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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.

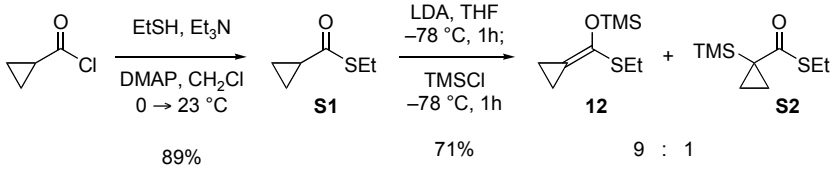
Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure.[2]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

[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.

[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%).

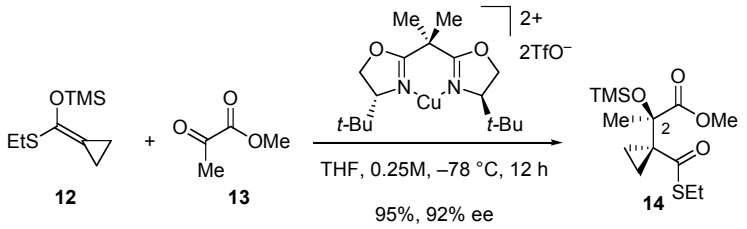
***S*-Ethyl cyclopropanecarbothioate (S1):**

^{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**$_3$)$_3$).

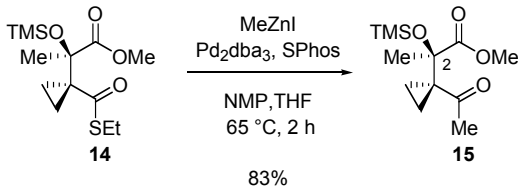
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	135.8, 100.5, 25.5, 15.4, 7.2, 5.1, 0.7.
FTIR (neat) cm^{-1}:	2965 (s), 1751 (s), 1449 (w), 1252 (s), 1189 (s), 1071 (m).
HRMS (ESI):	calcd for $C_9H_{19}OSSi$ $[M+H]^+$: 203.0920, found: 203.0926.
GC, t_R:	2.499 min
TLC (10% EtOAc in hexanes) R*f*:	0.5 (UV)



(+)-(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)

[4] For the preparation of (*R*,*R*)-2,2′-isopropylidene-bis(4-ᵗbutyl-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.



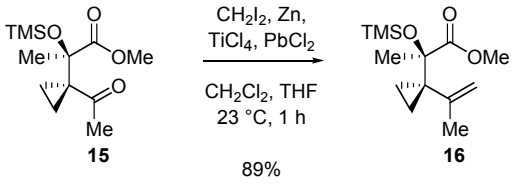
(+)-(2*R*)-2-(1-Acetyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (15):

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)

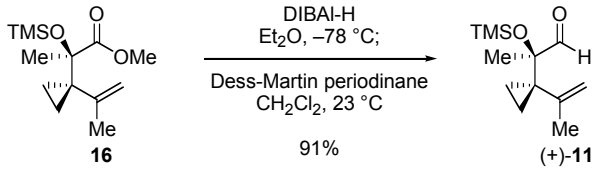
[5] Activated zinc dust was prepared by sequential washing of Zn dust with 1.2N HCl in H_2O, H_2O, methanol, and diethyl ether, and drying under vacuum; see: Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967, Vol. 1, p. 1267.



(+)-(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=CC**H**$_3$), 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):

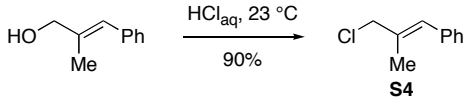
Diisobutylaluminum hydride (DIBAl-H, 1.5M in Toluene, 11.7 mL, 17.6 mmol, 3.00 equiv) was added drop-wise down the side of the flask into a solution of (2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester (**16,** 1.5 g, 5.80 mmol, 1 equiv) in diethyl ether (29 mL) 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):

^{1}H 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, $CDCl_3$) δ:	9.50 (s, 1H, C**H**O), 4.95 (br-s, 1H, C=C**H**$_2$), 4.87 (br-s, 1H, C=C**H**$_2$), 1.71 (br-s, 3H, C**H**$_3$C=CH$_2$), 1.29 (s, 3H, C**H**$_3$COTMS), 0.97 (ddd, *J* = 3.8, 5.8, 9.6 Hz, 1H, C**H**$_2$CH$_2$), 0.78 (ddd, *J* = 3.9, 5.8, 9.6 Hz, 1H, C**H**$_2$CH$_2$), 0.48 (ddd, *J* = 4.0, 5.8, 9.6 Hz, 1H, CH$_2$C**H**$_2$), 0.41 (ddd, *J* = 3.8, 5.8, 9.6 Hz, 1H, CH$_2$C**H**$_2$), 0.09 (s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) 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 $C_{12}H_{22}NaO_2Si$ $[M+Na]^+$: 249.1281, found: 249.1293.
TLC (100% hexanes) R*f*:	Prod. **11**: 0.17 (Anis)

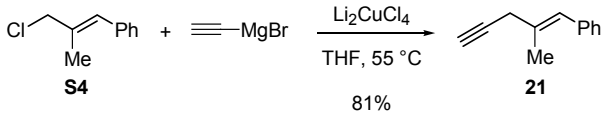


S4

***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.

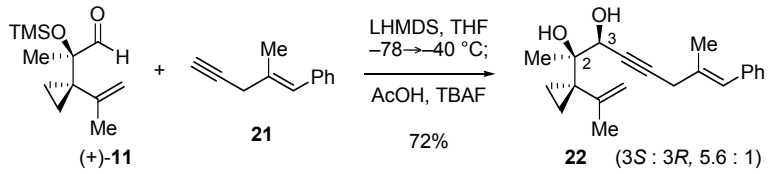
^{1}H NMR (500 MHz, $CDCl_3$) δ:	8.05-8.0 (m, 2H, Ar**H**), 7.98-7.90 (m, 3H, Ar**H**), 7.27 (br-s, 1H, C=C**H**), 4.87 (s, 2H, C**H**$_2$Cl), 2.67 (d, J = 1.5 Hz, 3H, C**H**$_3$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ:	136.9, 134.3, 130.0, 129.1, 128.4, 127.2, 53.1, 16.1.
FTIR (neat) cm^{-1}:	2985 (m, 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 ($KMnO_4$)



***E*-(2-Methyl-pent-1-en-4-ynyl)-benzene (21):**

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 ($KMnO_4$)



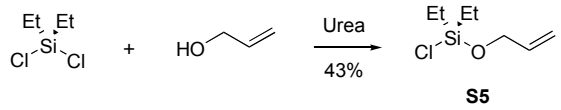
***E*-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-7-methyl-8-phenyl-oct-7-en-4-yne-2,3-diol (22):**

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$\mathbf{H}_2$), 5.12 (br-s, 1H, C=C$\mathbf{H}_2$*), 4.95 (br-s, 1H, C=C$\mathbf{H}_2$*), 4.91 (br-s, 1H, C=C$\mathbf{H}_2$), 4.54 (br-s, 1H, C**H**OH*), 4.48 (br-s, 1H, C**H**OH), 2.97 (s, 2H, C$\mathbf{H}_2$*), 2.82 (s, 2H, C$\mathbf{H}_2$), 1.93 (s, 1H, CHO**H**), 1.93 (s, 1H, CHO**H***), 1.87 (s, 3H, C$\mathbf{H}_3$*), 1.82 (s, 3H, C$\mathbf{H}_3$*), 1.77 (s, 3H, C$\mathbf{H}_3$), 1.71 (s, 3H, C$\mathbf{H}_3$), 1.64 (s, 1H, O**H**), 1.64 (s, 1H, O**H***), 1.30 (s, 3H, C$\mathbf{H}_3$), 1.29 (s, 3H, C$\mathbf{H}_3$*), 1.26 (ddd, *J* = 4.6, 6.0, 10.0 Hz, 1H, C$\mathbf{H}_2$CH$_2$), 1.02 (ddd, *J* = 10.0, 6.0, 4.6 Hz, 1H, C$\mathbf{H}_2$CH$_2$*), 0.93 (ddd, *J* = 4.0, 6.1, 9.8 Hz, 1H, C$\mathbf{H}_2$CH$_2$), 0.89 (ddd, *J* = 9.8, 6.1, 4.0 Hz, 1H, C$\mathbf{H}_2$CH$_2$*), 0.56 (ddd, *J* = 4.6, 6.1, 10.0 Hz, 1H, C$\mathbf{H}_2$CH$_2$), 0.52-0.45 (m, 2H, C$\mathbf{H}_2$CH$_2$*), 0.44 (ddd, *J* = 4.0, 6.0, 9.8 Hz, 1H, C$\mathbf{H}_2$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)



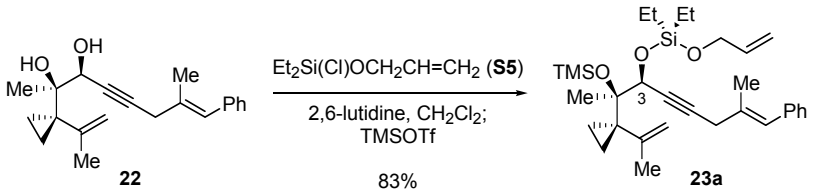
S5

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).

[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.



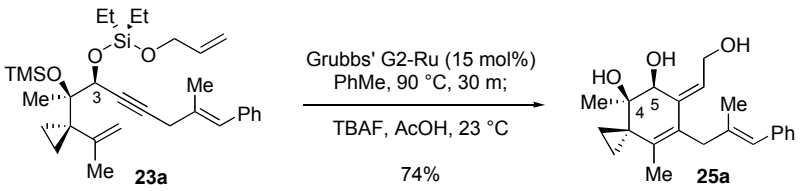
***E*-(2*R*,3*S*)-2-(1-Isopropenyl-cyclopropyl)-2-(trimethylsilyloxy)-3-(allyloxy-diethyl-silanyloxy)-7-methyl-8-phenyl-oct-7-en-4-yne (23a):**

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_2C**H**=CH_2), 6.06-5.98 (m, 1H, CH_2C**H**=CH_2*), 5.50 (dq, *J* = 17.0, 2.0 Hz, 1H, *trans*-$OCH_2CH=C$**H**$_2$), 5.49 (dq, *J* = 17.0, 2.0 Hz, 1H, *trans*-$OCH_2CH=C$**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*-$OCH_2CH=C$**H**$_2$, C=C**H**$_2$), 5.19-5.13 (m, 2H, *cis*-$OCH_2CH=C$**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_2C**H**$_2$, C**H**$_3$, C**H**$_3$*), 1.30-1.19 (m, 6H, $SiCH_2C$**H**$_3$), 1.05-0.8 (m, 5H, CH_2C**H**$_2$, SiC**H**$_2CH_3$), 0.76-0.70 (m, 1H, CH_2C**H**$_2$), 0.66-0.60 (m, 1H, CH_2C**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)

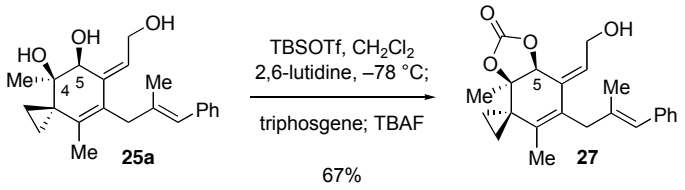


(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol (25a):

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_6D_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_2OH), 5.93 (t, *J* = 7.0 Hz, 1H, C=C**H**CH_2OH), 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_2C**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_2C**H**$_2$*), 0.88-0.83 (m, 1H, CH_2C**H**$_2$), 0.82-0.78 (m, 1H, CH_2C**H**$_2$*), 0.78-0.73 (m, 1H, CH_2C**H**$_2$), 0.72-0.65 (m, 1H, CH_2C**H**$_2$*), 0.61-0.56 (m, 1H, CH_2C**H**$_2$), 0.56-0.47 (m, 1H, CH_2C**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)

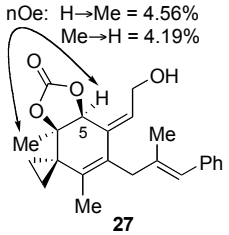


(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol-carbonate 27:

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:



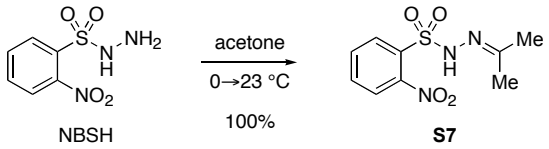
27

^{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)

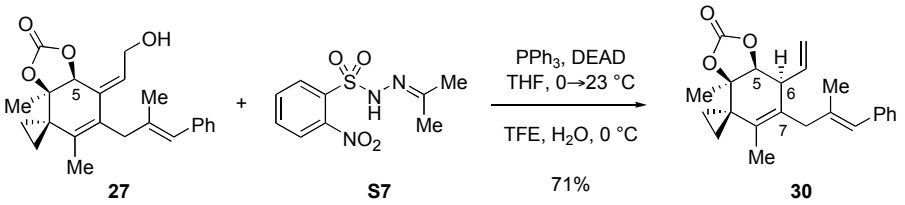


_N_-Isopropylidene-_N′_-2-nitrobenzenesulfonyl hydrazine (S7):

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)

[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).



(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_2C**H**$_2$), 0.77 (s, 3H, C**H****$_3$), 0.75 (s, 3H, C**H**$_3$), 0.73-0.66 (m, 2H, CH_2C**H***$_2$), 0.64 (s, 3H, C**H***$_3$), 0.44-0.38 (m, 2H, CH_2C**H**$_2$), 0.35-0.29 (m, 1H, CH_2C**H**$_2$), 0.23-0.18 (m, 1H, CH_2C**H****$_2$), 0.10-0.04 (m, 1H, CH_2C**H***$_2$).

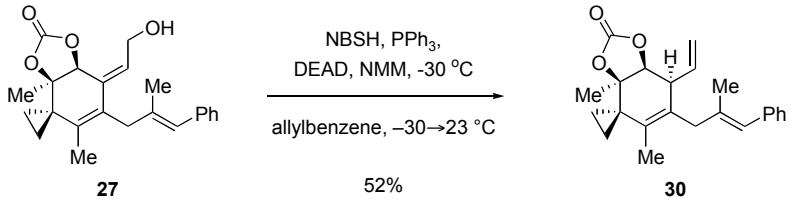
^{13}C NMR (125.8 MHz, C_6D_6, ~3:1:0.1 mixture of three diastereomers) δ: 154.2, 154.0, 139.0, 136.4, 136.3, 134.5, 134.4, 133.3, 131.4, 130.8, 129.7, 129.6, 128.9, 128.8, 127.8, 126.9, 126.8, 118.9, 118.3, 86.1, 85.0, 83.9, 47.7, 47.5, 43.8, 42.1, 34.5, 28.4, 27.5, 25.3, 24.2, 23.8, 23.3, 18.5, 18.2, 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)

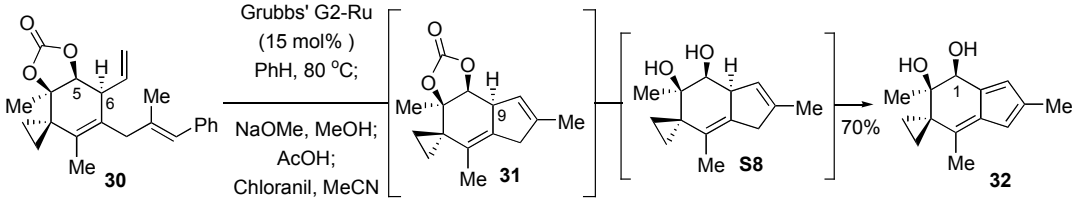
For the analogous reductive transposition using the reagent NBSH, see:



(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**.

[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.

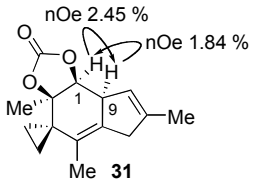


Fulvenediol 32:

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_2C**H**$_2$), 1.16 (s, 3H, C**H**$_3$), 1.05-1.00 (m, 1H, CH_2C**H**$_2$), 0.98-0.92 (m, 1H, CH_2C**H**$_2$), 0.87-0.82 (m, 1H, CH_2C**H**$_2$).

