Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Concise Total Synthesis of (–)-Calycanthine, (+)-Chimonanthine, and (+)-Folicanthine.

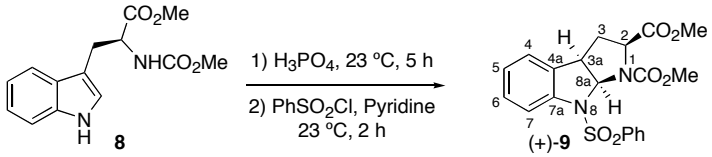
Massachusetts Institute of Technology, Department of Chemistry, Cambridge, Massachusetts 02139

General Procedures. All reactions were performed in oven-dried or flame-dried round-bottomed 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. Where necessary (so noted), solutions were deoxygenated by dinitrogen purging for a minimum of 10 min. 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).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and iodine vapors or an aqueous solution of ceric ammonium molybdate (CAM). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C.

Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile and toluene were purchased from J.T. Baker (Cycletainer^{TM}) and were purified by the method of Grubbs et al. under positive argon pressure.[2] Acetone was distilled from anhydrous calcium sulfate. Methanol (>99.9 % HPLC grade, ≤0.020 % water) was purchased from Aldrich chemical company and used as received. CH_2Cl_2 saturated with NH_3 was prepared by agitation of a 2:1 (v/v) biphasic mixture of CH_2Cl_2 and 28-30% aqueous NH_4OH, separation of the organic layer and drying over Na_2SO_4. AIBN was recrystallized from diethyl ether. Na_2HPO_4 was dried by flame–drying under reduced pressure for 5 min.

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

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with Varian inverse probe 500 INOVA and Varian 500 INOVA spectrometers and are recorded 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, DMSO-d_6: δ 2.50). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23, DMSO-d_6: δ 39.51). Data is reported as follows: chemical shift [assignment]. Infrared data (IR) 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)]. Optical rotations were measured on a Jasco-1010 polarimeter. Enantiomeric excess was determined by chiral HPLC analysis performed on an Agilent Technologies 1100 series HPLC system with a Daicel Chirapak AD-H column. We are grateful to Dr. Li Li for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. The structure of (+)-chimonanthine was obtained with the assistance of Dr. Peter Mueller at the X-ray crystallography laboratory of the Department of Chemistry, Massachusetts Institute of Technology.



Hexahydropyrroloindole (+)-9:[3]

A fine suspension of carbamate **8** (25.2 g, 95.4 mmol, 1 equiv) in aqueous phosphoric acid (85%) was vigorously stirred. After 5h, a homogenous light tan solution formed. The thick solution was added drop-wise to a vigorously stirred mixture of dichloromethane (600 mL) and an aqueous solution of sodium carbonate (11% wt/wt, 600 ml). The pH of the aqueous layer was monitored throughout the addition, and once it reached pH = 7, another portion of solid sodium carbonate (66 g) was added slowly. The addition was continued in this manner until completion (total Na_2CO_3 added = 198 g). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 200 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford a white foam (24.3 g, 96%). The hexahydropyrroloindole (1.7 g, 6.4 mmol, 1 equiv) was dissolved in pyridine (8.60 mL) and benzenesulfonyl chloride (1.65 mL, 12.8 mmol, 2.00 equiv) was added and the mixture vigorously stirred. After 2 h, pyridine was removed under reduced pressure and the residue was suspended in ethyl acetate (50 mL). The organic suspension was sequentially washed with aqueous hydrochloric acid solution (1N, 2 × 25 mL), saturated aqueous sodium bicarbonate solution (50 mL), and brine (100 mL). The organic layer was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure to afford a dark red residue. The residue was purified by flash column chromatography (eluent: 50% EtOAc in hexanes) to afford hexahydropyrroloindole (+)-**9** as a white solid (1.7 g, 64%; 61% from **8**). This compound was determined to be of >99% ee by chiral HPLC analysis (Chirapak AD-H, 90 % hexanes / 10% isopropanol, 3.0 mL/min, 254 nm, t_R (minor, not observed) = 11.9 min, t_R (major) = 23.0 min). All spectral data were in agreement with the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$, 50 ºC): δ 7.76 (d, *J* = 8.0 Hz, 2H, SO_2Ar-*o*-**H**), 7.51 (t, *J* = 7.5 Hz, 1H, SO_2Ar-*p*-**H**), 7.46 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.40 (t, *J* = 7.3 Hz, 2H, SO_2Ar-*m*-**H**), 7.23 (app-t, *J* = 8.0 Hz, 1H, C_6**H**), 7.03-7.07 (m, 2H, C_4**H**, C_5**H**), 6.29 (d, *J* = 6.0 Hz, 1H, C_{8a}**H**), 4.60 (d, *J* = 9.0 Hz, 1H, C_2**H**), 3.67 (t, *J* = 6.8 Hz, 1H, C_{3a}**H**), 3.60 (s, 3H, NCO_2C**H**$_3$), 3.16 (s, 3H, CO_2C**H**$_3$), 2.59 (d, *J* = 13.0 Hz, 1H, C_3**H**$_{endo}$), 2.46 (ddd, *J* =13.0, 9.0, 7.5 Hz, 1H, C_3**H**$_{exo}$).

