**H**Ph), 6.65 (br-s, 1H, C=C**H**Ph*), 5.16 (br-s, 1H, C=C**H**$_2$), 5.12 (br-s, 1H, C=C**H**$_2$*), 4.95 (br-s, 1H, C=C**H**$_2$*), 4.91 (br-s, 1H, C=C**H**$_2$), 4.54 (br-s, 1H, C**H**OH*), 4.48 (br-s, 1H, C**H**OH), 2.97 (s, 2H, C**H**$_2$*), 2.82 (s, 2H, C**H**$_2$), 1.93 (s, 1H, CHO**H**), 1.93 (s, 1H, CHO**H***), 1.87 (s, 3H, C**H**$_3$*), 1.82 (s, 3H, C**H**$_3$*), 1.77 (s, 3H, C**H**$_3$), 1.71 (s, 3H, C**H**$_3$), 1.64 (s, 1H, O**H**), 1.64 (s, 1H, O**H***), 1.30 (s, 3H, C**H**$_3$), 1.29 (s, 3H, C**H**$_3$*), 1.26 (ddd, J = 4.6, 6.0, 10.0 Hz, 1H, C**H**$_2$CH$_2$), 1.02 (ddd, J = 10.0, 6.0, 4.6 Hz, 1H, C**H**$_2$CH$_2$*), 0.93 (ddd, J = 4.0, 6.1, 9.8 Hz, 1H, C**H**$_2$CH$_2$), 0.89 (ddd, J = 9.8, 6.1, 4.0 Hz, 1H, C**H**$_2$CH$_2$*), 0.56 (ddd, J = 4.6, 6.1, 10.0 Hz, 1H, C**H**$_2$CH$_2$), 0.52-0.45 (m, 2H, C**H**$_2$CH$_2$*), 0.44 (ddd, J = 4.0, 6.0, 9.8 Hz, 1H, C**H**$_2$CH$_2$).

^{13}C NMR (125.8 MHz, C_6D_6, 5.6:1 mixture of (3*S*)- and (3*R*)-diastereomers; minor (3*R*)-isomer denoted by *) δ: 147.9, 147.9*, 138.7, 138.3*, 133.9*, 133.8, 129.5, 129.3*, 128.9*, 128.8, 127.2*, 127.1, 127.0, 127.0*, 118.4, 118.2*, 84.9, 84.1*, 83.1, 83.0*,

	75.6*, 75.1, 69.9, 69.9*, 33.5, 32.6*, 30.2, 30.1*, 23.6*, 23.5, 23.4, 22.4*, 18.1, 18.1*, 11.2, 10.2*, 10.1*, 9.6.
FTIR (neat) cm^{-1}:	3440 (br-s, O–H), 2923 (m, C–H), 2227 (w, C≡C), 1635 (w), 1491 (w), 1447 (m), 1375 (m), 1105 (m), 1024 (s).
HRMS (ESI):	calcd for $C_{21}H_{26}NaO_2$ $[M+Na]^+$: 333.1825, found: 333.1829.
TLC (20% EtOAc in hexanes), R*f*:	0.20 (CAM)



S5

Allyloxy-chloro-diethyl-silane (S5):[6]

Allyl alcohol (5.8 g, 100 mmol, 1.00 equiv) was added slowly via syringe over a 6 h period to a stirring mixture of dichloro-diethyl-silane (15.8 g, 100 mmol, 1 equiv), and urea (7.2 g, 120 mmol, 1.20 equiv) at 23 °C under argon. The reaction mixture was transferred via cannula to a distillation apparatus, and the residue was purified by vacuum distillation (65 °C, 15 mmHg) to afford allyloxy-chloro-diethyl-silane (**S5**, 7.52 g, 43%) as a clear colorless oil.

^{1}H NMR (500 MHz,C_6D_6) δ:	5.82-5.72 (m, 1H, C**H**), 5.23 (d, *J* = 17.1 Hz, 1H, C**H**), 4.99 (d, *J* = 10.4 Hz, 1H, C**H**), 4.12 (br-s, 2H, C**H**$_2$), 0.95 (t, *J* = 7.6 Hz, 6H, C**H**$_3$), 0.76-0.62 (m, 4H, C**H**$_2$).
^{13}C NMR (125.8 MHz, C_6D_6) δ:	136.7, 115.1, 64.7, 8.9, 6.8.
FTIR (neat) cm^{-1}:	3331.2 (br-w), 2959 (s), 1460 (m), 1414 (w), 1243 (m), 1086 (s), 1008 (s).
GC-LRMS:	calcd for $C_7H_{15}ClOSi$ [M]$^+$: 178 found: 178 (6.4 min).

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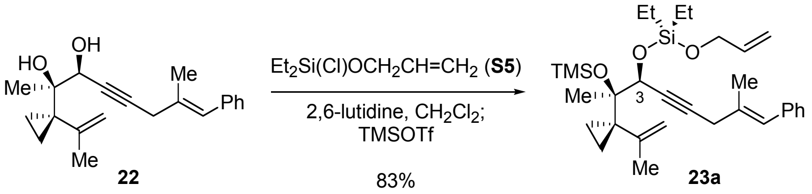
[6] Prepared according to the procedure of Krolevets, A. A.; Antipova, V. V.; Popov, A. G.; Adamov, A. V. *Zhurnal Obschchei Khimii*, **1988**, *58*, 2274-2281.



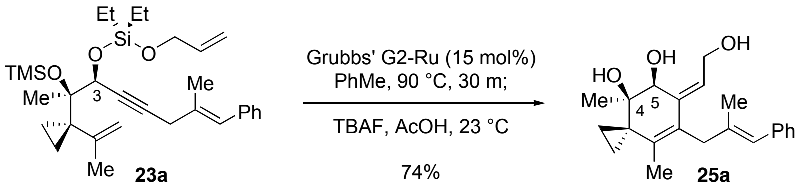
***E*-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethylsilyloxy)-3-(allyloxy-diethyl-silanyloxy)-7-methyl-8-phenyl-oct-7-en-4-yne (23a):**

Allyloxy-chloro-diethyl-silane (**S5**, 347 mg, 2.00 mmol, 2.00 equiv) was added drop-wise to a stirring solution of diol **22** (310 mg, 1.00 mmol, 1 equiv, [3*S*:3*R*, 5.6:1]), and 2,6-lutidine (674 µL, 6.00 mmol, 6.00 equiv) in dichloromethane (5 mL) at 23 °C under argon. After 2 h, the reaction mixture was cooled to –78 °C, and trimethylsilyl trifluoromethanesulfonate (550 µL, 3.00 mmol, 3.00 equiv) was added. After an additional 3 h, excess silylating reagent was quenched by the addition of saturated aqueous sodium bicarbonate solution (5 mL), the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel: diam. 2.5 cm, ht. 5 cm; hexanes–EtOAc [98:2]) afforded the sensitive (hydrolysis of alloxydiethylsilyl ether) compound **23a** (435 mg, 83%, [3*S*:3*R*, 6:1]) as a light yellow oil containing residual diallyloxydiethylsilane (**S6**) and were used directly in the next step. Samples of metathesis substrate **23a** lacking **S6** were obtained by further chromatographic purification, at the expense of additional loss of **23a**. The presence of residual diallyloxydiethylsilane does not interfere with the following metathesis reaction.

^{1}H NMR (500 MHz, C_6D_6, 6:1 mixture of (3*S*)- and (3*R*)-diastereomers; minor (3*R*)-isomer denoted by *) δ:7.48-7.1 (m, 5H, Ar**H***), 7.40-7.36 (m, 2H, Ar**H**), 7.31-7.27 (m, 2H, Ar**H**), 7.18-7.13 (m, 1H, Ar**H**), 6.81 (br-s, 1H, PhC**H**=CH$_2$), 6.79 (s, 1H, PhC**H**=CH$_2$*), 6.06-5.98 (m, 1H, OCH$_2$C**H**=CH$_2$), 6.06-5.98 (m, 1H, CH$_2$C**H**=CH$_2$*), 5.50 (dq, *J* = 17.0, 2.0 Hz, 1H, *trans*-OCH$_2$CH=C**H**$_2$), 5.49 (dq, *J* = 17.0, 2.0 Hz, 1H, *trans*-OCH$_2$CH=C**H**$_2$*), 5.42 (d, *J* = 2.7 Hz, 1H, C=C**H**$_2$), 5.40 (d, *J* = 2.7 Hz, 1H, C=C**H**$_2$*), 5.18-5.13 (m, 2H, *cis*-OCH$_2$CH=C**H**$_2$, C=C**H**$_2$), 5.19-5.13 (m, 2H, *cis*-OCH$_2$CH=C**H**$_2$*, C=C**H**$_2$*), 4.99 (t, *J* = 1.8 Hz, 1H, C**H**OSi), 4.95 (t, *J* = 1.8 Hz, 1H, C**H**OSi*), 4.49-3.98 (m, 2H, OC**H**$_2$CH=CH$_2$), 4.49-3.98 (m, 2H, OC**H**$_2$CH=CH$_2$*), 3.10 (s, 2H, C**H**$_2$C=C*), 3.02 (s, 2H, C**H**$_2$C=C), 2.05 (s, 3H, C**H**$_3$*), 2.02 (s, 3H, C**H**$_3$), 1.99 (s, 3H, C**H**$_3$*), 1.87 (s, 3H, C**H**$_3$), 1.53-1.48 (m, 7H, CH$_2$C**H**$_2$, C**H**$_3$, C**H**$_3$*), 1.30-1.19 (m, 6H, SiCH$_2$C**H**$_3$), 1.05-0.8 (m, 5H, CH$_2$C**H**$_2$, SiC**H**$_2$CH$_3$), 0.76-0.70 (m, 1H, CH$_2$C**H**$_2$), 0.66-0.60 (m, 1H, CH$_2$C**H**$_2$), 0.41 (s, 9H, Si(C**H**$_3$)$_3$), 0.41 (s, 9H, Si(C**H**$_3$)$_3$*).

^{13}C NMR (125.8 MHz, C_6D_6, 6:1 mixture of (3*S*)- and (3*R*)-diastereomers) δ: 148.1, 138.9, 137.9, 134.1, 129.5, 128.8, 127.1, 126.9, 118.6, 114.3, 84.0, 83.5, 79.9, 70.1, 64.2, 63.7, 34.2, 30.4, 24.1, 23.1, 18.2, 11.1, 10.3, 7.3, 7.2, 6.5, 5.6, 5.2, 3.4.

FTIR (neat) cm^{-1}:	2957 (m, C–H), 2229 (w, C≡C), 1635 (w), 1458 (w), 1415 (w), 1374 (w), 1248 (m), 1133 (m), 1064 (m), 922 (m), 839 (m).
HRMS (ESI):	calcd for $C_{31}H_{48}NaO_3Si_2$ $[M+Na]^+$: 547.3040, found: 547.3028.
TLC (5% EtOAc in hexanes) R*f*:	0.62 (UV, CAM, Anis)



(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol (25a):

Silyldiether **23a** (435 mg, 0.830 mmol, 1 equiv, [3*S*:3*R*, 6:1]) was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL). The residue was dissolved in toluene (83 mL), and the resulting solution deoxygenated by a stream of argon for 5 min. Grubbs' 1,3-dimesityl-4,5-dihydroimidazol-2-ylidenetricyclohexylphosphine benzylidene ruthenium dichloride catalyst (106 mg, 0.124 mmol, 0.15 equiv) was added as a solid at 23 ºC, the reaction vessel was purged quickly by a stream of argon, sealed, and the resulting dark-pink solution was stirred until complete dissolution occurred. The reaction mixture was heated to 90 ºC by placement in a pre-heated oil bath. After 30 min, the metathesis catalyst was quenched by the addition of ethyl vinyl ether (4 mL). The resulting mixture was cooled to 23 ºC, and was filtered through a plug of silica (diam. 4 cm, ht. 1.5 cm; hexanes-EtOAc 95:5). The filtrate was partially concentrated under reduced pressure (to ~ 5 mL) volume, and a mixture of TBAF (1M in THF, 3.32 mL, 3.32 mmol, 4.00 equiv) and acetic acid (95.0 µL, 1.66 mmol, 2.00 equiv) was slowly added at 23 °C under an argon atmosphere. After 2 h, the reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (10 ml) and extracted with ethyl acetate (4 × 15 ml). The combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel: diam. 2.5 cm, ht. 2.5 cm; hexanes-EtOAc [1:1] to EtOAc-MeOH [99:1]) afforded the desired triol **25a** (209 mg, 74%, [5*S*:5*R*, 6:1]) as a light brown oil.

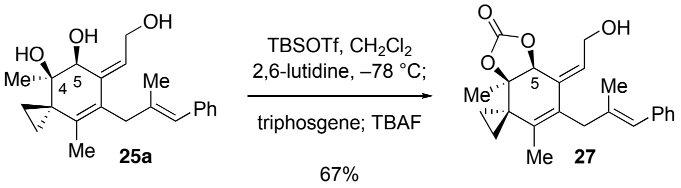
^{1}H NMR (500 MHz, C$_6$D$_6$, 6:1 mixture of (5*S*)- and (5*R*)-diastereomers; minor (5*R*)-isomer denoted by *) δ: 7.27-7.22 (m, 2H, Ar**H**), 7.26-7.00 (m, 5H, Ar**H***), 7.20-7.15 (m, 2H, Ar**H**), 7.06-7.01 (m, 1H, Ar**H**), 6.39 (s, 1H, PhC**H**=CH$_2$*), 6.31 (s, 1H, PhC**H**=CH$_2$), 5.97 (t, *J* = 7.0 Hz, 1H, C=C**H***CH$_2$OH), 5.93 (t, *J* = 7.0 Hz, 1H, C=C**H**CH$_2$OH), 4.56 (s, 1H, C**H**OH*), 4.47 (s, 1H, C**H**OH), 4.36 (dd, *J* = 12.5, 7.6 Hz, 1H, C**H**$_2$OH), 4.22 (dd, *J* = 12.5, 7.6 Hz, 1H, C**H**$_2$OH*), 4.06 (dd, *J* = 12.8, 6.4 Hz, 1H, C**H**$_2$OH), 3.93 (dd, *J* = 12.8, 6.4 Hz, 1H, C**H**$_2$OH*), 3.40-3.28 (m, 3H, C**H**$_2$*, O**H**), 3.12 (d, *J* = 17.7 Hz, 1H, C**H**$_2$), 3.03 (d, *J* = 17.7 Hz, 1H, C**H**$_2$), 2.96 (br-s, 1H, O**H**), 2.73 (br-s, 1H, O**H**), 1.72 (s, 3H, C**H**$_3$*), 1.79 (s, 3H, C**H**$_3$), 1.35-1.30 (m, 1H, CH$_2$C**H**$_2$), 1.28 (s, 3H, C**H**$_3$), 1.25 (s, 3H, C**H**$_3$), 1.16 (s, 3H, C**H**$_3$*), 1.13 (s, 3H, C**H**$_3$*), 0.96-0.90 (m, 1H, CH$_2$C**H**$_2$*), 0.88-0.83 (m, 1H, CH$_2$C**H**$_2$), 0.82-0.78 (m, 1H, CH$_2$C**H**$_2$*), 0.78-0.73 (m, 1H, CH$_2$C**H**$_2$), 0.72-0.65 (m, 1H, CH$_2$C**H**$_2$*), 0.61-0.56 (m, 1H, CH$_2$C**H**$_2$), 0.56-0.47 (m, 1H, CH$_2$C**H**$_2$*).

^{13}C NMR (125.8 MHz, C_6D_6, 6:1 mixture of (5*S*)- and (5*R*)-diastereomers) δ: 141.2, 139.4, 138.8, 136.7, 129.6, 128.7, 126.7, 126.6, 126.6, 125.0, 72.9, 70.9, 58.9, 39.8, 28.4, 24.3, 18.9, 15.0, 10.2, 5.4.

FTIR (neat) cm^{-1}: 3385 (br-s, O–H), 2930 (m, C–H), 1724 (w), 1626 (w), 1597 (w), 1443 (m), 1377 (m), 1266 (m), 1173 (m).

HRMS (ESI): calcd for $C_{22}H_{28}NaO_3$ $[M+Na]^+$: 363.1936, found: 363.1936.

TLC (1% MeOH in EtOAc) R*f*: 0.40 (UV, CAM)

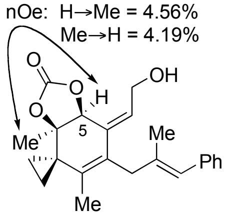


(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol-carbonate 27:

A solution of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 91.9 µL, 0.40 mmol, 1.00 equiv) in dichloromethane (1 mL) was added drop-wise via cannula transfer (down the side of the flask) to a solution of triol **25a** (136 mg, 0.40 mmol, 1 equiv, [5*S*:5*R*, 6:1]), and 2,6-lutidine (269 µL, 2.40 mmol, 6.00 equiv) in dichloromethane (1 mL) at –78 °C under an argon atmosphere. During the addition, the progress of the silylation reaction was monitored by TLC analysis to ensure monosilylation of the starting triol **25a**. After completion of the addition of TBSOTf, a solution of triphosgene (178 mg, 0.60 mmol, 1.50 equiv) in dichloromethane (200 µL) was added via cannula and the resulting reaction mixture was allowed to warmed to 23 °C. After 3 h, the resulting dark-red mixture was cooled to 0 °C, treated with TBAF (1M in THF, 4.00 mL, 4.00 mmol, 10.0 equiv), and the resulting mixture was allowed to warm to 23 °C. After 12 h, the reaction mixture was diluted with saturated aqueous ammonium chloride solution (10 mL), and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, and were concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel: diam. 3 cm, ht. 15 cm; hexanes-EtOAc [1:1]) afforded the desired carbonate **27** (98.6 mg, 67%, [5*S*:5*R*, 20:1]) as an oil. This step has not yet been optimized for the minor diastereomer, leading to enrichment of the major diastereomer in the product; this procedure has thus far been more practical rather than chromatographic separation of the diastereomers and their independent conversion to the corresponding carbonate.

^{1}H NMR (500 MHz, C_6D_6, 20:1 mixture of (5*S*)- and (5*R*)-diastereomers; minor (5*R*)-isomer denoted by *) δ: 7.20-7.10 (m, 4H, Ar**H**), 7.19-7.00 (m, 5H, Ar**H***), 7.03-6.99 (m, 1H, Ar**H**), 6.30 (s, 1H, PhC**H**=CH_2*), 6.08 (s, 1H, PhC**H**=CH_2), 5.95 (t, *J* = 6.9 Hz, 1H, C=C**H**CH_2OH), 5.67 (t, *J* = 6.9 Hz, 1H, C=C**H**CH_2OH*), 4.58 (s, 1H, C**H**O), 4.49 (s, 1H, C**H**OH*), 4.13-4.02 (m, 2H, C**H**$_2$OH), 3.99-3.95 (m, 2H, C**H**$_2$OH*), 3.19 (d, *J* = 15.8 Hz, 1H, C**H**$_2$*), 3.09 (d, *J* = 15.8 Hz, 1H, C**H***$_2$), 2.89 (d, *J* = 17.1 Hz, 1H, C**H**$_2$), 2.80 (d, *J* = 17.1 Hz, 1H, C**H**$_2$), 1.62 (s, 3H, C**H**$_3$), 1.50 (s, 3H, C**H**$_3$*), 1.32 (br-s, 1H, O**H**), 1.15-1.09 (m, 1H, CH_2C**H**$_2$), 1.09 (s, 3H, C**H**$_3$), 0.99 (s, 3H, C**H**$_3$*), 0.92 (s, 3H, C**H**$_3$), 0.86 (s, 3H, C**H**$_3$*), 0.57-0.51 (m, 1H, CH_2C**H**$_2$), 0.50-0.44 (m, 1H, CH_2C**H**$_2$*), 0.41-35 (m, 1H, CH_2C**H**$_2$), 0.35-0.30 (m, 1H, CH_2C**H**$_2$*), 0.25-0.19 (m, 1H, CH_2C**H**$_2$), 0.18-0.12 (m, 1H, CH_2C**H**$_2$*).

The C5-stereochemistry of the major diastereomer of **27** was secured by the following nOe data:



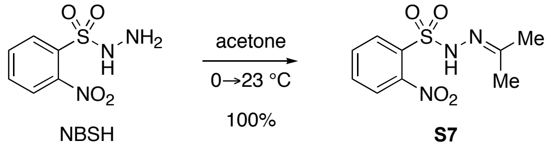
27

^{13}C NMR (125.8 MHz, C_6D_6, 20:1 mixture of (5*S*)- and (5*R*)-diastereomers) δ: 154.4, 139.0, 138.8, 136.0, 135.9, 133.9, 133.5, 130.1, 129.7, 129.6, 129.5, 128.9, 128.7, 127.4, 127.1, 126.8, 125.6, 81.7, 80.3, 80.2, 59.9, 40.4, 32.9, 32.7, 30.5, 27.6, 23.5, 23.3, 22.9, 22.3, 22.2, 18.6, 16.0, 15.9, 14.7, 10.1, 9.9, 6.8, 6.7.

FTIR (neat) cm^{-1}: 3424 (br-m, O–H), 2923 (m, C–H), 1801 (s, C=O), 1653 (w), 1598 (w), 1444 (m), 1381 (m), 1245 (m), 1149 (m), 1024 (m).

HRMS (ESI): calcd for $C_{23}H_{26}NaO_4$ [M+Na]$^+$: 389.1723, found: 389.1732.

TLC (50% EtOAc in hexane) R*f*: 0.30 (UV, Anis)



N-Isopropylidene-N'-2-nitrobenzenesulfonyl hydrazine (S7):

o-Nitrobenzenesulfonylhydrazide[7] (NBSH, 601 mg, 2.77 mmol, 1 equiv) was dissolved in acetone (3.00 mL, 40.9 mmol, 14.7 equiv) and the mixture was stirred vigorously under argon at 0 °C for 1 h. The mixture was warmed to 23 °C and concentrated under reduced pressure to afford hydrazone **S7** (712 mg, 100%)[8] as a white solid.

^{1}H NMR (500 MHz, CD_3CN) δ:	8.25 (br-s, 1H, N**H**), 8.10-8.06 (m, 1H, Ar**H**), 7.86-7.78 (m, 3H, Ar**H**), 1.87 (s, 3H, C**H**$_3$), 1.86 (s, 3H, C**H**$_3$)
^{13}C NMR (125.8 MHz, CD_3CN) δ:	160.3, 135.7, 133.6, 133.0, 132.1, 125.9, 120.4, 25.2, 17.7.
FTIR (neat) cm^{-1}:	3264 (m, N–H), 3093-2916 (w, C–H), 1550 (s, N=C), 1374 (m), 1177 (s).
HRMS (ESI):	calcd for $C_9H_{12}N_3O_4S$ $[M+H]^+$: 258.0543, found: 258.0546.
mp:	121-123 °C
TLC (hexanes:EtOAc 1:1) R*f*:	0.50 (CAM)

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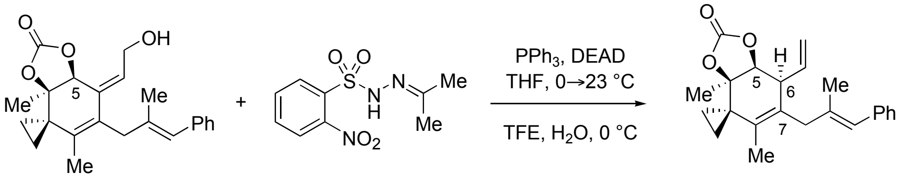
[7] For synthesis of NBSH, see: Myers, A. G.; Zheng, B.; Movassaghi, M. *J. Org. Chem.* **1997**, *62*, 7507.

[8] For a prior discussion of **S7**, see: Movassaghi, M. Ph.D. Dissertation, Harvard University (2001).



27 **S7** **30**

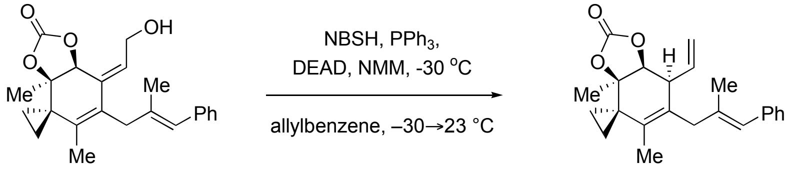
(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate 30:

The alcohol **27** (20.0 mg, 0.054 mmol, 1 equiv, [5*S*:5*R*, 20:1]) was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL). Triphenylphosphine (28.3 mg, 0.108 mmol, 2.00 equiv) and hydrazone **S7** (27.8 mg, 0.108 mmol, 2.00 equiv) were added as solids and the reaction vessel was sealed under an argon atmosphere. Anhydrous THF (540 μL, purged with a stream of argon for ~5 min) was added and the resulting solution was cooled to 0 ºC prior to slow addition of diethyldiazocarboxylate (16.9 μL, 0.108 mmol, 2.00 equiv) via syringe. After 2 h, the reaction mixture was allowed to warm to 23 ºC over 15 min. The mixture was then cooled to 0 ºC and a mixture of trifluoroethanol and water (1:1, 1.08 mL, purged with a stream of argon for ~5 min) was added. After 14 h at 0 °C, the reaction mixture was warmed to 23 °C, was diluted with brine (10 mL), and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the residue by flash column chromatography (silica gel: diam. 1.5 cm, ht 5 cm; eluent: EtOAc:hexane [1:3]) provided triene **30** as a mixture of diastereomers (13.6 mg, 71%; [6*S*:6*R*, 3:1]). The C6-stereochemistry of the major diastereomer of **30** was secured using nOe data for a derivative (carbonate **31**, see page S24).

^{1}H NMR (500 MHz, C_6D_6, ~3:1:0.1 mixture of three diastereomers (5*S*,6*S*:5*S*,6*R*:5*R*; the minor (5*S*,6*R*)-diastereomer and the corresponding (5*R*)-diastereomer are noted as * and **, respectively) δ: 7.40-7.0 (m, 5H, Ar**H**), 6.35 (s, 1H, PhC**H****), 6.30 (s, 1H, PhC**H***), 6.16 (s, 1H, PhC**H**), 6.03 (dt, *J* = 16.9, 9.2 Hz, 1H, C**H**=CH$_2$), 5.82 (dt, *J* = 16.9, 9.2 Hz, 1H, C**H****=CH$_2$), 5.45 (dt, *J* = 16.9, 9.2 Hz, 1H, C**H***=CH$_2$), 5.07-5.01 (m, 2H, CH=C**H**$_2$), 4.93-4.85 (m, 2H, CH=C**H***$_2$), 4.84-4.62 (m, 2H, CH=C**H****$_2$), 3.98 (d, *J* = 5.3 Hz, 1H, C**H**O), 3.95 (d, *J* = 5.3 Hz, 1H, C**H***O), 3.86 (d, *J* = 5.3 Hz, 1H, C**H****O), 3.22-3.18 (m, 1H, C**H***CH=CH$_2$), 3.00 (dd, *J* = 8.7, 6.3 Hz, 1H, C**H**CH=CH$_2$), 2.94 (d, *J* = 15.4 Hz, 1H, C**H***$_2$), 2.82 (d, *J* = 15.4 Hz, 1H, C**H**$_2$), 2.64 (d, *J* = 15.5 Hz, 1H, C**H**$_2$), 2.59 (d, *J* = 15.5 Hz, 1H, C**H***$_2$), 1.81 (s, 3H, C**H***$_3$), 1.62 (s, 3H, C**H**$_3$), 1.56 (s, 3H, C**H****$_3$), 1.21 (s, 3H, C**H***$_3$), 1.20 (s, 3H, C**H**$_3$), 1.10 (s, 3H, C**H****$_3$), 0.95-0.90 (m, 1H, CH$_2$C**H**$_2$), 0.77 (s, 3H, C**H****$_3$), 0.75 (s, 3H, C**H**$_3$), 0.73-0.66 (m, 2H, CH$_2$C**H***$_2$), 0.64 (s, 3H, C**H***$_3$), 0.44-0.38 (m, 2H, CH$_2$C**H**$_2$), 0.35-0.29 (m, 1H, CH$_2$C**H**$_2$), 0.23-0.18 (m, 1H, CH$_2$C**H****$_2$), 0.10-0.04 (m, 1H, CH$_2$C**H***$_2$).

^{13}C NMR (125.8 MHz, C_6D_6, ~3:1:0.1 mixture of three diastereomers) δ:	154.2, 154.0, 139.0, 136.4, 136.3, 134.5, 134.4, 133.3, 131.4, 130.8, 129.7, 129.6, 128.9, 128.8, 127.8, 126.9, 126.8, 118.9, 118.3, 86.1, 85.0, 83.9, 47.7, 47.5, 43.8, 42.1, 34.5, 28.4, 27.5, 25.3, 24.2, 23.8, 23.3, 18.5, 18.2, 15.7, 15.4, 11.9, 11.8, 10.8, 9.1, 8.8, 8.5.
FTIR (neat) cm^{-1}:	3080 (w, C–H), 2934 (w, C–H), 1798 (s, C=O), 1650 (w), 1598 (w), 1444 (w), 1381 (w), 1360 (w), 1238 (m), 1077 (m).
HRMS (ESI):	calcd for $C_{23}H_{26}NaO_3$ [M+Na]$^+$: 373.1780, found: 373.1776.
TLC (hexanes:EtOAc 3:1) R*f*:	0.40 (Anis)

For the analogous reductive transposition using the reagent NBSH, see:



27 **30**

(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate 30:

The alcohol **27** (41 mg, 0.112 mmol, 1 equiv) was placed in a flame-dried flask and the sample was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL) and placed under an argon atmosphere. Freshly distilled *N*-methylmorpholine (NMM, 0.37 mL)[9] was added followed by triphenylphosphine (91 mg, 0.347 mmol, 3.10 equiv) as a solid and the mixture was sealed under an argon atmosphere. After complete dissolution of the solids, the solution was cooled to –30 ºC and diethyl-diazocarboxylate (54 µL, 0.336 mmol, 3.00 equiv) was slowly introduced via syringe. After 10 min, *O*-nitrobenzenesulfonylhydrazide (NBSH, 73 mg, 0.336 mmol, 3.00 equiv) was added as solid, the reaction vessel was immediately sealed under an argon atmosphere, and the resulting deep-yellow solution was maintained at –30 ºC.[10] After 40 min, allylbenzene (0.150 mL, 1.12 mmol, 10.0 equiv)[11] was added and the reaction mixture was allowed to warm to 23 ºC. During the warming step the mixture turned deep-orange. After an additional 40 min, the reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (4 mL) and extracted with diethyl ether (3 × 3 mL). Purification of the residue by flash column chromatography (silica gel: diam. 1.5 cm, ht 5 cm; eluent: EtOAc:hexane [1:3]) provided the desired triene **30** (20 mg, 52%) as described above. For characterization of **30**, please see the data presented for the experimental procedure employing the hydrazone of NBSH **S7**.

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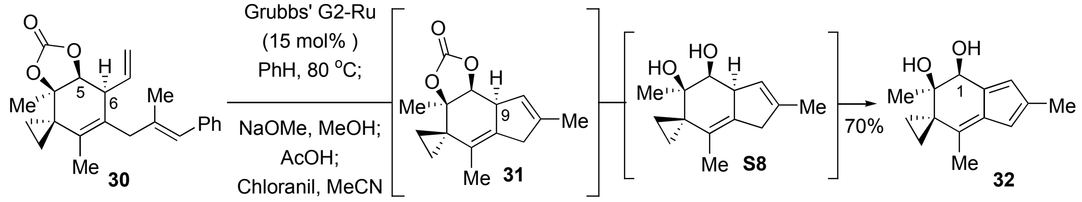
[9] NMM was the optimal solvent when employing NBSH for this reductive transposition. While THF (or THF-NMM) provided superior solubility of the reagents and additives, a significant drop in efficiency of the Mitsunobu reaction was observed.

[10] While addition of neopentyl alcohol accelerated the Mitsunobu displacement step, its introduction to the highly concentrated reaction mixture resulted in significant precipitation of excess reagents. Use of more dilute reaction concentrations led to a significant decrease in efficiency of the reductive transposition.

[11] In the absence of this additive the C6-vinyl group was reduced to give a significant amount of the corresponding C6-ethyl derivative of **30**. This undesired reduction is likely due to diimide (generated from excess NBSH) reduction of the C6-vinyl group.

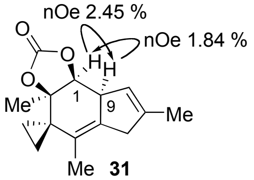


Fulvenediol 32:

The triene **30** (5.7 mg, 0.016 mmol, 1 equiv, [(5*S*,6*S*)-**30**:(5*S*,6*R*)-**30**:(5*R*)-**30**, 3:1:0.1]) was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL). Benzene (320 μL) was added followed by Grubbs' 1,3-dimesityl-4,5-dihydroimidazol-2-ylidenetricyclohexylphosphine benzylidene ruthenium dichloride catalyst (2.0 mg, 2.4 μmol, 0.15 equiv) at 23 ºC, the mixture was sealed under an argon atmosphere, and the resulting dark-pink solution was heated to 80 ºC. After 30 min, ethyl vinyl ether (0.1 mL) was introduced via a syringe, and the mixture was cooled to 23 ºC. The resulting mixture was charged with a methanolic solution of sodium methoxide (1.0 M in MeOH, 33.0 μL, 0.033 mmol, 2.00 equiv) at 23 °C. After 24 h, conversion to diol **S8** was complete by TLC analysis. Acetonitrile (600 μL) was added and the mixture was concentrated under reduced pressure to 30% of the total volume (ca. 300 μL). Acetic acid (1.72 μL, 0.033 mmol, 2.00 equiv) and chloranil (12.5 mg, 0.051 mmol, 3.00 equiv) were added sequentially, and the reaction mixture was stirred at 23 °C. After 13 h, saturated aqueous sodium thiosulfate solution (5 mL) was added and the reaction mixture was extracted with diethyl ether (4 × 5 mL), and the combined organic extracts were washed with saturated aqueous sodium bicarbonate solution (5 mL). The organic layer was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel: diam. 0.5 cm, ht 5 cm; eluent: EtOAc:hexane [1:3]) afforded the fulvenediol **32** (2.4 mg, 70%)[12] as a yellow oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ:	6.34 (br-s, 1H, C**H**=C), 6.08 (br-s, 1H, C**H**=C), 4.34 (d, *J* = 6.9 Hz, 1H, C**H**OH), 2.86 (br-s, 1H, O**H**), 2.07 (br-s, 3H, C**H**$_3$), 1.84 (s, 3H, C**H**$_3$), 1.61 (d, *J* = 7.7, 1H, O**H**), 1.28-1.22 (m, 1H, CH$_2$C**H**$_2$), 1.16 (s, 3H, C**H**$_3$), 1.05-1.00 (m, 1H, CH$_2$C**H**$_2$), 0.98-0.92 (m, 1H, CH$_2$C**H**$_2$), 0.87-0.82 (m, 1H, CH$_2$C**H**$_2$).

The C9-stereochemistry of the major diastereomer of **31** was secured by the following nOe data:



31

^{13}C NMR (125.8 MHz, CDCl$_3$) δ:	151.2, 142.1, 138.8, 133.6, 131.4, 114.7, 73.5, 72.8, 30.5, 23.6, 16.6, 16.0, 13.3, 6.8.
FTIR (neat) cm^{-1}:	3421 (br-s, O–H), 2916 (s, C–H), 1630 (s), 1443 (m), 1376 (m), 1333 (m), 1114 (m).

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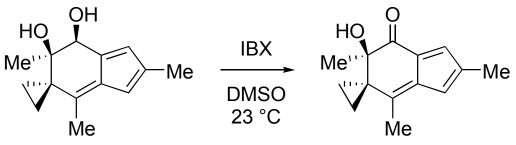
[12] The C1-diastereomers ((1*R*)-fulvenediol **32**) are chromatographically separable. Crude samples of fulvenediol **32** contain trace amounts of the 1*R*-diastereomer and the oxidation to acylfulvene can be performed on the mixture of these C1-diastereomers.