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

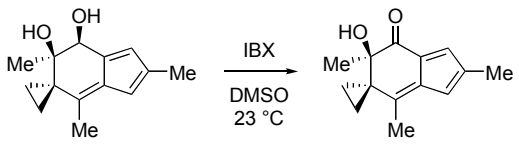


^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 151.2, 142.1, 138.8, 133.6, 131.4, 114.7, 73.5, 72.8, 30.5, 23.6, 16.6, 16.0, 13.3, 6.8.

FTIR (neat) cm^{-1}: 3421 (br-s, O–H), 2916 (s, C–H), 1630 (s), 1443 (m), 1376 (m), 1333 (m), 1114 (m).

[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**)

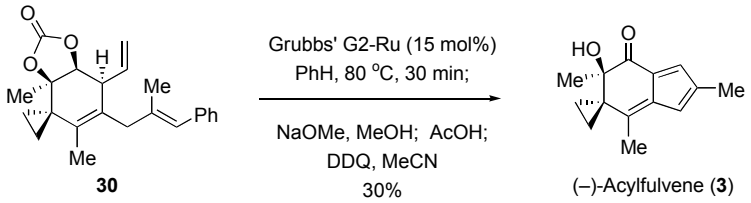
(–)-Acylfulvene (3):

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 ºC. 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_2C**H**$_2$), 1.39 (s, 3H, C**H**$_3$), 1.33-1.29 (m, 1H, CH_2C**H**$_2$), 1.10-1.06 (m, 1H, CH_2C**H**$_2$), 0.75-0.71 (m, 1H, CH_2C**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)

[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.

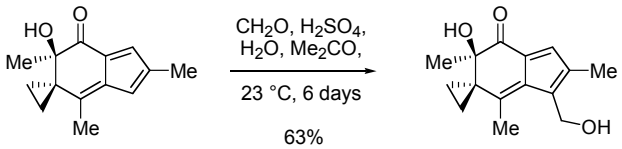


(–)-Acylfulvene (3):

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 ºC, and the resulting dark-pink solution was sealed under an argon atmosphere and heated to 80 ºC. After 30 min, the reaction ethyl vinyl ether (0.1 mL) was added via syringe, and the reaction mixture was cooled to 23 ºC. 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.

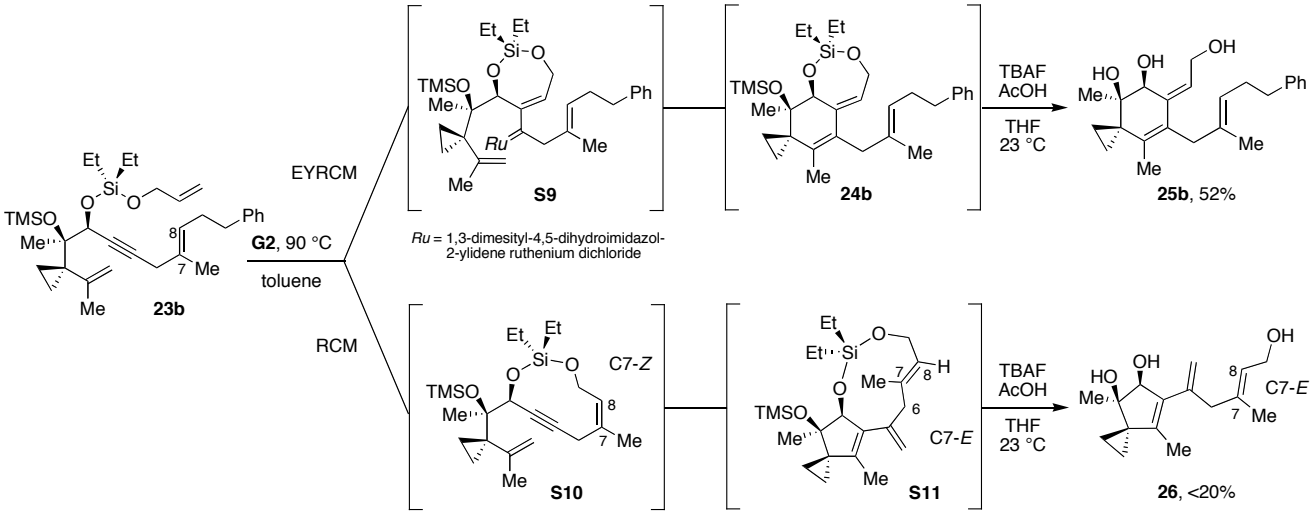
Our synthetic (–)-irofulven (**4**) was determined to be 92% ee by chiral HPLC analysis [Chirapak AD-H; 1.5 mL/min; 20% ^{i}PrOH in hexanes; t_R(major) = 4.88 min, t_R(minor) = 6.51 min].

^{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)

[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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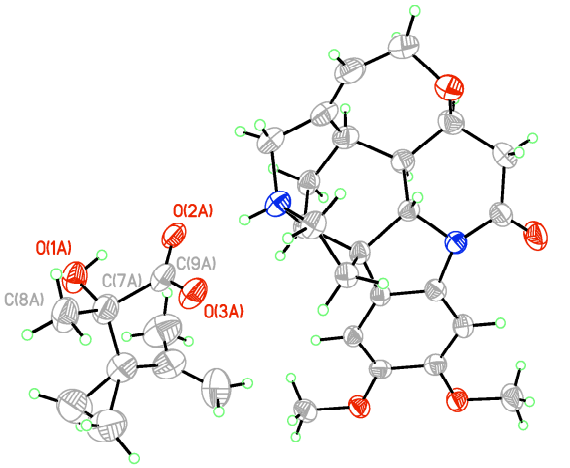
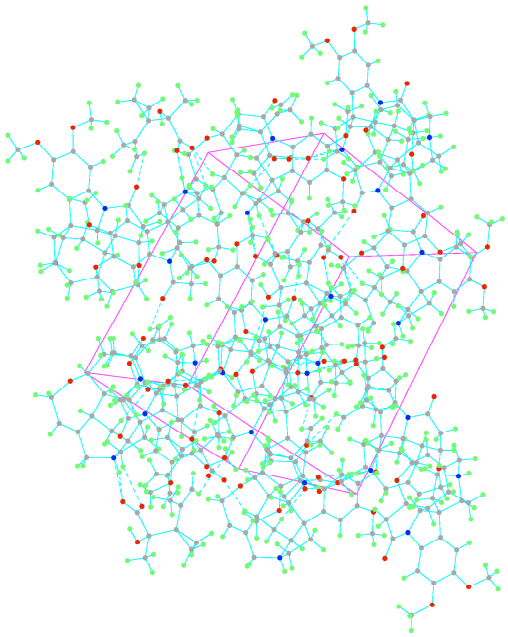
[16] Characterization data for triene **26**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.84 (t, *J* = 7.0 Hz, 1H, $HOCH_2C\mathbf{H}$), 4.72 (br-s, 1H, C=C$\mathbf{H}_2$), 4.52 (br-s, 1H, C=C$\mathbf{H}_2$), 4.46 (dd, 1H, *J* = 7.0, 12.7 Hz, HOC$\mathbf{H}_2$), 4.34 (br-s, 1H, HOC**H**), 4.30 (dd, *J* = 7.0, 12.7 Hz, 1H, HOC$\mathbf{H}_2$), 3.02 (d, *J* = 17.7 Hz, 1H, C$\mathbf{H}_2$-C=C), 2.89 (d, *J* = 17.7 Hz, 1H, C$\mathbf{H}_2$-C=), 2.54 (br-s, 1H, O**H**), 1.77 (s, 3H, HC=CC$\mathbf{H}_3$), 1.44 (s, 3H, C=CC$\mathbf{H}_3$), 1.15 (m, 1H, $CH_2C\mathbf{H}_2$), 1.13 (s, 3H, HOCC$\mathbf{H}_3$), 0.88 (m, 1H, $CH_2C\mathbf{H}_2$), 0.69 (m, 2H, $CH_2C\mathbf{H}_2$). ^{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 ºC, 15 min) and the corresponding triol was fully characterized: ^{1}H NMR (400 MHz, C_6D_6) δ: 5.29 (t, *J* = 7.0 Hz, 1H, $HOCH_2C\mathbf{H}$), 5.11 (br-s, 1H, C=C$\mathbf{H}_2$), 4.90 (br-s, 1H, C=C$\mathbf{H}_2$), 4.40 (d, *J* = 6.4, 1H, Hz, HOC**H**), 3.91-3.83 (m, 2H, HOC$\mathbf{H}_2$), 2.69 (d, *J* = 17.4 Hz, 1H, C≡CC$\mathbf{H}_2$C=C), 2.64 (d, *J* = 17.4 Hz, 1H, C≡CC$\mathbf{H}_2$C=C), 2.02 (br-s, 1H, O**H**), 1.79 (br-s, 1H, O**H**), 1.75 (s, 3H, HC=CC$\mathbf{H}_3$), 1.66 (s, 3H, H_2C=CC$\mathbf{H}_3$), 1.28 (s, 3H, HOCC$\mathbf{H}_3$), 1.21 (m, 1H, C$\mathbf{H}_2CH_2$), 0.90 (m, 1H, C$\mathbf{H}_2CH_2$), 0.54 (m, 1H, C$\mathbf{H}_2CH_2$), 0.41 (m, 1H, C$\mathbf{H}_2CH_2$). ^{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:

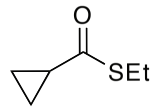
Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for S12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	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



exp1 s2pul

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sw	9998.8	dm	nnn
fb	not used	dmm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.2	dres	1.0
d1	5.000	homo	n
tof	1498.1	PROCESSING	
nt	16	wtfile	
ct	16	proc	ft
alock	n	fn	65536
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
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vs	84		
sc	0		
wc	250		
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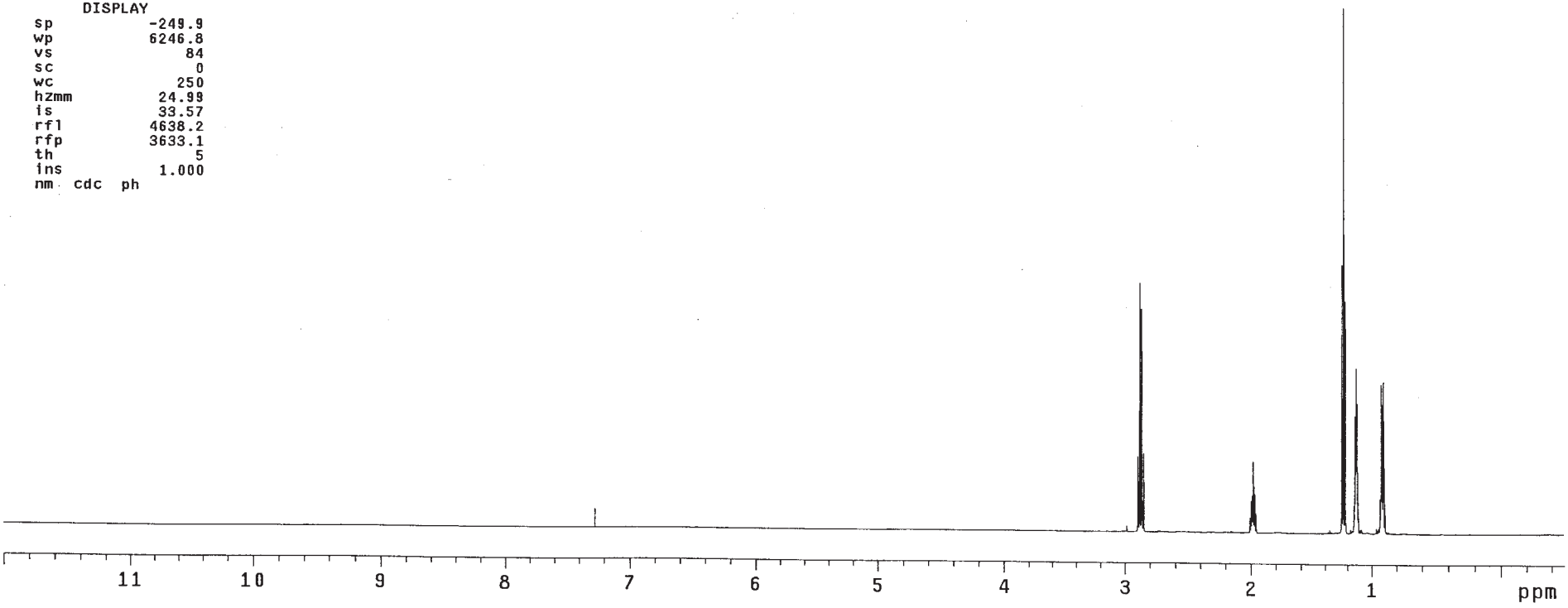

exp1 s2pul

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ss	1	dseq	
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pw	6.9	homo	n
d1	0.763	PROCESSING	
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gain	not used	math	f
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il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
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vs	280		
sc	0		
wc	250		
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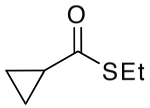
ai	ph		



S-ethyl cyclopropanecarbothioate

(cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane

exp1 s2pul

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tn	H1
at	3.277
np	65536
sw	9998.8
fb	not used
bs	1
tpwr	56
pw	8.2
d1	10.000
tof	1498.1
nt	16
ct	16
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	

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	
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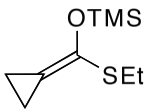
math	f
werr	
wexp	
wbs	
wnt	