^{13}C NMR (125.8 MHz, $CDCl_3$, 50 ºC): 171.5 (**C**=O), 154.9 (N**C**=O), 142.9 (**C**$_{7a}$), 140.3 (SO_2Ar-*i*-**C**), 133.1 (**C**$_{4a}$), 132.9 (SO_2Ar-*p*-**C**), 129.08 (SO_2Ar-*m*-**C**), 129.07 (**C**$_6$), 126.9 (SO_2Ar-*o*-**C**), 125.3 (**C**$_5$), 124.5 (**C**$_4$), 118.5 (**C**$_7$), 80.3 (**C**$_{8a}$), 59.2 (**C**$_2$), 52.9 (NCO**C**H$_3$), 52.1 (CO**C**H$_3$), 45.9 (**C**$_{3a}$), 33.9 (**C**$_3$).

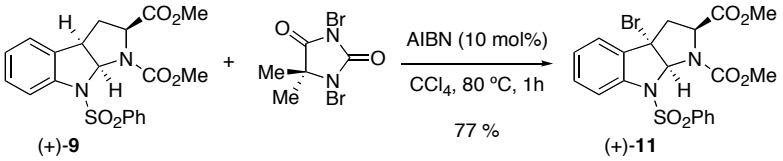
[3] C.-O. Chan, C. J. Cooksey, D. Crich, *J. Chem. Soc. Perkin Trans. 1* **1992**, 777.

FTIR (thin film) cm^{-1}: 3065 (m), 2953 (s) 1753 (s), 1712 (s), 1384 (s), 1359 (s).

HRMS (ESI): calc for $C_{20}H_{21}N_2O_6S$ $[M+H]^+$: 417.1115
Found: 417.1105

M.p. (ethyl acetate–hexanes): 160.5–161.5 ºC

$[\alpha]^{20}_D$: +88 º (*c* = 1.00, CH_2Cl_2)



Tricyclic bromide (+)-11:[4]

Dibromohydantoin (2.90 g, 10.0 mmol, 1.00 equiv) followed by AIBN (164 mg, 1.00 mmol, 0.100 equiv) were added to a suspension of the tricycle (+)-**9** (4.16 g, 10.0 mmol, 1 equiv) in CCl_4 (250 mL) at room temperature. The mixture was heated to 80 ºC for 1 h at which point the solution became dark orange–red and a white solid precipitated. The reaction mixture was cooled to room temperature, the volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (eluent: 0 → 40% ethyl acetate in hexanes) to afford the tricyclic bromide (+)-**11** as a white foam (3.80 g, 77 %). This compound was determined to be of >99% ee by chiral HPLC analysis (Chirapak AD-H, 10 % isopropanol in hexanes, 3.0 mL/min, 254 nm, t_R (minor, not observed) = 8.2 min, t_R (major) = 14.8 min)).

^{1}H NMR (500 MHz, $CDCl_3$, 50 ºC): 7.87 (d, *J* = 7.5 Hz, 2H, SO_2Ph-*o*-**H**), 7.55 (d, *J* = 8.0 Hz, 1H, C_4**H**), 7.52 (app tt, *J* = 7.5, 1.0 Hz, 1H, SO_2Ph-*p*-**H**), 7.42 (t, *J* = 8.0 Hz, 2H, SO_2Ph-*m*-**H**), 7.34 (app td, *J* = 7.5, 1.0 Hz, 1H, C_6**H**), 7.26 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.14, (td, *J* = 7.5 Hz, 1.0 Hz, 1H, C_5**H**), 6.36 (s, 1H, C_{8a}**H**), 4.62 (d, *J* = 9.0 Hz, 1H, C_2**H**), 3.70 (s, 3H, NCO_2C**H**$_3$), 3.27 (d, *J* = 13.0 Hz, 1H, C_3**H**), 3.17 (s, 3H, CO_2C**H**$_3$), 3.04 (dd, *J* = 13.0, 9.0 Hz, 1H, C_3**H**).