HRMS (ESI):	calcd for $C_{14}H_{18}NaO_2$ $[M+Na]^+$: 241.1199, found: 241.1206.
TLC (hexanes:EtOAc 1:1) R*f*:	0.50 (CAM, UV)



32 83% (–)-Acylfulvene (**3**)

(–)-Acylfulvene (3):

The fulvenediol **32** (2.5 mg, 11 μmol, 1 equiv) was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL). Anhydrous DMSO (0.5 mL) was added followed by IBX (5.0 mg, 18 μmol, 1.6 equiv) and the resulting suspension was sealed under an argon atmosphere and stirred at 23 °C. After 3 h, another portion of IBX (2.5 mg, 9 μmol, 0.8 equiv) was added and reaction vessel was again sealed under an argon atmosphere. After 1h, water was added (5 mL) followed by EtOAc (3 mL) and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 2 mL) and the combined organic layers were washed sequentially with water (4 mL) and with brine (4 mL). The organic layer was dried over anhydrous sodium sulfate. The organic phase was filtered and concentrated under reduced pressure to afford (–)-acylfulvene (**3**, 2.0 mg, 83%, 91% ee, $[\alpha]^{20}_{D}$ = –265.5 (*c* 0.10, EtOH)) that had spectroscopic data consistent with those reported in the literature.[13]

(–)-Acylfulvene (**3**) was determined to be 91% ee by chiral HPLC analysis [Chirapak AD-H; 1.0 mL/min; 10% ^{i}PrOH in hexanes; t_R(major) = 8.30 min, t_R(minor) = 10.21 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ:	7.17 (br-s, 1H, C**H**=C), 6.43 (br-s, 1H, C**H**=C), 3.94 (br-s, 1H, O**H**), 2.16 (s, 3H, C**H**$_3$), 2.01 (s, 3H, C**H**$_3$),1.57-1.52 (m, 1H, CH$_2$C**H**$_2$), 1.39 (s, 3H, C**H**$_3$), 1.33-1.29 (m, 1H, CH$_2$C**H**$_2$), 1.10-1.06 (m, 1H, CH$_2$C**H**$_2$), 0.75-0.71 (m, 1H, CH$_2$C**H**$_2$).
^{13}C NMR (100.6 MHz, $CDCl_3$) δ:	198.3, 159.1, 143.2, 141.2, 136.6, 127.0, 121.2, 77.0, 37.8, 28.3, 17.4, 15.7, 14.8, 10.2.
FTIR (neat) cm^{-1}:	3460 (br-m, O–H), 2918 (m, C–H), 1803 (w), 1667 (s, C=O), 1615 (s), 1490 (m), 1445 (m).
HRMS (ESI):	calcd for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043, found: 239.1044.
TLC (hexanes:EtOAc 1:1) R*f*:	0.60 (CAM, UV)

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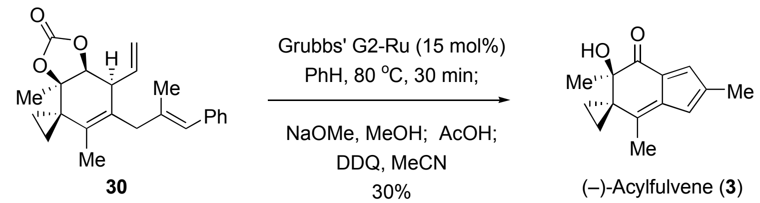
[13] Our characterization data for acylfulvene was in agreement with those reported in McMorris, T. C.; Staake, M. D.; Kelner, M. J.; *J. Org. Chem.* **2004**, *69*, 619. For optical rotation values reported for (–)-acylfulvene, see: $[\alpha]^{25}_{D}$ = –493.4 (*c* 2.1 mg/mL, EtOH) in McMorris, T. C.; Staake, M. D.; Kelner, M. J.; *J. Org. Chem.* **2004**, *69*, 619 (please see ref. 12 in this paper) and $[\alpha]^{25}_{D}$ = –606 (*c* 0.078, EtOH) in McMorris, T. C.; Kelner, M. J.; Wang, W.; Diaz, M. A.; Estes, L. A.; Taetle, R. *Experientia*, **1996**, *52*, 75. Our measurements were conducted using absolute ethanol (Aldrich, 200 Proof 99.5%) and at 20 °C (pure samples, multiple readings). The enantiomeric excess of our synthetic (–)-acylfulvene was determined by HPLC analysis as described above.



30

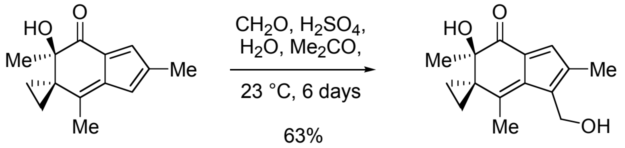
(–)-Acylfulvene (**3**)

(–)-Acylfulvene (3):

The triene **30** (6.9 mg, 20 μmol, 1 equiv) was dried azeotropically by concentration from anhydrous benzene (3 × 1 mL). Benzene (400 μL) was added followed by Grubbs' 1,3-dimesityl-4,5-dihydroimidazol-2-ylidenetricyclohexylphosphine benzylidene ruthenium dichloride catalyst (2.5 mg, 3.0 μmol, 0.15 equiv) at 23 °C, and the resulting dark-pink solution was sealed under an argon atmosphere and heated to 80 °C. After 30 min, the reaction ethyl vinyl ether (0.1 mL) was added via syringe, and the reaction mixture was cooled to 23 °C. The resulting mixture was charged with a methanolic solution of sodium methoxide (1.0 M in MeOH, 40.0 μL, 0.040 mmol, 2.00 equiv). After 24 h, acetonitrile (800 μL) was added and the mixture was concentrated to 30% of the total volume (ca. 400 μL). Acetic acid (1.72 μL, 0.033 mmol, 2.00 eq) and DDQ (13.6 mg, 0.060 mmol, 3.00 equiv) were added sequentially, and the reaction mixture was sealed under an argon atmosphere. After 13 h, a solution of ascorbic acid (7 mg), citric acid (12.6 mg), and sodium hydroxide (9.4 mg) in H_2O (1 mL) were added to quench the excess oxidant (DDQ). The reaction mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL), and the resulting mixture was extracted with hexanes (4 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel: diam. 0.5 cm, ht 5 cm; eluent: EtOAc:hexane [1:4]) afforded acylfulvene (**3**, 1.4 mg, 30%, 91% ee) as a yellow oil.

(–)-Acylfulvene (**3**) was determined to be 91% ee by chiral HPLC analysis [Chirapak AD-H; 1.0 mL/min; 10% ^{i}PrOH in hexanes; t_R(major) = 8.30 min, t_R(minor) = 10.21 min].

For full characterization of (–)-acylfulvene (**3**), please see the complete set of data presented above for the two-step procedure.



(–)-Acylfulvene (**3**) (–)-Irofulven (**4**)

(–)-Irofulven (4):

A solution of (–)-acylfulvene (**3**, 1.4 mg, 6.5 µmol, 1.0 equiv) in acetone (0.5 mL) was added to a solution of formaldehyde (37% wt. in H_2O, 35.0 µL, 0.44 mmol, 67.0 equiv) in a mixture of water (0.5 mL), acetone (0.5 mL), and aqueous hydrosulfuric acid (2.0 N, 0.5 mL) at 0 °C. After 5 min, the reaction mixture was allowed to warm to 23 ºC and maintained under an argon atmosphere for 6 days. The reaction mixture was diluted with dichloromethane (5 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (5 mL). The combined organic layers were washed sequentially with a saturated aqueous sodium bicarbonate solution (5 mL) and brine (5 mL). The organic layer was dried over anhydrous sodium sulfate, was filtered, and was further diluted by the addition of benzene (5 mL). The volatiles were removed and the total volume reduced (to approximately 1–mL) and the remaining orange solution was immediately[14] purified by flash column chromatography (silica gel: diam. 1 cm, ht 5 cm; EtOAc-hexanes 1:1) to give (–)-irofulven (**4**, 1 mg, 63%, 92% ee, $[\alpha]^{20}_{D} = -512$ (*c* 0.03, EtOH)[15])) as an orange oil.

Our synthetic (–)-irofulven (**4**) was determined to be 92% ee by chiral HPLC analysis [Chirapak AD-H; 1.5 mL/min; 20% ^{i}PrOH in hexanes; t_R(major) = 4.88 min, t_R(minor) = 6.51 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ:	7.11 (br-s, 1H, C**H**=C), 4.66 (dd, *J* = 11.6, 8.3 Hz, 2H, C**H**OH), 3.91 (br-s, 1H, O**H**), 2.20 (s, 3H, C**H**$_3$), 2.16 (s, 3H, C**H**$_3$), 1.53-1.49 (m, 1H, CH_2C**H**$_2$), 1.39 (s, 3H, C**H**$_3$), 1.39-1.33 (m, 1H, CH_2C**H**$_2$), 1.11-1.07 (m, 1H, CH_2C**H**$_2$), 0.75-0.72 (m, 1H, CH_2C**H**$_2$).
^{13}C NMR (100.6 MHz, $CDCl_3$) δ:	198.3, 160.5, 142.4, 138.9, 135.0, 132.5, 127.1, 76.5, 56.6, 38.0, 27.8, 16.5, 14.6, 13.3, 9.8.
FTIR (neat) cm^{-1}:	3442 (br-m, O–H), 2920 (m, C–H), 1653 (m, C=O), 1593 (m), 1345 (m), 1280 (m).
HRMS (ESI):	calcd for $C_{15}H_{18}O_3$ $[M+]^+$: 247.1329, found: 247.1331.
TLC (hexanes:EtOAc 1:1) R*f*:	0.38 (CAM, UV)

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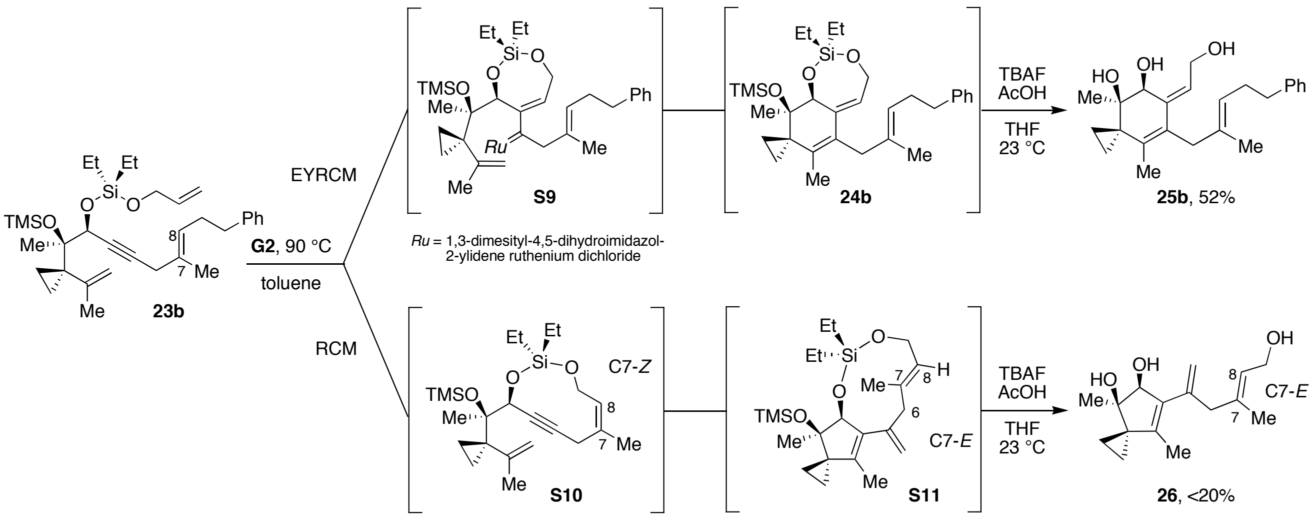
[14] This is necessary to minimize bisacylfulvene formation; please see: Weinreb, S. M.; McMorris, T. C.; Anchel, M. *Tetrahedron Lett.* **1971**, *38*, 3489 and McMorris, T. C.; Kelner, M. J.; Wang W.; Yu, J.; Estes, L. A.; Taetle, R. *J. Nat. Prod.* **1996**, *59*, 896.

[15] Our characterization data for irofulven was in agreement with those reported in McMorris, T. C.; Kelner, M. J.; Wang W.; Yu, J.; Estes, L. A.; Taetle, R. *J. Nat. Prod.* **1996**, *59*, 896. For an optical rotation value reported for (–)-irofulven, see: $[\alpha]^{25}_{D} = -639$ (*c* 0.096, EtOH) in McMorris, T. C.; Kelner, M. J.; Wang W.; Yu, J.; Estes, L. A.; Taetle, R. *J. Nat. Prod.* **1996**, *59*, 896. Our optical rotation measurements were conducted using absolute ethanol (Aldrich, 200 Proof 99.5%) and at 20 °C (pure samples, multiple readings). The enantiomeric excess of our synthetic (–)-irofulven was determined by HPLC analysis as described above.

Scheme S1. Proposed Mechanism for the Formation of Triol **26**.



Due to the central importance of the EYRCM cascade in development of our general strategy for securing the spirocyclic AB-ring system of illudins, we investigated the formation of the minor byproduct **26** when using the trienyne **23b** as substrate. Our proposed mechanism for the formation of triol **26** is illustrated in Scheme S1. Monitoring the EYRCM reaction of trienyne **23b** by in situ ^{1}H NMR spectroscopy (toluene-d_8) revealed clear conversion to the desired dihydrodioxasilepine **24b**, leading to isolation of the desired triol **25b** after desilylation (52%). Interestingly, a competitive pathway (major:minor, ~3.5:1) leading to formation of the triene **S11** was observed. The observed nOe data confirmed the 7*E*-stereochemistry of triene **S11** (C8-H→C6-H, 2.2% nOe) consistent with the 7*E*-stereochemistry of triol **26** (C8-H→C6-H, 4.6% nOe).[16] Careful inspection revealed formation of the triene **S11** via a transient 10-membered ring (7*Z*)-dienyne **S10** (desilylation gave the corresponding dienyne triol, C7-Me→C8-H, 6.9% nOe).[17,18] Conversion of dienyne **S10** to triene **S11** is catalyzed by **G2** at >70 °C. Isolation of the highly sensitive dienyne **S10** and its exposure to **G2** (toluene, 90 °C) led to exclusive formation of triene **S11**.

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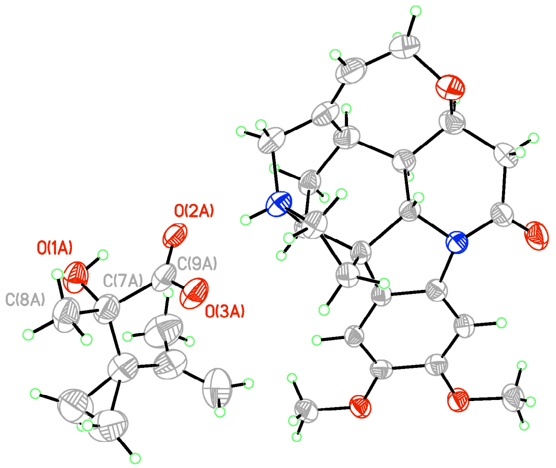
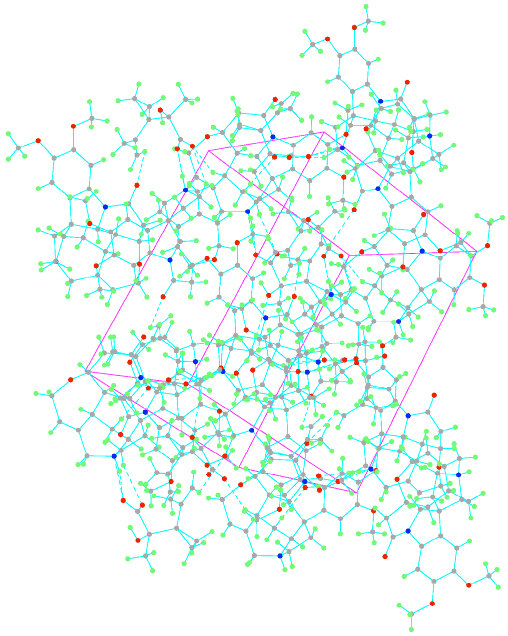
[16] Characterization data for triene **26**: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.84 (t, *J* = 7.0 Hz, 1H, HOCH$_2$C**H**), 4.72 (br-s, 1H, C=C**H**$_2$), 4.52 (br-s, 1H, C=C**H**$_2$), 4.46 (dd, 1H, *J* = 7.0, 12.7 Hz, HOC**H**$_2$), 4.34 (br-s, 1H, HOC**H**), 4.30 (dd, *J* = 7.0, 12.7 Hz, 1H, HOC**H**$_2$), 3.02 (d, *J* = 17.7 Hz, 1H, C**H**$_2$-C=C), 2.89 (d, *J* = 17.7 Hz, 1H, C**H**$_2$-C=), 2.54 (br-s, 1H, O**H**), 1.77 (s, 3H, HC=CC**H**$_3$), 1.44 (s, 3H, C=CC**H**$_3$), 1.15 (m, 1H, CH$_2$C**H**$_2$), 1.13 (s, 3H, HOCC**H**$_3$), 0.88 (m, 1H, CH$_2$C**H**$_2$), 0.69 (m, 2H, CH$_2$C**H**$_2$). ^{13}C NMR (125 MHz, CDCl$_3$) δ: 142.8, 140.6, 138.0, 126.4, 125.9, 110.0, 72.8, 70.4, 59.0, 37.2, 27.5, 23.6, 23.4, 14.8, 9.4, 4.9. FTIR (neat) cm^{-1}: 3382 (s, O-H), 2922 (s, C-H), 1742 (m), 1376 (m), 1272 (m), 1029 (m). HRMS (ESI) calcd for $C_{16}H_{24}O_3$ [M+Na]$^+$: 287.1618, found: 287.1624. TLC (100% EtOAc), *Rf*: 0.44 (UV, anisaldehyde).

[17] For examples of olefin isomerization catalyzed by ruthenium complexes, see: S. H. Hong, D. P. Sanders, C. W. Lee, R. H. Grubbs, *J. Am. Chem. Soc.* **2005**, *127*, 17160.

[18] The dienyne **S10** was deprotected (TBAF, AcOH, 23 °C, 15 min) and the corresponding triol was fully characterized: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ: 5.29 (t, *J* = 7.0 Hz, 1H, HOCH$_2$C**H**), 5.11 (br-s, 1H, C=C**H**$_2$), 4.90 (br-s, 1H, C=C**H**$_2$), 4.40 (d, *J* = 6.4, 1H, Hz, HOC**H**), 3.91-3.83 (m, 2H, HOC**H**$_2$), 2.69 (d, *J* = 17.4 Hz, 1H, C≡CC**H**$_2$C=C), 2.64 (d, *J* = 17.4 Hz, 1H, C≡CC**H**$_2$C=C), 2.02 (br-s, 1H, O**H**), 1.79 (br-s, 1H, O**H**), 1.75 (s, 3H, HC=CC**H**$_3$), 1.66 (s, 3H, H$_2$C=CC**H**$_3$), 1.28 (s, 3H, HOCC**H**$_3$), 1.21 (m, 1H, C**H**$_2$CH$_2$), 0.90 (m, 1H, C**H**$_2$CH$_2$), 0.54 (m, 1H, C**H**$_2$CH$_2$), 0.41 (m, 1H, C**H**$_2$CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$) δ: 147.4, 135.4, 125.8, 118.1, 85.2, 79.7, 75.2, 69.5, 59.1, 33.0, 24.0, 23.4, 22.5, 22.0, 10.4, 9.1. FTIR (neat) cm^{-1}: 3398 (s, O-H), 2921 (s, C-H), 1635 (m), 1376 (m), 1272 (m), 1023 (s). HRMS (ESI) calcd for $C_{16}H_{24}NaO_3$ [M+Na]$^+$: 287.1618, found: 287.1626. TLC (100% EtOAc), R*f*: 0.6 (UV, anisaldehyde).

X-ray Structure of (2*S*)-2-Hydroxy-2-(1-isopropenyl-cyclopropyl)-propionic acid–(–)-Brucine Complex (S12).





(2*S*)-2-Hydroxy-2-(1-isopropenyl-cyclopropyl)-propionic acid–(–)-Brucine Complex (S12):

Lithium hydroxide (24 mg, 0.58 mmol, 5.0 equiv) was added to a solution of (2*S*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (*ent*-**16**, 30 mg, 0.12 mmol, 1 equiv) in methanol (0.75 mL) and water (0.25 mL) at 23 °C. After 24 h, the volatiles were removed under reduced pressure and the resulting aqueous solution acidified to pH 3 by addition of aqueous hydrogen chloride solutions (1N). The mixture was extracted with ethyl acetate (3 × 4 mL), and the combined organic layers were dried over anhydrous sodium sulfate and were concentrated under reduced pressure to afford (2*S*)-2-hydroxy-2-(1-isopropenyl-cyclopropyl)-propionic acid (**S13**, 13.0 mg, 66%) as a white solid. (–)-Brucine (30 mg, 0.07 mmol, 1 eq) was added to a solution of (2*S*)-2-hydroxy-2-(1-isopropenyl-cyclopropyl)-propionic acid (**S13**, 13.0 mg, 0.07 mmol, 1eq) in ethyl acetate (500 μL). The resulting complex was crystallized by slow diffusion of hexanes into the ethyl acetate solution over 4 days at 23 ºC.

Table S1. Crystal data and structure refinement for S12.

Identification code	05204	
Empirical formula	C32 H40 N2 O7	
Formula weight	564.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.4406(13) Å	α= 90°.
	b = 13.6892(15) Å	β= 90°.
	c = 16.1340(17) Å	γ = 90°.
Volume	2747.7(5) Å^3	
Z	4	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	1208	
Crystal size	0.30 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.95 to 25.02°.	
Index ranges	-14<=h<=14, -16<=k<=16, -19<=l<=19	
Reflections collected	43545	
Independent reflections	2742 [R(int) = 0.0711]	
Completeness to theta = 25.02°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9810 and 0.9718	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2742 / 409 / 456	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0580, wR2 = 0.1512	
R indices (all data)	R1 = 0.0729, wR2 = 0.1677	
Absolute structure parameter	0(2)	
Largest diff. peak and hole	0.315 and -0.305 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for S12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	9473(3)	6082(3)	-2842(2)	35(1)
N(2)	10377(3)	6501(3)	-100(2)	30(1)
O(4)	12864(3)	5655(3)	-1324(2)	53(1)
O(5)	11097(3)	6283(3)	1188(2)	52(1)
O(6)	7161(2)	6624(3)	1702(2)	41(1)
O(7)	5981(2)	6243(2)	429(2)	35(1)
C(10)	9832(4)	7101(3)	-2656(3)	36(1)
C(11)	9278(4)	7360(3)	-1851(3)	31(1)
C(12)	9336(3)	6396(3)	-1356(2)	28(1)
C(13)	9040(4)	5636(3)	-2037(2)	30(1)
C(14)	9483(4)	4617(3)	-1903(3)	37(1)
C(15)	10718(4)	4687(3)	-1839(3)	41(1)
C(16)	11164(4)	5174(4)	-2606(3)	43(1)
C(17)	10339(4)	5470(4)	-3243(3)	41(1)
C(18)	12203(4)	5326(4)	-2707(4)	54(1)
C(19)	13005(5)	5051(5)	-2058(4)	64(2)
C(20)	10961(4)	5217(3)	-1021(3)	34(1)
C(21)	12135(4)	5262(4)	-731(3)	42(1)
C(22)	12226(3)	5957(4)	20(3)	38(1)
C(23)	11193(3)	6252(3)	433(3)	37(1)
C(24)	10490(3)	6250(3)	-992(2)	29(1)
C(25)	9267(3)	6519(3)	112(3)	30(1)
C(26)	8643(3)	6380(3)	-590(2)	28(1)
C(27)	7527(3)	6299(3)	-513(3)	29(1)
C(28)	7058(3)	6346(3)	264(3)	31(1)
C(29)	7714(4)	6538(3)	964(3)	33(1)
C(30)	8815(4)	6620(3)	891(3)	34(1)
C(31)	5311(3)	6010(4)	-250(3)	44(1)
C(32)	7805(4)	6867(5)	2409(3)	55(1)
C(1A)	5708(9)	5576(7)	-3063(6)	79(3)
C(2A)	5716(7)	6631(6)	-3133(5)	61(2)
C(3A)	5941(11)	7234(9)	-2519(7)	72(3)
C(5A)	4474(7)	7101(8)	-4286(7)	75(2)
C(6A)	4969(8)	8037(6)	-4086(6)	73(2)
C(4A)	5614(7)	7092(7)	-3969(5)	57(1)
C(7A)	6528(7)	6832(6)	-4593(5)	47(1)
O(1A)	6351(5)	5865(4)	-4901(3)	45(1)
C(8A)	6566(7)	7506(6)	-5339(4)	52(2)
C(9A)	7602(9)	6885(6)	-4123(8)	40(1)
O(2A)	8042(6)	6065(6)	-3985(4)	38(1)
O(3A)	7974(11)	7697(7)	-3939(8)	46(2)
C(1B)	5740(40)	6970(20)	-2524(16)	70(5)
C(2B)	5582(18)	7480(13)	-3296(11)	61(2)
C(3B)	5200(20)	8377(14)	-3388(17)	71(5)
C(5B)	4474(18)	6637(17)	-4436(17)	69(3)
C(6B)	4967(18)	5866(14)	-3945(15)	68(3)
C(4B)	5555(16)	6870(16)	-4052(11)	57(2)
C(7B)	6546(15)	6975(13)	-4633(11)	47(1)
O(1B)	6622(13)	6180(10)	-5207(9)	45(1)
C(8B)	6550(20)	7916(14)	-5138(13)	52(2)
C(9B)	7570(20)	7000(18)	-4090(20)	40(1)
O(2B)	7830(20)	6166(18)	-3806(14)	38(1)
O(3B)	7880(30)	7790(20)	-3800(30)	46(2)

Table S3. Bond lengths [Å] and angles [°] for S12.

N(1)-C(10)	1.496(6)
N(1)-C(17)	1.510(6)
N(1)-C(13)	1.532(5)
N(2)-C(23)	1.373(6)
N(2)-C(25)	1.423(5)
N(2)-C(24)	1.487(5)
O(4)-C(21)	1.423(6)
O(4)-C(19)	1.456(6)
O(5)-C(23)	1.224(6)
O(6)-C(29)	1.380(5)
O(6)-C(32)	1.433(6)
O(7)-C(28)	1.374(5)
O(7)-C(31)	1.413(5)
C(10)-C(11)	1.513(6)
C(11)-C(12)	1.544(5)
C(12)-C(26)	1.506(6)
C(12)-C(13)	1.558(5)
C(12)-C(24)	1.563(6)
C(13)-C(14)	1.515(6)
C(14)-C(15)	1.544(6)
C(15)-C(16)	1.512(7)
C(15)-C(20)	1.536(6)
C(16)-C(18)	1.319(7)
C(16)-C(17)	1.508(7)
C(18)-C(19)	1.494(8)
C(20)-C(24)	1.532(6)
C(20)-C(21)	1.535(7)
C(21)-C(22)	1.544(7)
C(22)-C(23)	1.503(6)
C(25)-C(30)	1.384(6)
C(25)-C(26)	1.386(6)
C(26)-C(27)	1.399(6)
C(27)-C(28)	1.383(6)
C(28)-C(29)	1.418(6)
C(29)-C(30)	1.379(6)
C(1A)-C(2A)	1.449(13)
C(2A)-C(3A)	1.319(14)
C(2A)-C(4A)	1.495(12)
C(5A)-C(6A)	1.458(13)
C(5A)-C(4A)	1.508(11)
C(6A)-C(4A)	1.534(12)
C(4A)-C(7A)	1.561(9)
C(7A)-O(1A)	1.431(8)
C(7A)-C(8A)	1.516(9)
C(7A)-C(9A)	1.538(9)
C(9A)-O(3A)	1.239(8)
C(9A)-O(2A)	1.270(8)
C(1B)-C(2B)	1.44(2)
C(2B)-C(3B)	1.326(19)
C(2B)-C(4B)	1.479(17)
C(5B)-C(6B)	1.45(2)
C(5B)-C(4B)	1.514(17)
C(6B)-C(4B)	1.57(2)
C(4B)-C(7B)	1.556(15)
C(7B)-O(1B)	1.432(15)
C(7B)-C(8B)	1.524(16)
C(7B)-C(9B)	1.543(15)
C(9B)-O(3B)	1.247(15)
C(9B)-O(2B)	1.274(16)
C(10)-N(1)-C(17)	113.0(4)
C(10)-N(1)-C(13)	107.8(3)
C(17)-N(1)-C(13)	113.1(3)
C(23)-N(2)-C(25)	124.9(4)
C(23)-N(2)-C(24)	118.6(4)
C(25)-N(2)-C(24)	109.1(3)
C(21)-O(4)-C(19)	114.1(4)
C(29)-O(6)-C(32)	115.3(3)
C(28)-O(7)-C(31)	116.6(3)
N(1)-C(10)-C(11)	104.8(3)
C(10)-C(11)-C(12)	102.9(3)
C(26)-C(12)-C(11)	114.2(3)
C(26)-C(12)-C(13)	115.7(3)
C(11)-C(12)-C(13)	101.2(3)
C(26)-C(12)-C(24)	102.5(3)
C(11)-C(12)-C(24)	110.3(3)
C(13)-C(12)-C(24)	113.4(3)
C(14)-C(13)-N(1)	111.1(4)
C(14)-C(13)-C(12)	115.3(3)
N(1)-C(13)-C(12)	104.4(3)
C(13)-C(14)-C(15)	108.3(4)
C(16)-C(15)-C(20)	115.0(4)
C(16)-C(15)-C(14)	109.7(4)
C(20)-C(15)-C(14)	106.4(4)
C(18)-C(16)-C(17)	122.8(5)
C(18)-C(16)-C(15)	122.0(5)
C(17)-C(16)-C(15)	115.2(4)
C(16)-C(17)-N(1)	110.0(4)
C(16)-C(18)-C(19)	121.9(6)
O(4)-C(19)-C(18)	110.3(4)
C(24)-C(20)-C(21)	108.5(4)
C(24)-C(20)-C(15)	112.8(4)
C(21)-C(20)-C(15)	117.9(4)
O(4)-C(21)-C(20)	114.6(4)
O(4)-C(21)-C(22)	104.3(4)
C(20)-C(21)-C(22)	109.5(4)
C(23)-C(22)-C(21)	116.8(4)
O(5)-C(23)-N(2)	122.8(4)
O(5)-C(23)-C(22)	122.3(4)
N(2)-C(23)-C(22)	114.9(4)
N(2)-C(24)-C(20)	106.2(3)
N(2)-C(24)-C(12)	104.3(3)
C(20)-C(24)-C(12)	117.2(3)
C(30)-C(25)-C(26)	122.0(4)
C(30)-C(25)-N(2)	127.8(4)
C(26)-C(25)-N(2)	110.2(4)
C(25)-C(26)-C(27)	119.5(4)
C(25)-C(26)-C(12)	110.4(3)
C(27)-C(26)-C(12)	130.0(4)
C(28)-C(27)-C(26)	119.8(4)
O(7)-C(28)-C(27)	125.6(4)
O(7)-C(28)-C(29)	115.2(4)
C(27)-C(28)-C(29)	119.2(4)
C(30)-C(29)-O(6)	124.2(4)
C(30)-C(29)-C(28)	121.3(4)
O(6)-C(29)-C(28)	114.6(4)
C(29)-C(30)-C(25)	118.2(4)
C(3A)-C(2A)-C(1A)	124.6(9)
C(3A)-C(2A)-C(4A)	115.5(8)
C(1A)-C(2A)-C(4A)	119.4(8)

C(6A)-C(5A)-C(4A)	62.3(6)
C(5A)-C(6A)-C(4A)	60.5(5)
C(2A)-C(4A)-C(5A)	113.0(7)
C(2A)-C(4A)-C(6A)	120.8(7)
C(5A)-C(4A)-C(6A)	57.3(6)
C(2A)-C(4A)-C(7A)	115.1(7)
C(5A)-C(4A)-C(7A)	117.9(7)
C(6A)-C(4A)-C(7A)	119.6(7)
O(1A)-C(7A)-C(8A)	107.0(6)
O(1A)-C(7A)-C(9A)	110.4(6)
C(8A)-C(7A)-C(9A)	109.6(7)
O(1A)-C(7A)-C(4A)	108.8(6)
C(8A)-C(7A)-C(4A)	113.3(7)
C(9A)-C(7A)-C(4A)	107.7(7)
O(3A)-C(9A)-O(2A)	126.1(8)
O(3A)-C(9A)-C(7A)	119.0(8)
O(2A)-C(9A)-C(7A)	114.8(6)
C(3B)-C(2B)-C(1B)	127(2)
C(3B)-C(2B)-C(4B)	115.0(17)
C(1B)-C(2B)-C(4B)	116.2(18)
C(6B)-C(5B)-C(4B)	63.7(10)
C(5B)-C(6B)-C(4B)	60.0(9)
C(2B)-C(4B)-C(5B)	118.5(16)
C(2B)-C(4B)-C(7B)	115.3(14)
C(5B)-C(4B)-C(7B)	118.5(16)
C(2B)-C(4B)-C(6B)	114.5(15)
C(5B)-C(4B)-C(6B)	56.3(9)
C(7B)-C(4B)-C(6B)	121.2(16)
O(1B)-C(7B)-C(8B)	107.3(14)
O(1B)-C(7B)-C(9B)	109.3(15)
C(8B)-C(7B)-C(9B)	106.4(15)
O(1B)-C(7B)-C(4B)	111.8(14)
C(8B)-C(7B)-C(4B)	113.7(16)
C(9B)-C(7B)-C(4B)	108.2(17)
O(3B)-C(9B)-O(2B)	124(2)
O(3B)-C(9B)-C(7B)	120(2)
O(2B)-C(9B)-C(7B)	113.3(17)