exp1 s2pul

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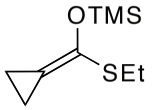
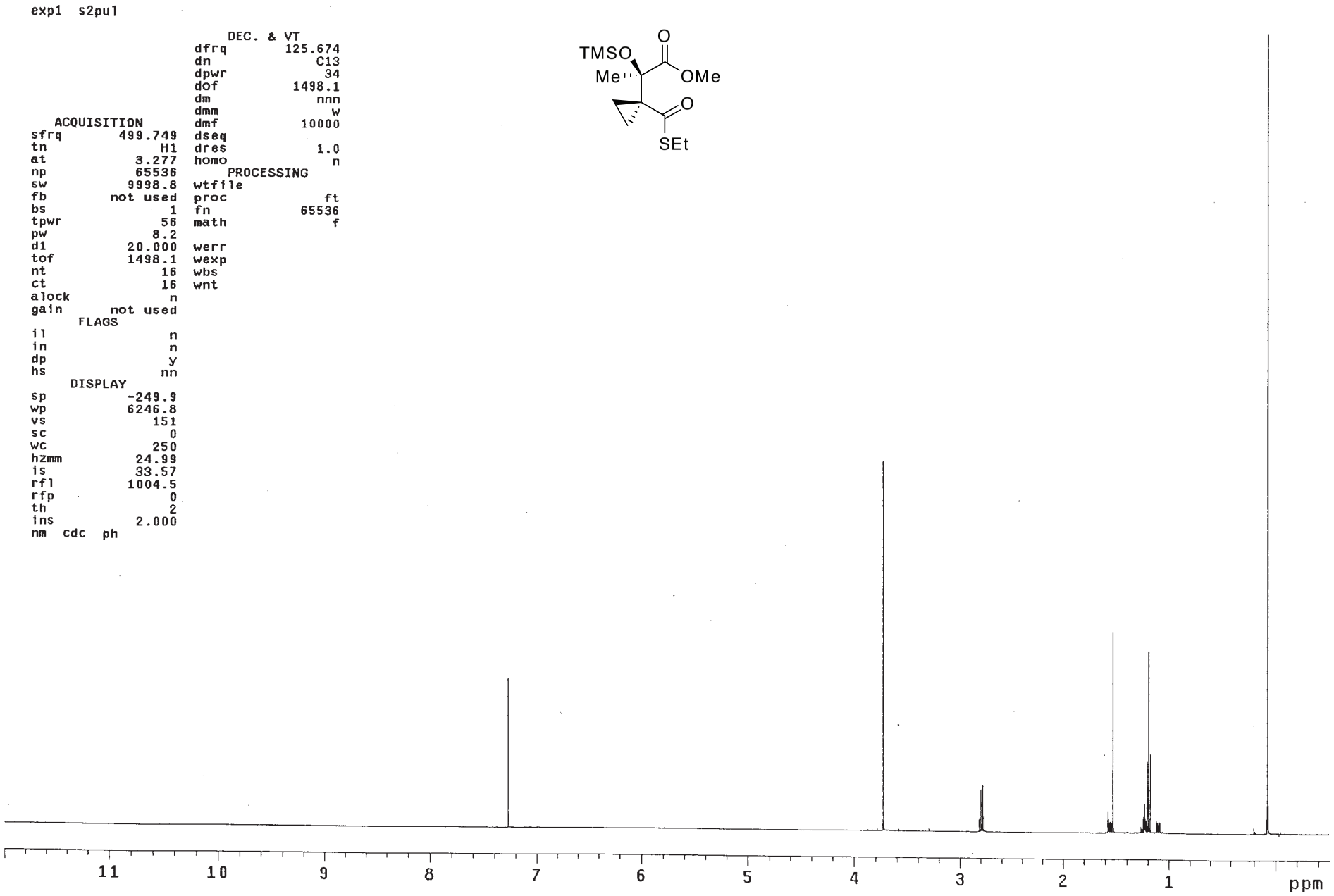
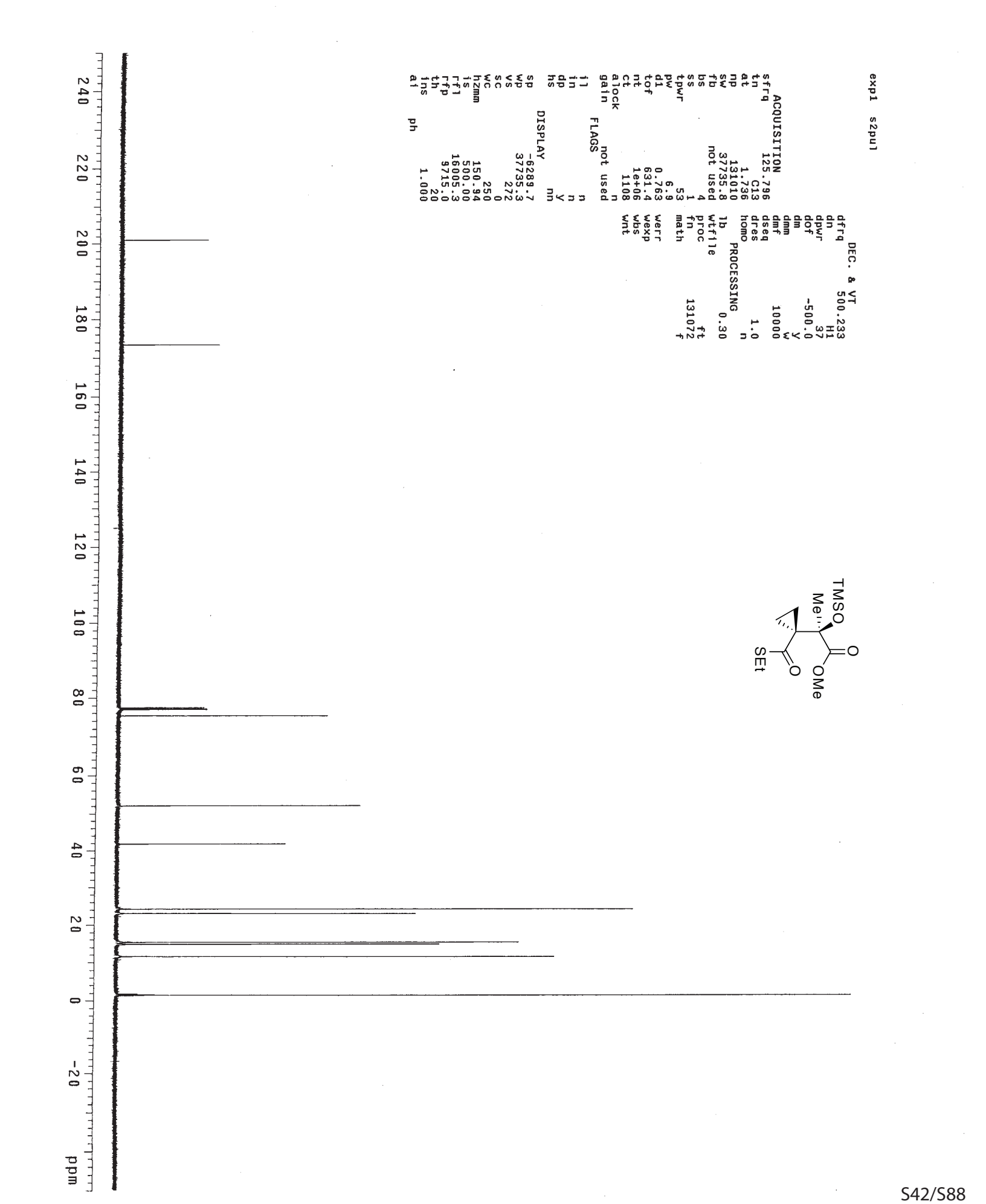
rfp	9715.0		
th	20		
ins	1.000		
ai	ph		



(cyclopropylidene-ethylsulfanyl-methoxy)-trimethyl-silane

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





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

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==========================================================================
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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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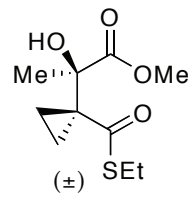
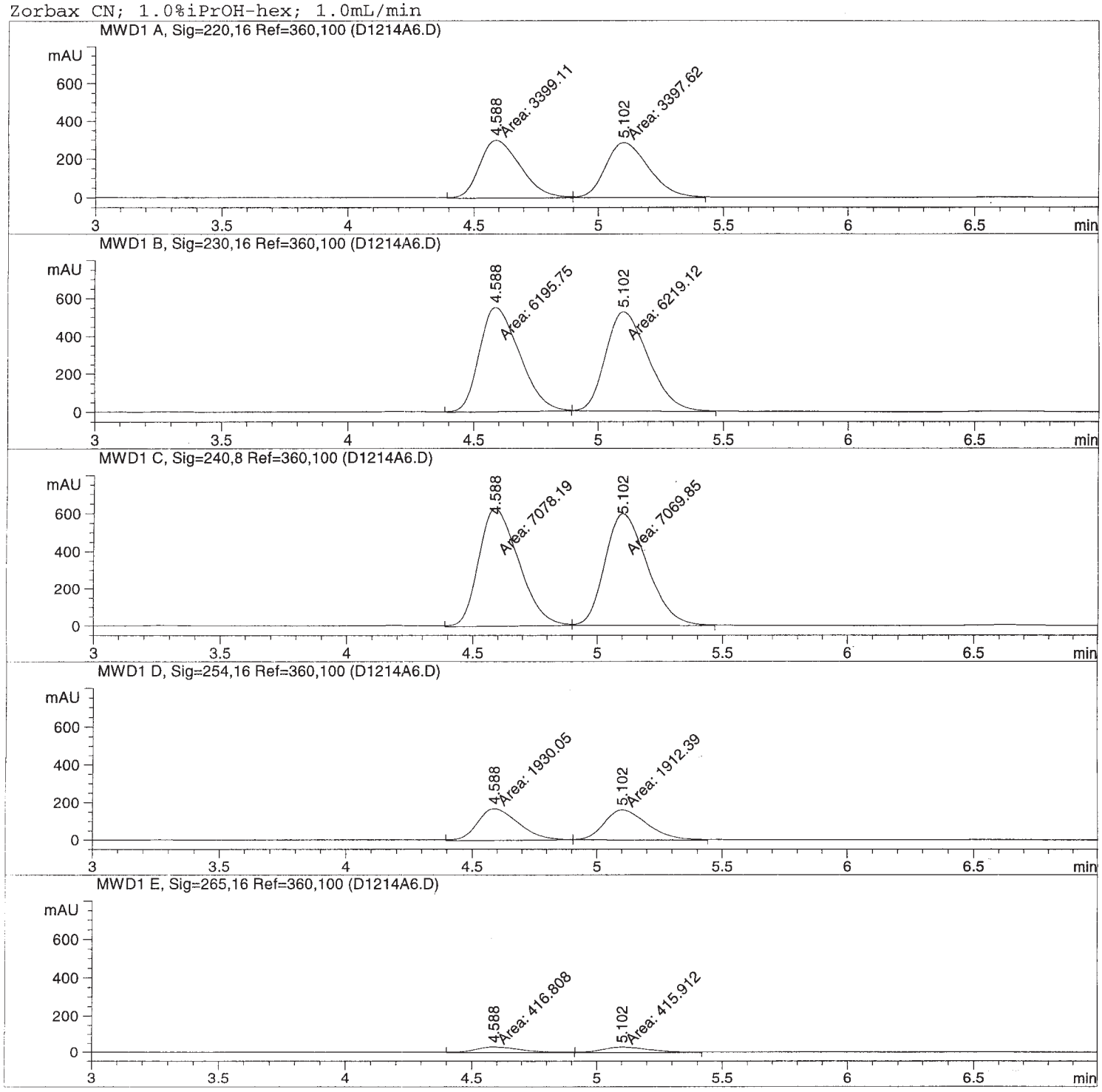
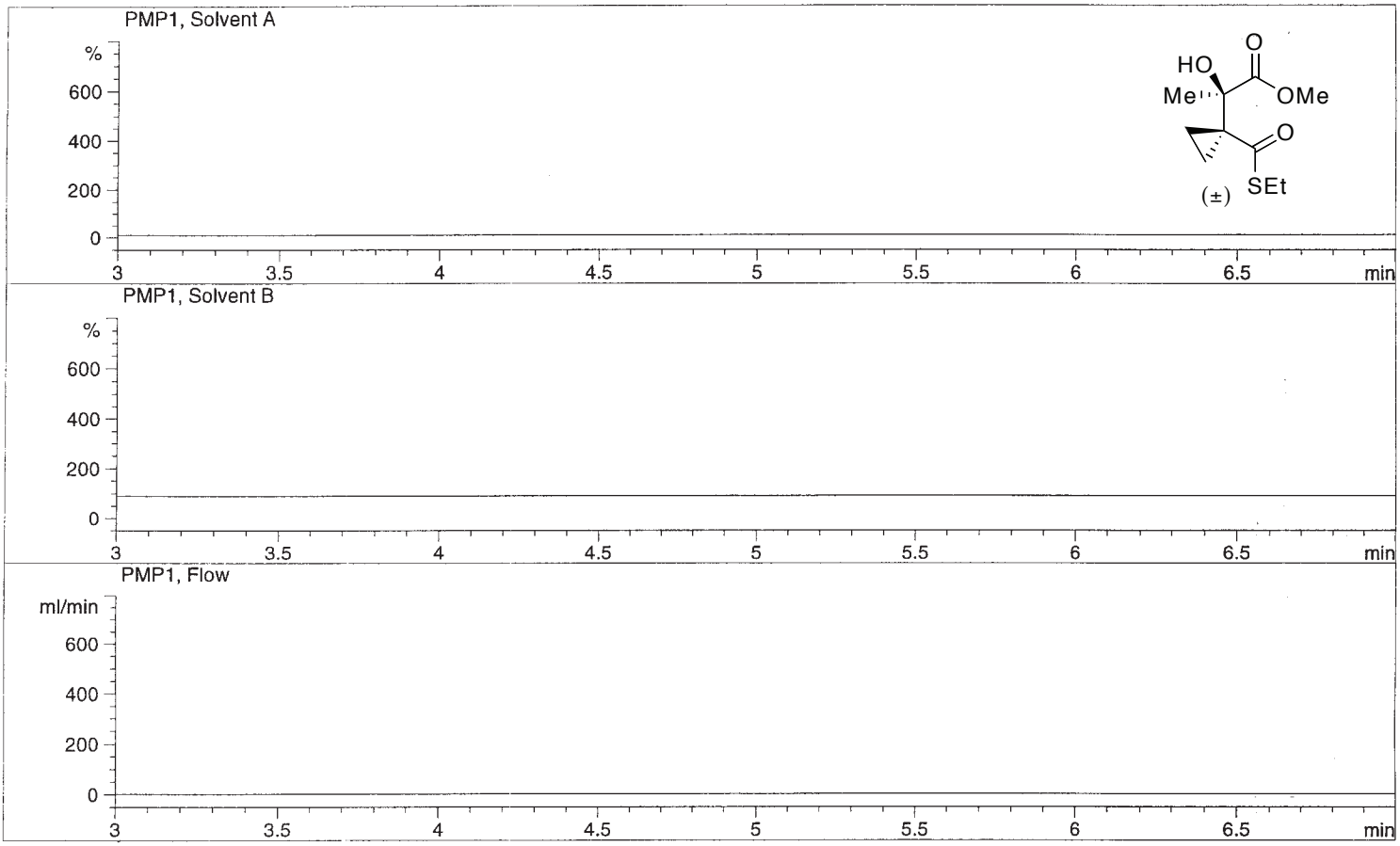




methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate



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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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

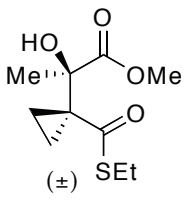
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.588	MM	0.1867	6195.75098	553.00427	49.9059
2	5.102	MM	0.1972	6219.11719	525.51385	50.0941

Totals : 1.24149e4 1078.51813

Results obtained with enhanced integrator!

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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	

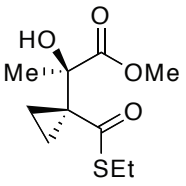
Results obtained with enhanced integrator!