^{13}C NMR (125.8 MHz, $CDCl_3$, 50 ºC): 170.16 (**C**=O), 154.34 (N**C**=O), 142.13 (**C**$_{7a}$), 140.09 (SO_2Ph-*i*-**C**), 133.48 (**C**$_{4a}$), 133.40 (SO_2Ph-*p*-**C**), 131.32 (SO_2Ph-*m*-**C**), 129.15 (**C**$_6$), 127.67 (SO_2Ph-*o*-**C**), 125.87 (**C**$_5$), 124.80 (**C**$_4$), 118.41 (**C**$_7$), 87.43 (**C**$_{8a}$), 60.21 (**C**$_{3a}$), 59.85 (**C**$_2$), 53.22 (NCO_2**C**H_3), 52.40 (CO_2**C**H_3), 44.90 (**C**$_3$).

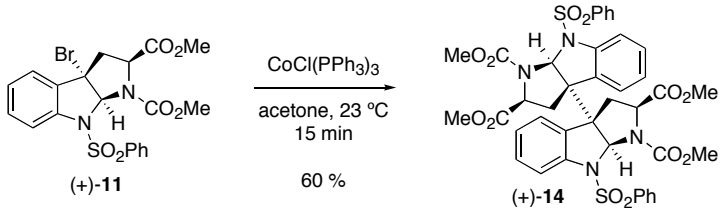
FTIR (thin film): 2954 (s), 1755 (s), 1716 (s), 1601 (m), 1447 (s).

[4] a) M. Bruncko, D. Crich, R. Samy, *Heterocycles*, **1993**, *36*, 1735. b) M. Bruncko, D. Crich, R. Samy, *J. Org. Chem.* **1994**, *59*, 5543.

HRMS-ESI (*m*/*z*): calc'd for $C_{20}H_{19}BrN_2NaO_6S$ $[M+Na]^+$: 517.0039, found: 517.0016.

$[\alpha]_D^{22}$: +107 (*c* = 1.00, $CHCl_3$).

TLC (40% EtOAc in hexanes), R*f*: 0.33 (UV, I_2).



Dimeric hexahydropyrroloindole (+)-14:

A solid sample of freshly prepared tristriphenylphosphine cobalt chloride ($CoCl(PPh_3)_3$[5], 6.40 g, 72.7 mmol, 1.20 equiv) was added rapidly to a degassed (dinitrogen purge, 10 min) solution of tricyclic bromide (+)-**11** (3.00 g, 6.06 mmol, 1 equiv) in acetone (61.0 mL) under an argon atmosphere. The solution immediately turned blue and a precipitate resulted. After 15 min, the reaction mixture was diluted with deionized water (200 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic extracts were washed with brine (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting yellow oil was purified by flash column chromatography (10% acetone in CH_2Cl_2) to yield the dimeric hexahydropyrroloindole (+)-**14** (1.50 g, 60%) as white foam. The hexacycle (+)-**14** was found to be of >99% ee by chiral HPLC analysis (Chirapak AD-H, 20% isopropanol in hexanes, 3.0 mL/min, 254 nm, t_R (minor, not observed) = 8.3 min, t_R (major) = 13.5 min).

^{1}H NMR (500 MHz, DMSO-d_6, 100 °C): 8.00 (d, *J* = 7.0 Hz, 4H, SO_2Ph-*o*-**H**), 7.70 (t, *J* = 7.3 Hz, 2H, SO_2Ph-*p*-**H**), 7.63 (t, *J* = 7.8 Hz, 4H, SO_2Ph-*m*-**H**), 7.27 (d, *J* = 7.5 Hz, 2H, C_4**H**), 7.16 (t, *J* = 7.8 Hz, 2H, C_6**H**), 7.08 (br d, *J* = 7.5 Hz, 2H, C_7**H**), 6.92 (t, *J* = 7.5 Hz, 2H, C_5**H**), 6.43 (s, 2H, C_{8a}**H**), 4.67 (d, *J* = 9.0 Hz, 2H, C_2**H**), 3.31 (br s, 6H, NCO_2C**H**$_3$), 3.12 (s, 6H, CO_2C**H**$_3$), 2.72 (dd, *J* = 12.8, 9.3 Hz, 2H, C_3**H**), 2.47 (d, *J* = 13.0 Hz, 2H, C_3**H**).

^{13}C NMR (125.8 MHz, DMSO-d_6, 100 °C): 169.62 (**C**=O), 153.04 (N**C**=O), 142.00 ($\mathbf{C}_{7a}$), 141.22 (SO_2Ph-*i*-**C**), 132.37 ($\mathbf{C}_{4a}$), 129.12 (SO_2Ph-*p*-**C**), 129.02 (SO_2Ph-*m*-**C**), 128.68 (SO_2Ph-*o*-**C**), 125.00 ($\mathbf{C}_6$), 124.34 ($\mathbf{C}_5$), 122.68 ($\mathbf{C}_4$), 114.01 ($\mathbf{C}_7$), 81.00 ($\mathbf{C}_{8a}$), 60.80 ($\mathbf{C}_{3a}$), 58.54 ($\mathbf{C}_2$), 51.81 ($NCO_2\mathbf{C}H_3$), 51.13 ($CO_2\mathbf{C}H_3$), 36.75 ($\mathbf{C}_3$).