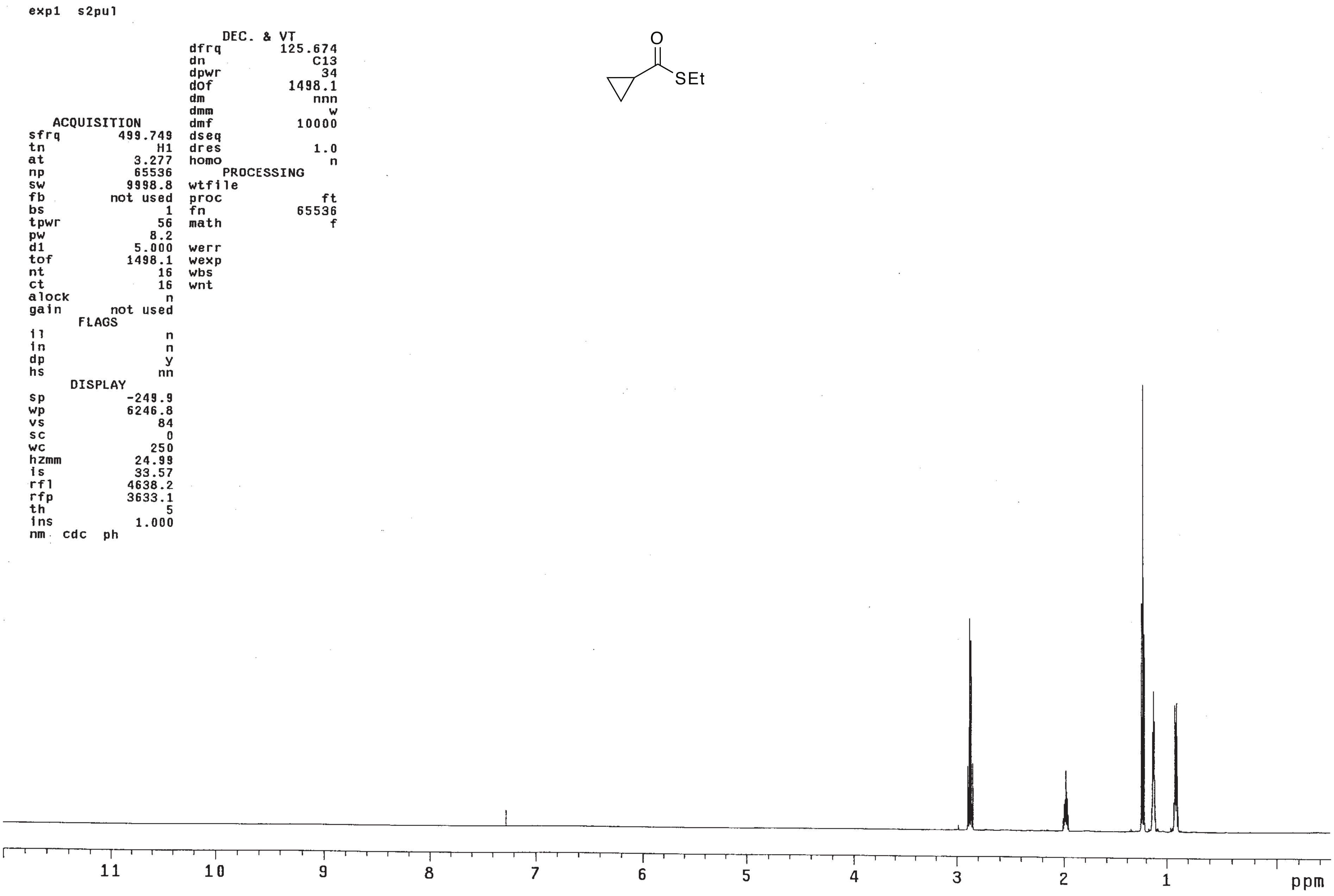
Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for S12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	45(2)	30(2)	31(2)	1(2)	4(2)	0(2)
N(2)	30(2)	29(2)	32(2)	-2(2)	-1(2)	1(1)
O(4)	33(2)	69(2)	57(2)	-15(2)	5(2)	0(2)
O(5)	40(2)	82(3)	33(2)	-2(2)	-7(2)	3(2)
O(6)	33(2)	60(2)	30(2)	-6(1)	2(1)	0(2)
O(7)	28(1)	41(2)	38(2)	0(2)	-2(1)	-1(1)
C(10)	47(3)	28(2)	32(2)	1(2)	0(2)	-2(2)
C(11)	37(2)	23(2)	33(2)	3(2)	-4(2)	-1(2)
C(12)	31(2)	24(2)	30(2)	-1(2)	-3(2)	-2(2)
C(13)	35(2)	26(2)	29(2)	-1(2)	-2(2)	-2(2)
C(14)	47(3)	27(2)	36(2)	-5(2)	-5(2)	-1(2)
C(15)	46(3)	30(2)	46(3)	-5(2)	0(2)	6(2)
C(16)	50(3)	38(2)	41(3)	-12(2)	7(2)	4(2)
C(17)	51(3)	36(2)	35(2)	-6(2)	7(2)	-1(2)
C(18)	51(3)	60(3)	52(3)	-18(3)	12(3)	1(3)
C(19)	43(3)	90(5)	58(4)	-25(3)	8(3)	9(3)
C(20)	36(2)	26(2)	41(2)	-2(2)	-3(2)	3(2)
C(21)	38(2)	38(2)	50(3)	0(2)	-4(2)	6(2)
C(22)	29(2)	41(2)	42(3)	5(2)	-4(2)	-1(2)
C(23)	32(2)	38(2)	40(3)	0(2)	-6(2)	1(2)
C(24)	31(2)	26(2)	29(2)	-2(2)	-1(2)	1(2)
C(25)	29(2)	26(2)	36(2)	0(2)	-3(2)	-2(2)
C(26)	32(2)	23(2)	29(2)	0(2)	-4(2)	0(2)
C(27)	31(2)	25(2)	30(2)	-2(2)	-6(2)	1(2)
C(28)	27(2)	27(2)	39(2)	-2(2)	2(2)	1(2)
C(29)	35(2)	32(2)	33(2)	0(2)	1(2)	2(2)
C(30)	34(2)	37(2)	29(2)	0(2)	-5(2)	1(2)
C(31)	26(2)	59(3)	45(3)	-6(2)	0(2)	0(2)
C(32)	41(3)	91(4)	32(2)	-9(3)	-2(2)	1(3)
C(1A)	99(7)	66(4)	71(5)	5(4)	24(5)	3(5)
C(2A)	62(4)	61(3)	58(3)	-6(3)	13(3)	1(3)
C(3A)	76(7)	75(5)	64(4)	-2(4)	-14(5)	-19(5)
C(5A)	66(3)	80(4)	79(4)	2(4)	-3(3)	7(4)
C(6A)	83(4)	66(4)	71(4)	-2(3)	15(4)	15(3)
C(4A)	59(3)	57(3)	55(3)	-10(2)	0(2)	4(3)
C(7A)	61(2)	40(2)	38(2)	-5(2)	-6(2)	5(2)
O(1A)	60(3)	36(2)	39(3)	-2(2)	-8(2)	-5(2)
C(8A)	76(4)	38(3)	42(3)	-2(3)	-12(3)	3(4)
C(9A)	56(2)	37(2)	28(2)	-7(2)	1(2)	0(2)
O(2A)	48(4)	36(2)	28(3)	-10(2)	2(2)	5(2)
O(3A)	66(3)	36(2)	35(5)	-6(2)	0(3)	2(2)
C(1B)	77(11)	79(11)	54(5)	2(7)	19(9)	-14(10)
C(2B)	66(5)	59(5)	59(4)	-9(4)	7(4)	3(4)
C(3B)	68(10)	59(7)	87(11)	-20(6)	-19(10)	4(8)
C(5B)	65(4)	68(7)	75(6)	-9(6)	-11(5)	2(6)
C(6B)	65(7)	65(6)	72(7)	-5(5)	-12(6)	-8(5)
C(4B)	58(3)	57(4)	57(3)	-6(3)	-2(3)	4(4)
C(7B)	61(2)	40(2)	38(2)	-5(2)	-6(2)	5(2)
O(1B)	60(3)	36(2)	39(3)	-2(2)	-8(2)	-5(2)
C(8B)	76(4)	38(3)	42(3)	-2(3)	-12(3)	3(4)
C(9B)	56(2)	37(2)	28(2)	-7(2)	1(2)	0(2)
O(2B)	48(4)	36(2)	28(3)	-10(2)	2(2)	5(2)
O(3B)	66(3)	36(2)	35(5)	-6(2)	0(3)	2(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for S12.

	x	y	z	U(eq)
H(1N)	8940(30)	6160(40)	-3190(20)	42
H(10A)	9614	7554	-3104	43
H(10B)	10623	7130	-2592	43
H(11A)	8523	7559	-1947	37
H(11B)	9660	7893	-1559	37
H(13)	8239	5595	-2077	36
H(14A)	9279	4189	-2372	44
H(14B)	9183	4335	-1388	44
H(15)	11018	4010	-1804	49
H(17A)	10014	4879	-3493	49
H(17B)	10690	5848	-3690	49
H(18)	12449	5619	-3206	65
H(19A)	12912	4354	-1909	77
H(19B)	13741	5138	-2279	77
H(20)	10570	4841	-583	41
H(21)	12378	4593	-566	50
H(22A)	12688	5640	440	45
H(22B)	12599	6557	-165	45
H(24)	10998	6718	-1263	34
H(27)	7093	6211	-991	35
H(30)	9251	6743	1363	40
H(31A)	5337	6540	-658	65
H(31B)	4570	5925	-56	65
H(31C)	5560	5402	-508	65
H(32A)	8312	6336	2520	82
H(32B)	7339	6962	2892	82
H(32C)	8204	7471	2297	82
H(1A1)	6406	5316	-3237	118
H(1A2)	5142	5307	-3419	118
H(1A3)	5570	5390	-2486	118
H(3A1)	6113	6983	-1987	86
H(3A2)	5931	7920	-2610	86
H(5A1)	4360	6948	-4880	90
H(5A2)	3905	6858	-3911	90
H(6A1)	4716	8380	-3582	88
H(6A2)	5171	8470	-4551	88
H(1OA)	6870(50)	5620(50)	-4630(40)	54
H(8A1)	7166	7317	-5698	78
H(8A2)	6666	8181	-5152	78
H(8A3)	5890	7454	-5648	78
H(1B1)	5490	7378	-2065	105
H(1B2)	6507	6827	-2452	105
H(1B3)	5334	6357	-2532	105
H(3B1)	4998	8748	-2915	86
H(3B2)	5125	8649	-3927	86
H(5B1)	3835	6966	-4200	83
H(5B2)	4450	6544	-5044	83
H(6B1)	5264	5294	-4244	81
H(6B2)	4648	5717	-3397	81
H(1OB)	7210(70)	6050(160)	-4950(40)	54
H(8B1)	5904	7942	-5485	78
H(8B2)	7190	7933	-5491	78
H(8B3)	6557	8478	-4762	78



S-ethyl cyclopropanecarbothioate

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exp1  s2pul

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                    dn              H1
                    dpwr            37
                    dof         -500.0
                    dm               y
                    dmm              w
   ACQUISITION      dmf          10000
sfrq       125.796  dseq
tn             C13  dres           1.0
at           1.736  homo             n
np          131010       PROCESSING
sw         37735.8  lb            0.30
fb        not used  wtfile
bs               4  proc            ft
ss               1  fn          131072
tpwr            53  math             f
pw             6.9
d1           0.763  werr
tof          631.4  wexp
nt           1e+06  wbs
ct             224  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -6291.4
wp         37735.3
vs             280
sc               0
wc             250
hzmm        150.94
is        11464.55
rfl        16007.0
rfp         9715.0
th              20
ins          1.000
ai    ph
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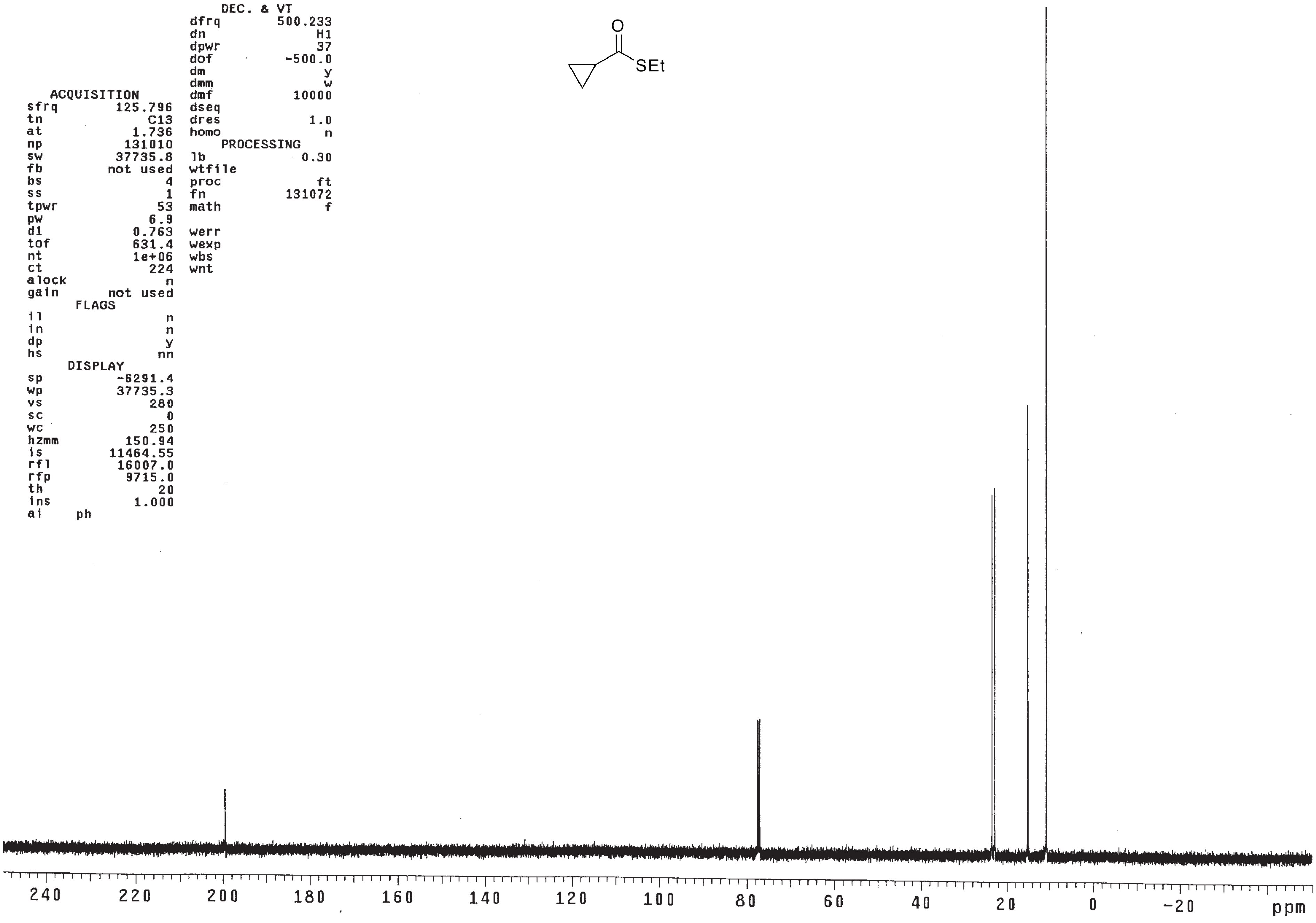
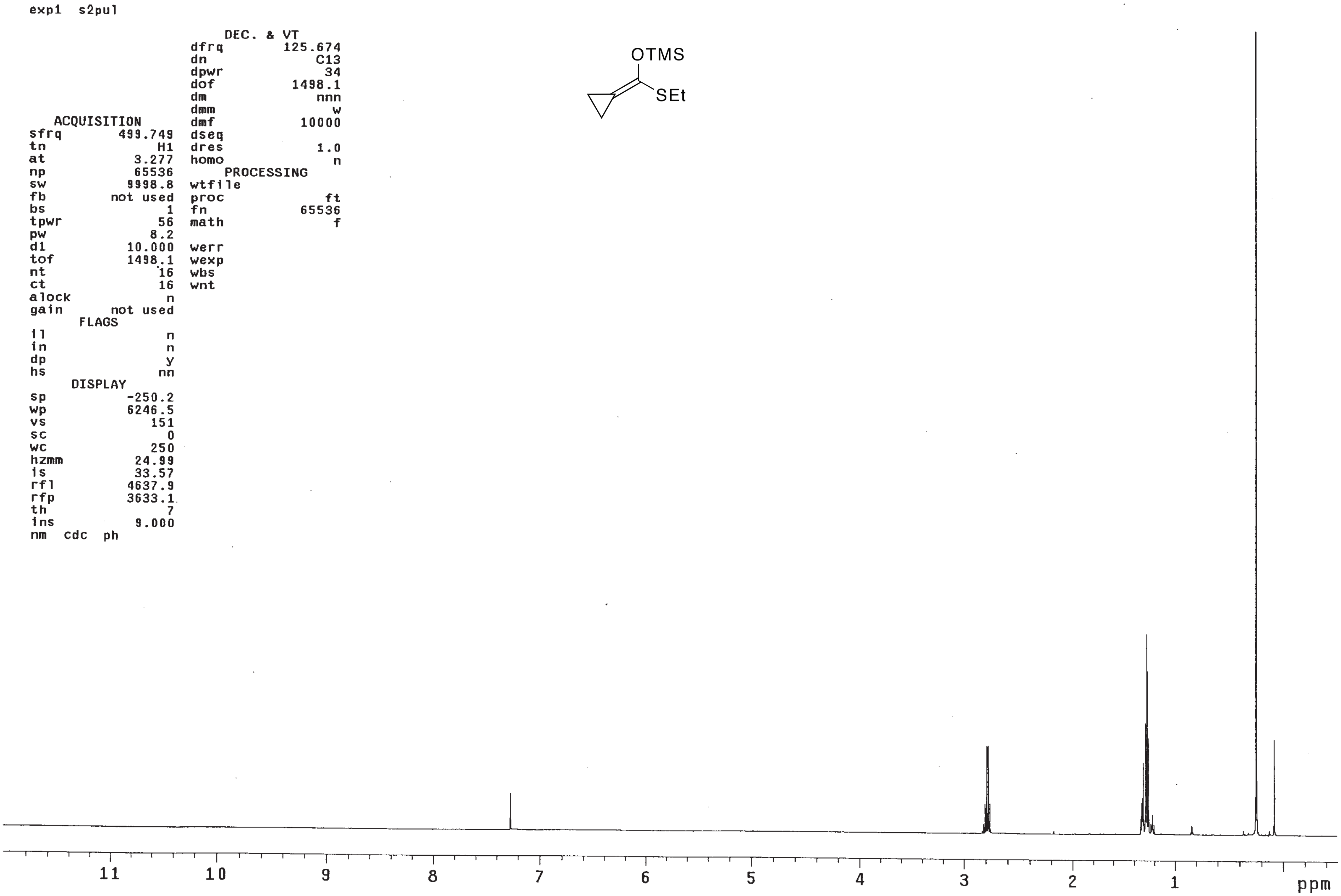


S-ethyl cyclopropanecarbothioate



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exp1  s2pul

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                        dn             C13
                        dpwr            34
                        dof         1498.1
                        dm             nnn
                        dmm              w
    ACQUISITION         dmf          10000
sfrq       499.749      dseq
tn              H1      dres           1.0
at           3.277      homo             n
np           65536          PROCESSING
sw          9998.8      wtfile
fb        not used      proc            ft
bs               1      fn           65536
tpwr            56      math             f
pw             8.2
d1          10.000      werr
tof         1498.1      wexp
nt              16      wbs
ct              16      wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.2
wp          6246.5
vs             151
sc               0
wc             250
hzmm         24.99
is           33.57
rfl         4637.9
rfp         3633.1
th               7
ins          9.000
nm  cdc  ph
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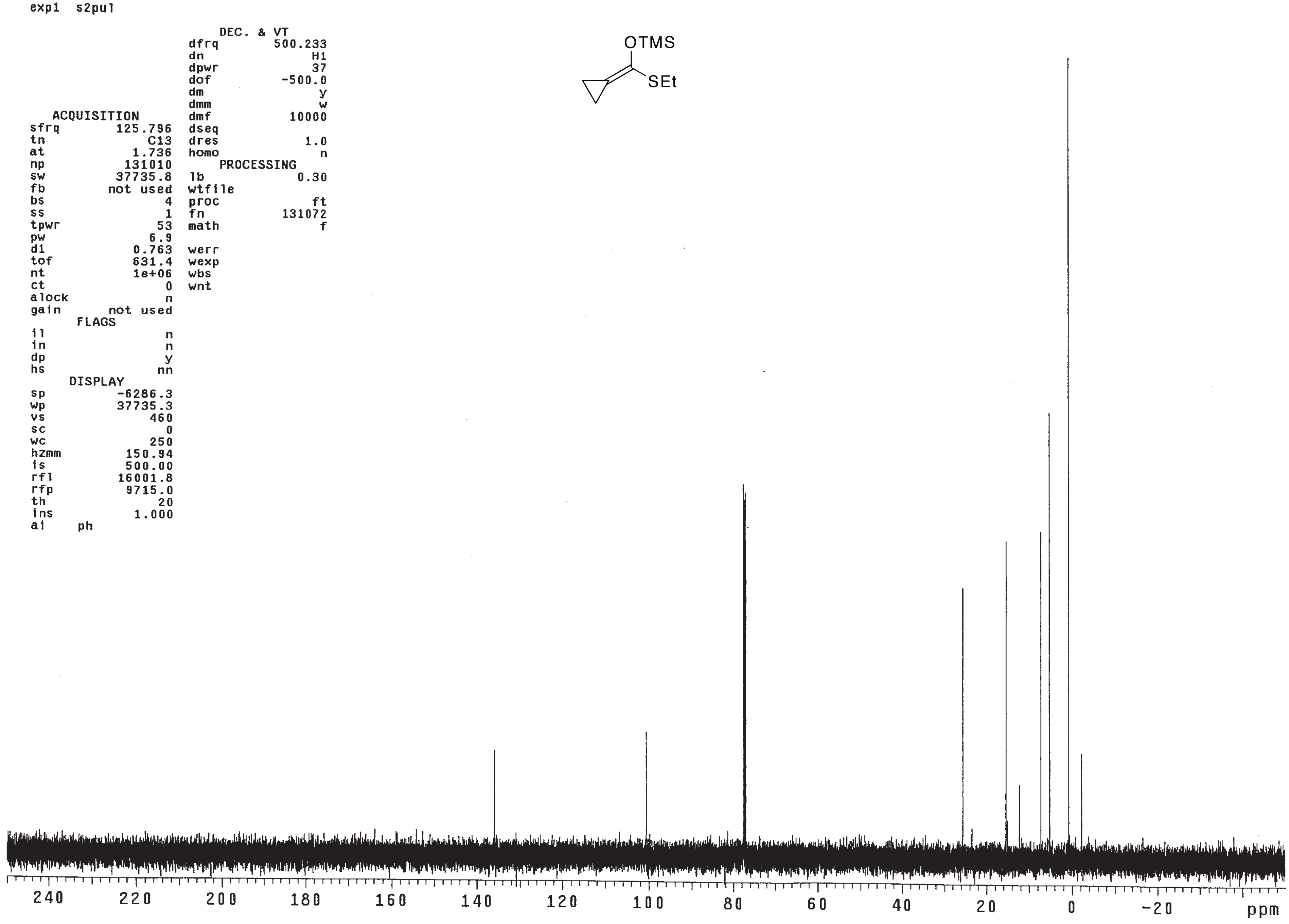
(cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane



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                     dn              H1
                     dpwr            37
                     dof         -500.0
                     dm               y
                     dmm              w
    ACQUISITION      dmf          10000
sfrq        125.796  dseq
tn              C13  dres           1.0
at            1.736  homo             n
np           131010     PROCESSING
sw          37735.8  lb            0.30
fb         not used  wtfile
bs                4  proc            ft
ss                1  fn          131072
tpwr             53  math             f
pw              6.9
d1            0.763  werr
tof           631.4  wexp
nt            1e+06  wbs
ct                0  wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6286.3
wp          37735.3
vs              460
sc                0
wc              250
hzmm         150.94
is           500.00
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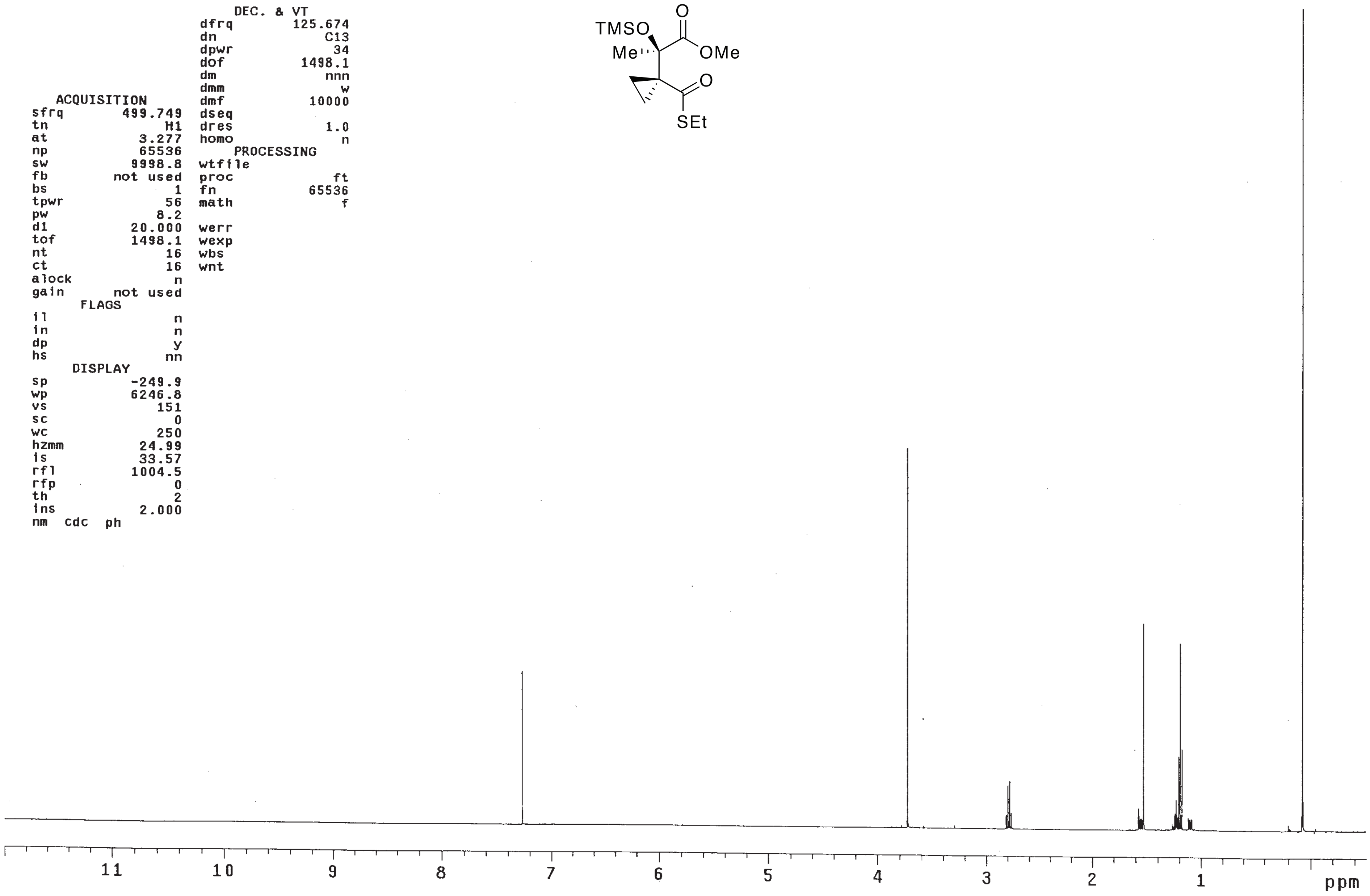
rfp          9715.0
th               20
ins           1.000
ai    ph
```

(cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane



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exp1  s2pul

                      DEC. & VT
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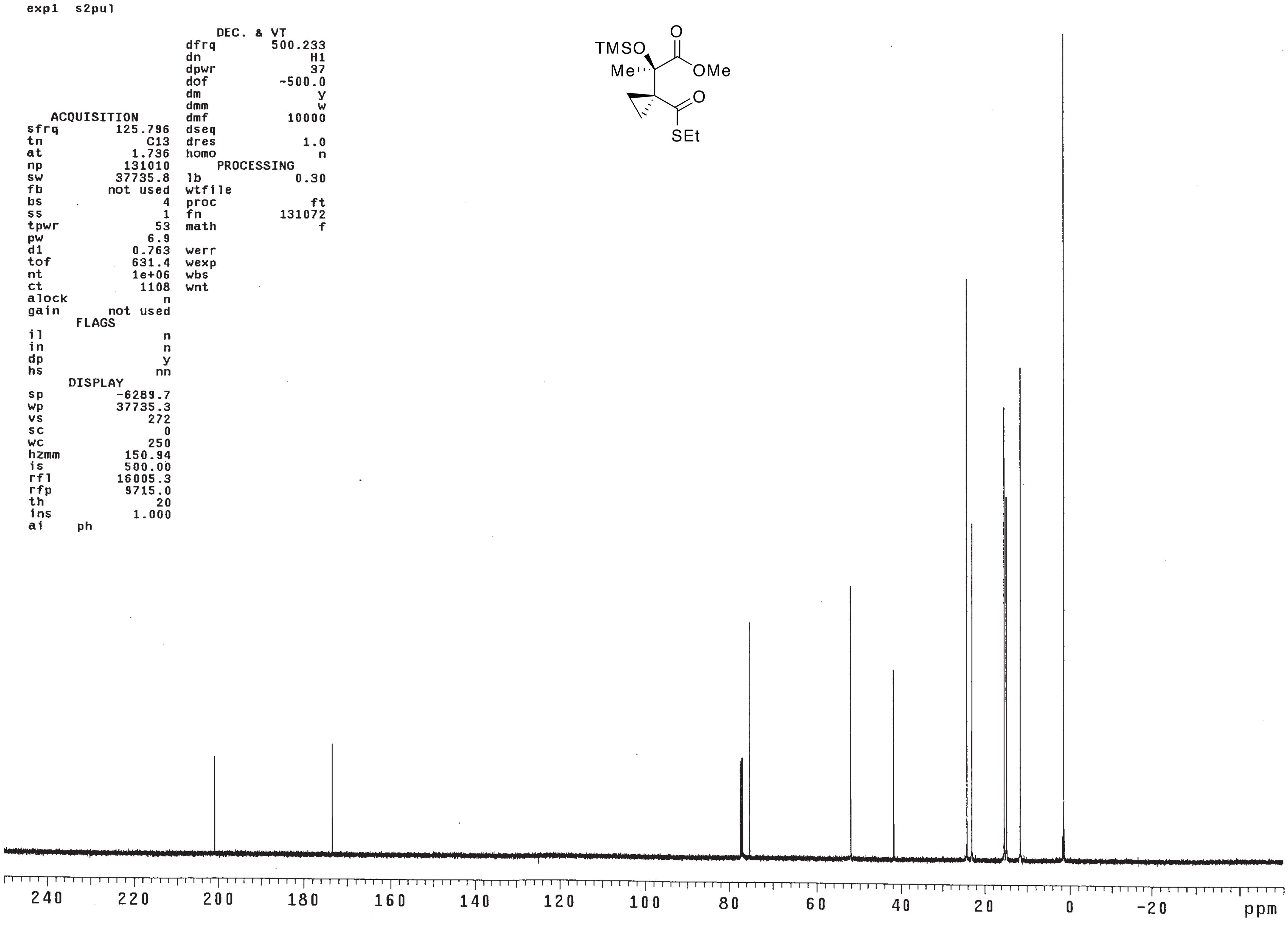
                    dn             C13
                    dpwr            34
                    dof         1498.1
                    dm             nnn
                    dmm              w
   ACQUISITION      dmf          10000
sfrq       499.749  dseq
tn              H1  dres           1.0
at           3.277  homo             n
np           65536     PROCESSING
sw          9998.8  wtfile
fb        not used  proc            ft
bs               1  fn           65536
tpwr            56  math             f
pw             8.2
d1          20.000  werr
tof         1498.1  wexp
nt              16  wbs
ct              16  wnt
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
hs              nn
    DISPLAY
sp          -249.9
wp          6246.8
vs             151
sc               0
wc             250
hzmm         24.99
is           33.57
rfl         1004.5
rfp              0
th               2
ins          2.000
nm  cdc  ph
```

(2*R*)-2-(1-ethylsulfanylcarbonyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester



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exp1  s2pul

                         DEC. & VT
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                    dn               H1
                    dpwr             37
                    dof          -500.0
                    dm                y
                    dmm               w
     ACQUISITION    dmf           10000
sfrq       125.796  dseq
tn             C13  dres            1.0
at           1.736  homo              n
np          131010     PROCESSING
sw         37735.8  lb             0.30
fb        not used  wtfile
bs               4  proc             ft
ss               1  fn           131072
tpwr            53  math              f
pw             6.9
d1           0.763  werr
tof          631.4  wexp
nt           1e+06  wbs
ct            1108  wnt
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -6289.7
wp         37735.3
vs             272
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        16005.3
rfp         9715.0
th              20
ins          1.000
ai     ph
```

(2*R*)-2-(1-ethylsulfanylcarbonyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester

```
=====================================================================
Injection Date    :                              Seq. Line :    2
Sample Name       :                               Location : Vial 91
Acq. Operator     :                                    Inj :    1
                                               Inj Volume : 1 µl
Acq. Method       : C:\HPCHEM\2\METHODS\DSI214A.M
Last changed      : 8/13/2005 2:57:07 PM by Movassaghi Group
Analysis Method : C:\HPCHEM\2\METHODS\182_9.M
Last changed      : 2/15/2006 1:25:40 PM by Bin
                    (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
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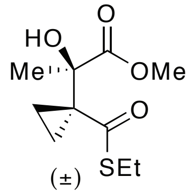
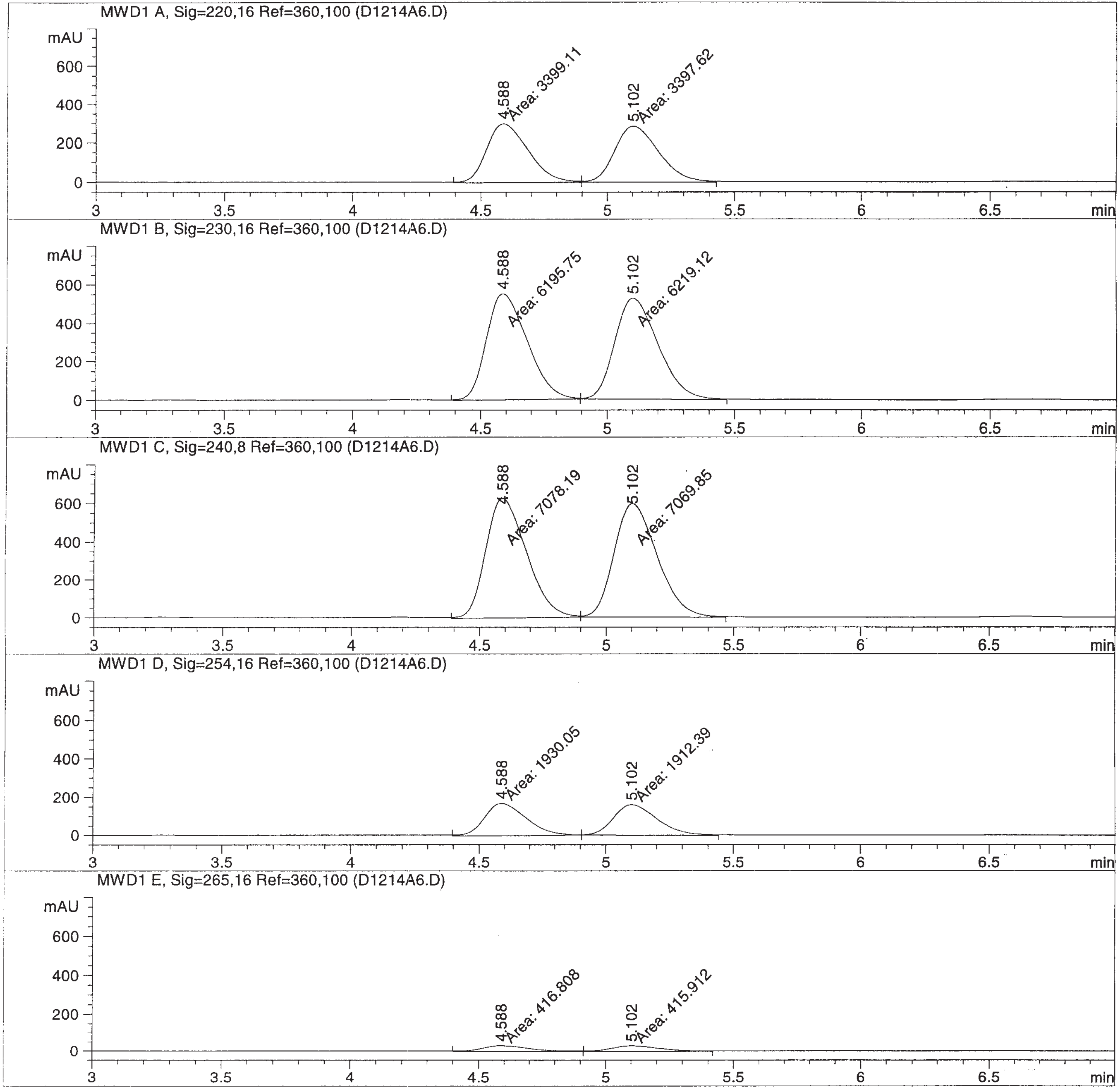
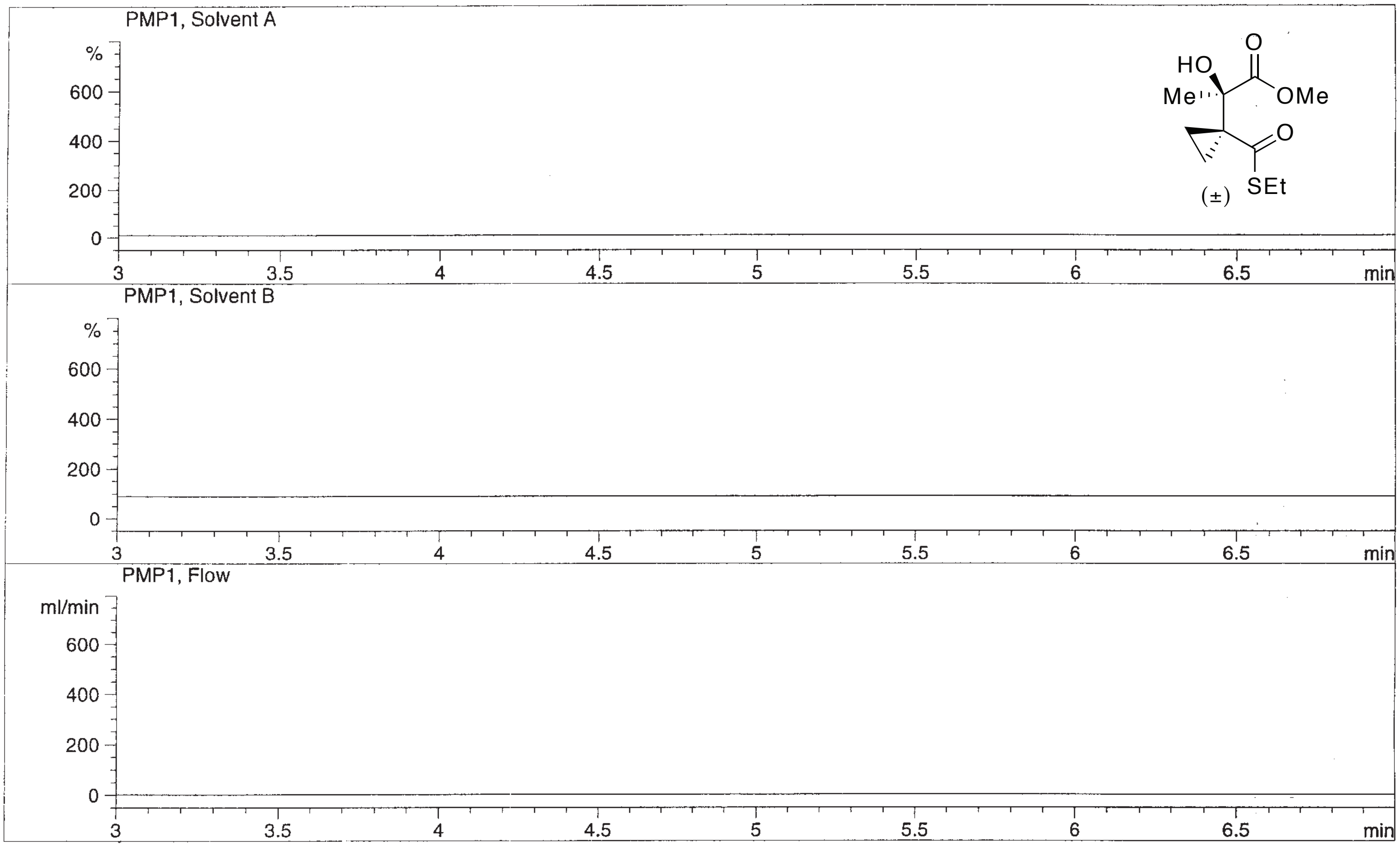




methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.588 MM    0.1896 3399.11206  298.79694  50.0110
   2   5.102 MM    0.1992 3397.62256  284.23749  49.9890

Totals :                  6796.73462  583.03442

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.588 MM    0.1867 6195.75098  553.00427  49.9059
   2   5.102 MM    0.1972 6219.11719  525.51385  50.0941

Totals :                  1.24149e4  1078.51813

 Results obtained with enhanced integrator!
```

methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate

```
Signal 3: MWD1 C, Sig=240,8 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.588 MM    0.1882 7078.19482  626.99695  50.0295
   2   5.102 MM    0.1979 7069.85059  595.39844  49.9705

Totals :                  1.41480e4  1222.39539

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.588 MM    0.1918 1930.04724  167.68768  50.2297
   2   5.102 MM    0.2014 1912.39209  158.27319  49.7703

Totals :                  3842.43933  325.96088

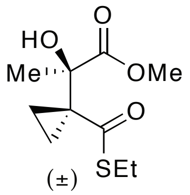
 Results obtained with enhanced integrator!