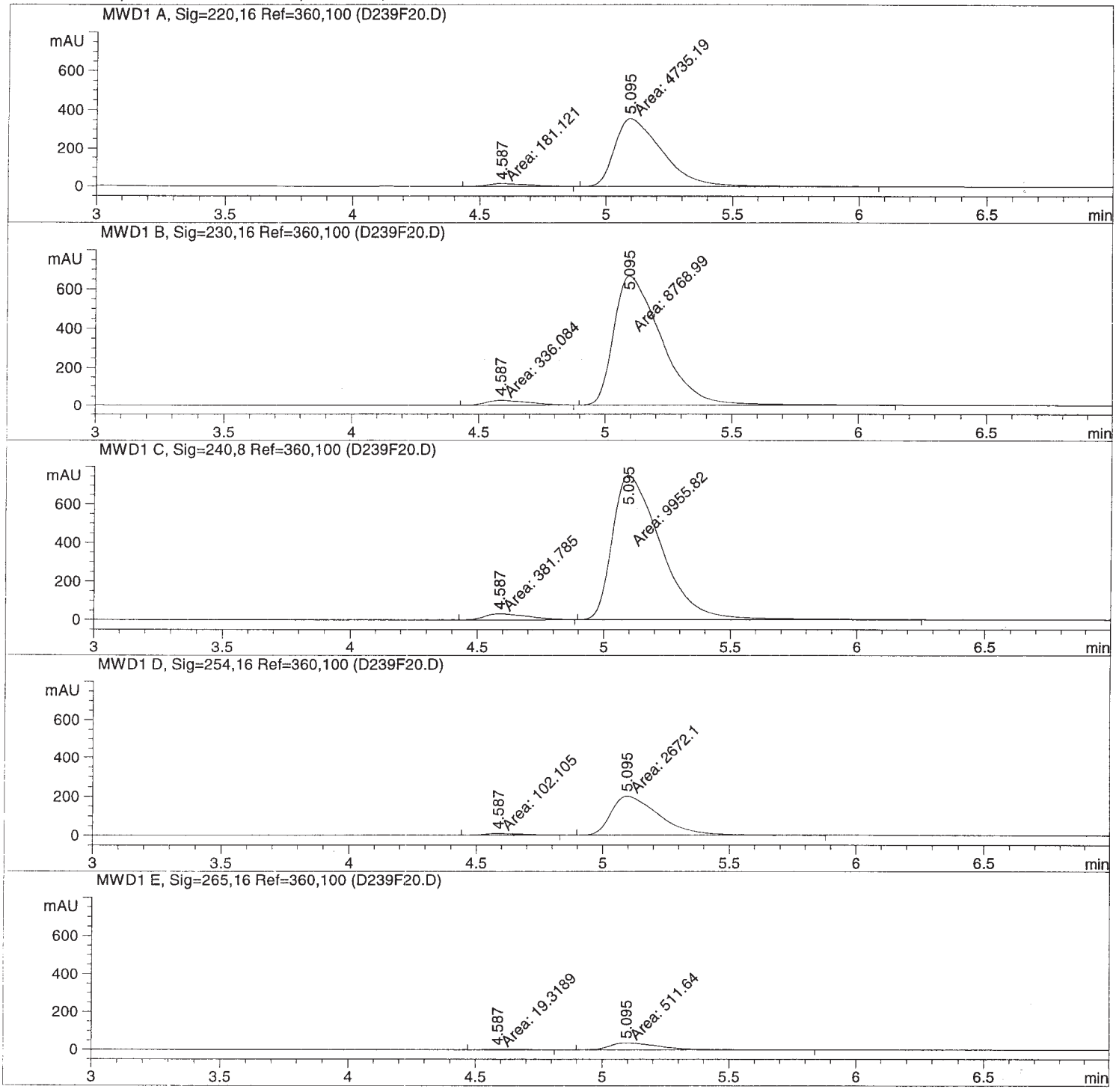
==========

*** End of Report ***

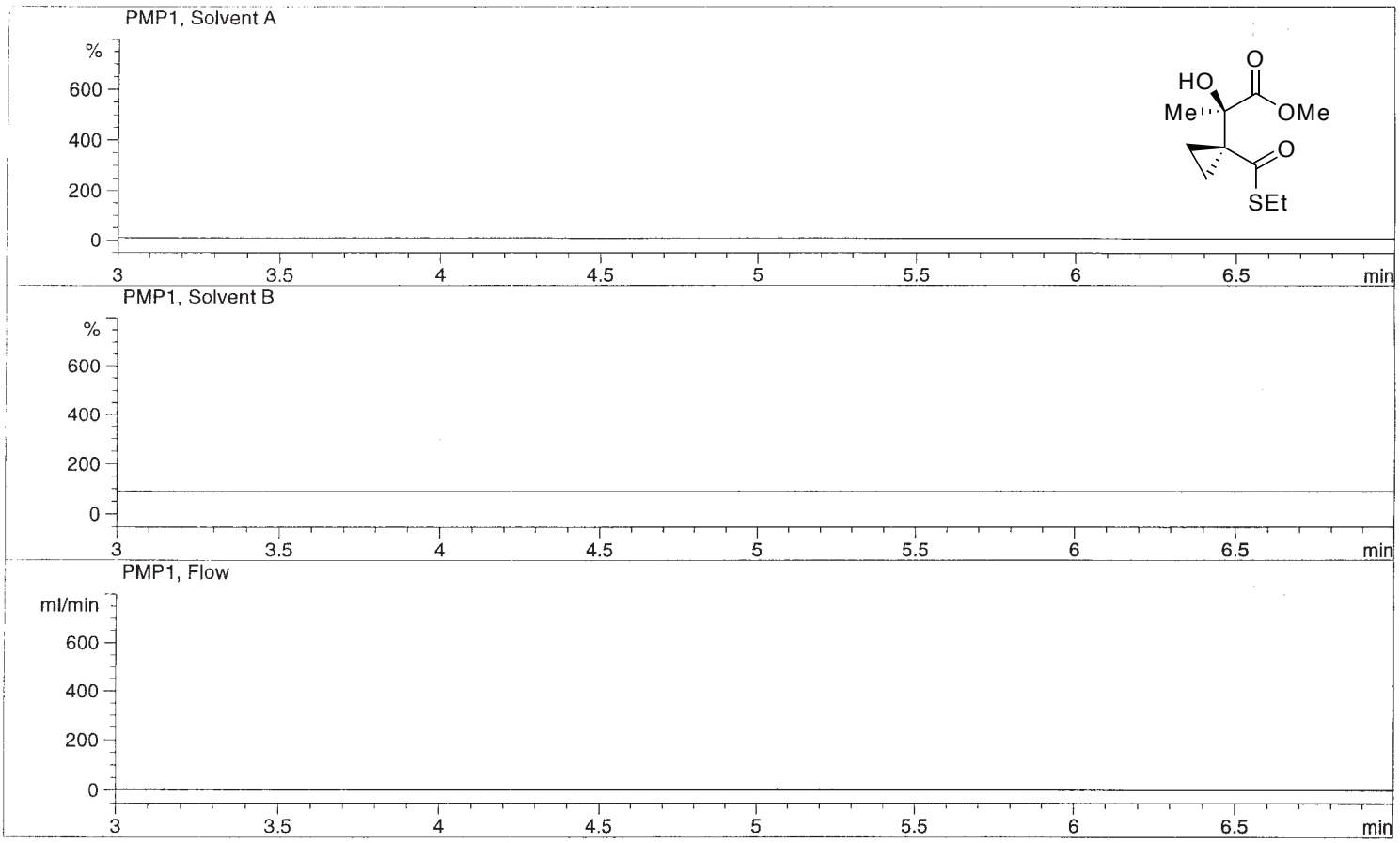
methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate

```
================================================================================
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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!

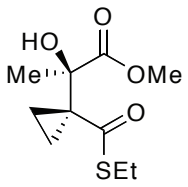
Signal 2: MWD1 B, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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!

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



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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!

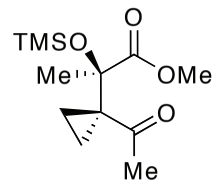
==========

*** End of Report ***

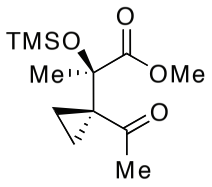
(2*R*)-methyl 2-(1-((ethylthio)carbonyl)cyclopropyl)-2-hydroxypropanoate

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

```
exp1  s2pul

                          DEC. & VT
                      dfrq        125.795
                      dn              C13
                      dpwr             37
                      dof               0
                      dm              nnn
                      dmm               c
                      dmf           10000
                      dseq
                      dres            1.0
                      homo              n
                          PROCESSING
                      wtfile
                      proc             ft
                      fn           131072
                      math              f

                      werr
                      wexp
                      wbs
                      wnt

    ACQUISITION
sfrq          500.235
tn                H1
at               3.200
np              64000
sw            10000.0
fb          not used
bs                 1
ss                 1
tpwr              59
pw               9.8
d1                 0
tof            1498.2
nt                16
ct                16
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            4632.6
rfp            3636.7
th                  7
ins             1.000
nm     ph
```



(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
```

exp1 s2pul

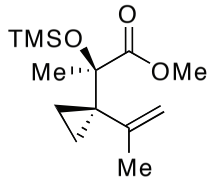
ACQUISITION	
sfrq	500.235
tn	H1
at	3.200
np	64000
sw	10000.0
fb	not used
bs	1
ss	1
tpwr	59
pw	9.8
d1	0
tof	1498.2
nt	16
ct	16
alock	n
gain	not used

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

DEC. & VT	
dfrq	125.795
dn	C13
dpwr	37
dof	0
dm	nnn
dmm	c
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	

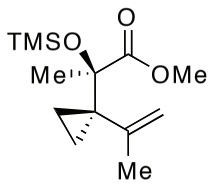


(2*R*)-2-(1-isopropenyl-cyclopropyl)-2-(trimethyl-silanyloxy)-propionic acid methyl ester

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

exp1 s2pul

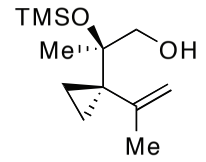
ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	1.736	dpwr	37
np	131010	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	4	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	631.4	lb	0.30
nt	1e+06	wtfile	
ct	200	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS			
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	
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)-propan-1-ol

exp903 s2pul

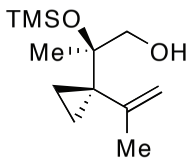
ACQUISITION		DEC. & VT	
sfrq	500.235	dfrq	125.795
tn	H1	dn	C13
at	3.200	dpwr	37
np	64000	dof	0
sw	10000.0	dm	nnn
fb	not used	dmm	c
bs	4	dmf	10000
ss	1	dseq	
tpwr	59	dres	1.0
pw	9.8	homo	n
d1	15.000	PROCESSING	
tof	1498.2	wtfile	
nt	32	proc	ft
ct	32	fn	131072
alock	n	math	f
gain	not used		
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
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

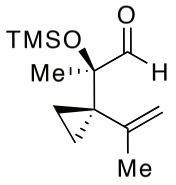
SAMPLE		DEC. & VT	
date	Sep 7 2005	dfrq	500.233
solvent	CDCl3	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	-500.0
sfrq	125.796	dm	y
tn	C13	dmm	w
at	1.736	dmf	10000
np	131010	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
ss	1	lb	0.30
tpwr	53	wtfile	
pw	6.9	proc	ft
d1	0.763	fn	131072
tof	631.4	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)-propionaldehyde

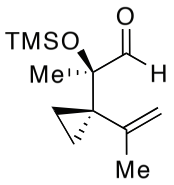
exp1 s2pul

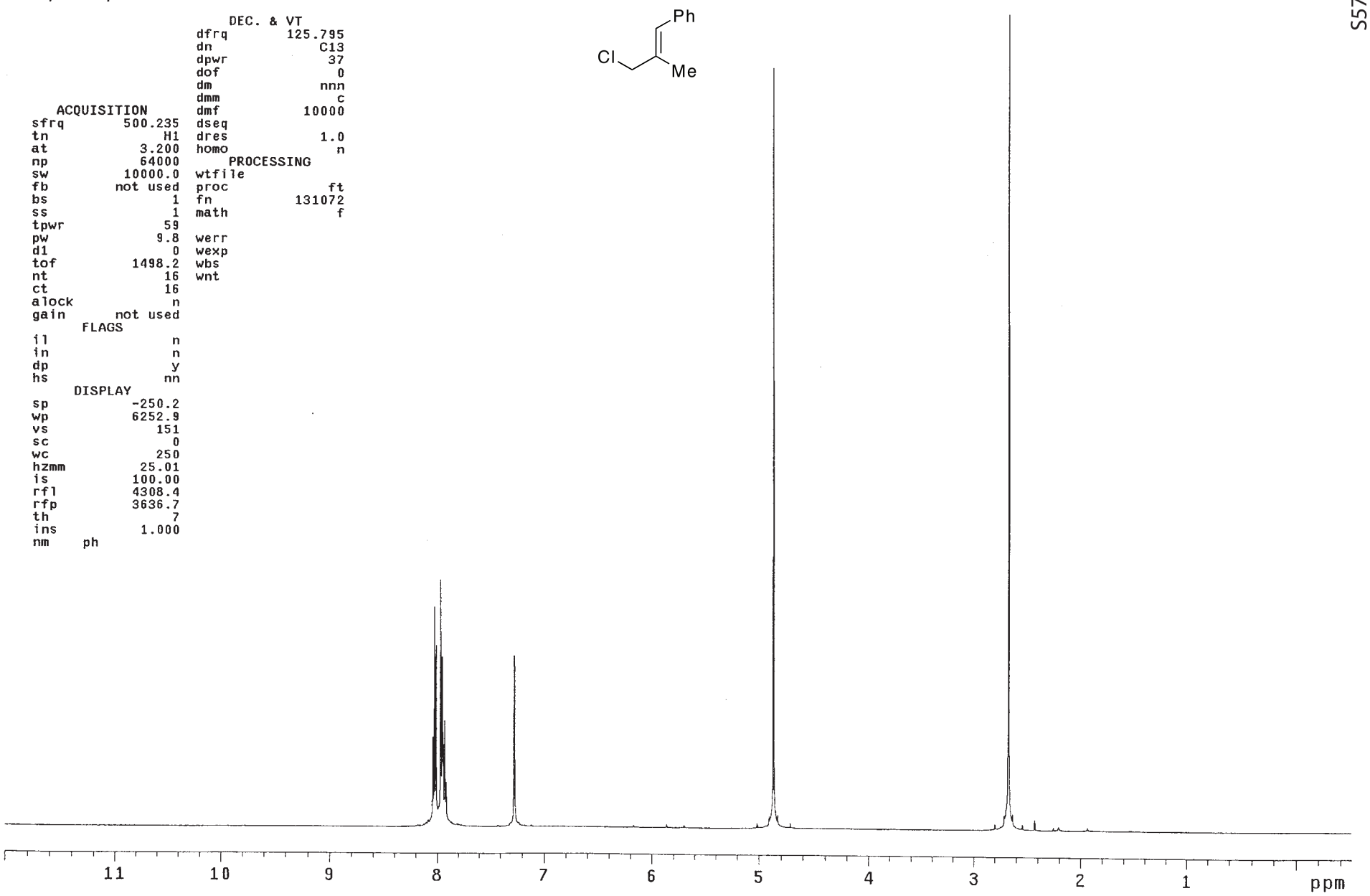
ACQUISITION		DEC. & VT	
sfrq	500.235	dfrq	125.795
tn	H1	dn	C13
at	3.200	dpwr	37
np	64000	dof	0
sw	10000.0	dm	nnn
fb	not used	dmm	c
bs	1	dmf	10000
ss	1	dseq	
tpwr	59	dres	1.0
pw	9.8	homo	n
d1	0	PROCESSING	
tof	1498.2	wtfile	
nt	64	proc	ft
ct	64	fn	131072
alock	n	math	f
gain	not used		
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
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
date    Nov  1 2005
solvent       CDCl3
file             exp
    ACQUISITION
sfrq        125.796
tn              C13
at              1.736
np             131010
sw           37735.8
fb          not used
bs                 4
ss                 1
tpwr              53
pw               6.9
d1             0.763
tof            631.4
nt             1e+07
ct                12
alock              n
gain        not used
       FLAGS
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

      DEC. & VT
dfrq         500.233
dn                H1
dpwr              37
dof           -500.0
dm                 y
dmm                w
dmf            10000
dseq
dres             1.0
homo               n
     PROCESSING
lb              0.30
wtfile
proc              ft
fn            131072
math               f

werr
wexp
wbs
wnt
```

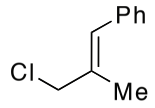




E-(5-Chloro-4-methyl-pent-3-enyl)-benzene

exp60 s2pul

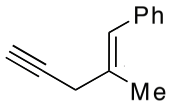
ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	1.736	dpwr	37
np	131010	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	4	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	631.4	lb	0.30
nt	1e+06	wtfile	
ct	44	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
sp	-6225.2		
wp	37735.3		
vs	159		
sc	0		
wc	250		
hzmm	74.58		
is	500.00		
rfl	15911.8		
rfp	9686.0		
th	20		
ins	1.000		
ai	ph		



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

exp2 s2pul

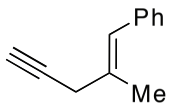
SAMPLE		DEC. & VT	
date	Jan 21 2006	dfrq	125.795
solvent	CDCl3	dn	C13
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.235	dm	nnn
tn	H1	dmm	c
at	3.200	dmf	10000
np	64000	dseq	
sw	10000.0	dres	1.0
fb	not used	homo	n
bs	1	PROCESSING	
ss	1	wtfile	
tpwr	59	proc	ft
pw	9.8	fn	131072
d1	0	math	f
tof	1498.2		
nt	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

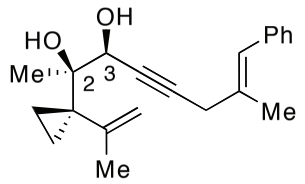
SAMPLE		DEC. & VT	
date	Jan 21 2006	dfrq	500.233
solvent	CDCl3	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	-500.0
sfrq	125.796	dm	y
tn	C13	dmm	w
at	1.736	dmf	10000
np	131010	dseq	
sw	37735.8	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
ss	1	lb	0.30
tpwr	53	wtfile	
pw	6.9	proc	ft
d1	0.763	fn	131072
tof	631.4	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

exp1 s2pul

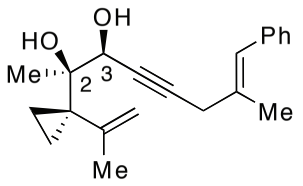
ACQUISITION		DEC. & VT	
sfrq	500.235	dfrq	125.795
tn	H1	dn	C13
at	3.200	dpwr	37
np	64000	dof	0
sw	10000.0	dm	nnn
fb	not used	dmm	c
bs	1	dmf	10000
ss	1	dseq	
tpwr	59	dres	1.0
pw	9.8	homo	n
d1	0	PROCESSING	
tof	1498.2	wtfile	
nt	16	proc	ft
ct	16	fn	131072
alock	n	math	f
gain	not used		
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
sp	-0.6		
wp	6002.7		
vs	151		
sc	0		
wc	250		
hzmm	24.01		
is	100.00		
rfl	4561.6		
rfp	3581.7		
th	7		
ins	1.000		
nm	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

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



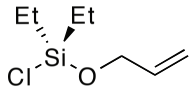
3S:3R, 5.6:1

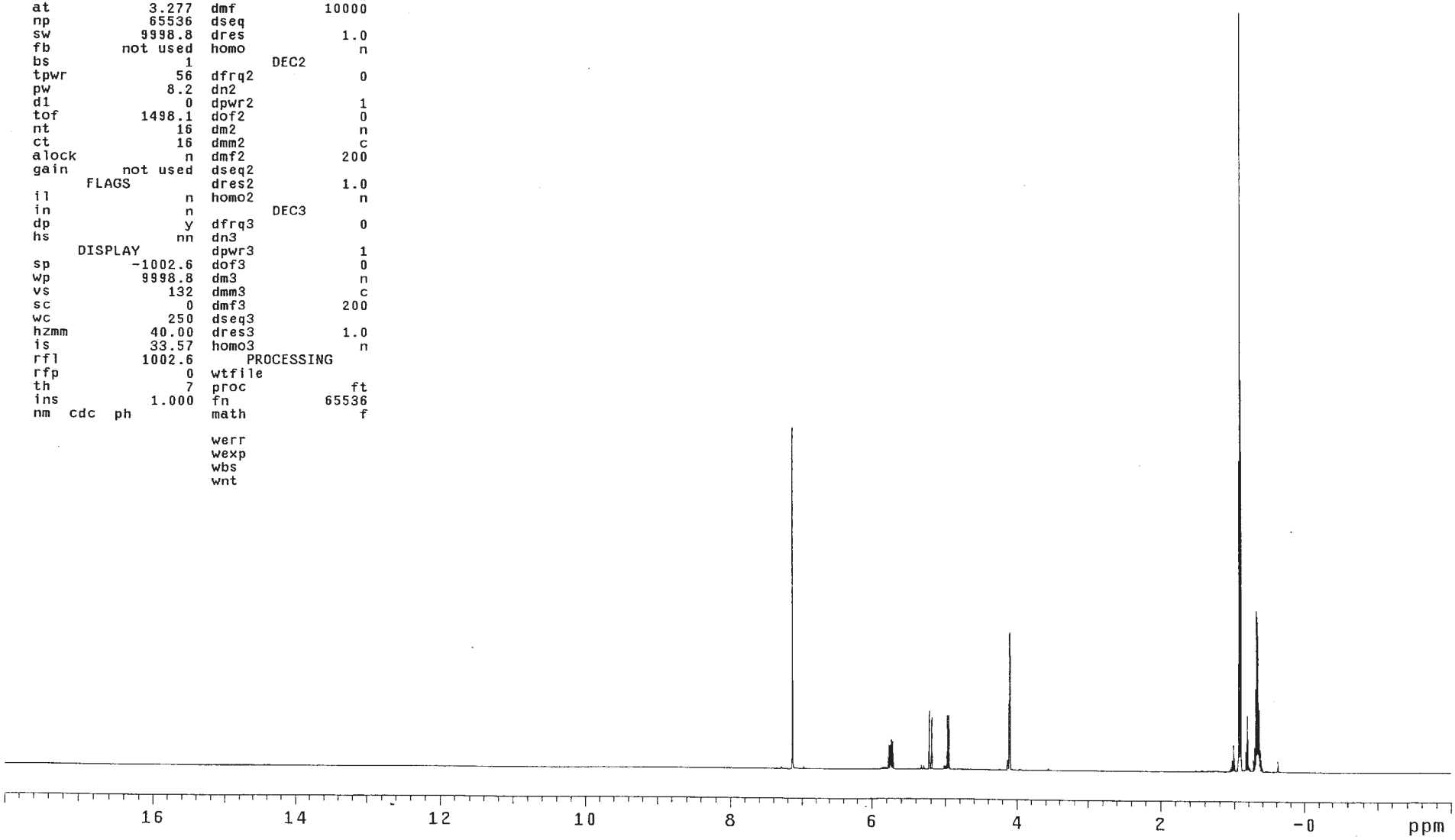
exp1 s2pul

ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	2.500	dpwr	37
np	188680	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	16	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	2.500	PROCESSING	
tof	631.4	lb	0.30
nt	1e+06	wtfile	
ct	7152	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
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		

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	

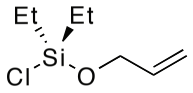




Allyloxy-chloro-diethyl-silane

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
dl	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		

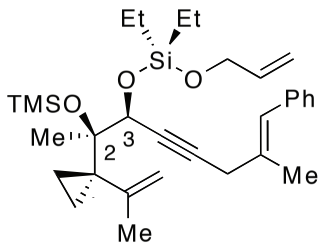


Allyloxy-chloro-diethyl-silane

exp1 s2pul

ACQUISITION		DEC. & VT	
sfrq	499.749	dfrq	125.674
tn	H1	dn	C13
at	3.277	dpwr	34
np	65536	dof	1498.1
sw	9998.8	dm	nnn
fb	not used	dmm	w
bs	4	dmf	10000
tpwr	56	dseq	
pw	8.2	dres	1.0
d1	0	homo	n
tof	1498.1	PROCESSING	
nt	64	wtfile	
ct	64	proc	ft
alock	n	fn	65536
gain	not used	math	f
FLAGS			
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	
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

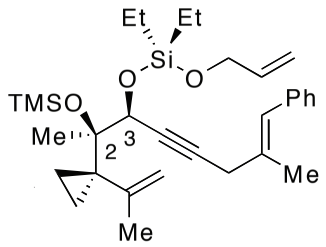


3S:3R, 6:1

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

ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	1.736	dpwr	37
np	131010	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	4	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	631.4	lb	0.30
nt	1e+06	wtfile	
ct	92	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS			
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	
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		

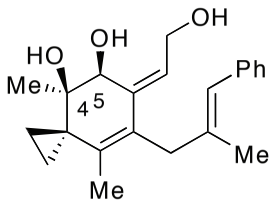


3S:3R, 6:1

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

ACQUISITION		DEC. & VT	
sfrq	499.749	dfrq	125.674
tn	H1	dn	C13
at	3.277	dpwr	34
np	65536	dof	1498.1
sw	9998.8	dm	nnn
fb	not used	dmm	W
bs	4	dmf	10000
tpwr	56	dseq	
pw	8.2	dres	1.0
d1	0	homo	n
tof	1498.1	PROCESSING	
nt	64	wtfile	
ct	64	proc	ft
alock	n	fn	65536
gain	not used	math	f
FLAGS			
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	
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			

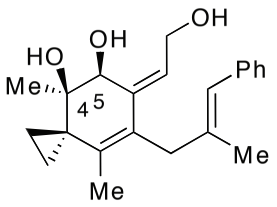


5S:5R, 6:1

(6Z)-(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

ACQUISITION		DEC. & VT	
sfrq	125.796	dfrq	500.233
tn	C13	dn	H1
at	1.736	dpwr	37
np	131010	dof	-500.0
sw	37735.8	dm	y
fb	not used	dmm	w
bs	4	dmf	10000
ss	1	dseq	
tpwr	53	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	631.4	lb	0.30
nt	1e+06	wtfile	
ct	372	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	
hs	nn		
DISPLAY			
sp	-6224.7		
wp	37735.3		
vs	337		
sc	0		
wc	250		
hzmm	40.69		
is	500.00		
rfl	22374.6		
rfp	16149.3		
th	20		
ins	1.000		
ai	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

exp1 s2pul

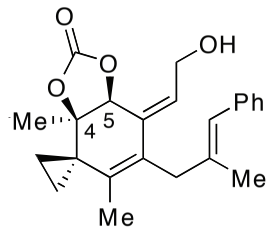
ACQUISITION	
sfrq	500.235
tn	H1
at	3.200
np	64000
sw	10000.0
fb	not used
bs	4
ss	1
tpwr	59
pw	9.8
d1	0
tof	1498.2
nt	64
ct	0
alock	n
gain	not used

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

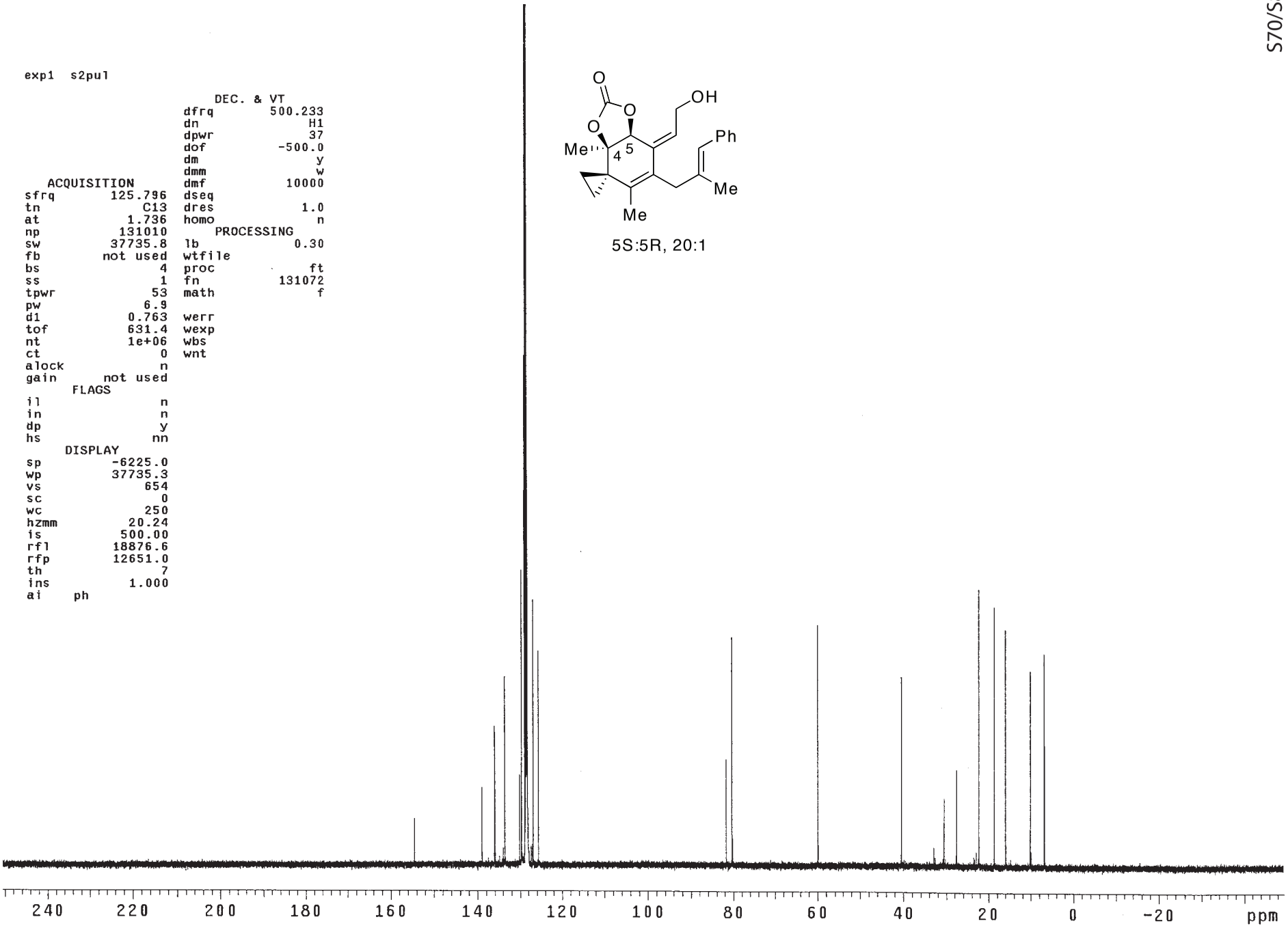
DEC. & VT	
dfrq	125.795
dn	C13
dpwr	37
dof	0
dm	nnn
dmm	c
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
wtfile	
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	



5S:5R, 20:1

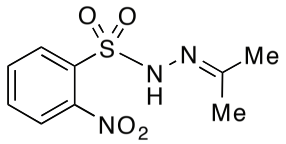
(6*Z*)-(4*R*,5*S*)-6-(2-Hydroxy-ethylidene)-4,8-dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-spiro[2.5]oct-7-ene-4,5-diol-carbonate



(6Z)-(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

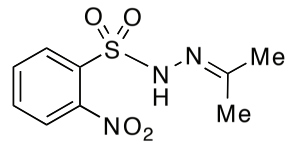
ACQUISITION		DEC. & VT	
sfrq	499.750	dfrq	125.673
tn	H1	dn	C13
at	3.001	dpwr	30
np	63050	dof	0
sw	10504.2	dm	nnn
fb	not used	dmm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.9	dres	1.0
d1	2.000	homo	n
tof	1519.5	PROCESSING	
nt	16	wtfile	
ct	16	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS		werr	
il	n	wexp	
in	n	wbs	
dp	y	wnt	wft
hs	nn		
DISPLAY			
sp	-249.9		
wp	6246.8		
vs	151		
sc	0		
wc	250		
hzmm	24.99		
is	33.57		
rfl	3746.9		
rfp	969.5		
th	1		
ins	6.000		
nm cdc ph			

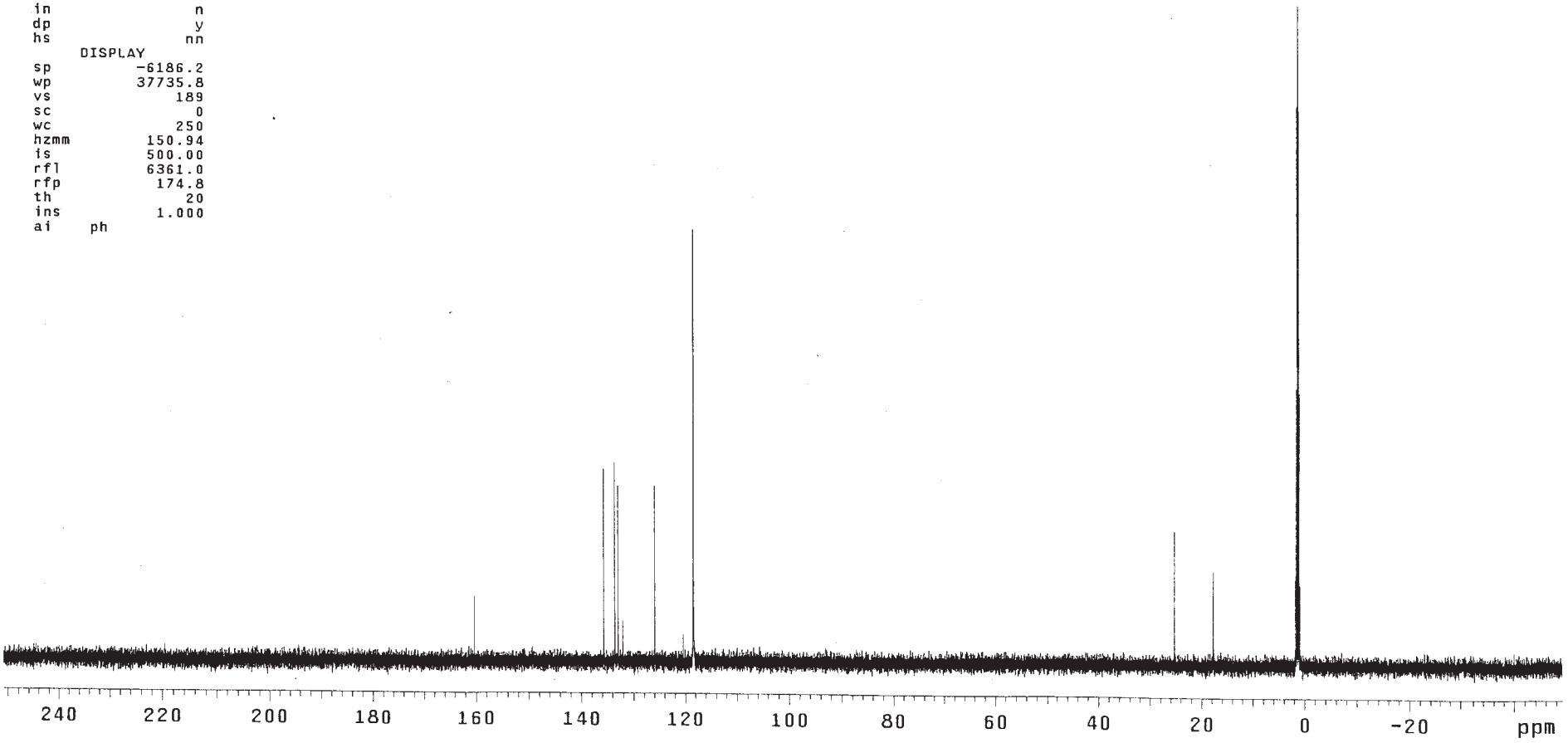


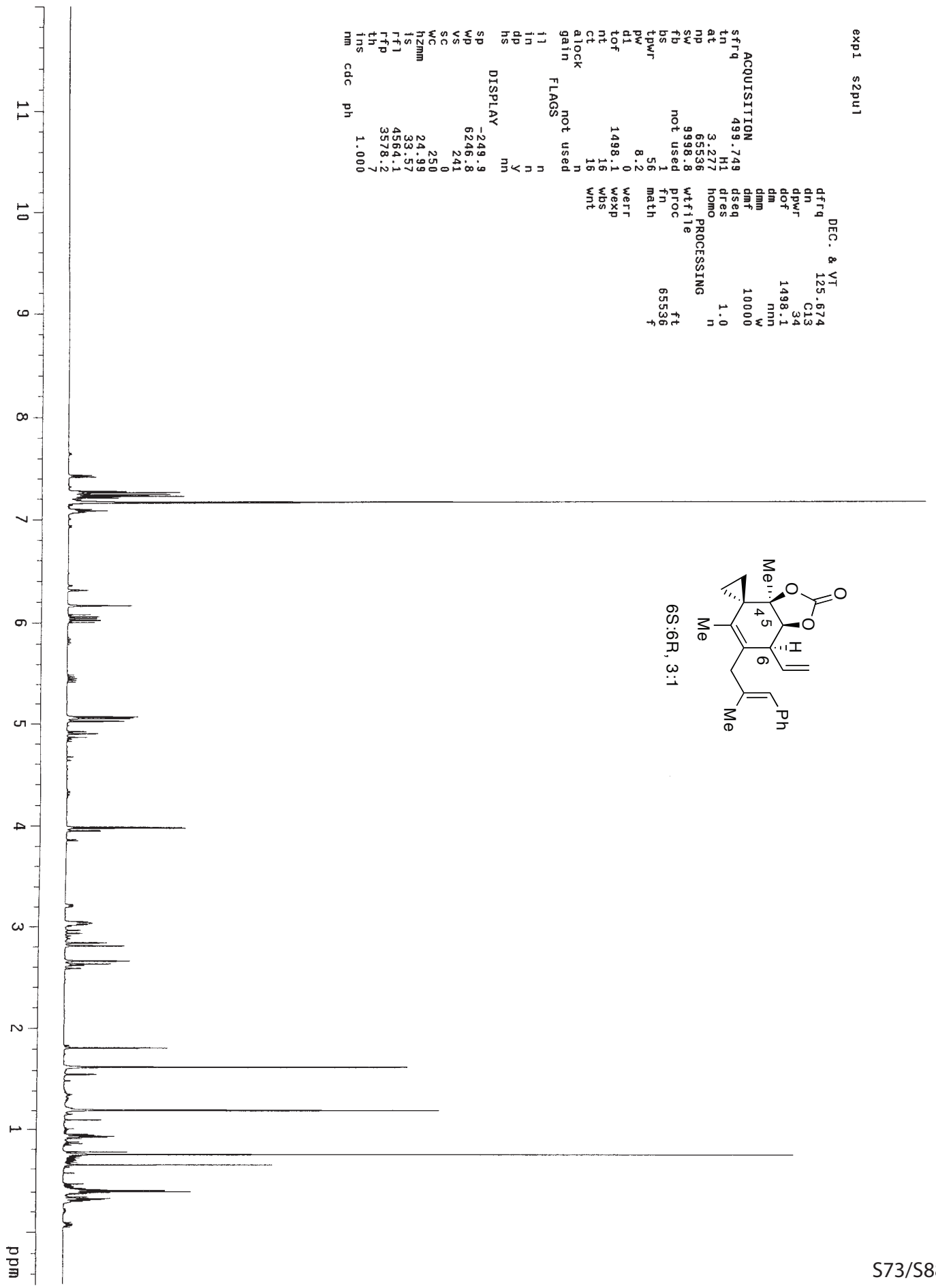
N-Isopropylidene-*N*′-2-nitrobenzenesulfonyl hydrazine

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