Signal 5: MWD1 E, Sig=265,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.588 MM    0.2159  416.80847   32.17342  50.0538
   2   5.102 MM    0.2246  415.91214   30.85807  49.9462

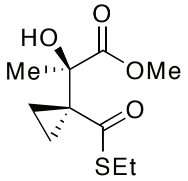
Totals :                   832.72061   63.03149

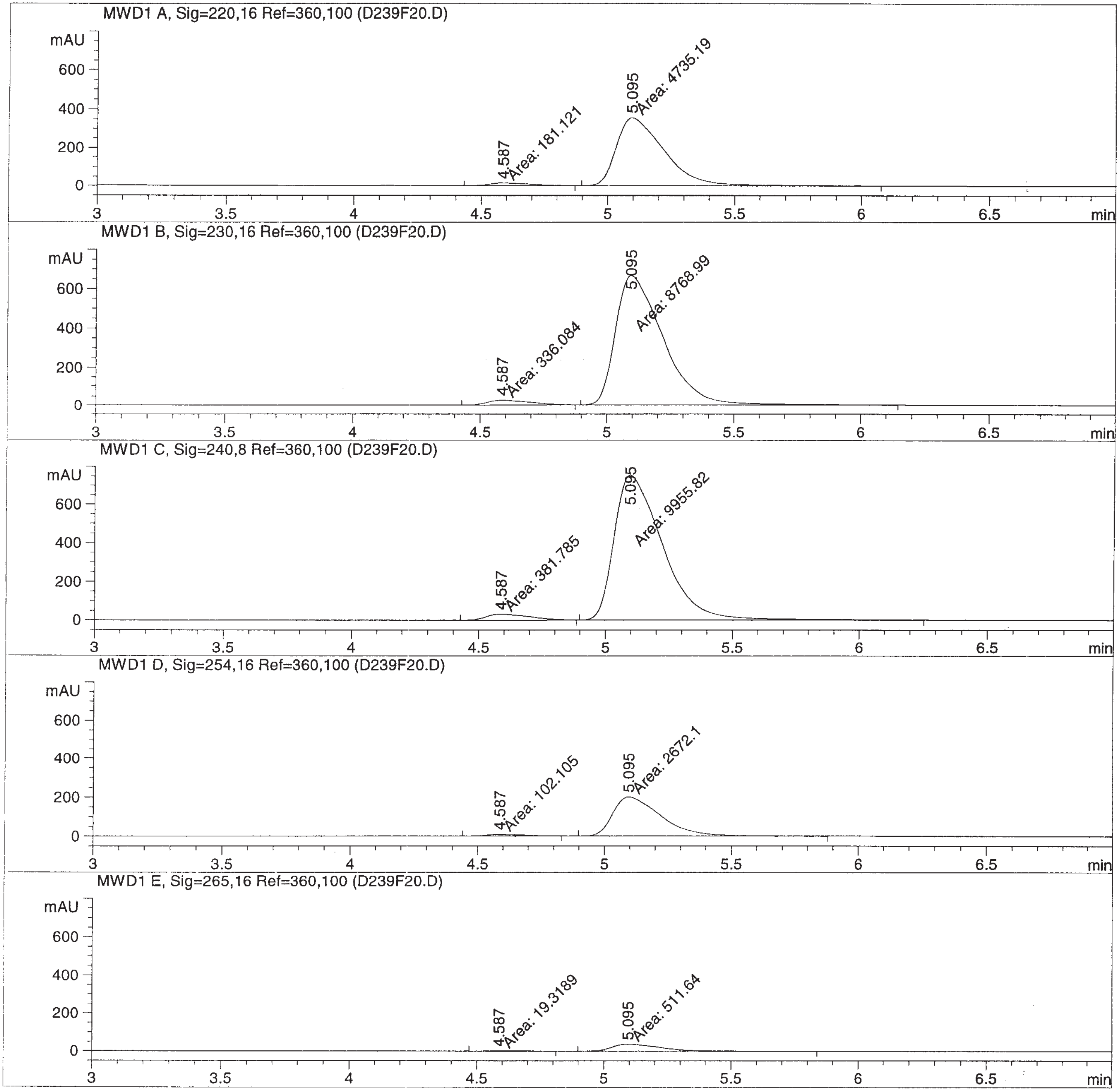
 Results obtained with enhanced integrator!
=====================================================================
                              *** End of Report ***
```



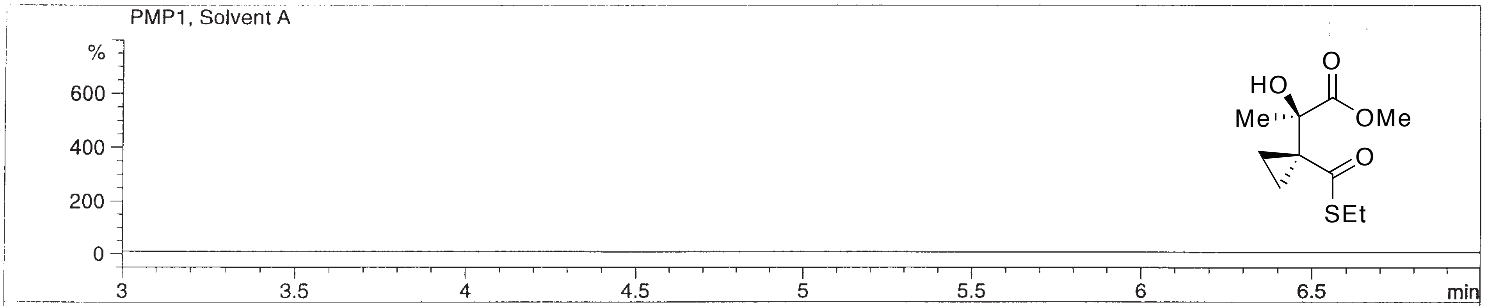
methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate

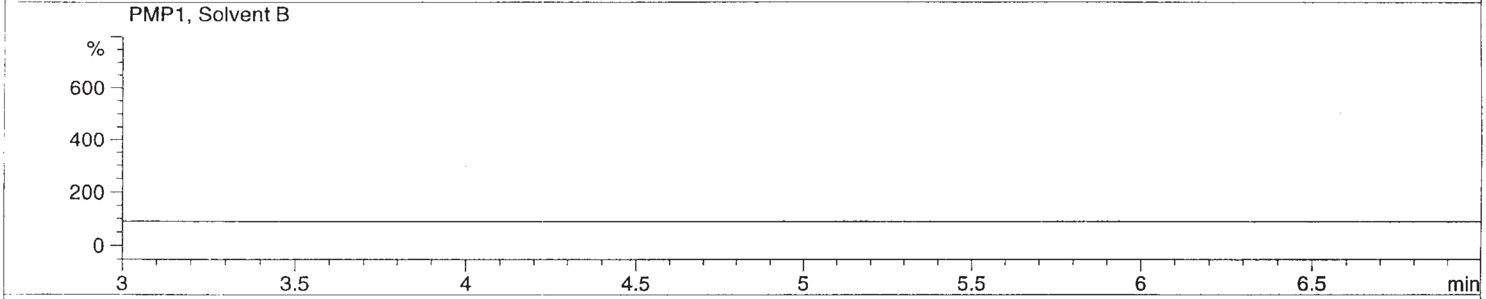
```
=====================================================================
Injection Date  :                               Seq. Line :   1
Sample Name     :                                Location : Vial 91
Acq. Operator   :                                     Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\2\METHODS\DSI1621.M
Last changed    : 8/20/2005 9:02:36 AM by Movassaghi Group
Analysis Method : C:\HPCHEM\2\METHODS\182_9.M
Last changed    : 2/15/2006 1:28:53 PM by Bin
                  (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
```

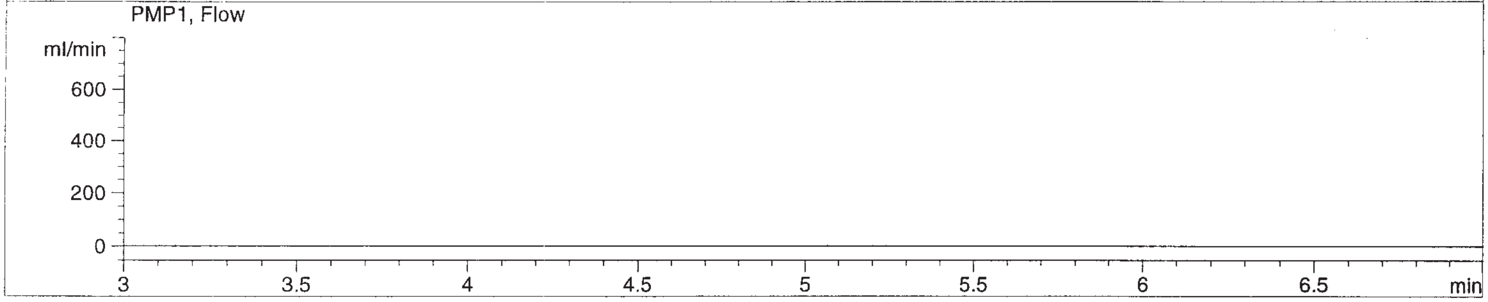




(2*R*)-methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate







```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.587 MM    0.1984  181.12068   15.21405   3.6841
   2   5.095 MM    0.2209 4735.18701  357.24994  96.3159

Totals :                  4916.30769  372.46399

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.587 MM    0.1964  336.08368   28.51702   3.6912
   2   5.095 MM    0.2197 8768.99316  665.32880  96.3088

Totals :                  9105.07684  693.84582

 Results obtained with enhanced integrator!
```

(2*R*)-methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate

```
Signal 3: MWD1 C, Sig=240,8 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.587 MM    0.1971  381.78519   32.28540   3.6932
   2   5.095 MM    0.2201 9955.81836  753.86084  96.3068

Totals :                  1.03376e4   786.14624

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.587 MM    0.1951  102.10541    8.72269   3.6805
   2   5.095 MM    0.2212 2672.10400  201.31873  96.3195

Totals :                 2774.20941  210.04141

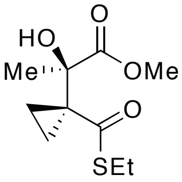
 Results obtained with enhanced integrator!

Signal 5: MWD1 E, Sig=265,16 Ref=360,100

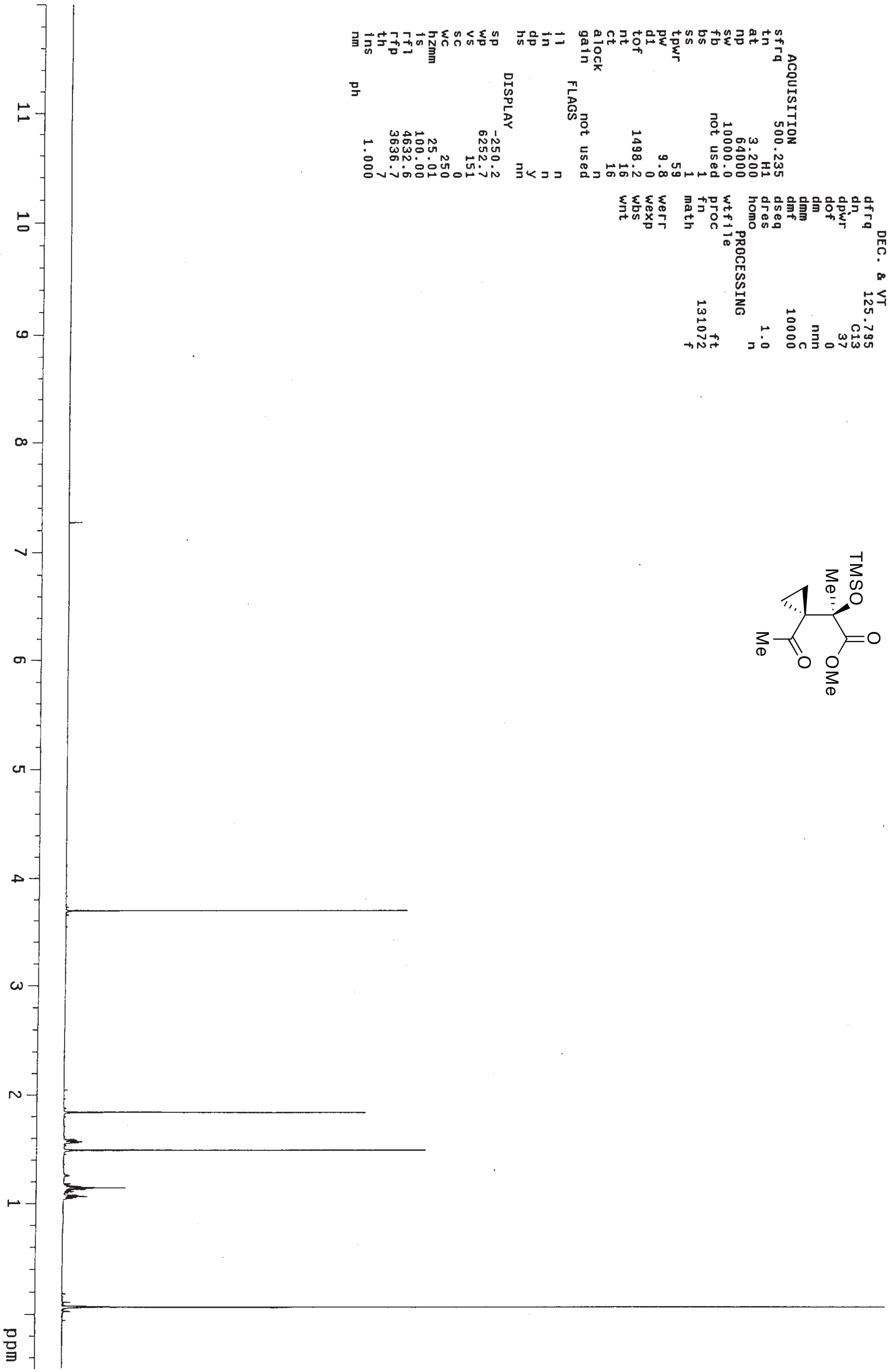
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.587 MM    0.1958   19.31890    1.64459   3.6385
   2   5.095 MM    0.2330  511.64023   36.59689  96.3615

Totals :                  530.95913   38.24148

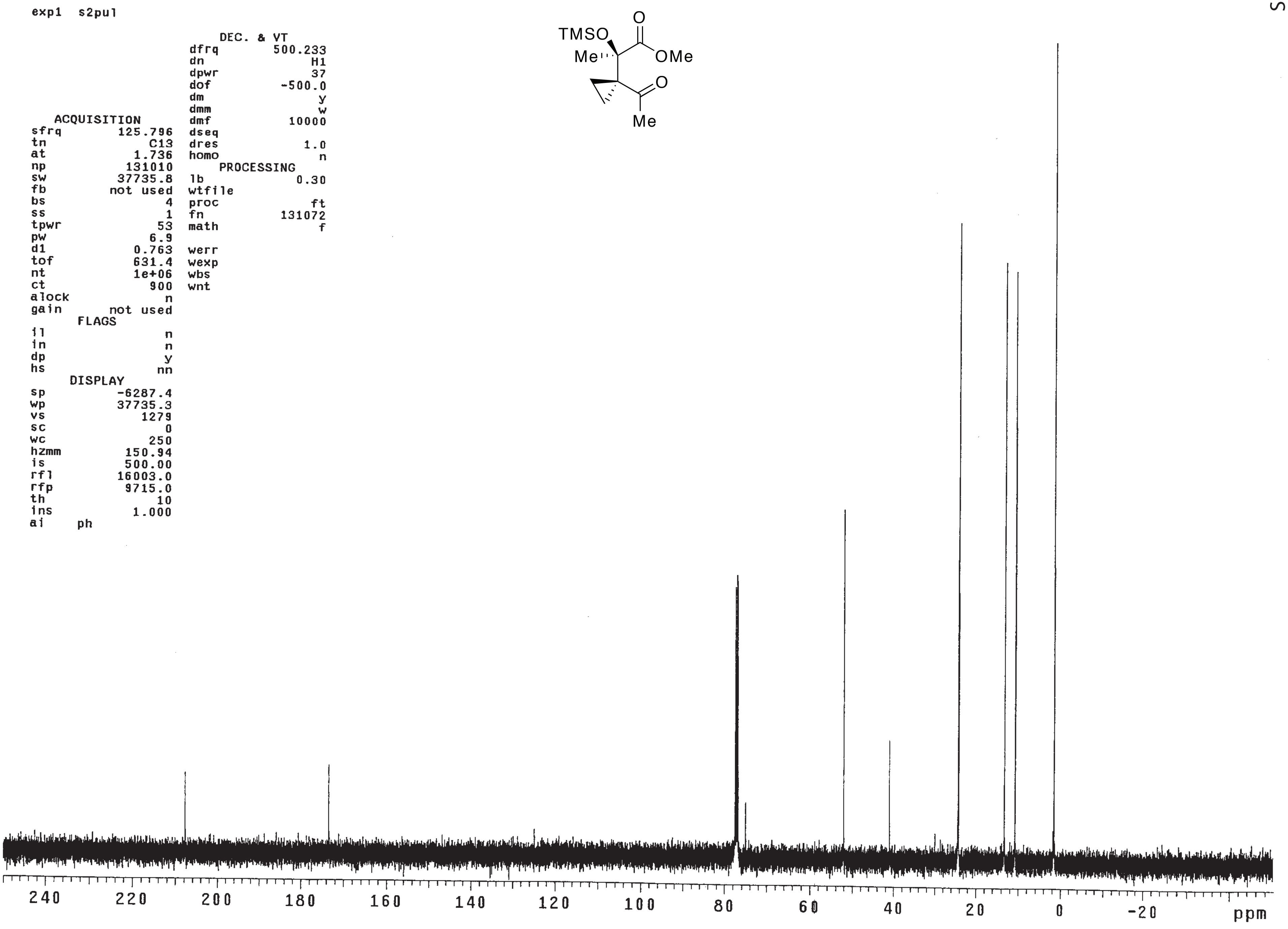
 Results obtained with enhanced integrator!
=====================================================================
                          *** End of Report ***
```



(2*R*)-methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate



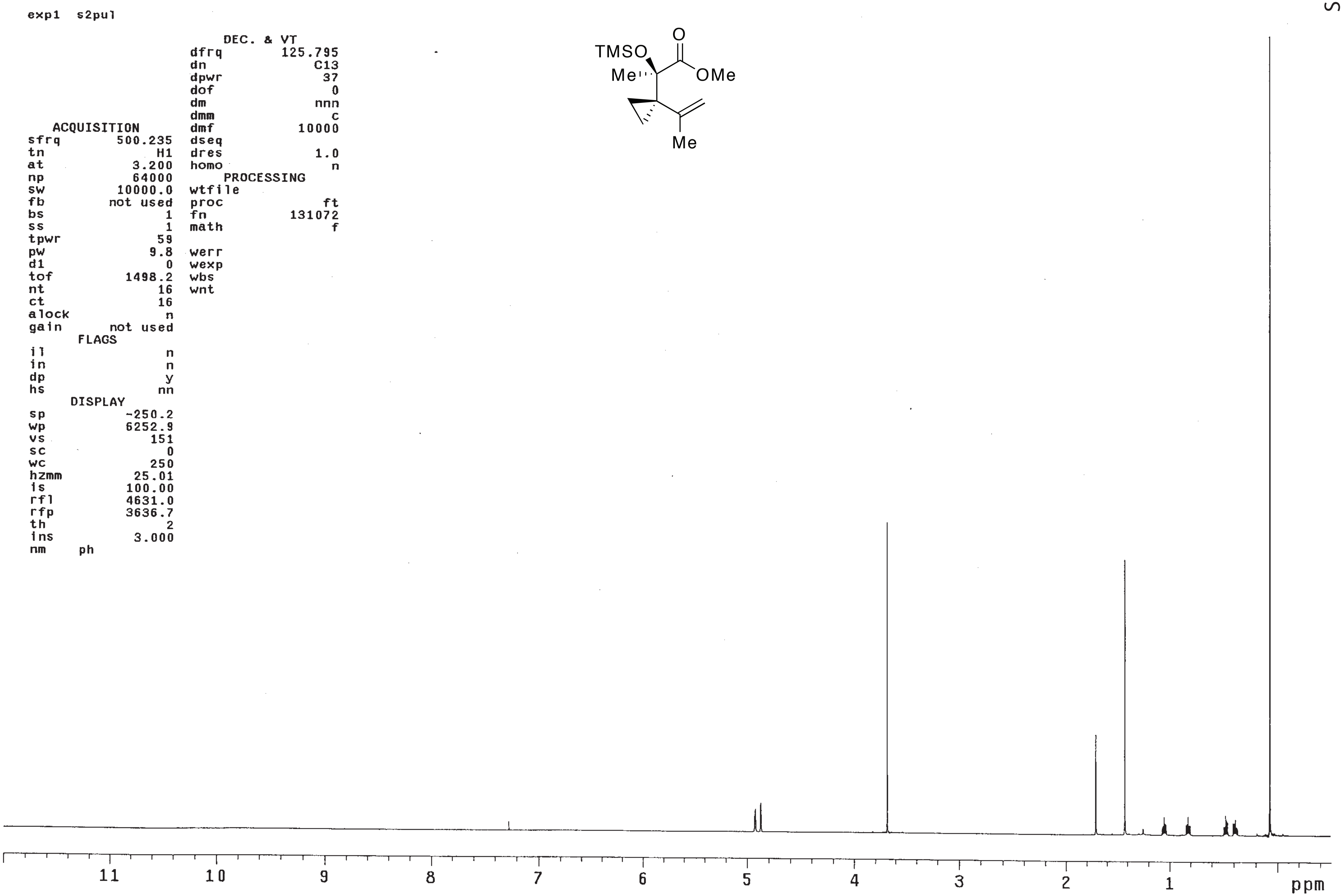
(2*R*)-2-(1-Acetyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester



```
exp1  s2pul

                              DEC. & VT
                      dfrq          500.233
                      dn                 H1
                      dpwr               37
                      dof            -500.0
                      dm                  y
                      dmm                 w
   ACQUISITION        dmf             10000
sfrq       125.796    dseq
tn             C13    dres              1.0
at           1.736    homo                n
np          131010        PROCESSING
sw         37735.8    lb               0.30
fb        not used    wtfile
bs               4    proc               ft
ss               1    fn             131072
tpwr            53    math                f
pw             6.9
d1           0.763    werr
tof          631.4    wexp
nt          1e+06     wbs
ct             900    wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -6287.4
wp         37735.3
vs            1279
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        16003.0
rfp         9715.0
th              10
ins          1.000
ai    ph
```

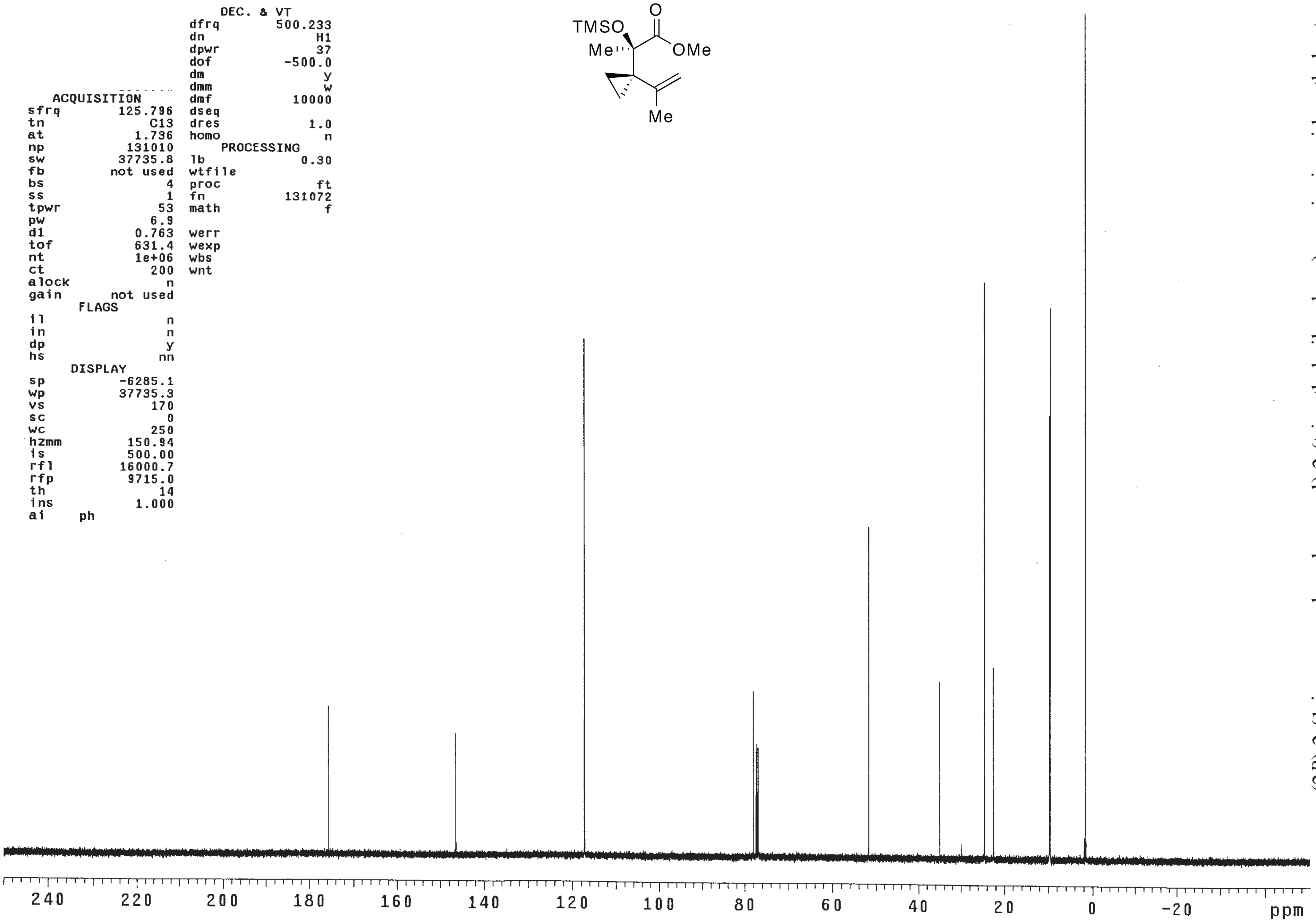
(2*R*)-2-(1-Acetyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester



```
exp1  s2pul

                            DEC. & VT
                         dfrq        125.795
                         dn              C13
                         dpwr             37
                         dof               0
                         dm              nnn
                         dmm               c
   ACQUISITION           dmf           10000
sfrq        500.235      dseq
tn               H1      dres            1.0
at            3.200      homo              n
np            64000         PROCESSING
sw          10000.0      wtfile
fb         not used      proc             ft
bs                1      fn           131072
ss                1      math              f
tpwr             59
pw              9.8      werr
d1                0      wexp
tof          1498.2      wbs
nt               16      wnt
ct               16
alock             n
gain       not used
     FLAGS
il                n
in                n
dp                y
hs               nn
    DISPLAY
sp           -250.2
wp           6252.9
vs              151
sc                0
wc              250
hzmm          25.01
is           100.00
rfl          4631.0
rfp          3636.7
th                2
ins           3.000
nm     ph
```

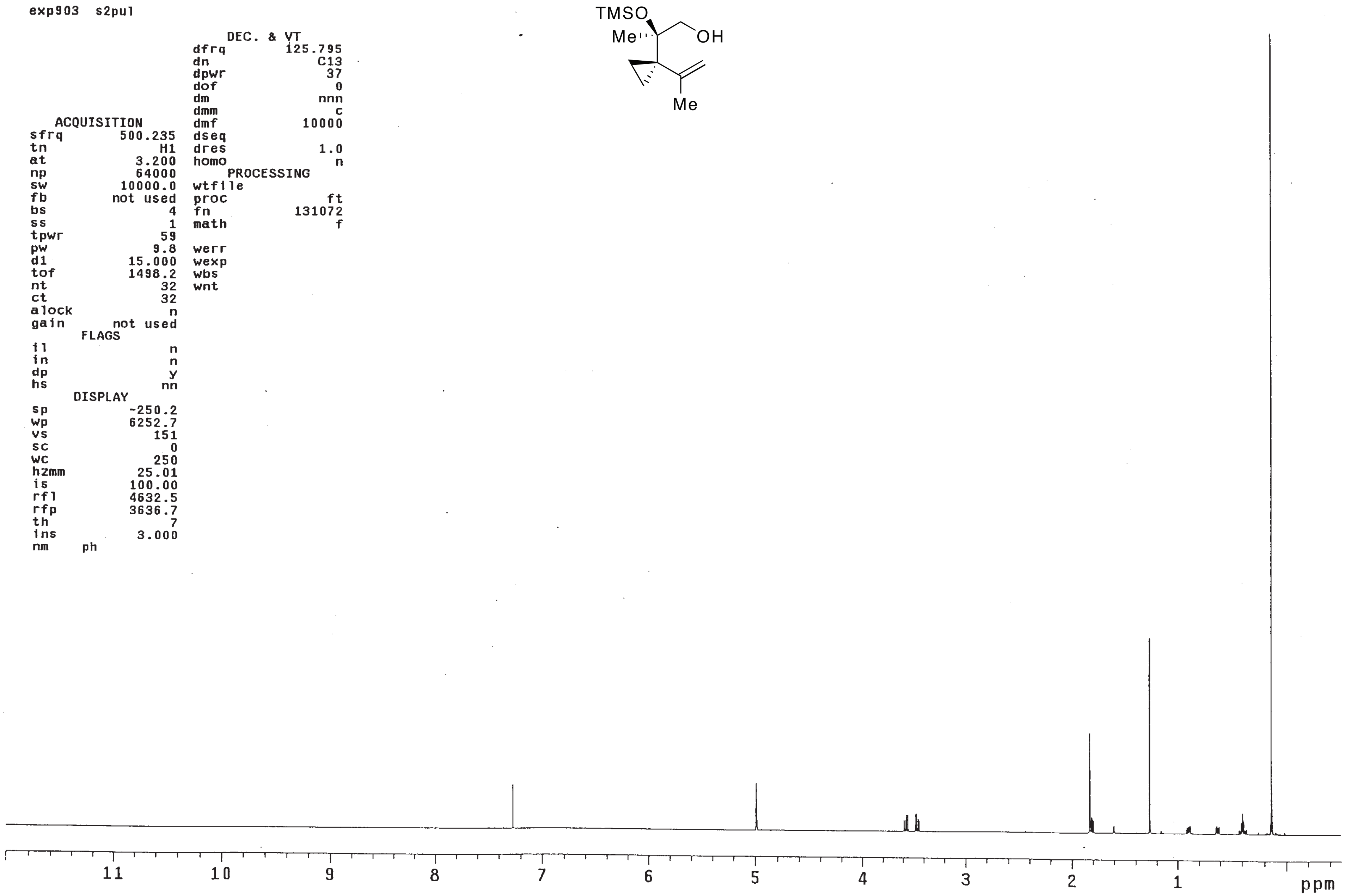
(2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester



```
exp1  s2pul

                          DEC. & VT
                     dfrq        500.233
                     dn               H1
                     dpwr             37
                     dof          -500.0
                     dm                y
                     dmm               w
   ACQUISITION       dmf           10000
sfrq       125.796   dseq
tn             C13   dres            1.0
at           1.736   homo              n
np          131010      PROCESSING
sw         37735.8   lb             0.30
fb        not used   wtfile
bs               4   proc             ft
ss               1   fn           131072
tpwr            53   math              f
pw             6.9
d1           0.763   werr
tof          631.4   wexp
nt           1e+06   wbs
ct             200   wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -6285.1
wp         37735.3
vs             170
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        16000.7
rfp         9715.0
th              14
ins          1.000
ai    ph
```

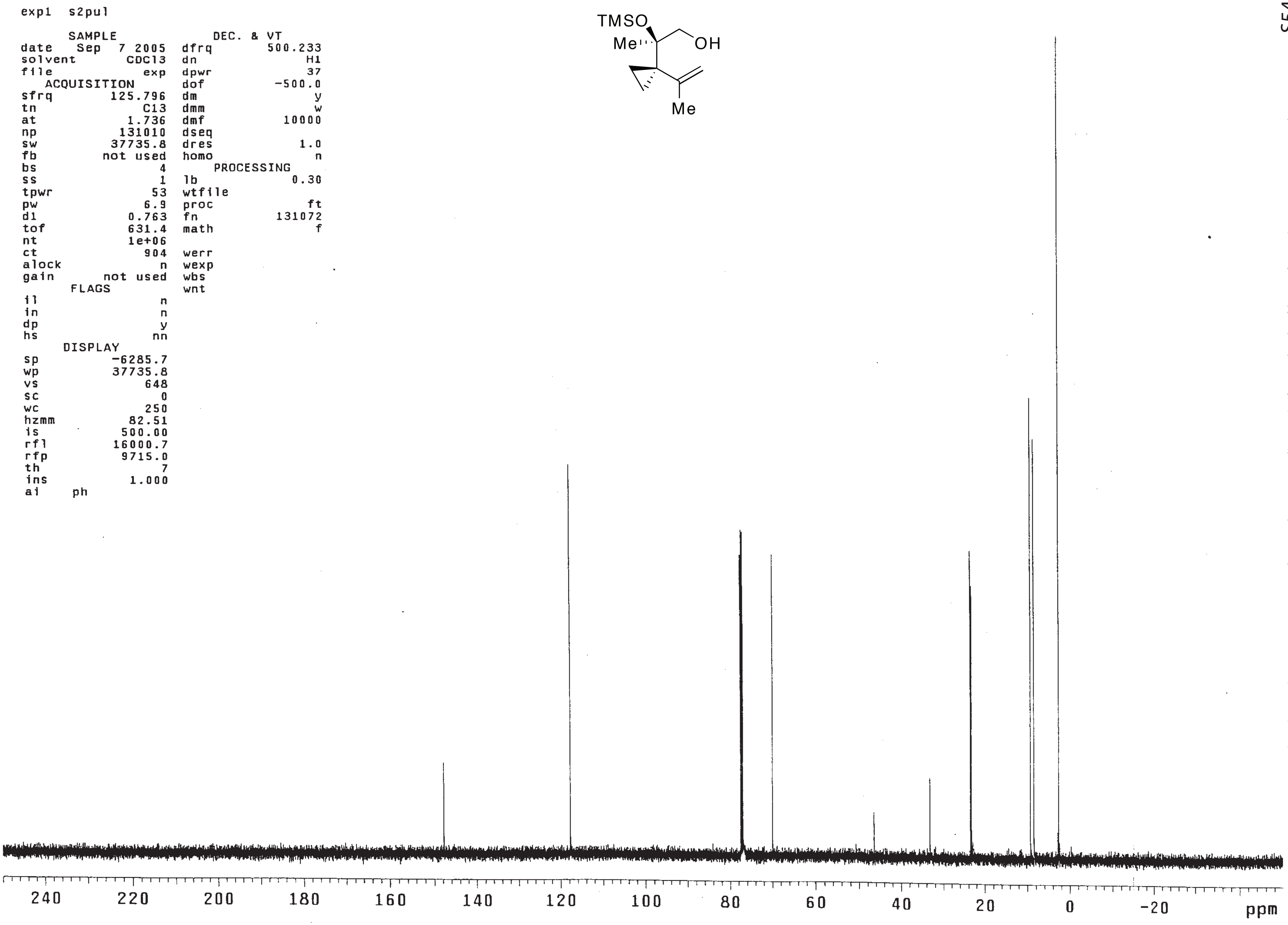
(2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester



```
exp903  s2pul

                     DEC. & VT
                 dfrq       125.795
                 dn             C13
                 dpwr            37
                 dof              0
                 dm             nnn
                 dmm              c
   ACQUISITION   dmf          10000
sfrq     500.235 dseq
tn            H1 dres           1.0
at         3.200 homo             n
np         64000     PROCESSING
sw       10000.0 wtfile
fb      not used proc            ft
bs             4 fn          131072
ss             1 math             f
tpwr          59
pw           9.8 werr
d1        15.000 wexp
tof       1498.2 wbs
nt            32 wnt
ct            32
alock          n
gain    not used
      FLAGS
il             n
in             n
dp             y
hs            nn
     DISPLAY
sp        -250.2
wp        6252.7
vs           151
sc             0
wc           250
hzmm       25.01
is        100.00
rfl       4632.5
rfp       3636.7
th             7
ins        3.000
nm    ph
```

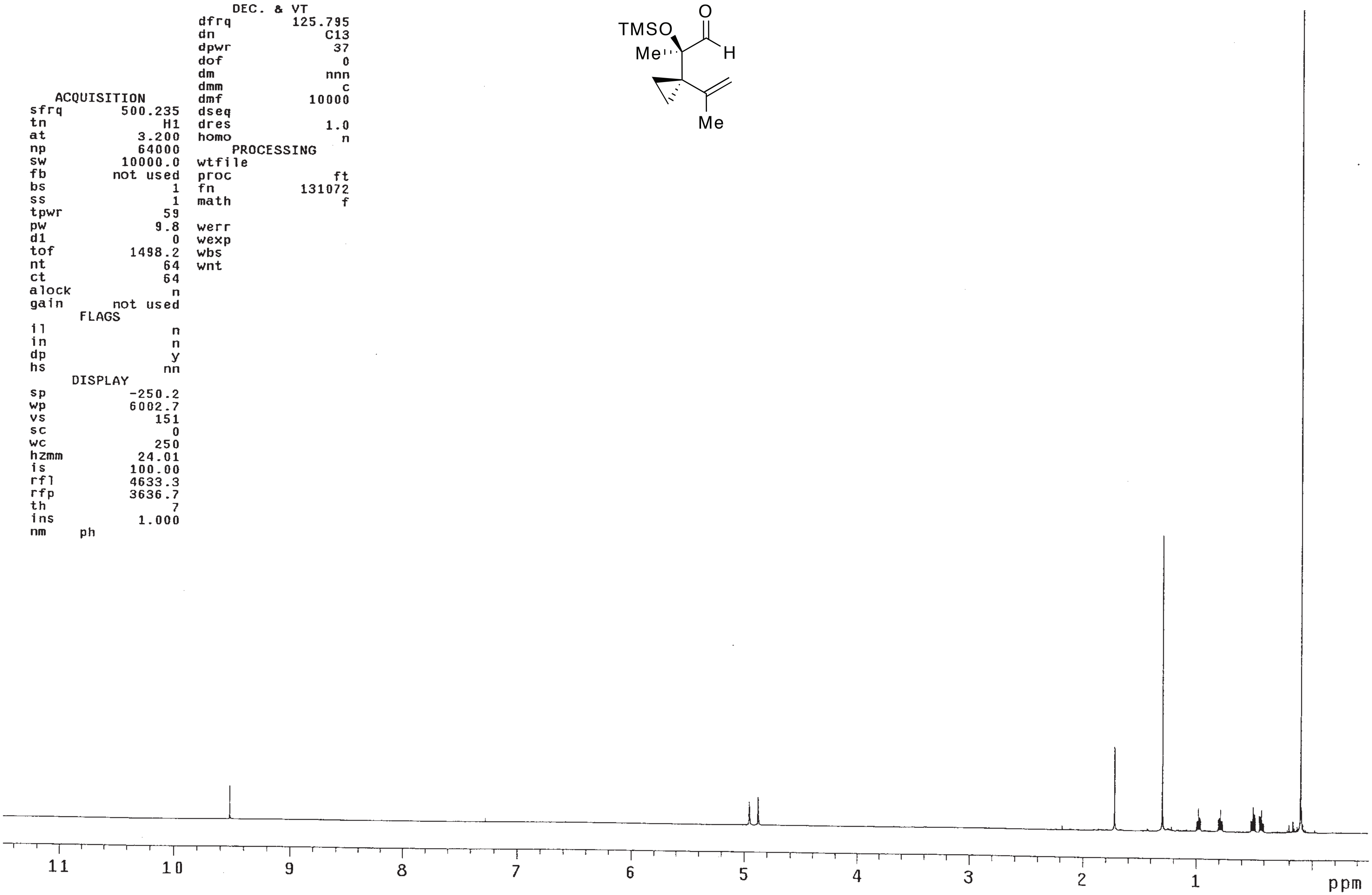
(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propan-1-ol



```
exp1  s2pul

      SAMPLE               DEC. & VT
date   Sep  7 2005  dfrq          500.233
solvent       CDCl3  dn                 H1
file            exp  dpwr               37
   ACQUISITION      dof            -500.0
sfrq        125.796  dm                  y
tn              C13  dmm                 w
at            1.736  dmf             10000
np           131010  dseq
sw          37735.8  dres              1.0
fb         not used  homo                n
bs                4      PROCESSING
ss                1  lb               0.30
tpwr             53  wtfile
pw              6.9  proc               ft
d1            0.763  fn             131072
tof           631.4  math                f
nt           1e+06
ct              904  werr
alock             n  wexp
gain       not used  wbs
      FLAGS          wnt
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6285.7
wp          37735.8
vs              648
sc                0
wc              250
hzmm          82.51
is           500.00
rfl         16000.7
rfp          9715.0
th                7
ins           1.000
ai     ph
```

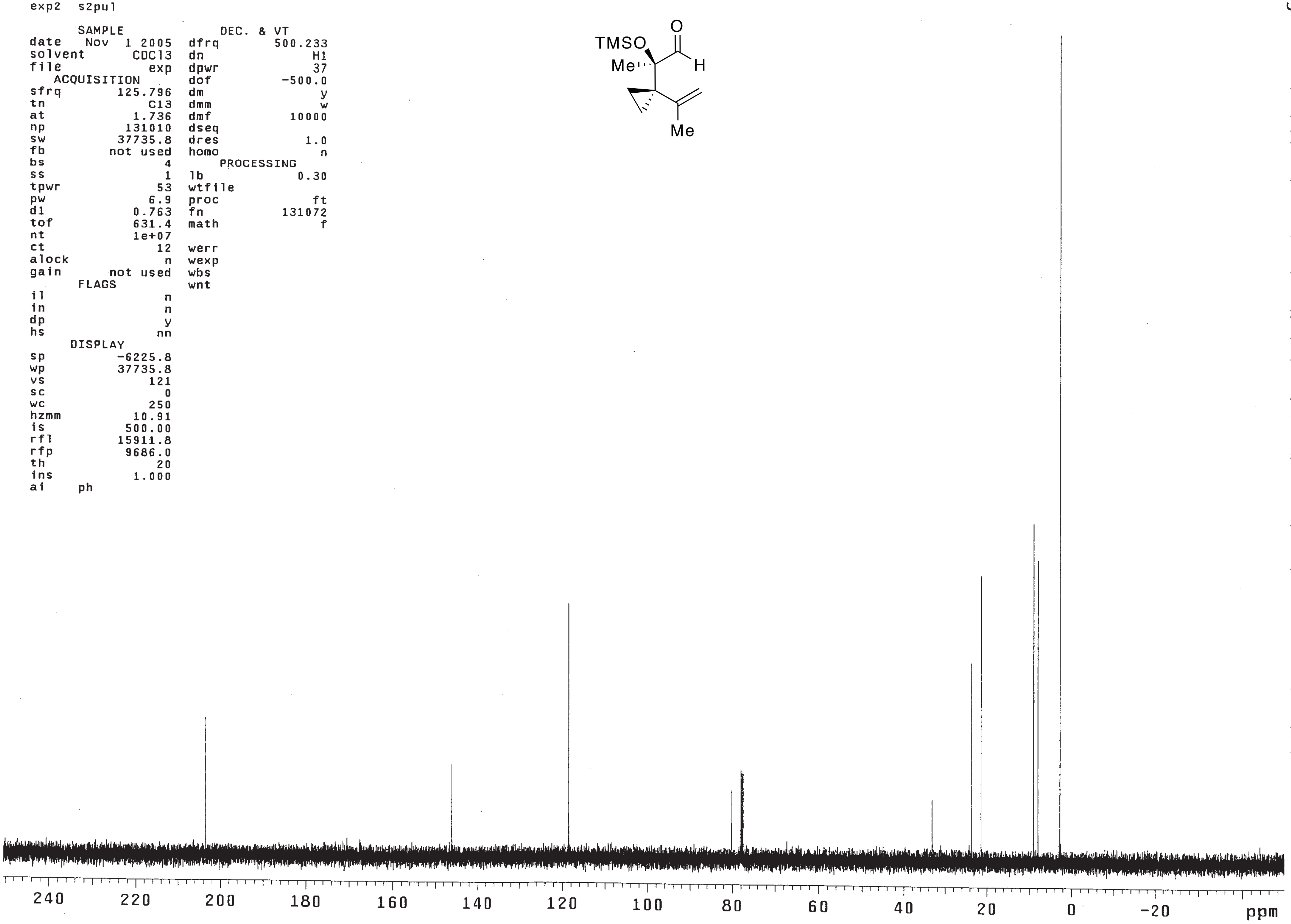
(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propan-1-ol



```
exp1  s2pul

                     DEC. & VT
               dfrq         125.795
               dn               C13
               dpwr              37
               dof                0
               dm               nnn
               dmm                c
   ACQUISITION dmf            10000
sfrq   500.235 dseq
tn          H1 dres             1.0
at       3.200 homo               n
np       64000     PROCESSING
sw     10000.0 wtfile
fb    not used proc              ft
bs           1 fn            131072
ss           1 math               f
tpwr        59
pw         9.8 werr
d1           0 wexp
tof     1498.2 wbs
nt          64 wnt
ct          64
alock        n
gain  not used
      FLAGS
il           n
in           n
dp           y
hs          nn
     DISPLAY
sp      -250.2
wp      6002.7
vs         151
sc           0
wc         250
hzmm     24.01
is      100.00
rfl     4633.3
rfp     3636.7
th           7
ins      1.000
nm    ph
```

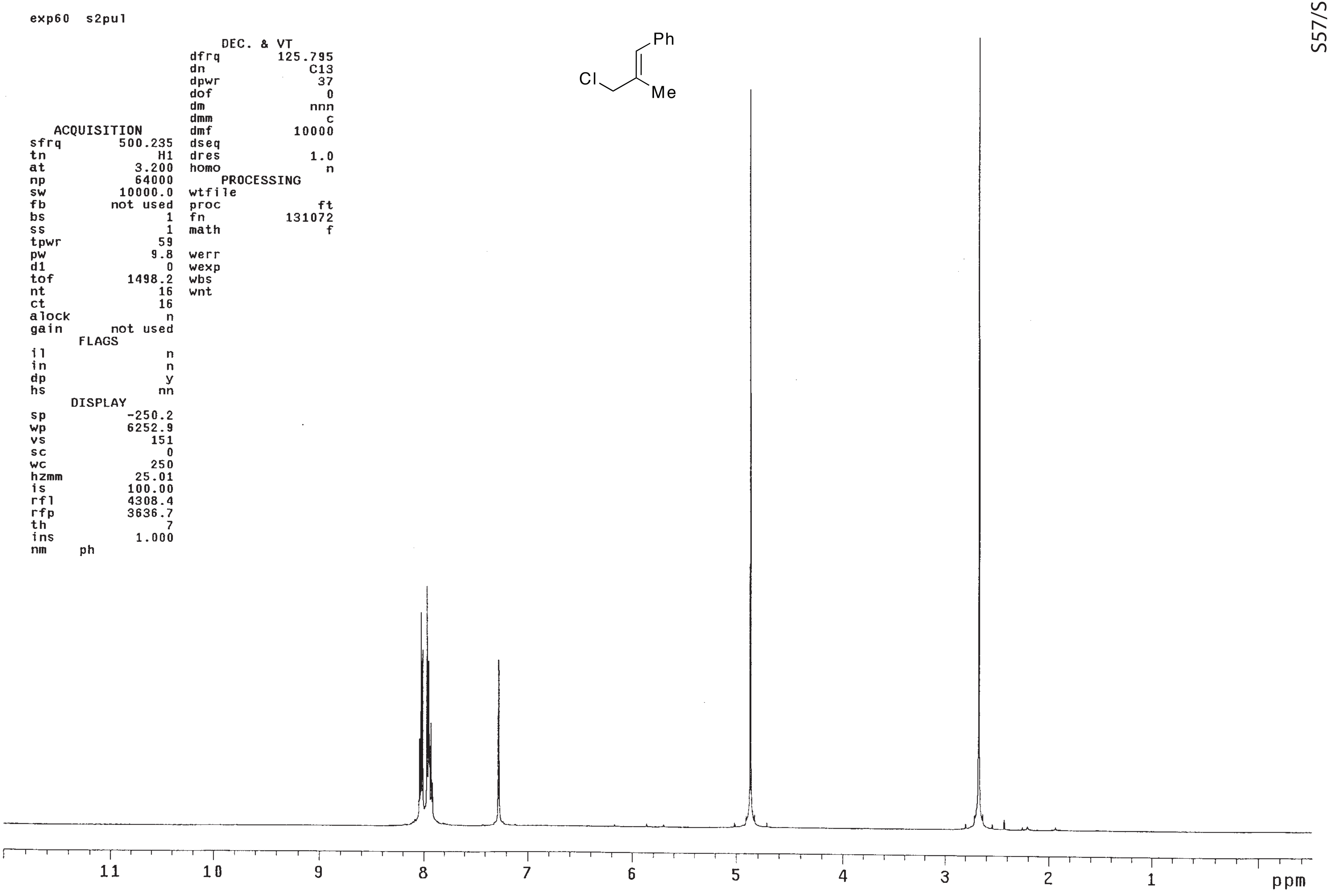
(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde



```
exp2  s2pul

      SAMPLE               DEC. & VT
date   Nov  1 2005   dfrq        500.233
solvent      CDCl3   dn               H1
file           exp   dpwr             37
   ACQUISITION       dof          -500.0
sfrq       125.796   dm                y
tn             C13   dmm               w
at           1.736   dmf           10000
np          131010   dseq
sw         37735.8   dres            1.0
fb        not used   homo              n
bs               4        PROCESSING
ss               1   lb             0.30
tpwr            53   wtfile
pw             6.9   proc             ft
d1           0.763   fn           131072
tof          631.4   math              f
nt           1e+07
ct              12   werr
alock            n   wexp
gain      not used   wbs
      FLAGS          wnt
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -6225.8
wp         37735.8
vs             121
sc               0
wc             250
hzmm         10.91
is          500.00
rfl        15911.8
rfp         9686.0
th              20
ins          1.000
ai     ph
```

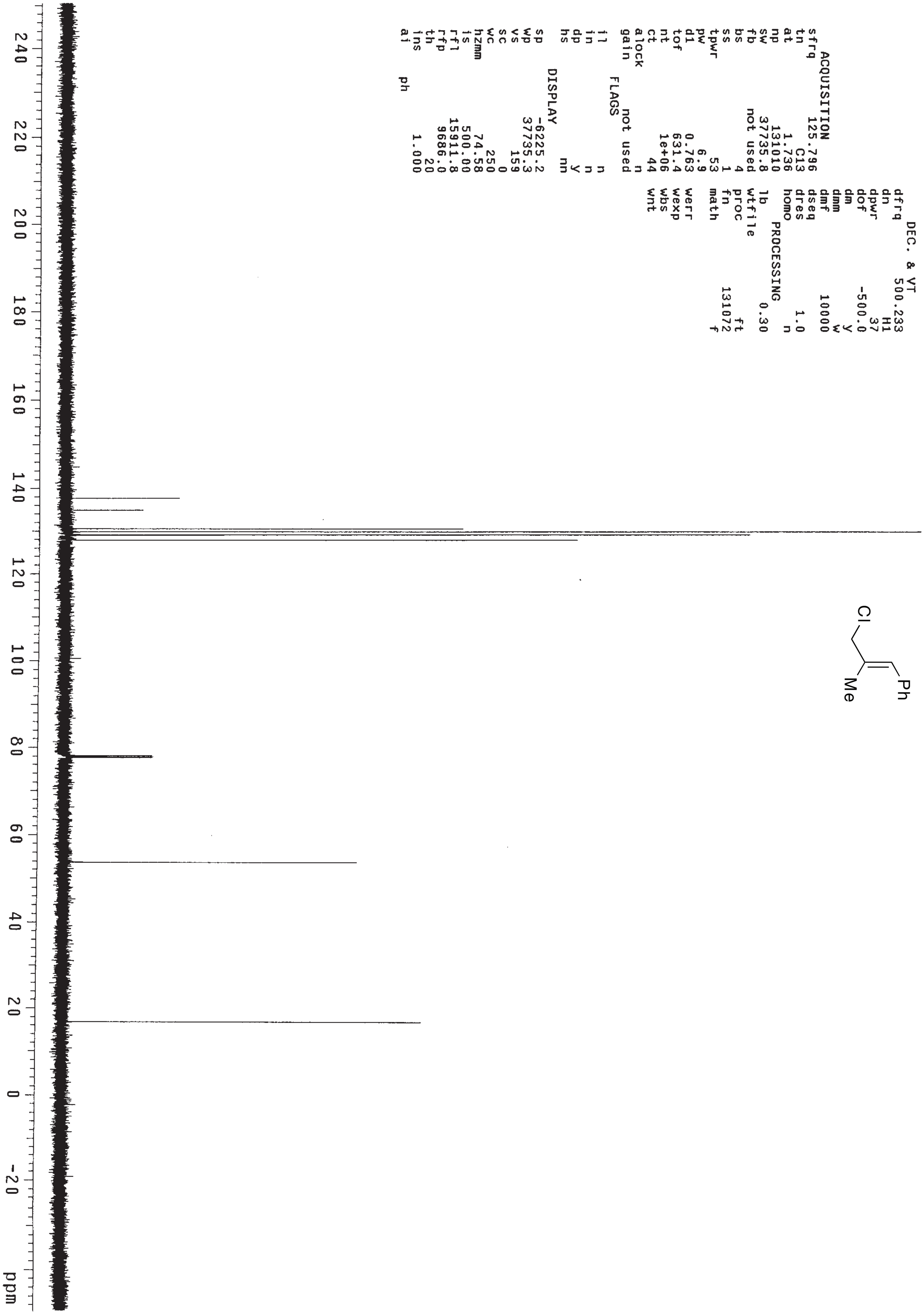
(2*R*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionaldehyde



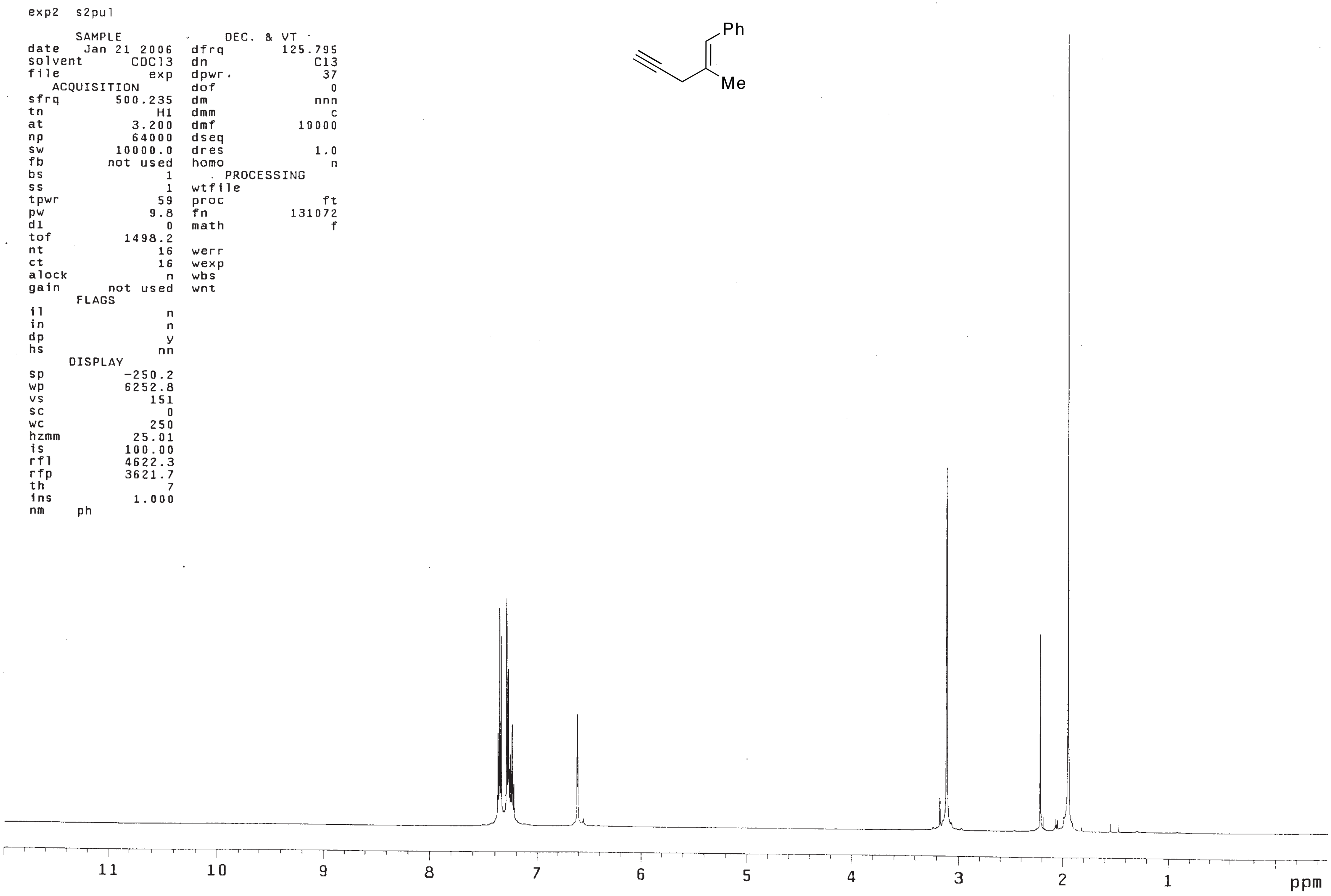
```
exp60  s2pul

                            DEC. & VT
                        dfrq        125.795
                        dn              C13
                        dpwr             37
                        dof               0
                        dm              nnn
                        dmm               c
   ACQUISITION          dmf           10000
sfrq        500.235     dseq
tn               H1     dres            1.0
at            3.200     homo              n
np            64000         PROCESSING
sw          10000.0     wtfile
fb         not used     proc             ft
bs                1     fn           131072
ss                1     math              f
tpwr             59
pw              9.8     werr
d1                0     wexp
tof          1498.2     wbs
nt               16     wnt
ct               16
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -250.2
wp           6252.9
vs              151
sc                0
wc              250
hzmm          25.01
is           100.00
rfl          4308.4
rfp          3636.7
th                7
ins           1.000
nm     ph
```

E-(5-Chloro-4-methyl-pent-3-enyl)-benzene



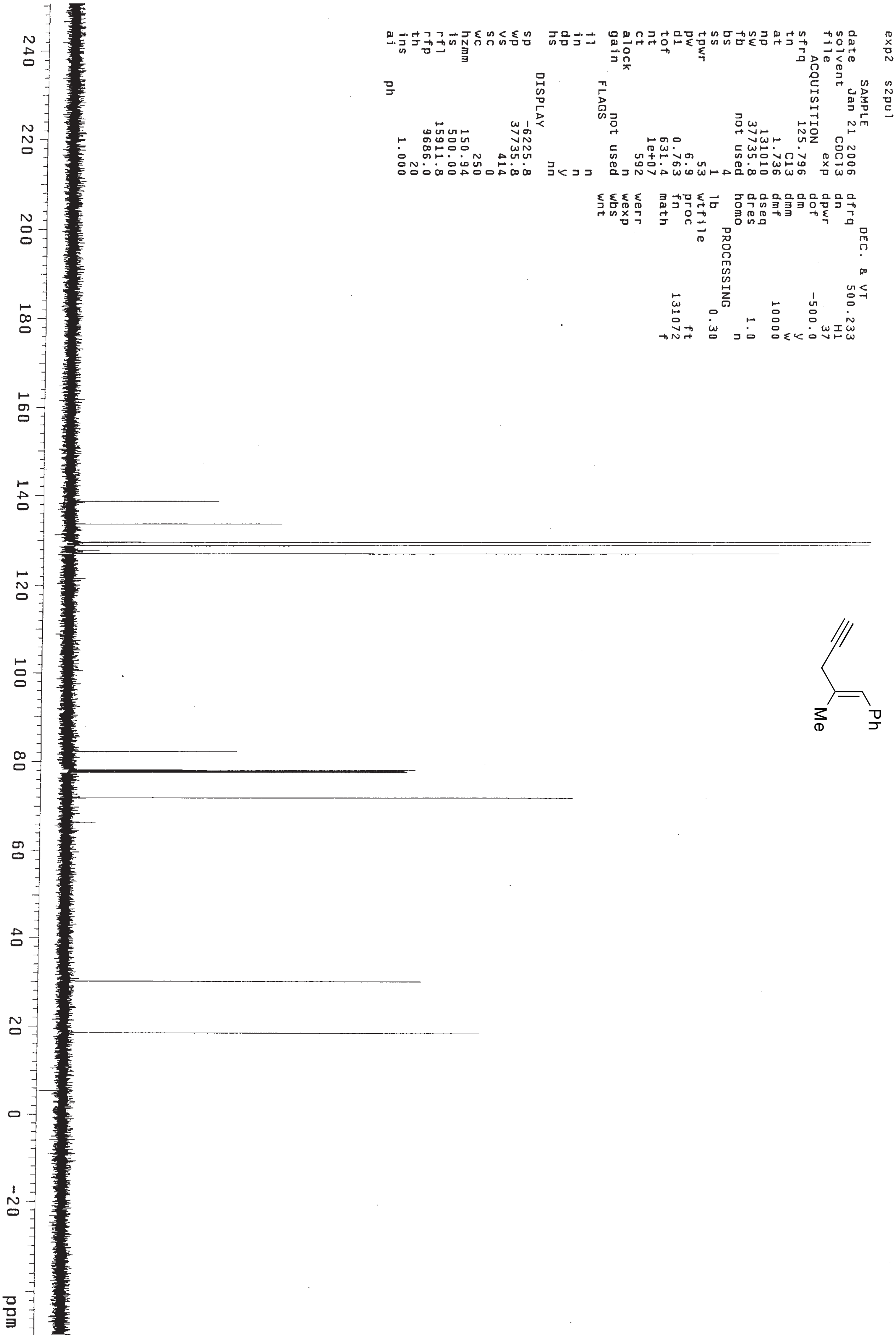
E-(5-Chloro-4-methyl-pent-3-enyl)-benzene



```
exp2  s2pul

      SAMPLE                 DEC. & VT
date   Jan 21 2006  dfrq        125.795
solvent      CDCl3  dn              C13
file           exp  dpwr             37
   ACQUISITION      dof               0
sfrq       500.235  dm              nnn
tn              H1  dmm               c
at           3.200  dmf           10000
np           64000  dseq
sw         10000.0  dres            1.0
fb        not used  homo              n
bs               1     PROCESSING
ss               1  wtfile
tpwr            59  proc             ft
pw             9.8  fn           131072
d1               0  math              f
tof         1498.2
nt              16  werr
ct              16  wexp
alock            n  wbs
gain      not used  wnt
      FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp          -250.2
wp          6252.8
vs             151
sc               0
wc             250
hzmm         25.01
is          100.00
rfl         4622.3
rfp         3621.7
th               7
ins          1.000
nm    ph
```

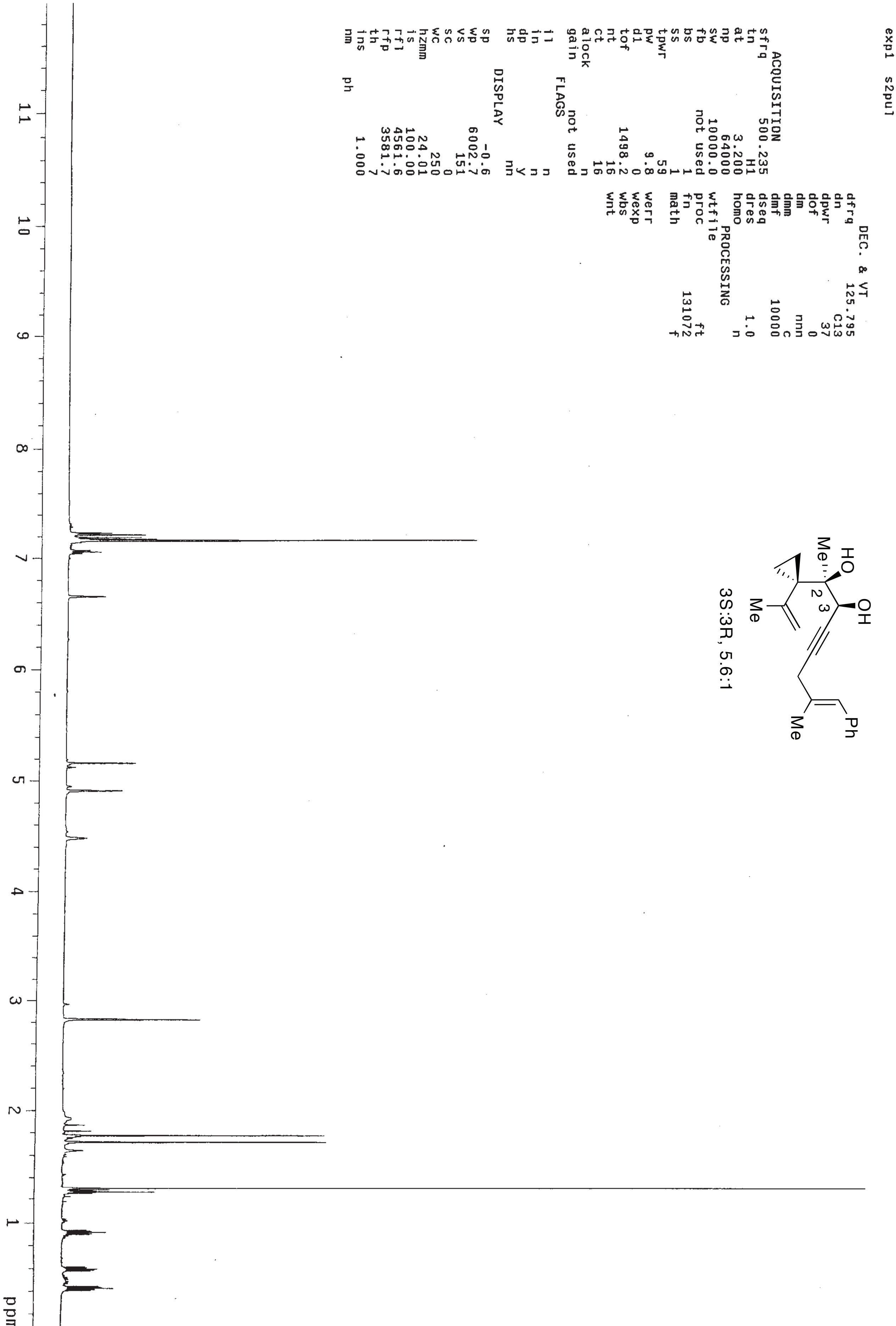
E-(2-Methyl-pent-1-en-4-ynyl)-benzene