```
exp2  s2pul

      SAMPLE
date    Jan 20 2006
solvent acetonitri~
                  le
file              exp
   ACQUISITION
sfrq        125.796
tn              C13
at              1.736
np             131010
sw           37735.8
fb         not used
bs                 4
ss                 1
tpwr              53
pw               6.9
d1             0.763
tof            631.4
nt             1e+06
ct                84
alock              n
gain       not used
       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

          DEC. & VT
dfrq         500.236
dn                H1
dpwr              37
dof           -500.0
dm                 y
dmm                w
dmf            10000
dseq
dres             1.0
homo               n
     PROCESSING
lb              0.30
wtfile
proc               ft
fn             131072
math               f
werr
wexp
wbs
wnt
```

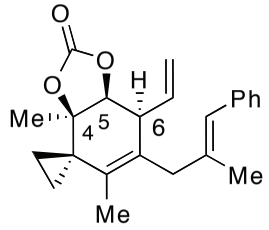






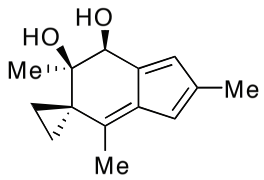
(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate

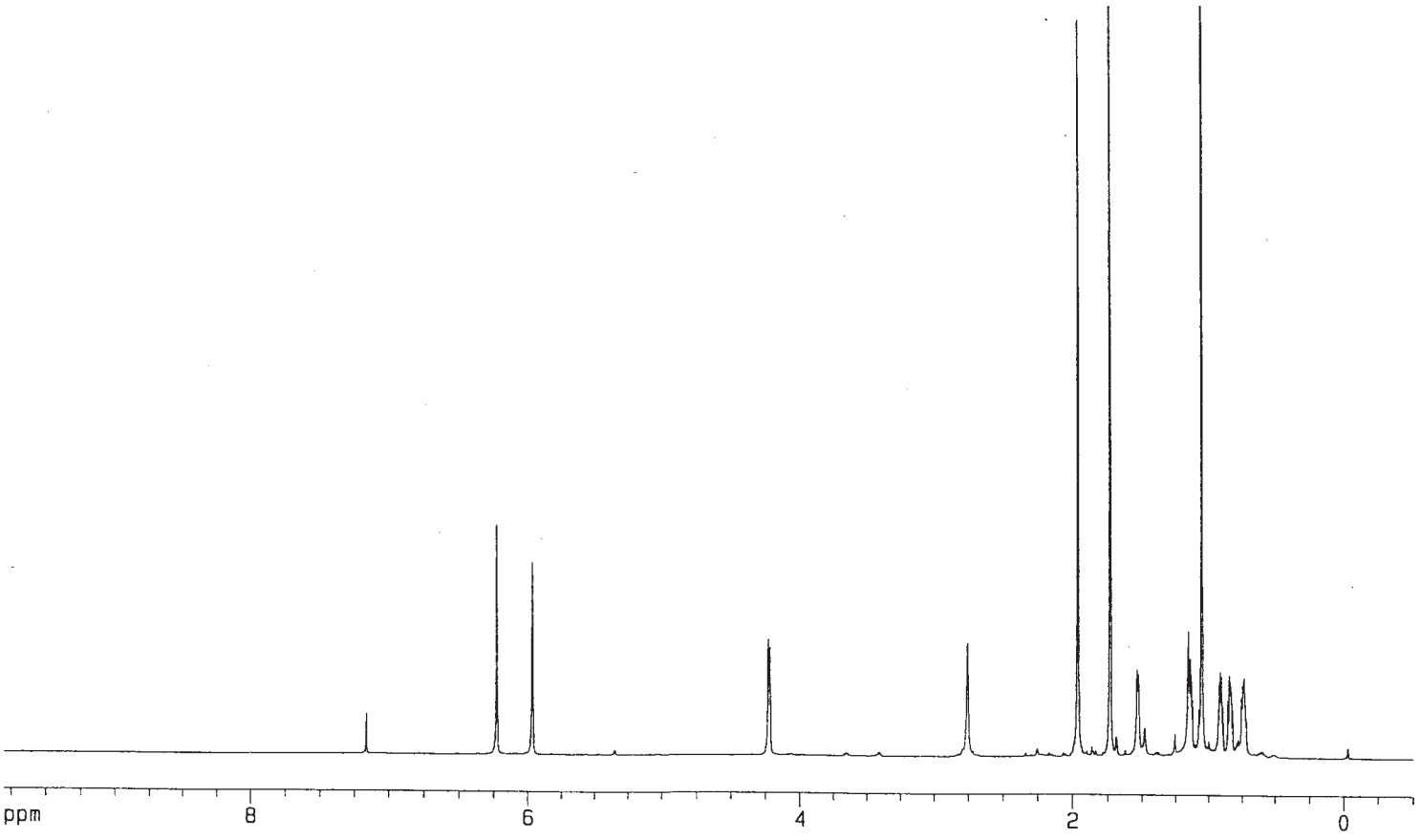
(4*R*,5*S*)-4,8-Dimethyl-7-([2*E*]-2-methyl-3-phenyl-allyl)-6-vinyl-spiro[2.5]oct-7-ene-4,5-diol-carbonate



6S:6R, 3:1

```
exp2  s2pul

      SAMPLE
date    Nov 17 2005
solvent     Benzene
file             exp
   ACQUISITION
sfrq         125.796
tn               C13
at             1.736
np            131010
sw           37735.8
fb         not used
bs                4
ss                1
tpwr             53
pw              6.9
d1            0.763
tof           631.4
nt            1e+06
ct              368
alock             n
gain       not used
       FLAGS
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

      DEC. & VT
dfrq         500.233
dn                H1
dpwr              37
dof           -500.0
dm                y
dmm               w
dmf           10000
dseq
dres            1.0
homo              n
    PROCESSING
lb             0.30
wtfile
proc              ft
fn            131072
math              f

werr
wexp
wbs
wnt
```





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

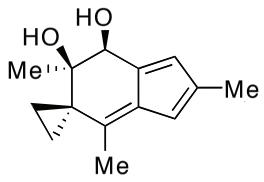
F2 - Processing parameters

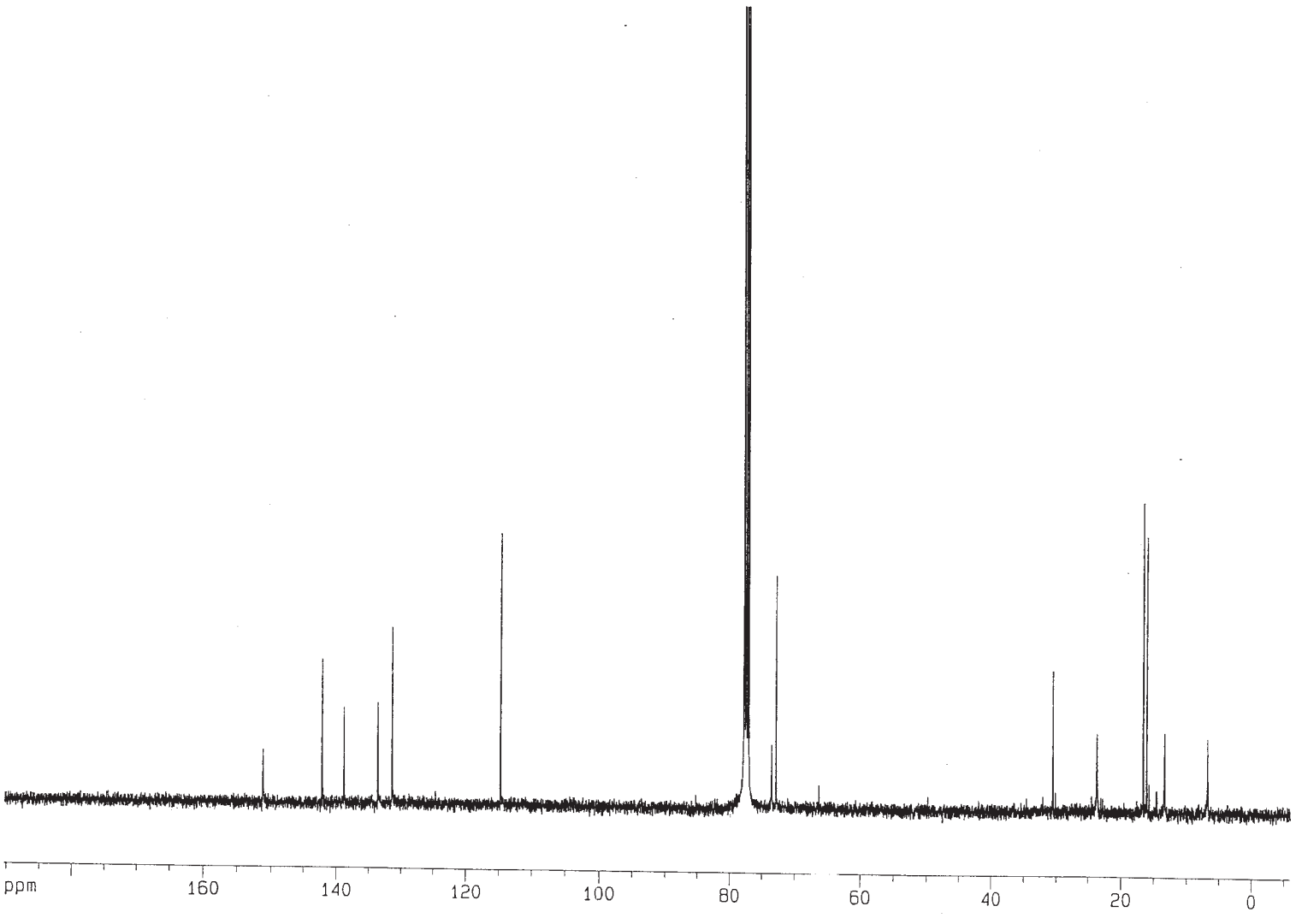
SI	32768
SF	600.1300773 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

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

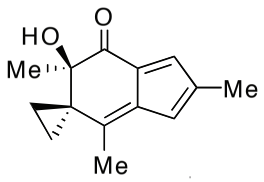
F2 - Processing parameters

SI	32768
SF	100.6127290 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

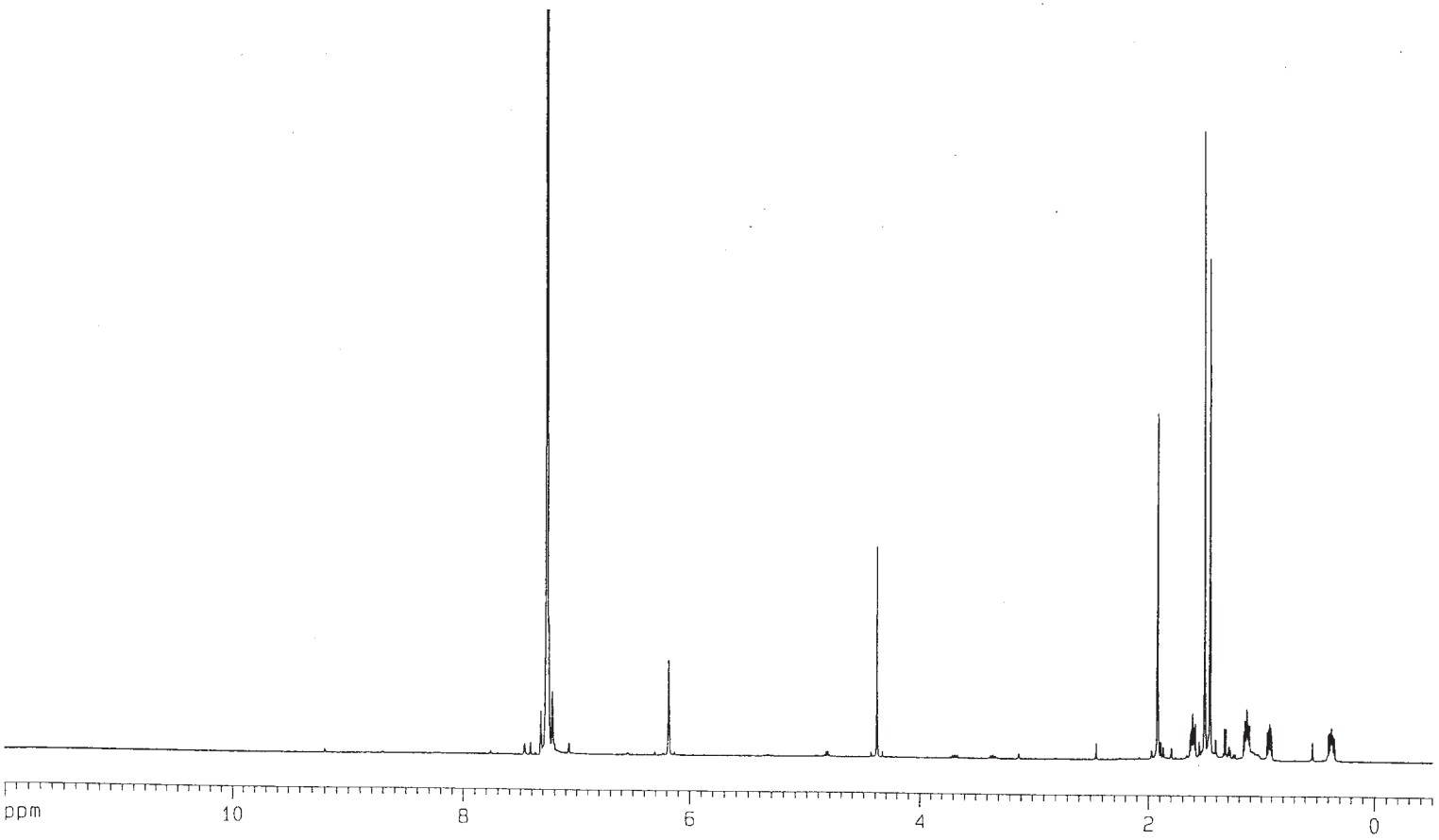
1D NMR plot parameters

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

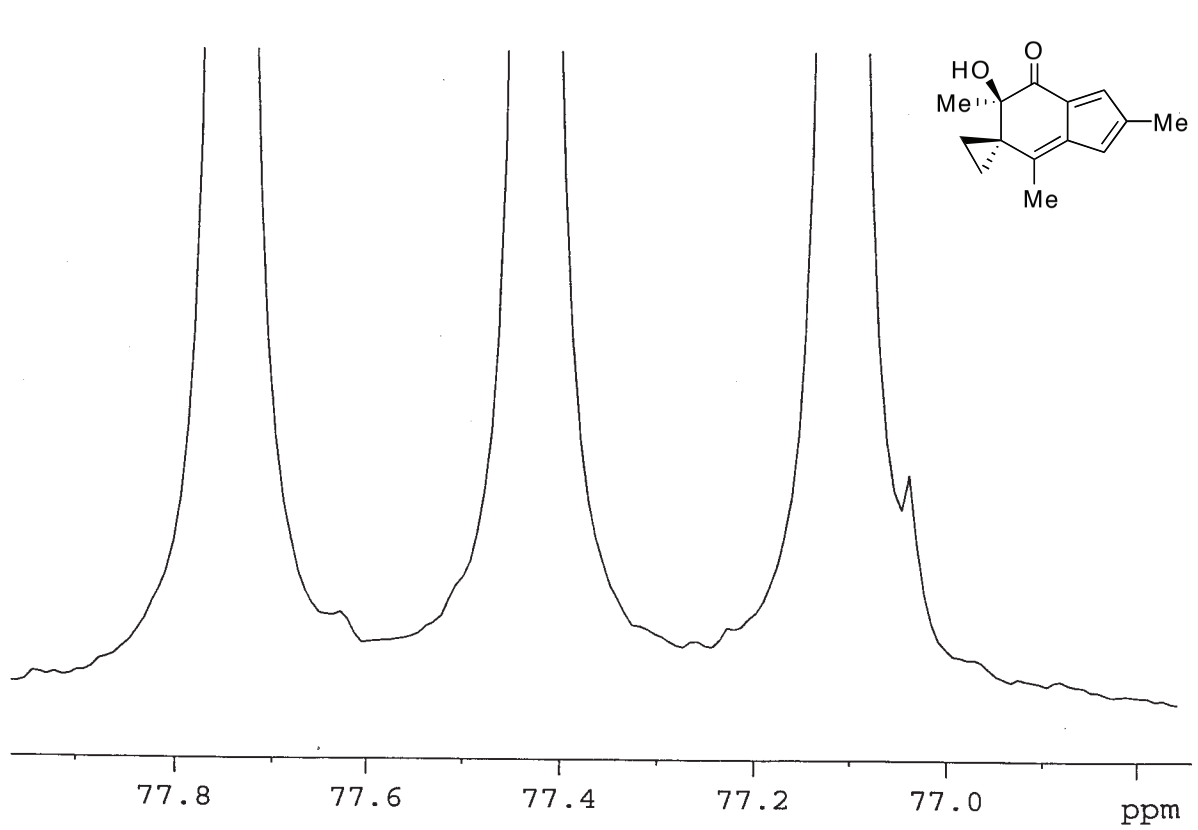
Fulvene diol



Acylfulvene




```
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
SFO1         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
```

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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
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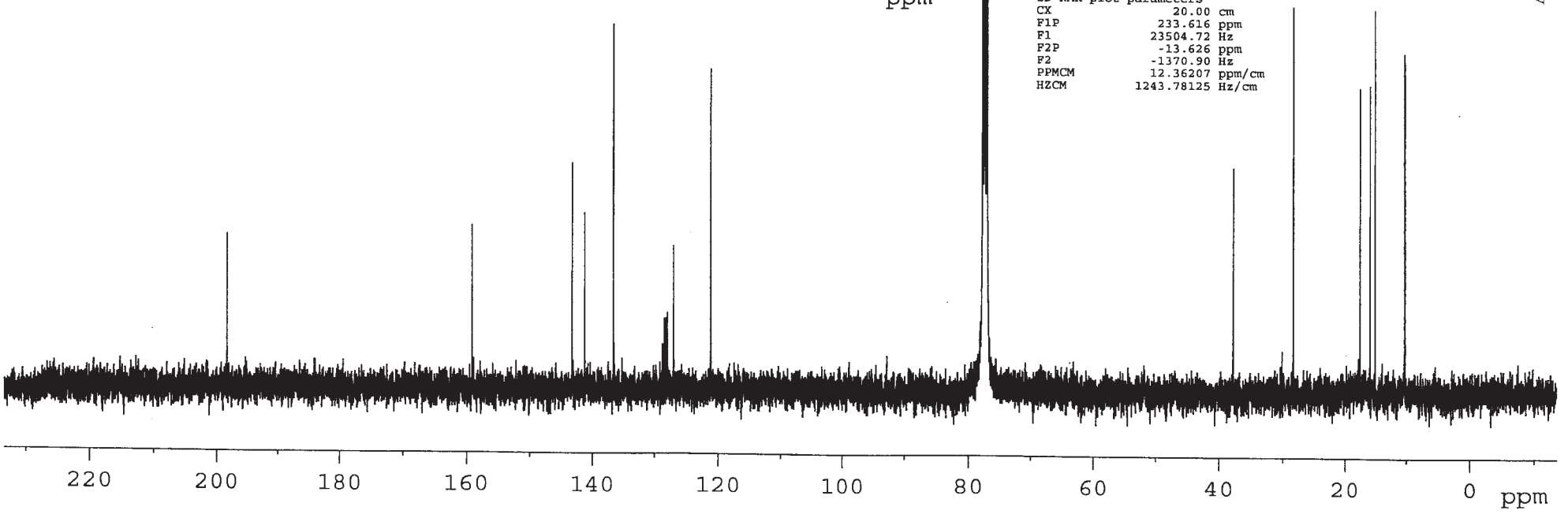
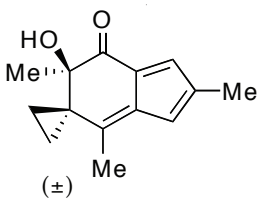
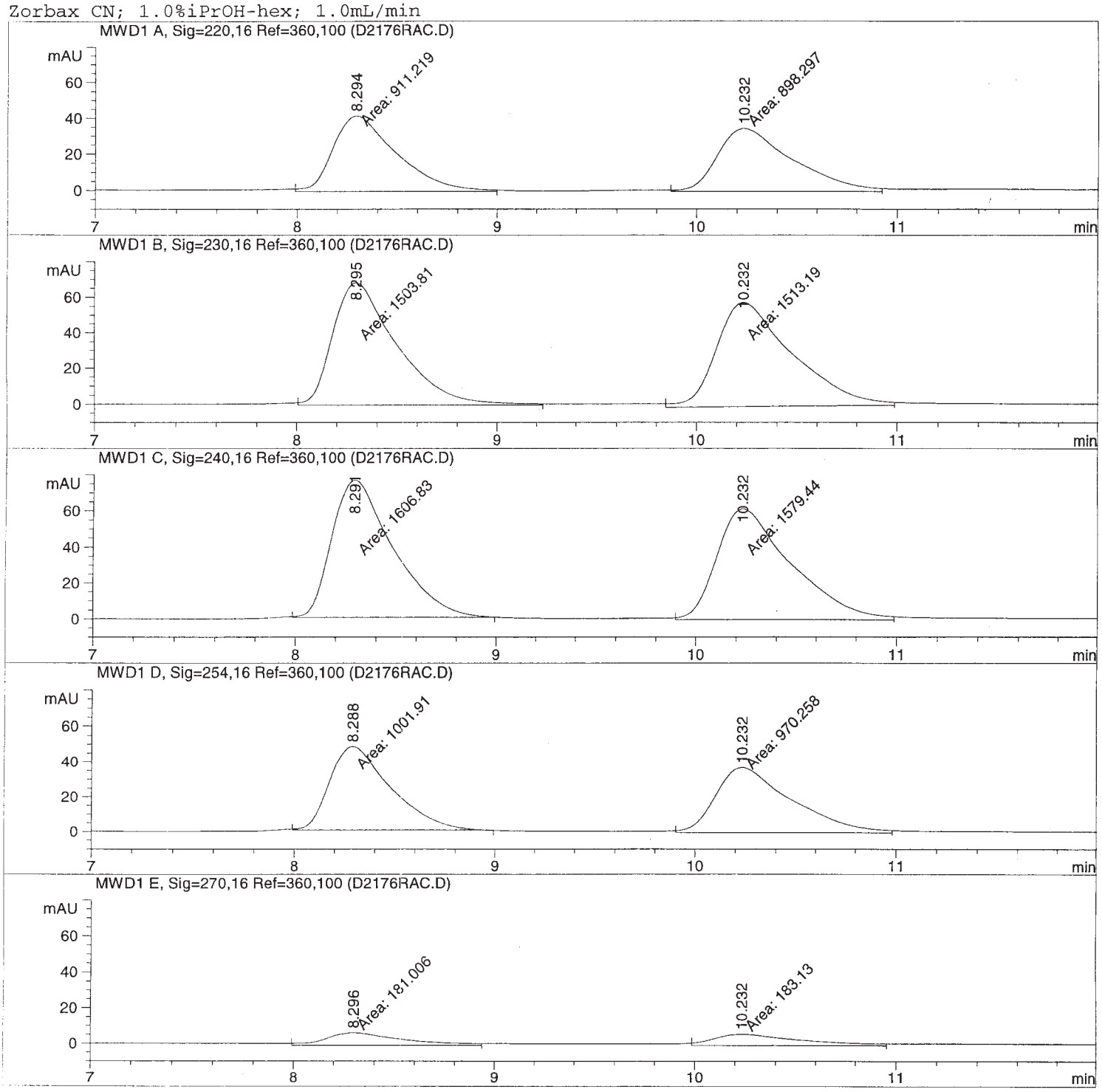
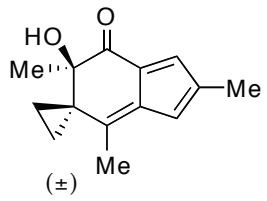


Acylfulvene

```
==========================================================================
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
```

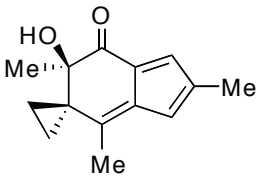


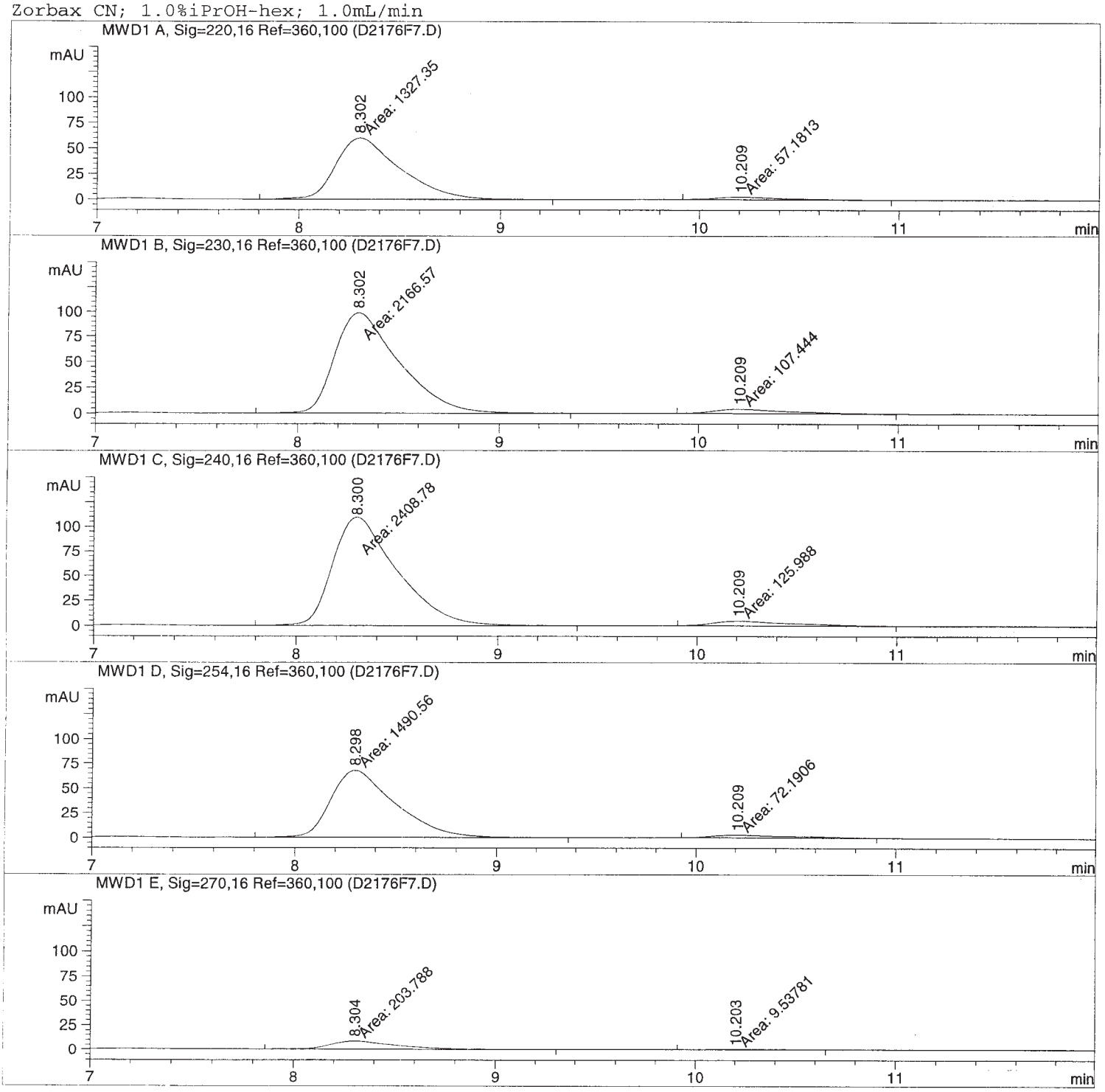




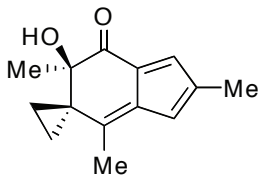

```
================================================================================
                              Area Percent Report
================================================================================

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
```

```
==========================================================================
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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!