```
exp2  s2pul

       SAMPLE                   DEC. & VT
date    Jan 21 2006   dfrq        500.233
solvent      CDCl3    dn               H1
file           exp    dpwr             37
   ACQUISITION        dof          -500.0
sfrq       125.796    dm                y
tn             C13    dmm               w
at           1.736    dmf           10000
np          131010    dseq
sw         37735.8    dres            1.0
fb        not used    homo              n
bs               4       PROCESSING
ss               1    lb             0.30
tpwr            53    wtfile
pw             6.9    proc             ft
d1           0.763    fn           131072
tof          631.4    math              f
nt           1e+07
ct             592    werr
alock            n    wexp
gain      not used    wbs
      FLAGS           wnt
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -6225.8
wp         37735.8
vs             414
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        15911.8
rfp         9686.0
th              20
ins          1.000
ai     ph
```

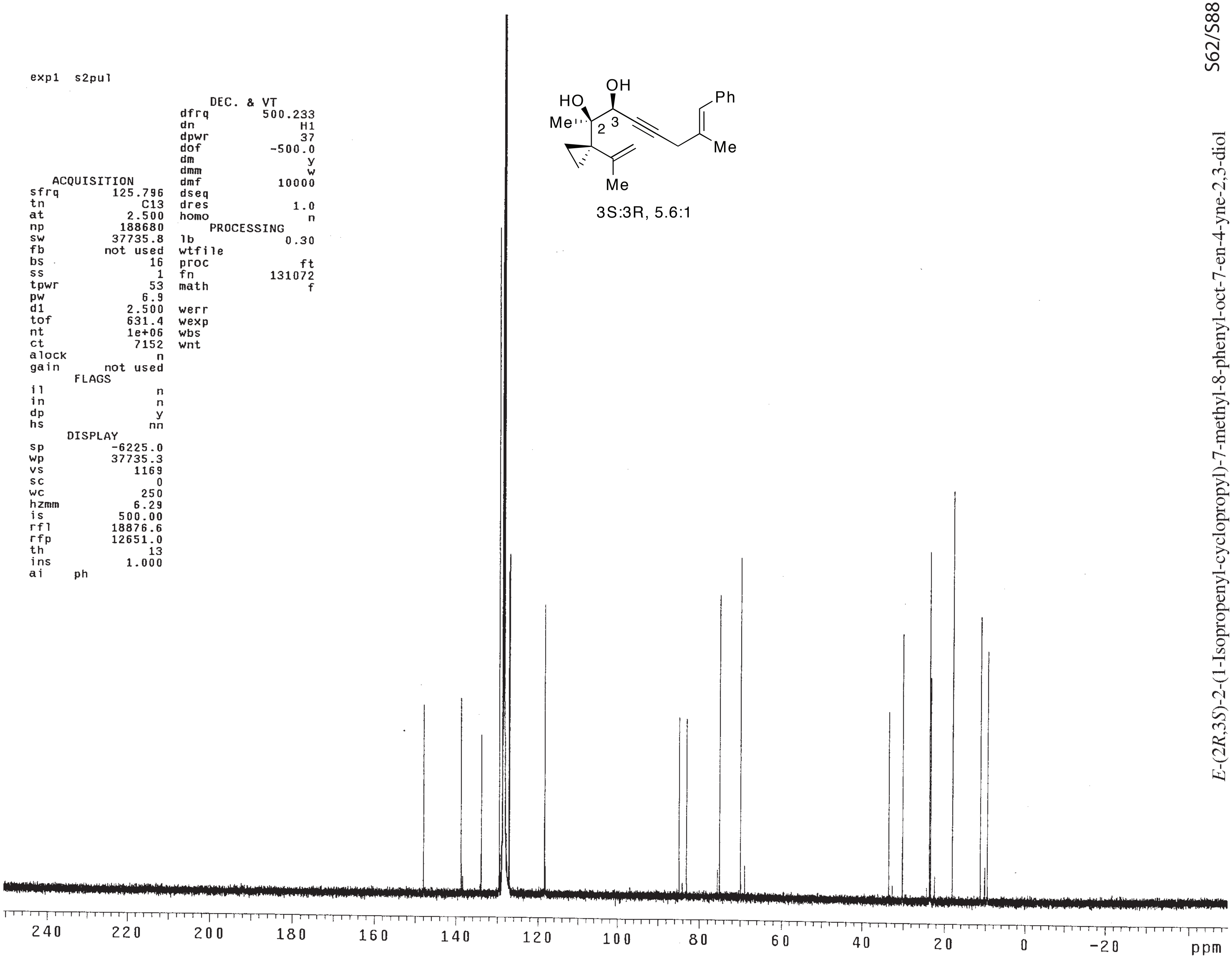
E-(2-Methyl-pent-1-en-4-ynyl)-benzene



E-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-7-methyl-8-phenyl-oct-7-en-4-yne-2,3-diol

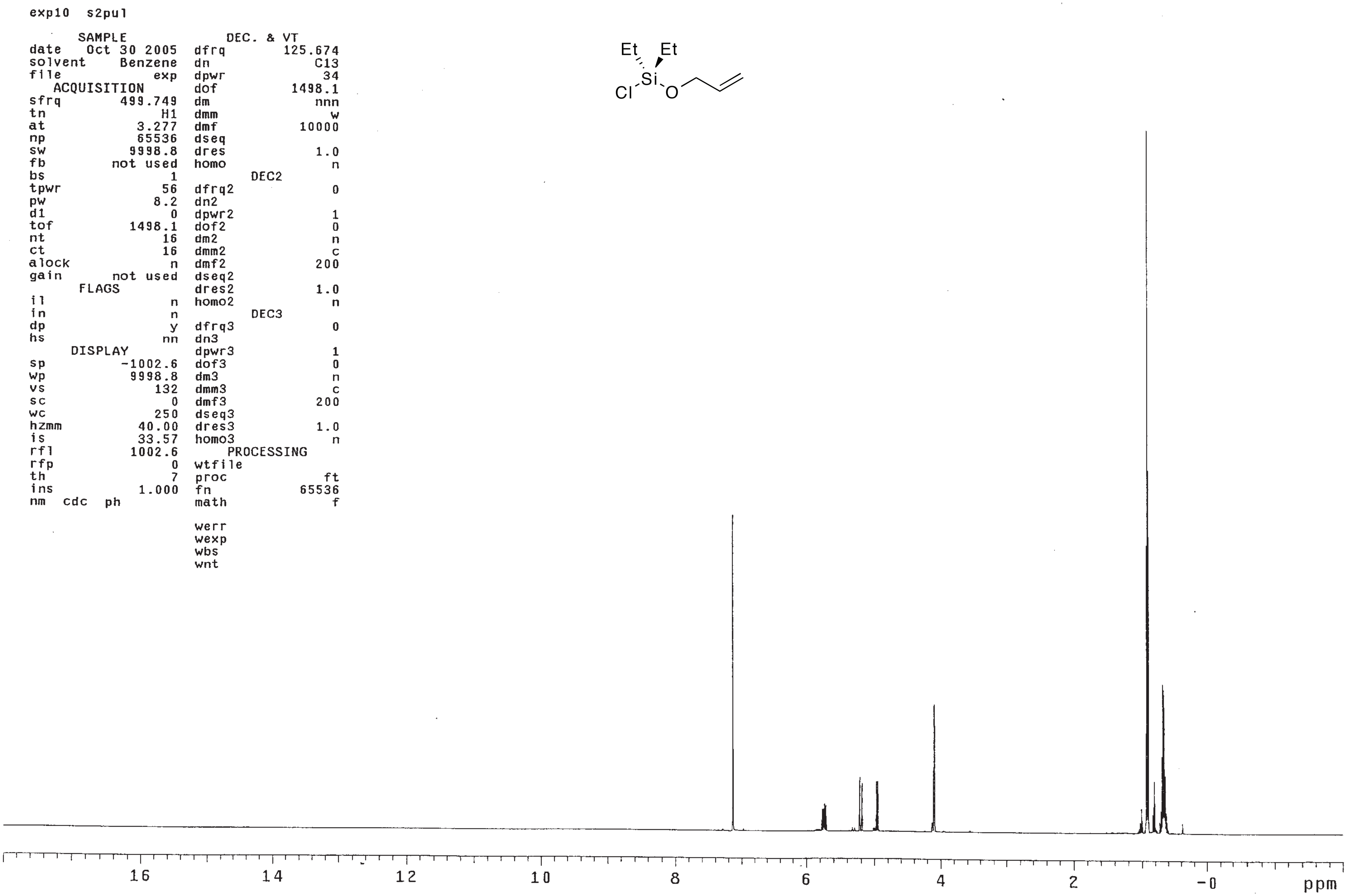
```
exp1  s2pul

                              DEC. & VT
                          dfrq         500.233
                          dn                H1
                          dpwr              37
                          dof           -500.0
                          dm                 y
                          dmm                w
   ACQUISITION            dmf            10000
sfrq        125.796       dseq
tn              C13       dres             1.0
at            2.500       homo               n
np           188680          PROCESSING
sw          37735.8       lb              0.30
fb         not used       wtfile
bs               16       proc              ft
ss                1       fn            131072
tpwr             53       math               f
pw              6.9
d1            2.500       werr
tof           631.4       wexp
nt            1e+06       wbs
ct             7152       wnt
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
hs               nn
      DISPLAY
sp          -6225.0
wp          37735.3
vs             1169
sc                0
wc              250
hzmm           6.29
is           500.00
rfl         18876.6
rfp         12651.0
th               13
ins           1.000
ai    ph
```



3S:3R, 5.6:1

E-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-7-methyl-8-phenyl-oct-7-en-4-yne-2,3-diol

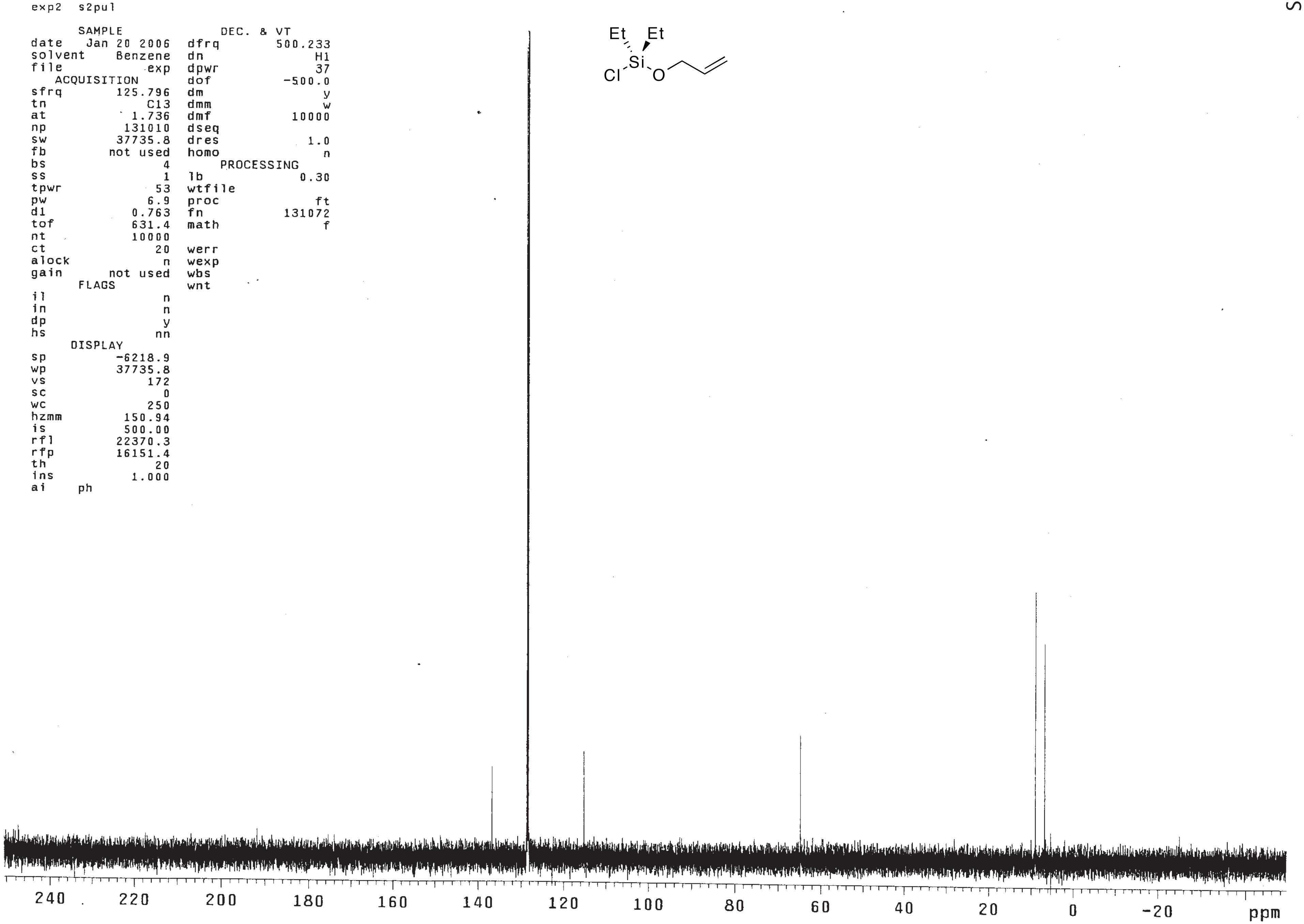


```
exp10  s2pul

     SAMPLE                DEC. & VT
date   Oct 30 2005  dfrq        125.674
solvent    Benzene  dn              C13
file           exp  dpwr             34
   ACQUISITION      dof          1498.1
sfrq       499.749  dm              nnn
tn              H1  dmm               w
at           3.277  dmf           10000
np           65536  dseq
sw          9998.8  dres            1.0
fb        not used  homo              n
bs               1           DEC2
tpwr            56  dfrq2             0
pw             8.2  dn2
d1               0  dpwr2             1
tof         1498.1  dof2              0
nt              16  dm2               n
ct              16  dmm2              c
alock            n  dmf2            200
gain      not used  dseq2
      FLAGS         dres2           1.0
il               n  homo2             n
in               n           DEC3
dp               y  dfrq3             0
hs              nn  dn3
     DISPLAY        dpwr3             1
sp         -1002.6  dof3              0
wp          9998.8  dm3               n
vs             132  dmm3              c
sc               0  dmf3            200
wc             250  dseq3
hzmm         40.00  dres3           1.0
is           33.57  homo3             n
rfl         1002.6       PROCESSING
rfp              0  wtfile
th               7  proc             ft
ins          1.000  fn            65536
nm  cdc  ph         math              f

                    werr
                    wexp
                    wbs
                    wnt
```

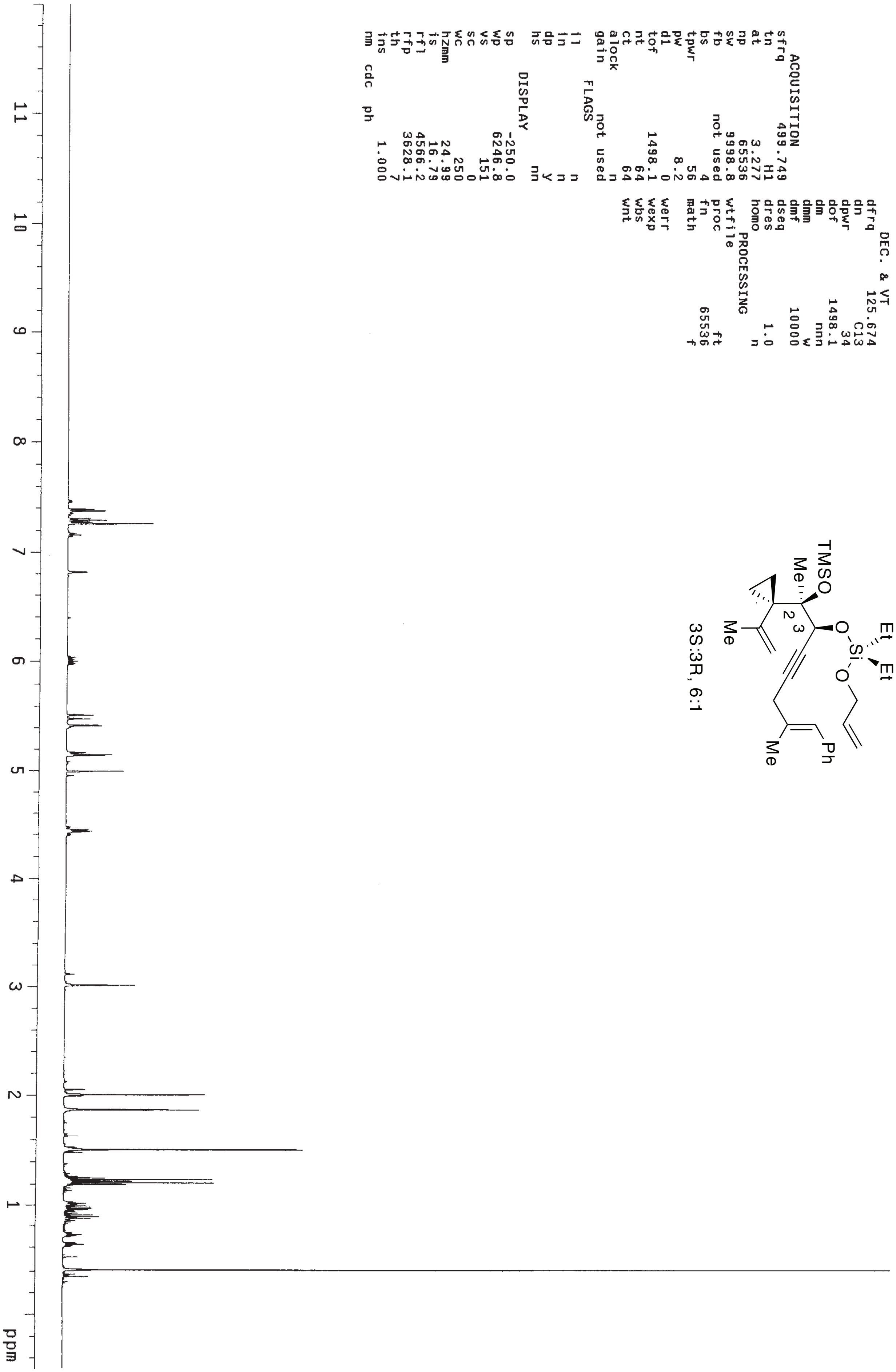
Allyloxy-chloro-diethyl-silane



```
exp2  s2pul

      SAMPLE                  DEC. & VT
date   Jan 20 2006   dfrq          500.233
solvent    Benzene   dn                 H1
file           exp   dpwr               37
   ACQUISITION       dof            -500.0
sfrq       125.796   dm                  y
tn             C13   dmm                 w
at           1.736   dmf             10000
np          131010   dseq
sw         37735.8   dres              1.0
fb        not used   homo                n
bs               4      PROCESSING
ss               1   lb               0.30
tpwr            53   wtfile
pw             6.9   proc               ft
d1           0.763   fn             131072
tof          631.4   math                f
nt           10000
ct              20   werr
alock            n   wexp
gain      not used   wbs
     FLAGS           wnt
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -6218.9
wp         37735.8
vs             172
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        22370.3
rfp        16151.4
th              20
ins          1.000
ai    ph
```

Allyloxy-chloro-diethyl-silane



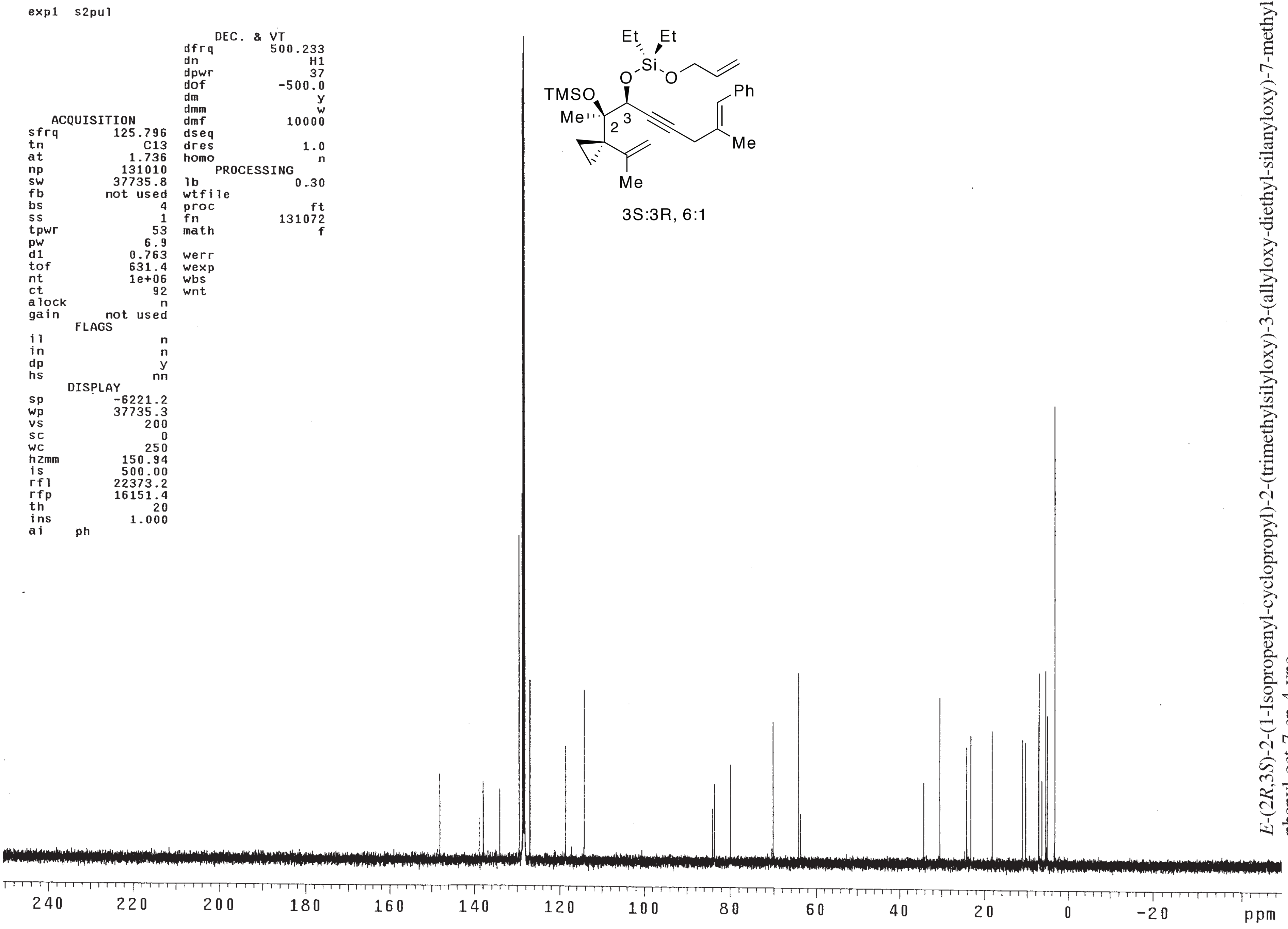
```
exp1  s2pul

      ACQUISITION
sfrq       499.749
tn              H1
at           3.277
np           65536
sw          9998.8
fb        not used
bs               4
tpwr            56
pw             8.2
d1               0
tof         1498.1
nt              64
ct              64
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp          -250.0
wp          6246.8
vs             151
sc               0
wc             250
hzmm         24.99
is           16.79
rfl         4566.2
rfp         3628.1
th               7
ins          1.000
nm  cdc  ph

      DEC. & VT
dfrq       125.674
dn             C13
dpwr            34
dof         1498.1
dm             nnn
dmm              w
dmf          10000
dseq
dres           1.0
homo             n
      PROCESSING
wtfile
proc            ft
fn           65536
math             f

werr
wexp
wbs
wnt
```

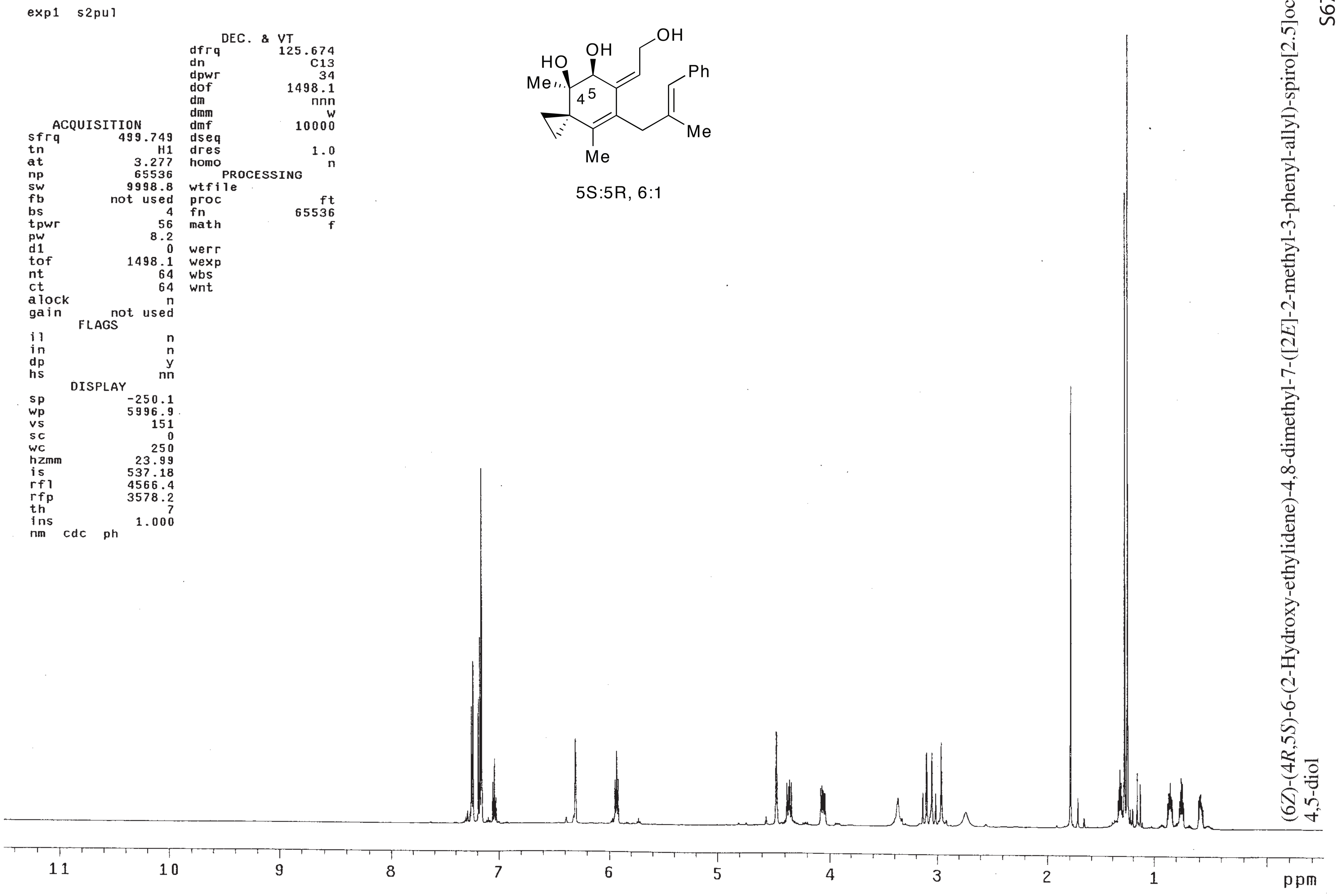
E-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethylsilyloxy)-3-(allyloxy-diethyl-silanyloxy)-7-methyl-8-phenyl-oct-7-en-4-yne



```
exp1  s2pul

                        DEC. & VT
                      dfrq        500.233
                      dn               H1
                      dpwr             37
                      dof          -500.0
                      dm                y
                      dmm               w
   ACQUISITION        dmf           10000
sfrq        125.796   dseq
tn              C13   dres            1.0
at            1.736   homo              n
np           131010       PROCESSING
sw          37735.8   lb             0.30
fb         not used   wtfile
bs                4   proc             ft
ss                1   fn           131072
tpwr             53   math              f
pw              6.9
d1            0.763   werr
tof           631.4   wexp
nt           1e+06    wbs
ct               92   wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -6221.2
wp          37735.3
vs              200
sc                0
wc              250
hzmm         150.94
is           500.00
rfl         22373.2
rfp         16151.4
th               20
ins           1.000
ai    ph
```

E-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethylsilyloxy)-3-(allyloxy-diethyl-silanyloxy)-7-methyl-8-phenyl-oct-7-en-4-yne

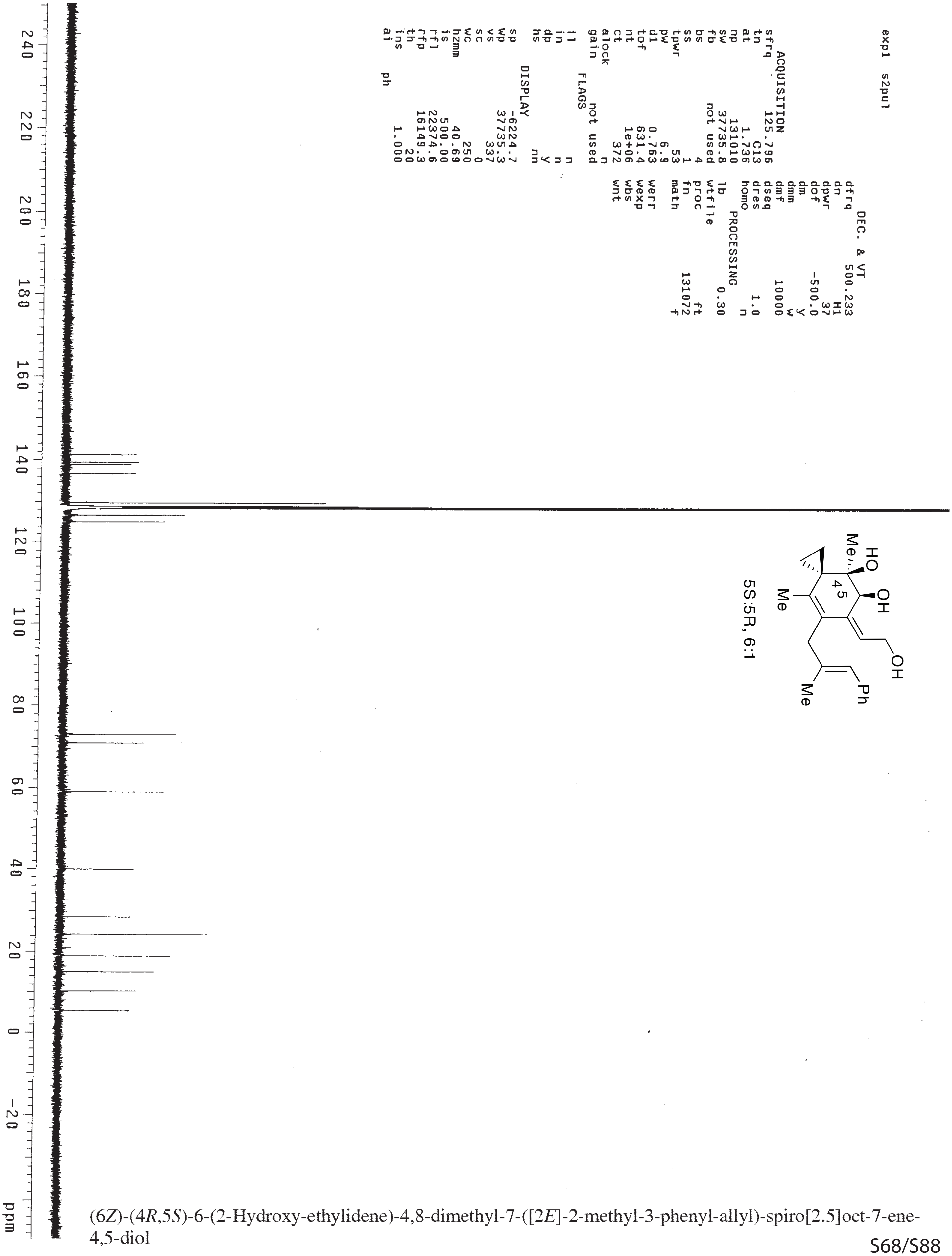


```
exp1  s2pul

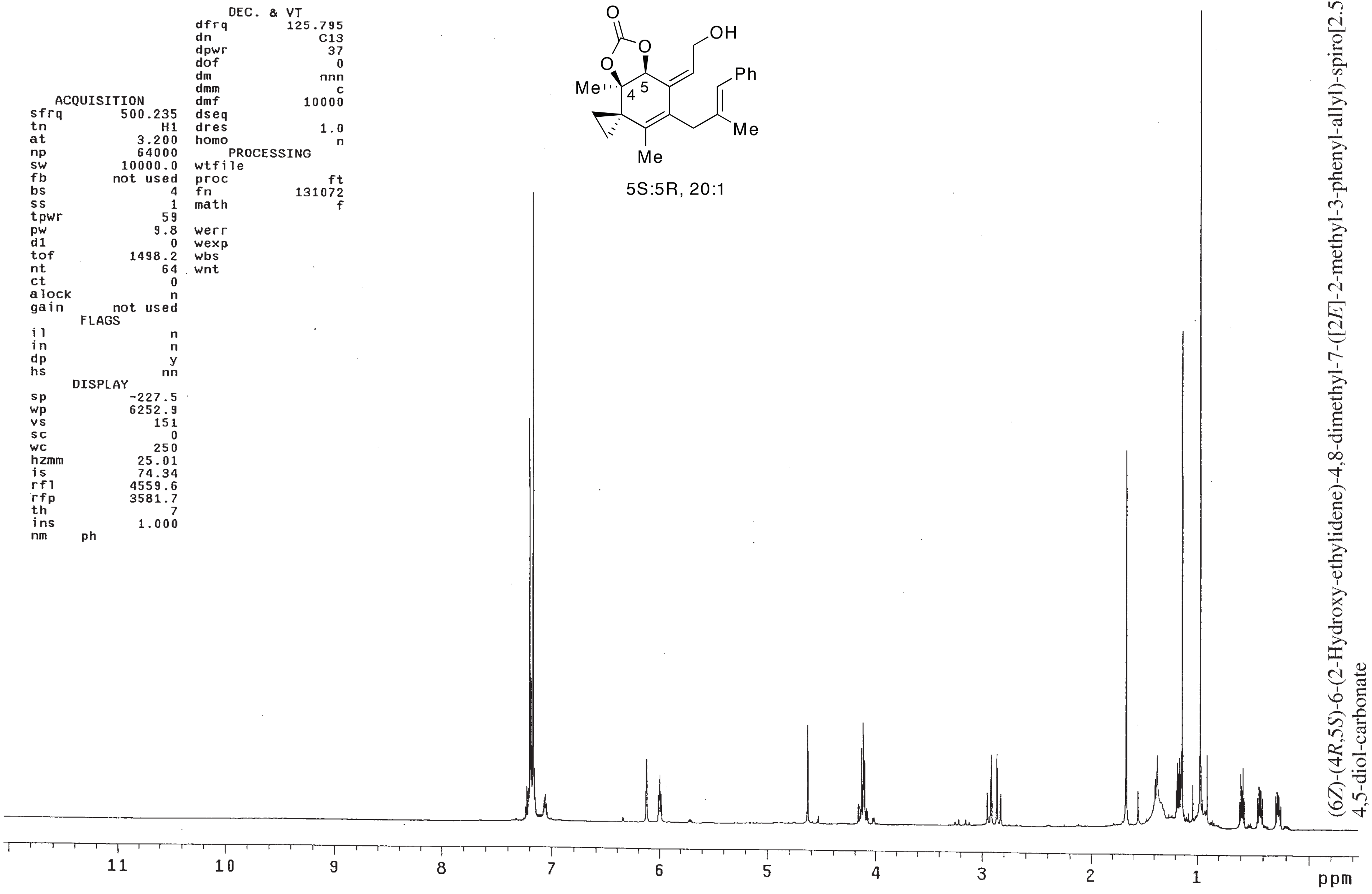
                          DEC. & VT
                   dfrq        125.674
                   dn              C13
                   dpwr             34
                   dof          1498.1
                   dm              nnn
                   dmm               w
   ACQUISITION     dmf           10000
sfrq      499.749  dseq
tn             H1  dres            1.0
at          3.277  homo              n
np          65536     PROCESSING
sw         9998.8  wtfile
fb       not used  proc             ft
bs              4  fn            65536
tpwr           56  math              f
pw            8.2
d1              0  werr
tof        1498.1  wexp
nt             64  wbs
ct             64  wnt
alock           n
gain     not used
      FLAGS
il              n
in              n
dp              y
hs             nn
     DISPLAY
sp         -250.1
wp         5996.9
vs            151
sc              0
wc            250
hzmm        23.99
is         537.18
rfl        4566.4
rfp        3578.2
th              7
ins         1.000
nm  cdc  ph
```

5S:5R, 6:1

(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol



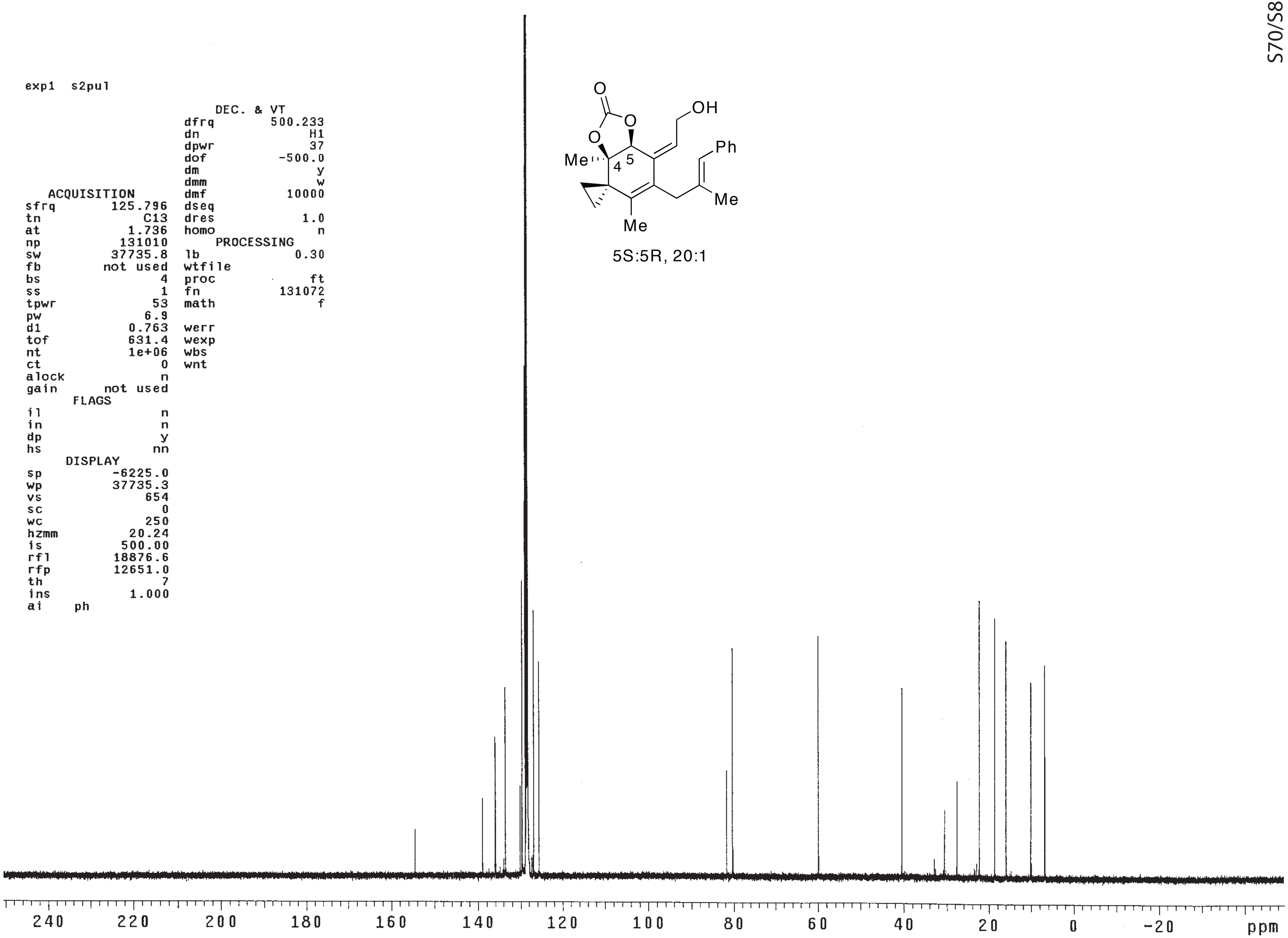
(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol



```
exp1  s2pul

                        DEC. & VT
                   dfrq         125.795
                   dn               C13
                   dpwr              37
                   dof                0
                   dm               nnn
                   dmm                c
   ACQUISITION     dmf            10000
sfrq     500.235   dseq
tn            H1   dres             1.0
at         3.200   homo               n
np         64000       PROCESSING
sw       10000.0   wtfile
fb      not used   proc              ft
bs             4   fn            131072
ss             1   math               f
tpwr          59
pw           9.8   werr
d1             0   wexp
tof       1498.2   wbs
nt            64   wnt
ct             0
alock          n
gain    not used
      FLAGS
il             n
in             n
dp             y
hs            nn
      DISPLAY
sp        -227.5
wp        6252.9
vs           151
sc             0
wc           250
hzmm       25.01
is         74.34
rfl       4559.6
rfp       3581.7
th             7
ins        1.000
nm    ph
```

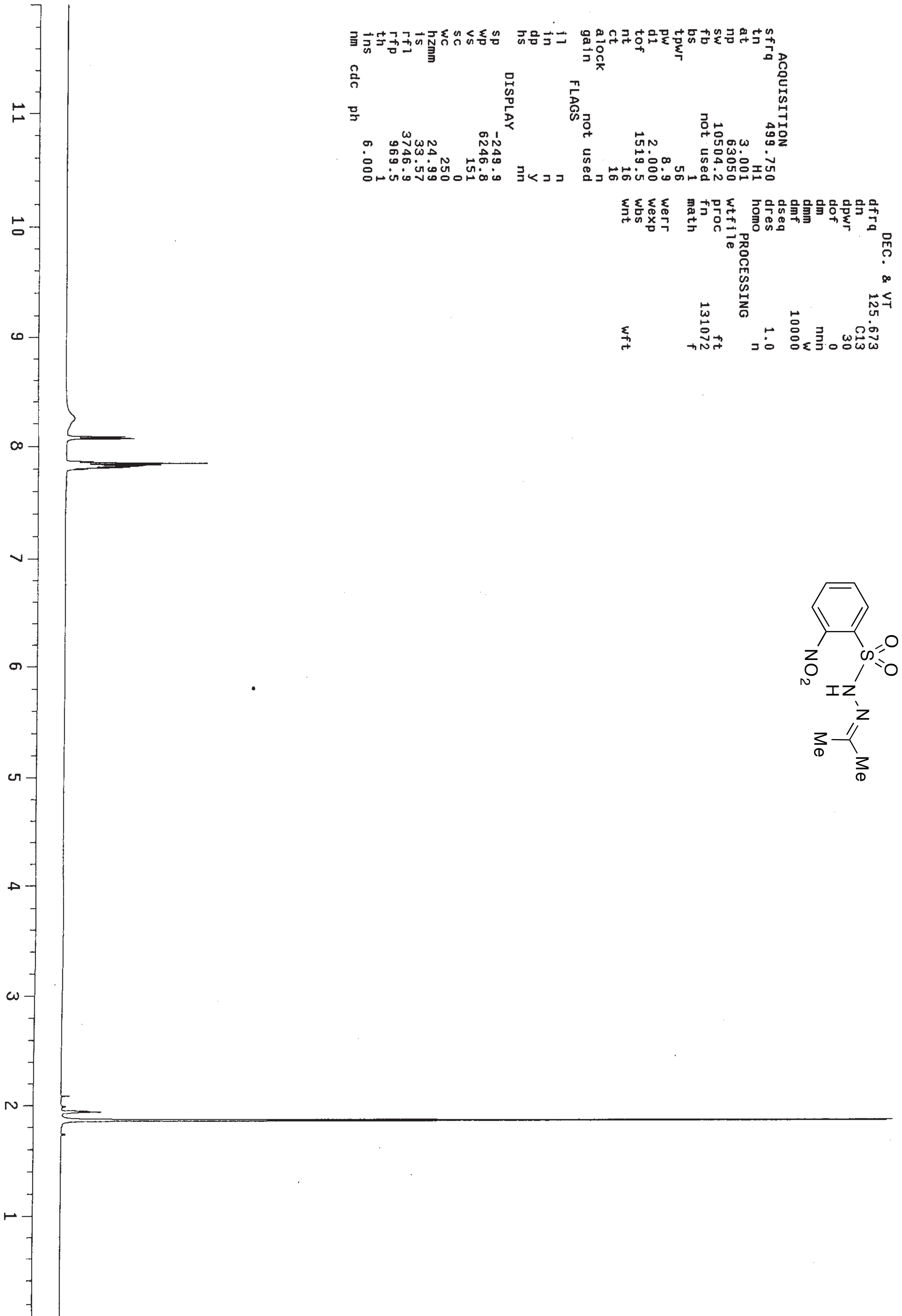
(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol-carbonate



```
exp1  s2pul

                          DEC. & VT
                     dfrq        500.233
                     dn               H1
                     dpwr             37
                     dof          -500.0
                     dm                y
                     dmm               w
   ACQUISITION       dmf           10000
sfrq        125.796  dseq
tn              C13  dres            1.0
at            1.736  homo              n
np           131010        PROCESSING
sw          37735.8  lb             0.30
fb         not used  wtfile
bs                4  proc             ft
ss                1  fn           131072
tpwr             53  math              f
pw              6.9
d1            0.763  werr
tof           631.4  wexp
nt           1e+06   wbs
ct                0  wnt
alock             n
gain       not used
        FLAGS
il                n
in                n
dp                y
hs               nn
       DISPLAY
sp          -6225.0
wp          37735.3
vs              654
sc                0
wc              250
hzmm          20.24
is           500.00
rfl         18876.6
rfp         12651.0
th                7
ins           1.000
ai     ph
```

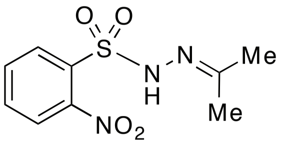
(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol-carbonate

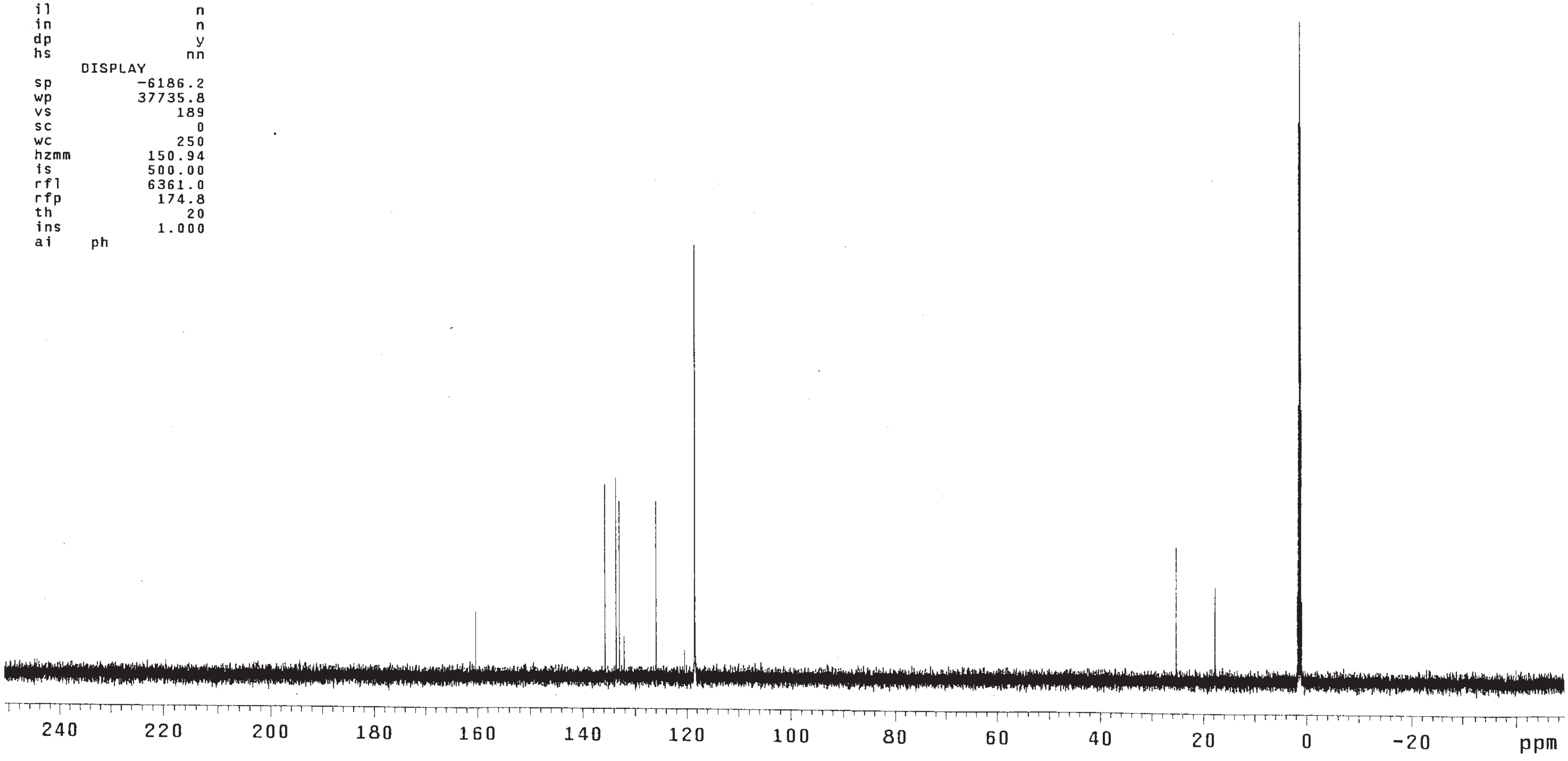


N-Isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine

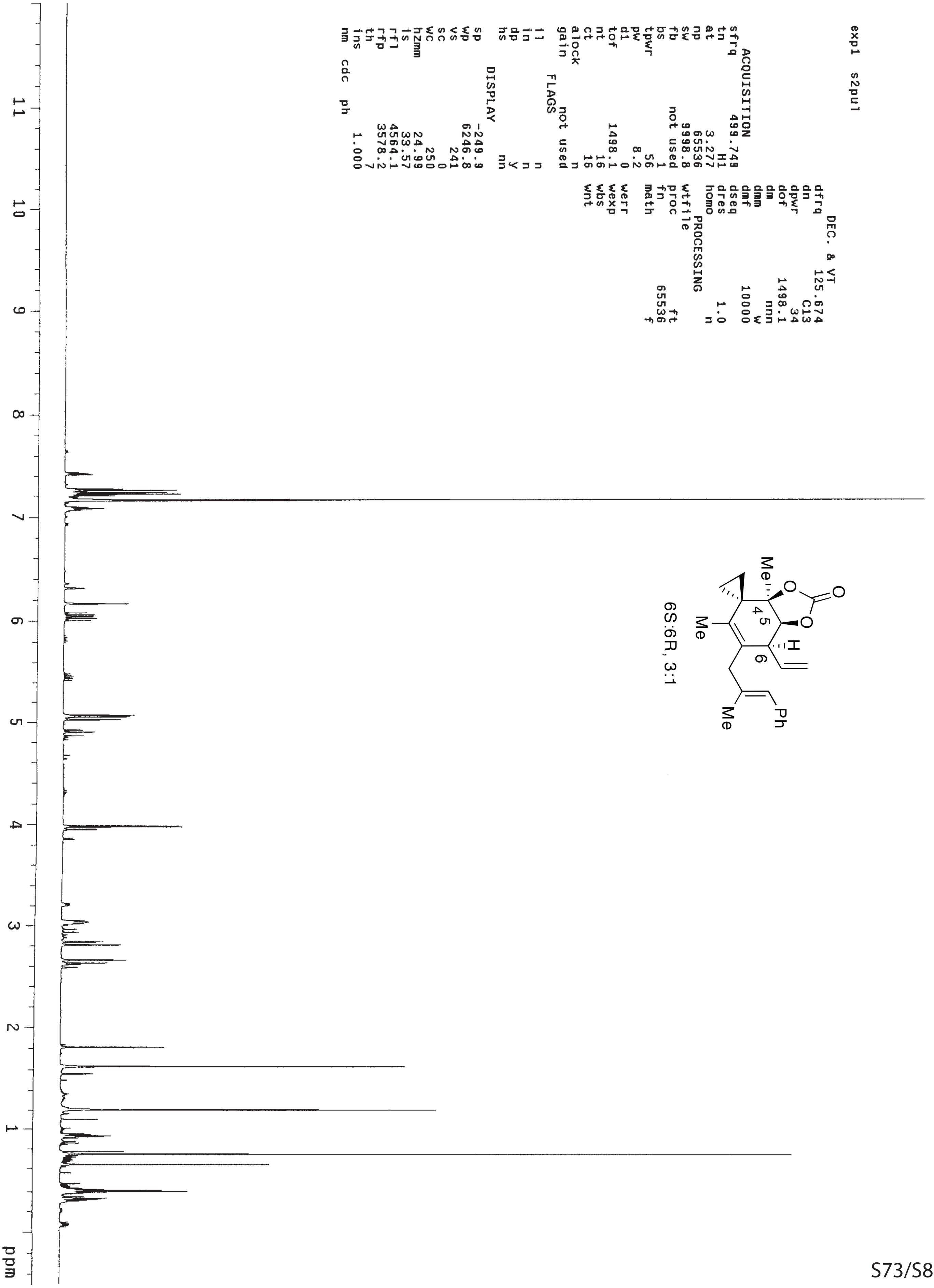
```
exp2  s2pul

      SAMPLE                DEC. & VT
date   Jan 20 2006  dfrq        500.236
solvent acetonitri~ dn               H1
                le  dpwr             37
file           exp  dof          -500.0
   ACQUISITION      dm                y
sfrq       125.796  dmm               w
tn             C13  dmf           10000
at           1.736  dseq
np          131010  dres            1.0
sw         37735.8  homo              n
fb        not used       PROCESSING
bs               4  lb             0.30
ss               1  wtfile
tpwr            53  proc             ft
pw             6.9  fn           131072
d1           0.763  math              f
tof          631.4
nt          1e+06   werr
ct              84  wexp
alock            n  wbs
gain      not used  wnt
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -6186.2
wp         37735.8
vs             189
sc               0
wc             250
hzmm        150.94
is          500.00
rfl         6361.0
rfp          174.8
th              20
ins          1.000
ai    ph
```





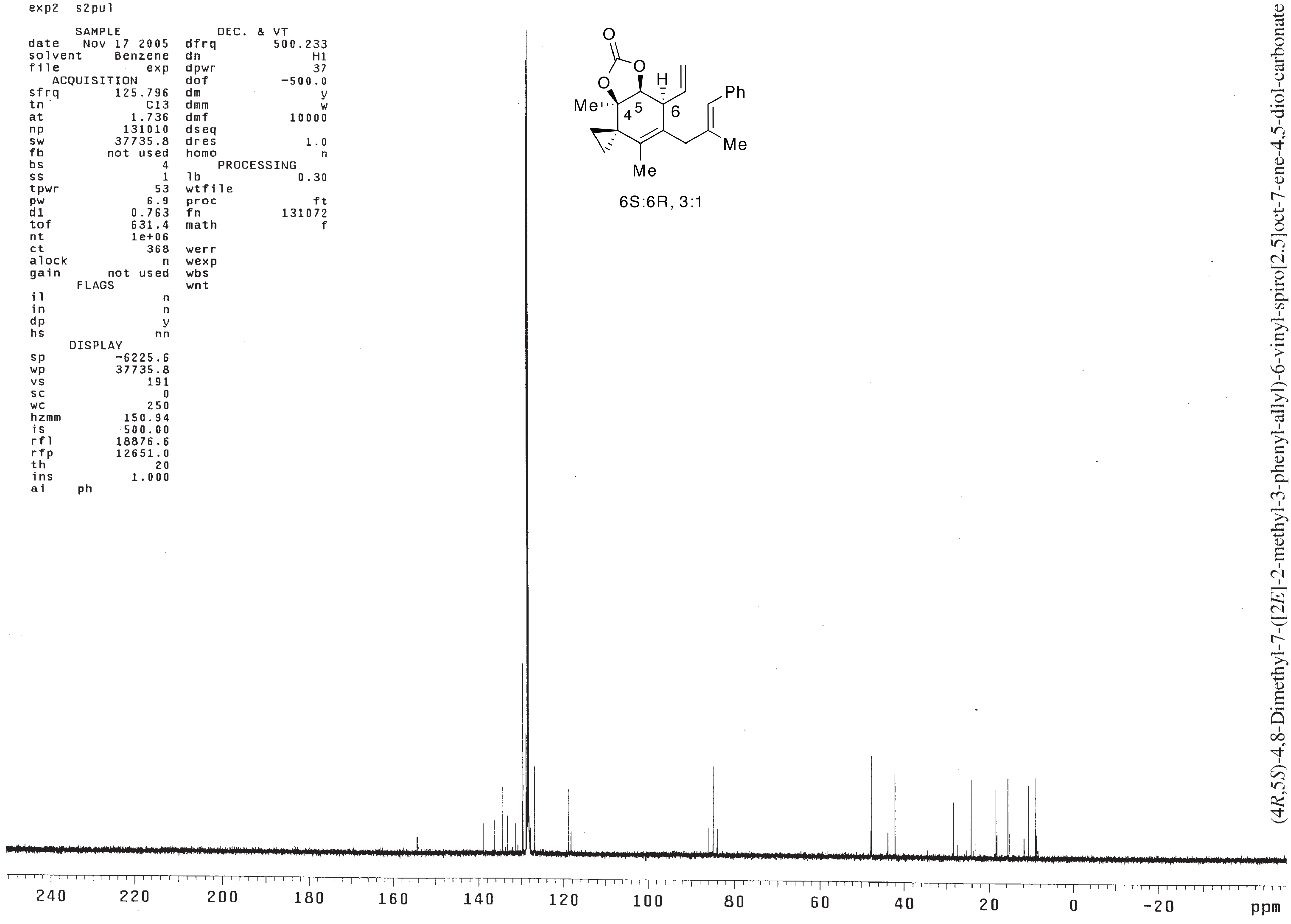
N-Isopropylidene-*N′*-2-nitrobenzenesulfonyl hydrazine



```
exp1  s2pul

                        DEC. & VT
                     dfrq      125.674
                     dn            C13
                     dpwr           34
                     dof        1498.1
                     dm            nnn
                     dmm             w
                     dmf         10000
   ACQUISITION       dseq
sfrq      499.749    dres          1.0
tn             H1    homo            n
at          3.277       PROCESSING
np          65536    wtfile
sw         9998.8    proc           ft
fb       not used    fn          65536
bs              1    math            f
tpwr           56
pw            8.2
d1              0
tof        1498.1
nt             16    werr
ct             16    wexp
alock           n    wbs
gain     not used    wnt
     FLAGS
il              n
in              n
dp              y
hs             nn
     DISPLAY
sp         -249.9
wp         6246.8
vs            241
sc              0
wc            250
hzmm        24.99
is          33.57
rfl        4564.1
rfp        3578.2
th              7
ins         1.000
nm  cdc  ph
```

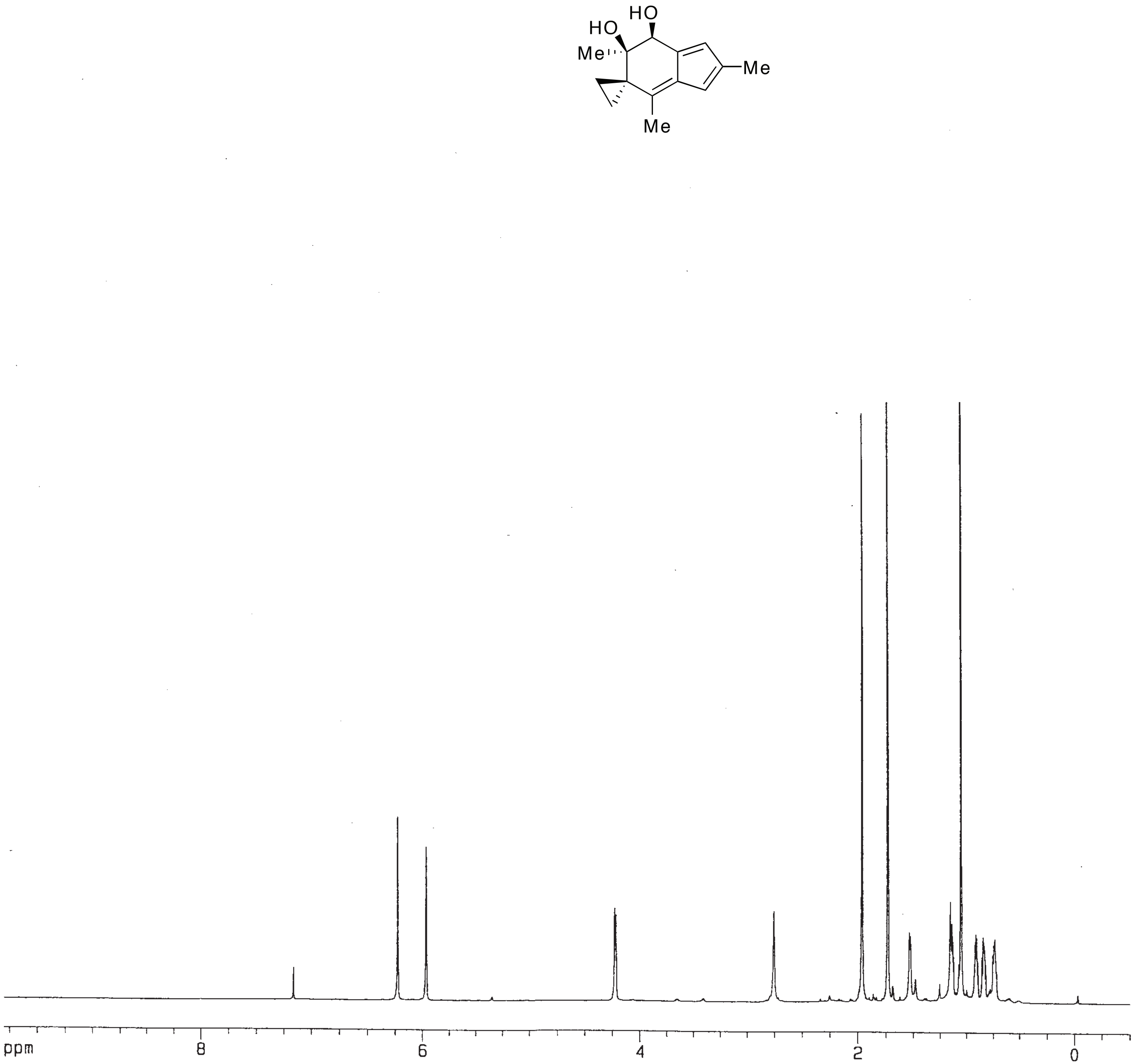
(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate



```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Nov 17 2005   dfrq         500.233
solvent    Benzene   dn                H1
file           exp   dpwr              37
  ACQUISITION        dof           -500.0
sfrq       125.796   dm                 y
tn             C13   dmm                w
at           1.736   dmf            10000
np          131010   dseq
sw         37735.8   dres             1.0
fb        not used   homo               n
bs               4      PROCESSING
ss               1   lb              0.30
tpwr            53   wtfile
pw             6.9   proc              ft
d1           0.763   fn            131072
tof          631.4   math               f
nt           1e+06
ct             368   werr
alock            n   wexp
gain      not used   wbs
      FLAGS          wnt
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -6225.6
wp         37735.8
vs             191
sc               0
wc             250
hzmm        150.94
is          500.00
rfl        18876.6
rfp        12651.0
th              20
ins          1.000
ai    ph
```

(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate



```
Current Data Parameters
NAME
EXPNO                    1
PROCNO                   1

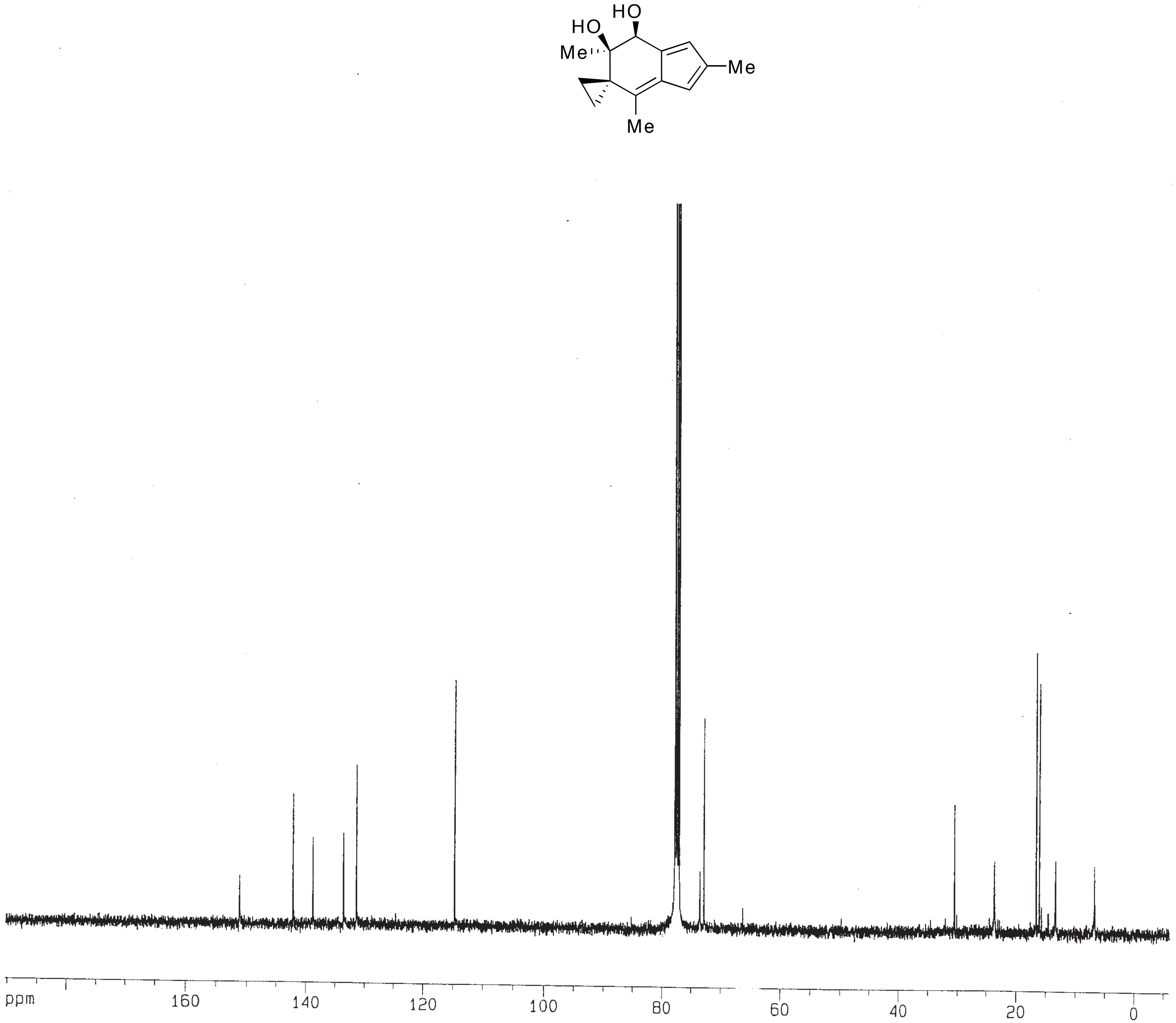
F2 - Acquisition Parameters
Date_             20060206
Time                 12.05
INSTRUM              spect
PROBHD   5 mm CPTCI 1H/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8992.806 Hz
FIDRES            0.137219 Hz
AQ               3.6439073 sec
RG                    22.6
DW                  55.600 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                   0.60 dB
SFO1           600.1314635 MHz

F2 - Processing parameters
SI                   32768
SF             600.1300773 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                   13.02 cm
F1P                 10.000 ppm
F1                 6001.30 Hz
F2P                 -0.500 ppm
F2                 -300.07 Hz
PPMCM              0.52500 ppm/cm
HZCM             315.06830 Hz/cm
```

Fulvene diol



```
Current Data Parameters
NAME
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060205
Time                11.58
INSTRUM             spect
PROBHD      5mm BBO BB-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 17355
DS                     4
SWH            24875.621 Hz
FIDRES          0.379572 Hz
AQ             1.3173236 sec
RG                1448.2
DW                20.100 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

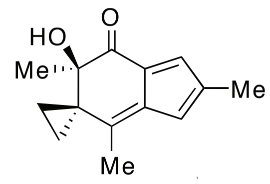
============ CHANNEL f1 ===========
NUC1                 13C
P1                 15.25 usec
PL1                 3.00 dB
SFO1         100.6237959 MHz

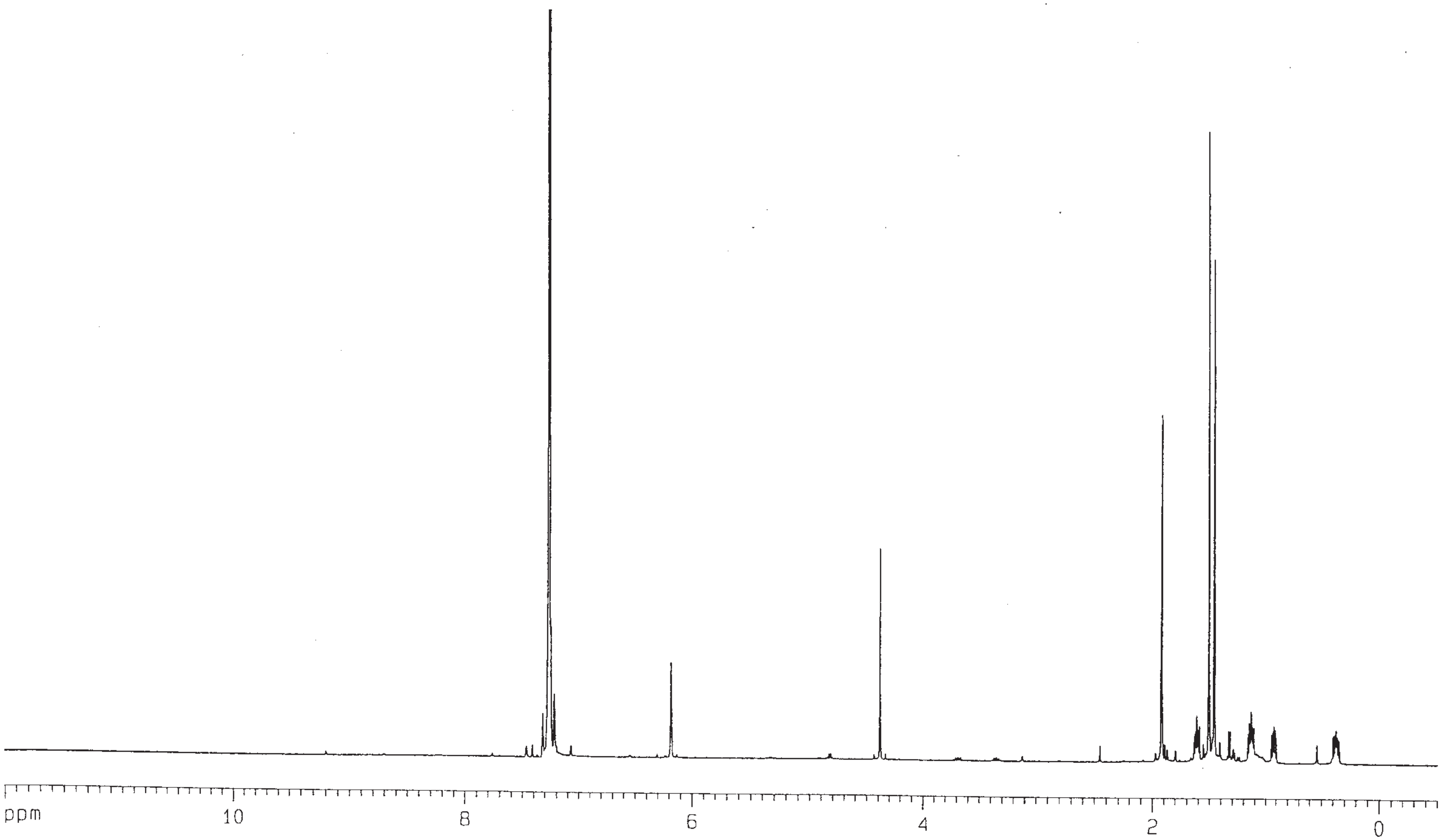
============ CHANNEL f2 ===========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             107.50 usec
PL2                 0.00 dB
PL12               24.00 dB
PL13               24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P              190.288 ppm
F1              19145.36 Hz
F2P               -6.043 ppm
F2               -608.01 Hz
PPMCM            9.81654 ppm/cm
HZCM           987.66852 Hz/cm
```

Fulvene diol





```
Current Data Parameters
NAME
EXPNO                      1
PROCNO                     1

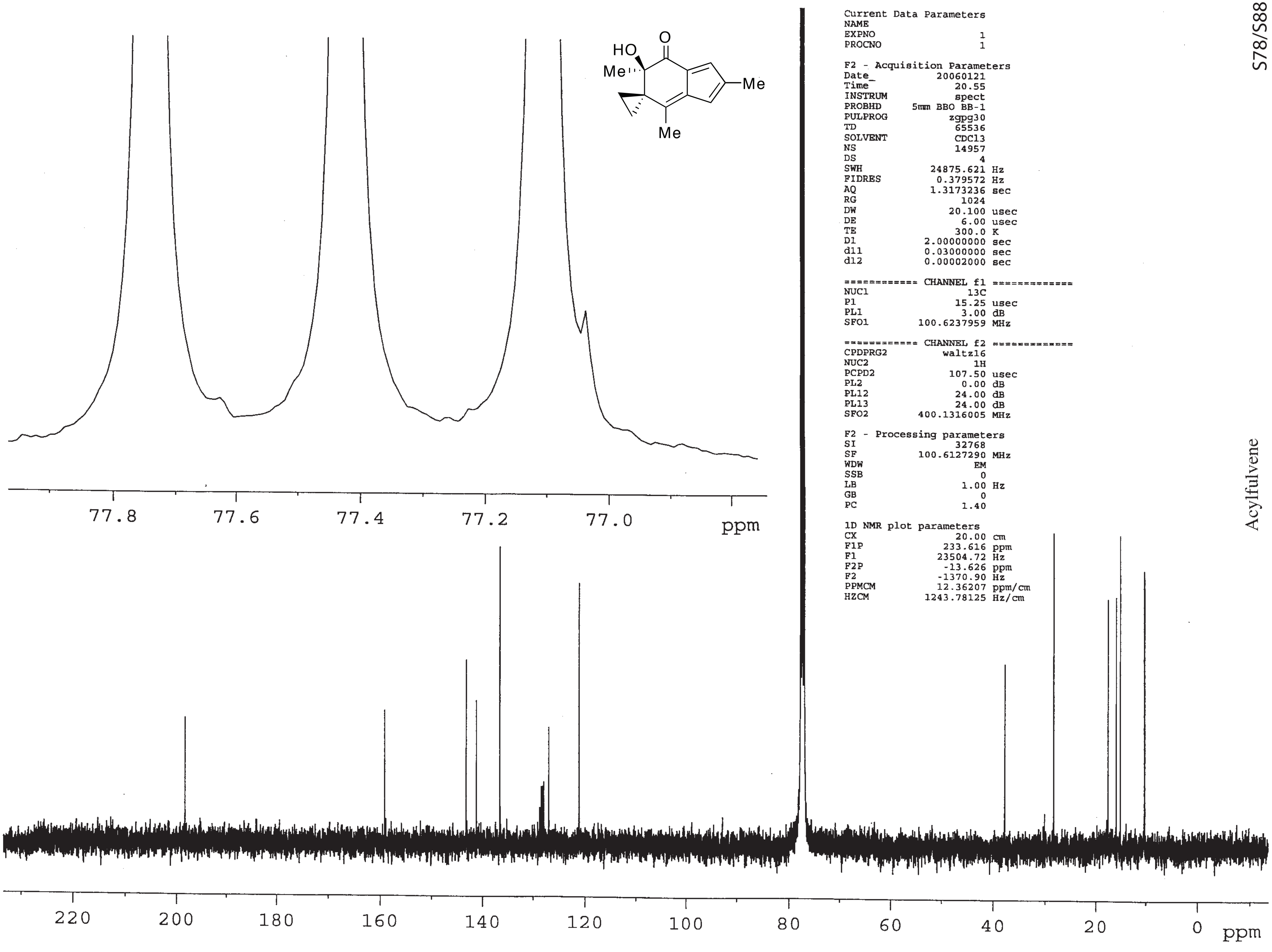
F2 - Acquisition Parameters
Date_               20060206
Time                   19.53
INSTRUM                spect
PROBHD          5mm BBO BB-1
PULPROG                 zg30
TD                     65536
SOLVENT                 C6D6
NS                        16
DS                         2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                 3.9584243 sec
RG                     287.4
DW                    60.400 usec
DE                      6.00 usec
TE                     300.0 K
D1                1.00000000 sec