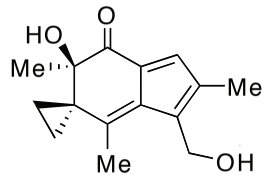
Signal 4: MWD1 D, Sig=254,16 Ref=360,100

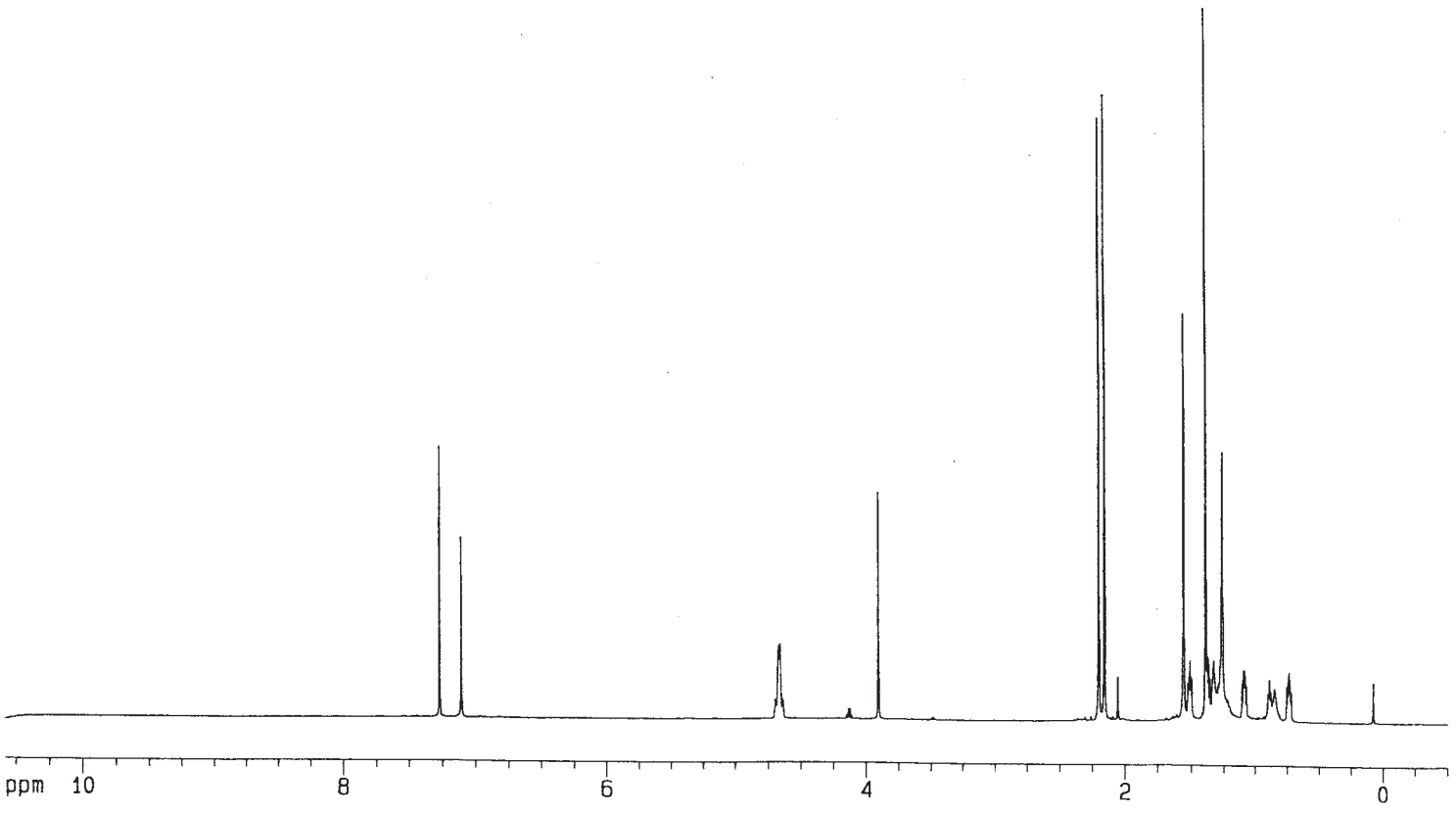
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.298	MM	0.3686	1490.56372	67.39674	95.3806
2	10.209	MM	0.4593	72.19061	2.61948	4.6194
Totals :				1562.75433	70.01622	

Results obtained with enhanced integrator!

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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	





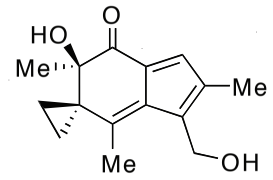
Current Data Parameters
NAME
EXPNO 1
PROCNO 1

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

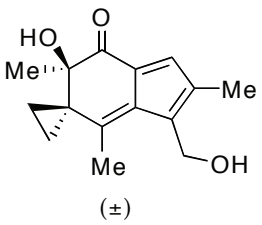
1D NMR plot parameters
CX 20.00 cm
CY 9.86 cm
F1P 10.800 ppm
F1 6481.40 Hz
F2P -0.500 ppm
F2 -300.07 Hz
PPMCM 0.56500 ppm/cm
HZCM 339.07346 Hz/cm



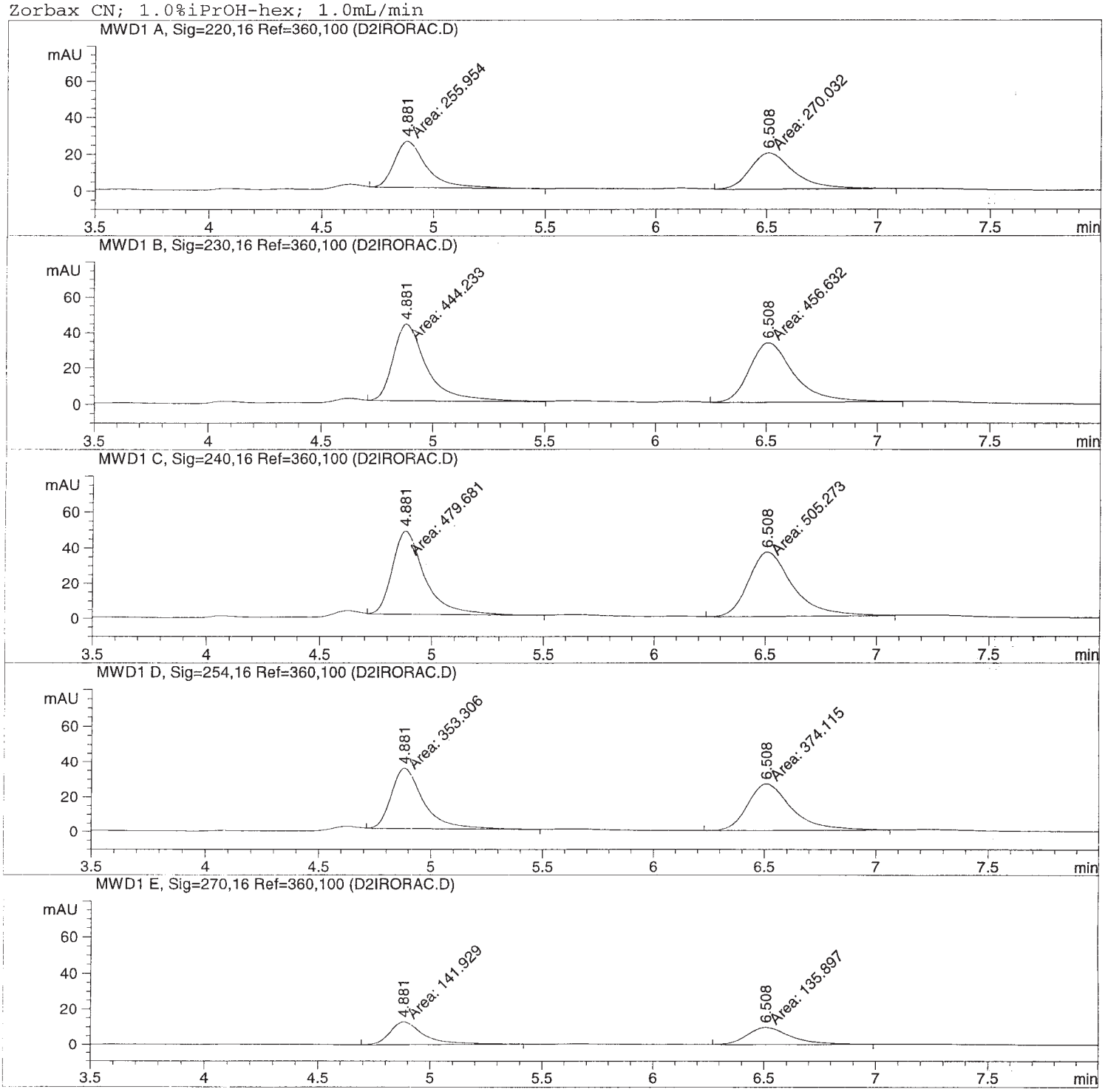
Irofulvene

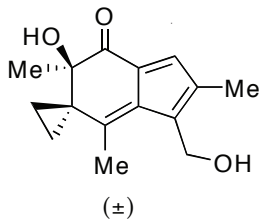
```
Current Data Parameters
NAME
EXPNO                  1
PROCNO                 1

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
```

```
================================================================================
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
```



(±)





(±)

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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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 [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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

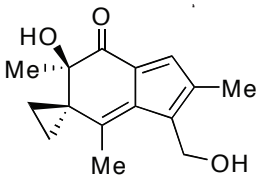
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.881	MM	0.1703	353.30612	34.58545	48.5697
2	6.508	MM	0.2314	374.11542	26.94118	51.4303
Totals :				727.42154	61.52663	

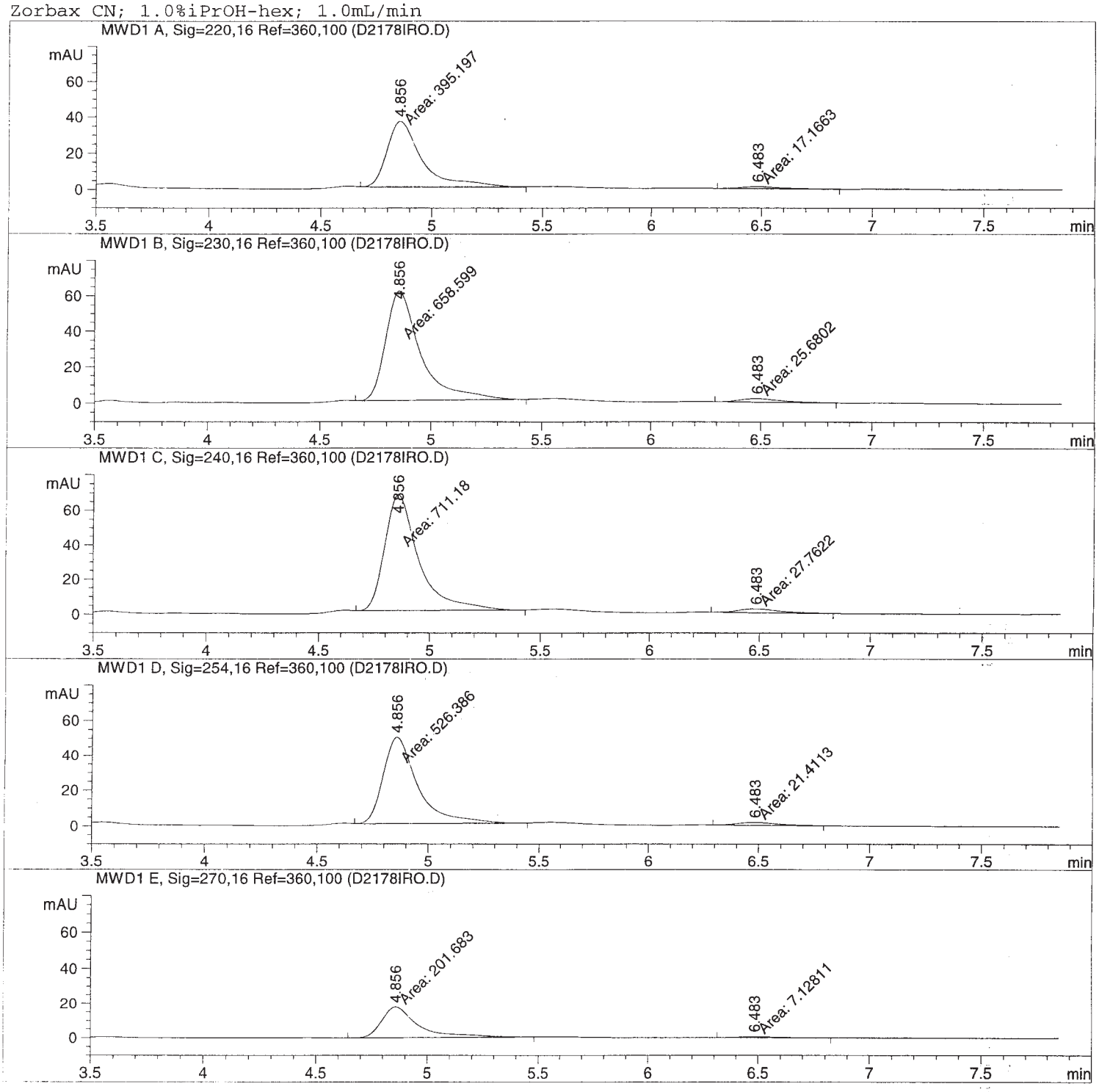
Results obtained with enhanced integrator!

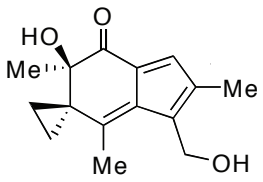
Signal 5: MWD1 E, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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	

```
==========================================================================
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
```








```
================================================================================
                          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
```