============ CHANNEL f1 ============
NUC1                      1H
P1                      7.90 usec
PL1                     0.00 dB
SF01             400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF               400.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
F1P                   12.012 ppm
F1                   4806.17 Hz
F2P                   -0.503 ppm
F2                   -201.07 Hz
PPMCM                0.62570 ppm/cm
HZCM               250.36191 Hz/cm
```

Acylfulvene



```
Current Data Parameters
NAME
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20060121
Time                   20.55
INSTRUM                spect
PROBHD       5mm BBO BB-1
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    14957
DS                        4
SWH               24875.621 Hz
FIDRES             0.379572 Hz
AQ                1.3173236 sec
RG                     1024
DW                   20.100 usec
DE                     6.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec

============ CHANNEL f1 ============
NUC1                    13C
P1                    15.25 usec
PL1                    3.00 dB
SFO1            100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2             waltz16
NUC2                     1H
PCPD2                107.50 usec
PL2                    0.00 dB
PL12                  24.00 dB
PL13                  24.00 dB
SFO2            400.1316005 MHz

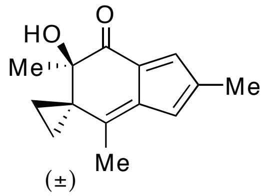
F2 - Processing parameters
SI                    32768
SF              100.6127290 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

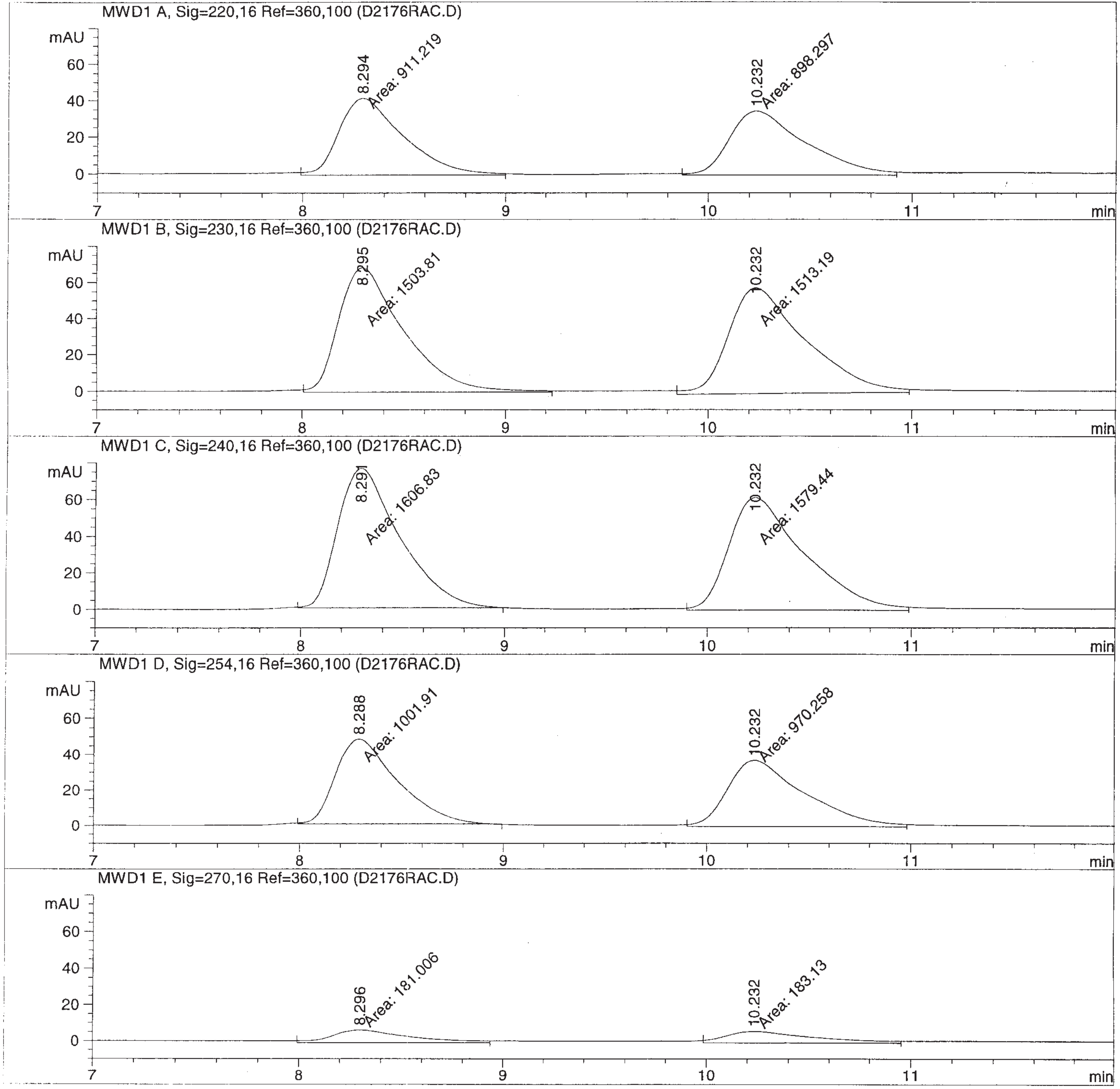
1D NMR plot parameters
CX                    20.00 cm
F1P                 233.616 ppm
F1                 23504.72 Hz
F2P                 -13.626 ppm
F2                 -1370.90 Hz
PPMCM              12.36207 ppm/cm
HZCM             1243.78125 Hz/cm
```

Acylfulvene

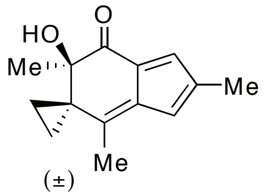
```
===================================================================
Injection Date   :                                Seq. Line :    1
Sample Name      :                                 Location : Vial 91
Acq. Operator    :                                      Inj :    1
                                                 Inj Volume : 1 µl

Acq. Method      : C:\HPCHEM\2\METHODS\ACYLFUL.M
Last changed     : 2/10/2006 10:33:35 AM by Bin
Analysis Method  : C:\HPCHEM\2\METHODS\182_9.M
Last changed     : 2/15/2006 12:41:43 PM by Bin
                   (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
```





Acylfulvene



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.294 MM    0.3635  911.21899   41.78366  50.3570
   2  10.232 MM    0.4289  898.29730   34.90594  49.6430

Totals :                  1809.51630   76.68960

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.295 MM    0.3657 1503.81494   68.54411  49.8446
   2  10.232 MM    0.4320 1513.18909   58.38517  50.1554

Totals :                  3017.00403  126.92929

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=240,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.291 MM    0.3521 1606.82849   76.06040  50.4298
   2  10.232 MM    0.4278 1579.44067   61.52729  49.5702

Totals :                  3186.26917  137.58769

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.288 MM    0.3491 1001.91046   47.83171  50.8025
   2  10.232 MM    0.4357  970.25781   37.11912  49.1975

Totals :                  1972.16827   84.95083

 Results obtained with enhanced integrator!

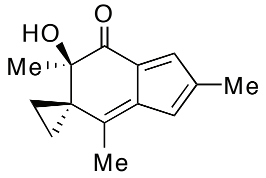
Signal 5: MWD1 E, Sig=270,16 Ref=360,100

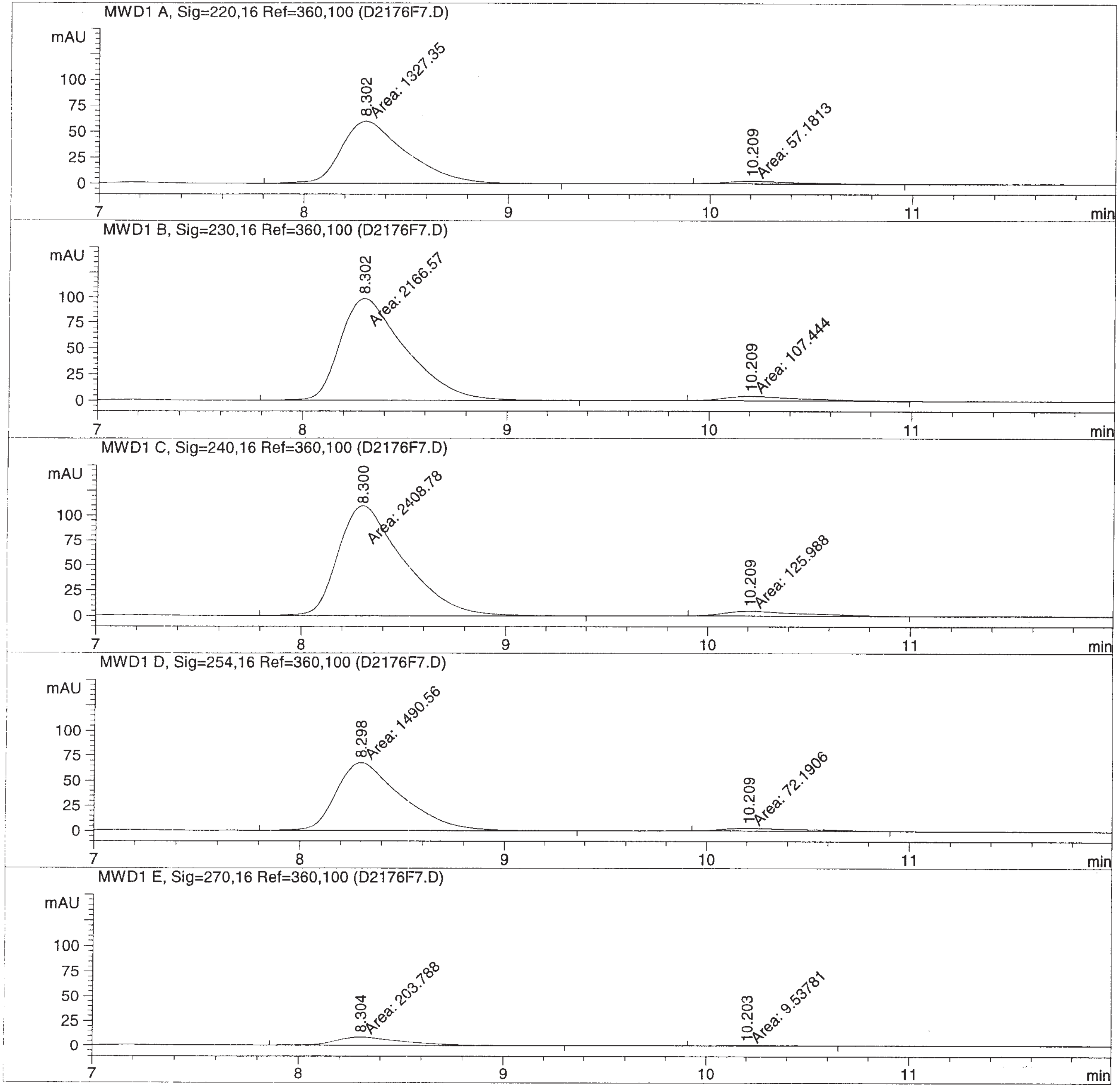
Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.296 MM    0.4375  181.00645    6.89578  49.7084
   2  10.232 MM    0.4941  183.12990    6.17725  50.2916

Totals :                   364.13635   13.07303
```

Acylfulvene

```
=====================================================================
Injection Date   :                                   Seq. Line :   1
Sample Name      :                                    Location : Vial 91
Acq. Operator    :                                         Inj :   1
                                                    Inj Volume : 1 µl
Acq. Method      : C:\HPCHEM\2\METHODS\ACYLFUL.M
Last changed     : 2/10/2006 10:33:35 AM by Bin
Analysis Method  : C:\HPCHEM\2\METHODS\182_9.M
Last changed     : 2/15/2006 12:50:15 PM by Bin
                   (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
```





Acylfulvene

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.302 MM    0.3690 1327.35315   59.95131  95.8700
   2  10.209 MM    0.3880   57.18126    2.45643   4.1300

Totals :                  1384.53440   62.40774

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.302 MM    0.3658 2166.57349   98.70364  95.2752
   2  10.209 MM    0.4169  107.44352    4.29493   4.7248

Totals :                  2274.01701  102.99857

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=240,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.300 MM    0.3678 2408.77856  109.15147  95.0296
   2  10.209 MM    0.4560  125.98849    4.60503   4.9704

Totals :                  2534.76705  113.75651

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.298 MM    0.3686 1490.56372   67.39674  95.3806
   2  10.209 MM    0.4593   72.19061    2.61948   4.6194

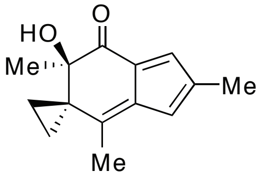
Totals :                  1562.75433   70.01622

 Results obtained with enhanced integrator!

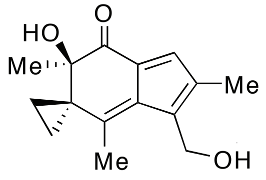
Signal 5: MWD1 E, Sig=270,16 Ref=360,100

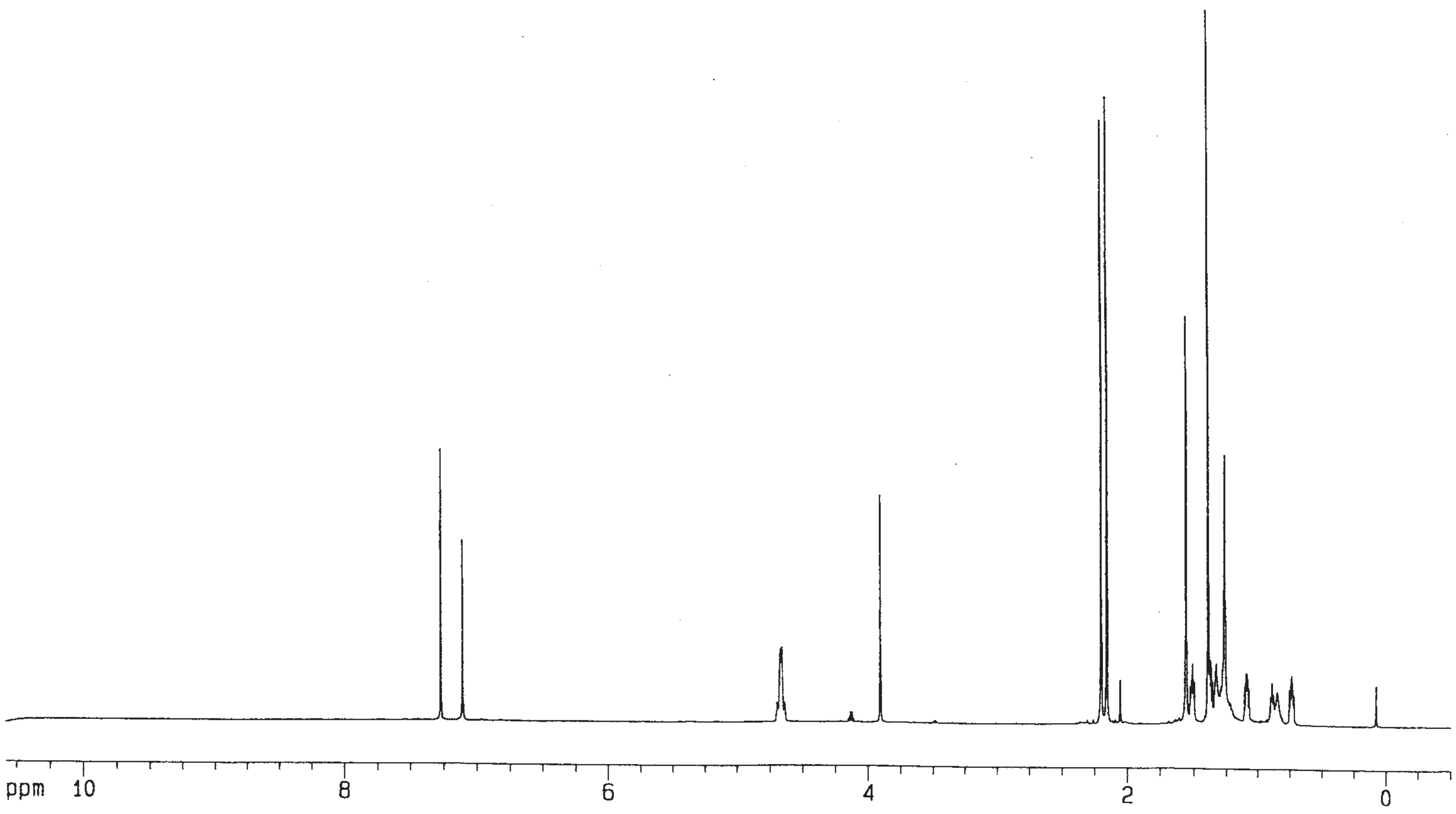
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   8.304 MM    0.3836  203.78841    8.85333  95.5290
   2  10.203 MM    0.3813    9.53781 4.16884e-1  4.4710

Totals :                   213.32622    9.27021
```



Acylfulvene





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Current Data Parameters
NAME
EXPNO                    1
PROCNO                   1

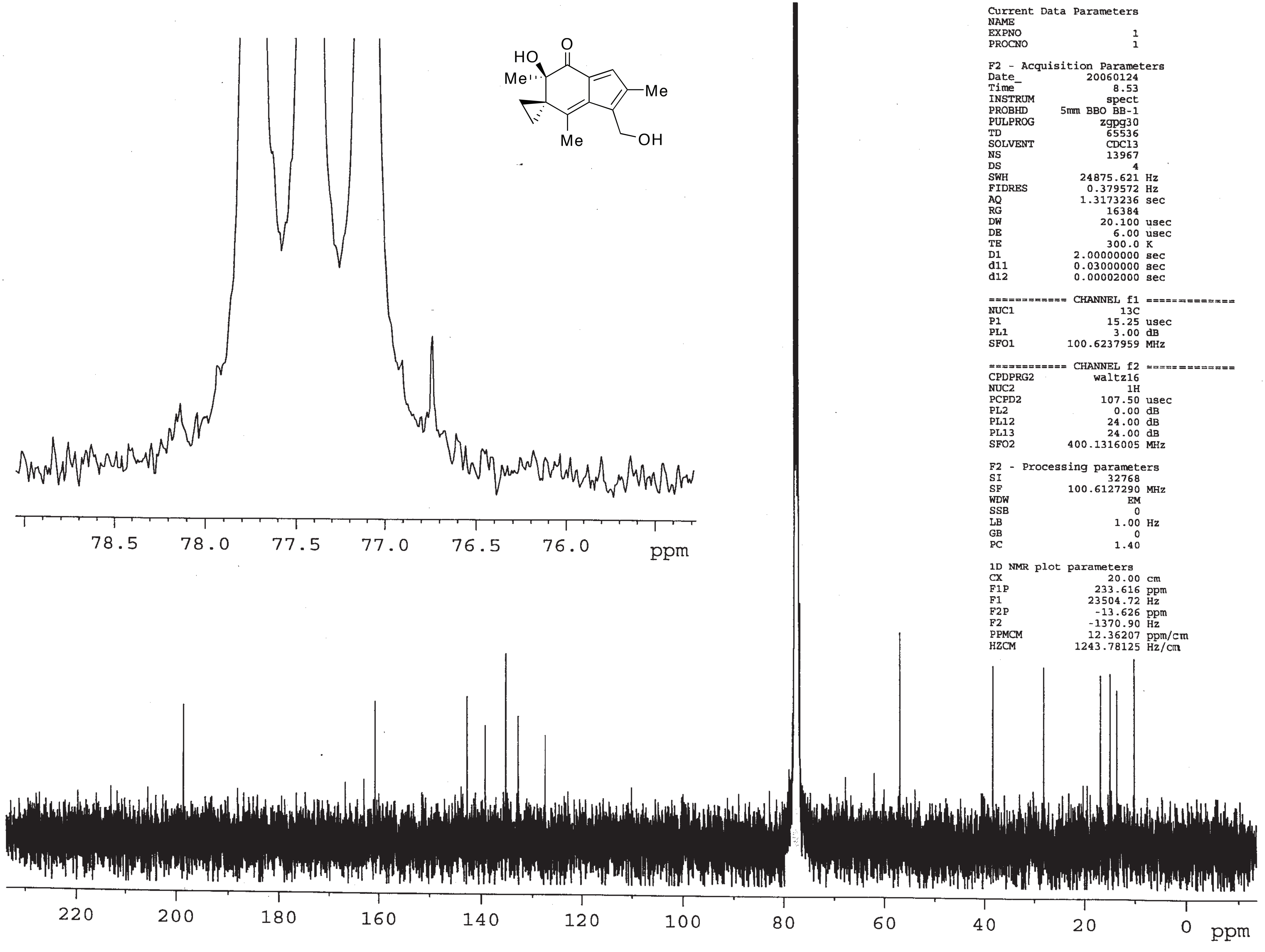
F2 - Acquisition Parameters
Date_             20060123
Time                 13.01
INSTRUM              spect
PROBHD   5 mm CPTCI 1H/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               7936.508 Hz
FIDRES            0.121102 Hz
AQ               4.1288805 sec
RG                    28.5
DW                  63.000 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.00 usec
PL1                  -4.00 dB
SFO1        600.1323934 MHz

F2 - Processing parameters
SI                   32768
SF          600.1300114 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                    9.86 cm
F1P                 10.800 ppm
F1                 6481.40 Hz
F2P                 -0.500 ppm
F2                 -300.07 Hz
PPMCM              0.56500 ppm/cm
HZCM             339.07346 Hz/cm
```

Irofulvene



```
Current Data Parameters
NAME
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060124
Time                  8.53
INSTRUM              spect
PROBHD      5mm BBO BB-1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  13967
DS                      4
SWH             24875.621 Hz
FIDRES           0.379572 Hz
AQ              1.3173236 sec
RG                  16384
DW                 20.100 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

============ CHANNEL f1 =============
NUC1                  13C
P1                  15.25 usec
PL1                  3.00 dB
SFO1          100.6237959 MHz

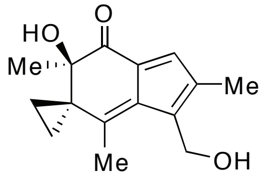
============ CHANNEL f2 =============
CPDPRG2           waltz16
NUC2                   1H
PCPD2              107.50 usec
PL2                  0.00 dB
PL12                24.00 dB
PL13                24.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127290 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P               233.616 ppm
F1               23504.72 Hz
F2P               -13.626 ppm
F2               -1370.90 Hz
PPMCM            12.36207 ppm/cm
HZCM           1243.78125 Hz/cm
```

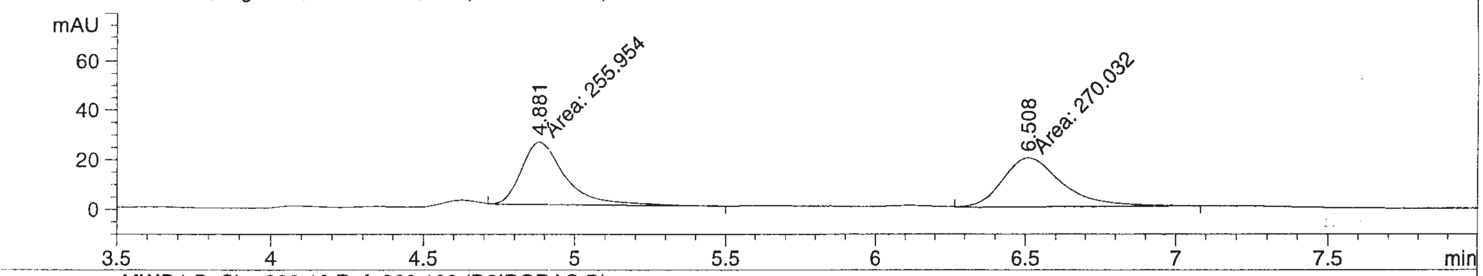
Irofulvene

```
=============================================================================
Injection Date   :                                    Seq. Line :    1
Sample Name      :                                     Location : Vial 91
Acq. Operator    :                                          Inj :    1
                                                     Inj Volume : 1 µl
Acq. Method      : C:\HPCHEM\2\METHODS\IROFULV.M
Last changed     : 2/9/2006 12:28:08 PM by Bin
Analysis Method  : C:\HPCHEM\2\METHODS\182_9.M
Last changed     : 2/15/2006 12:32:12 PM by Bin
                   (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
```

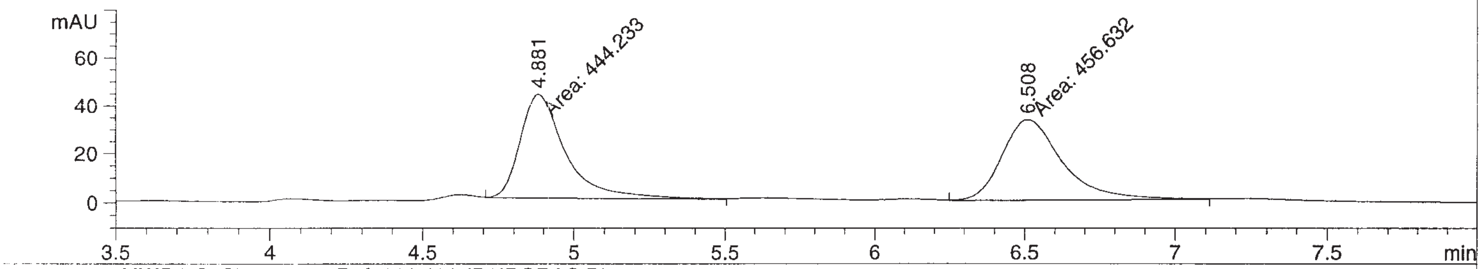


(±)

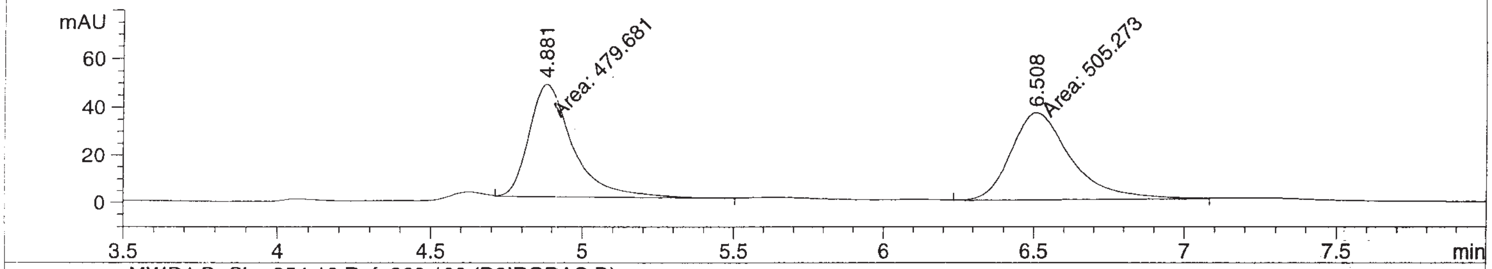
MWD1 A, Sig=220,16 Ref=360,100 (D2IRORAC.D)



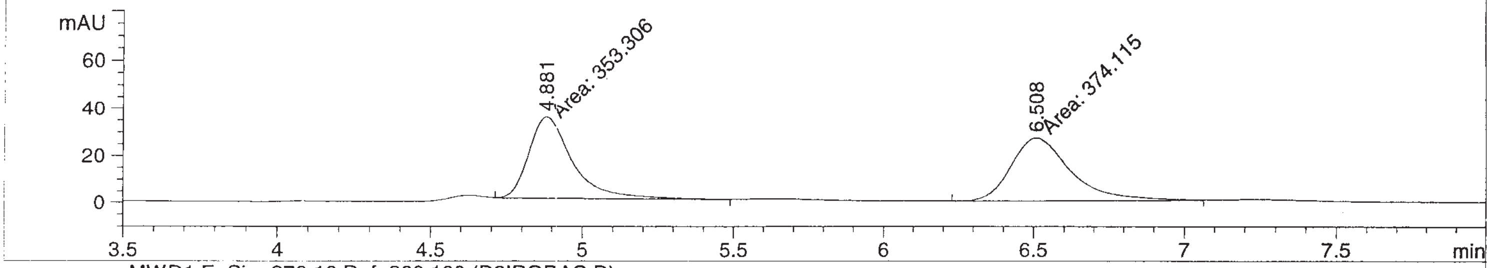
MWD1 B, Sig=230,16 Ref=360,100 (D2IRORAC.D)



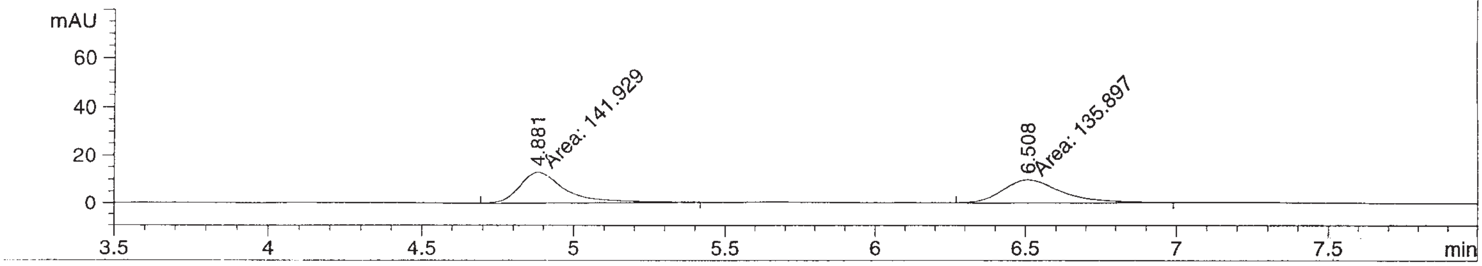
MWD1 C, Sig=240,16 Ref=360,100 (D2IRORAC.D)



MWD1 D, Sig=254,16 Ref=360,100 (D2IRORAC.D)



MWD1 E, Sig=270,16 Ref=360,100 (D2IRORAC.D)



Irofulvene

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.881 MM    0.1691  255.95450   25.22759  48.6618
   2   6.508 MM    0.2286  270.03177   19.68349  51.3382

Totals :                   525.98627   44.91107

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.881 MM    0.1724  444.23315   42.93738  49.3118
   2   6.508 MM    0.2301  456.63242   33.07205  50.6882

Totals :                   900.86557   76.00943

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=240,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.881 MM    0.1700  479.68124   47.03773  48.7008
   2   6.508 MM    0.2305  505.27335   36.53200  51.2992

Totals :                   984.95459   83.56973

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.881 MM    0.1703  353.30612   34.58545  48.5697
   2   6.508 MM    0.2314  374.11542   26.94118  51.4303

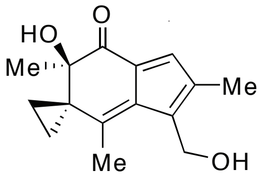
Totals :                   727.42154   61.52663

 Results obtained with enhanced integrator!

Signal 5: MWD1 E, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.881 MM    0.1827  141.92921   12.94412  51.0856
   2   6.508 MM    0.2336  135.89722    9.69631  48.9144

Totals :                   277.82643   22.64043
```

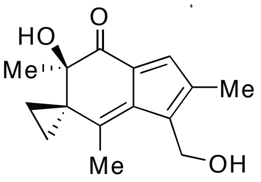


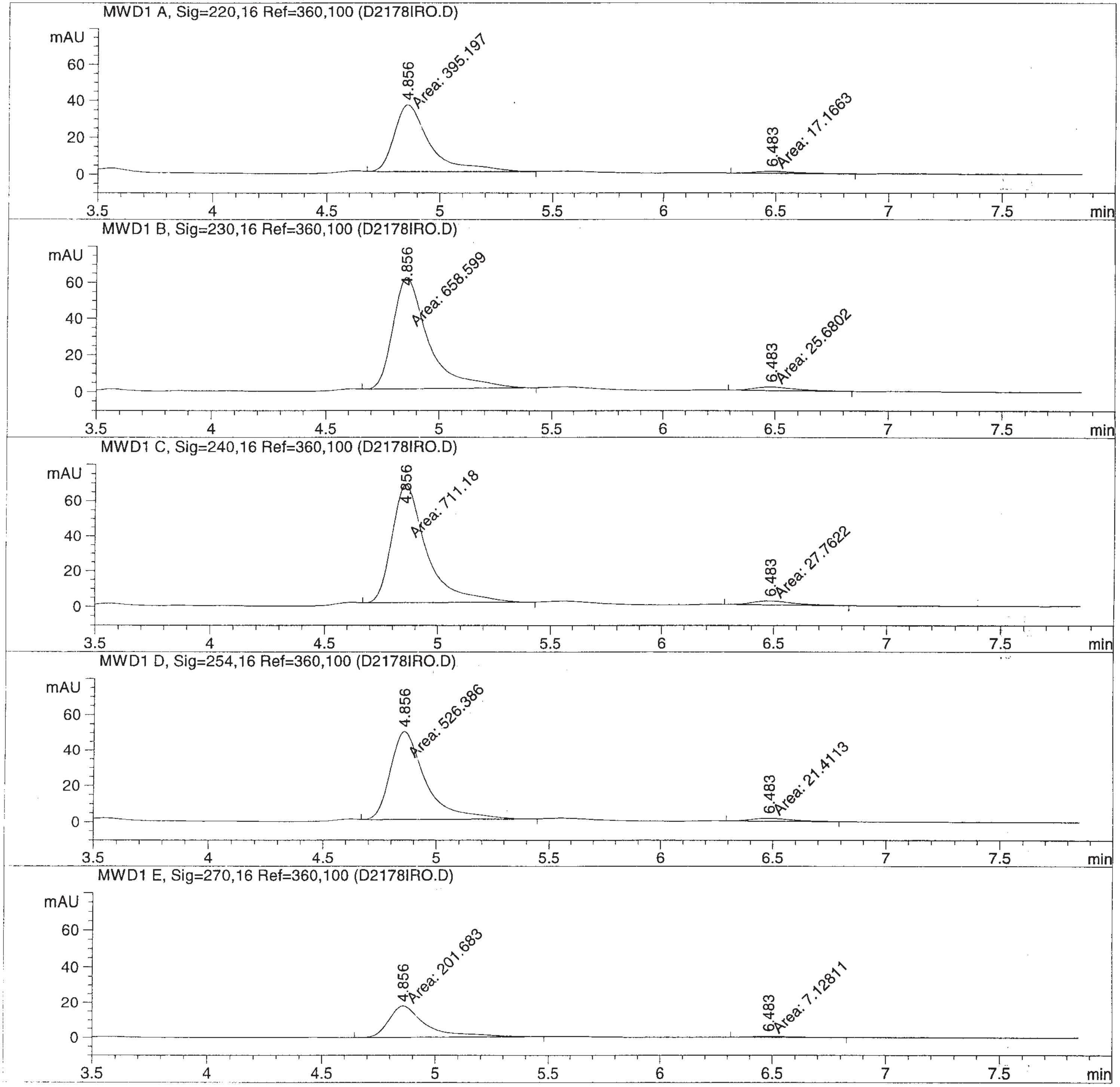
(±)

Irofulvene

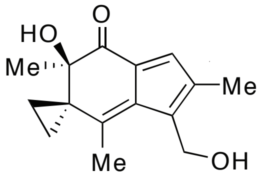
```
=====================================================================
Injection Date  :                                    Seq. Line :    1
Sample Name     :                                     Location : Vial 91
Acq. Operator   :                                          Inj :    1
                                                    Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\IROFULV.M
Last changed    : 2/9/2006 12:28:08 PM by Bin
Analysis Method : C:\HPCHEM\2\METHODS\182_9.M
Last changed    : 2/15/2006 12:32:12 PM by Bin
                  (modified after loading)
Zorbax CN; 1.0%iPrOH-hex; 1.0mL/min
```





Irofulvene



```
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.856 MM    0.1823  395.19705   36.14056  95.8371
   2   6.483 MM    0.2388   17.16626    1.19831   4.1629

Totals :                   412.36331   37.33887

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.856 MM    0.1798  658.59857   61.06145  96.2471
   2   6.483 MM    0.2199   25.68021    1.94622   3.7529

Totals :                   684.27878   63.00767

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=240,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.856 MM    0.1770  711.18018   66.97616  96.2430
   2   6.483 MM    0.2160   27.76224    2.14248   3.7570

Totals :                   738.94242   69.11864

 Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.856 MM    0.1777  526.38641   49.36498  96.0914
   2   6.483 MM    0.2169   21.41133    1.64554   3.9086

Totals :                   547.79775   51.01052

 Results obtained with enhanced integrator!

Signal 5: MWD1 E, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   4.856 MM    0.1871  201.68265   17.96253  96.5863
   2   6.483 MM    0.2061    7.12811 5.76507e-1   3.4137

Totals :                   208.81076   18.53904
```

Irofulvene