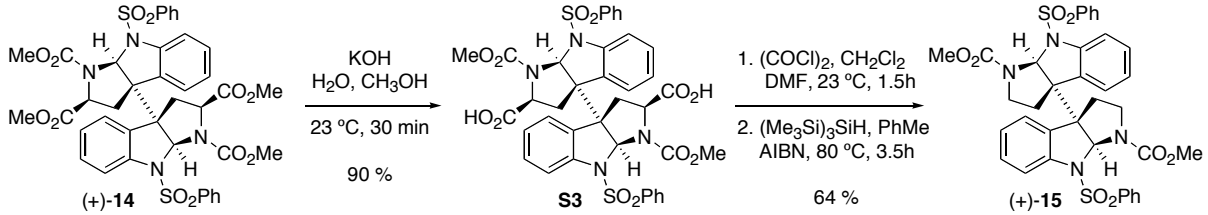
[5] Prepared according to M. Aresta, M. Rossi, A. Sacco, *Inorg. Chem. Acta*. **1969**, *3*, 227.

FTIR (thin film): 2954 (m), 1750 (s), 1721 (s), 1602 (m), 1447 (s).

HRMS-ESI (*m*/*z*): calc'd for $C_{40}H_{39}N_4O_{12}S_2$ $[M+H]^+$: 831.2000, found: 831.2025.

$[\alpha]_D^{22}$: +51 (*c* = 1.00, $CHCl_3$).

TLC (65% EtOAc in hexanes), R*f*: 0.23 (UV, I_2).

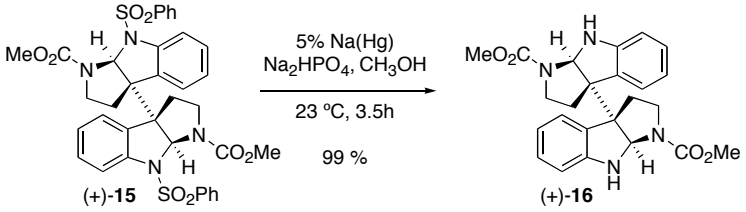


Hexacycle (+)-15:

An aqueous solution of potassium hydroxide (5 N, 10 mL) was added to a solution of dimer (+)-**14** (334 mg, 0.402 mmol, 1 equiv) in methanol (10 ml) at 23 °C. After 30 min, the resulting clear solution was cooled to 0 ºC and adjusted to pH ~ 2 by the drop-wise addition of aqueous hydrochloric acid solution (~12N). The reaction mixture was extracted with chloroform (10 × 20 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford the hexacyclic dicarboxylic acid as a white solid (291.3 mg, 90 %). The dicarboxyclic acid (263 mg, 0.328 mmol, 1 equiv) was concentrated from benzene (2 × 2.5 mL) under reduced pressure. Oxalyl chloride (114 μL, 1.31 mmol, 4.00 equiv) was added to a solution of dicarboxylic acid **S3** in CH_2Cl_2 (2.75 mL) at 23 °C. Dimethylformamide (DMF, 3.8 μL, 0.049 mmol, 0.15 equiv) was added, resulting in vigorous gas evolution. After 1.5 h, the volatiles were removed under reduced pressure and the residue was concentrated from benzene (2 × 3 mL) to remove the remaining oxalyl chloride. Tristrimethylsilylsilane ($(Me_3Si)_3SiH$, 305 μL, 0.985 mmol, 3.00 equiv) followed by AIBN (11 mg, 0.066 mmol, 0.20 equiv) were added to a solution of the crude dicarboxylic acid chloride in toluene (6.60 mL) and the mixture was heated to 80 ºC. After 30 min, an additional portion of tristrimethylsilylsilane (305 μL, 0.985 mmol, 3.00 equiv) and AIBN (11 mg, 0.066 mmol, 0.20 equiv) were added. After 1.5 h, an additional portion of AIBN (11 mg, 0.066 mmol, 0.20 equiv) was added. After 1.5 h, the reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (60% ethyl acetate in hexanes) to afford the hexacycle (+)-**15** as a white solid (149.0 mg, 64%).

^{1}H NMR (500 MHz, DMSO-d_6, 100 ºC): 7.91 (app d, *J* = 7.5 Hz, 4H, SO_2Ph-*o*-**H**), 7.71 (app t, *J* = 7.5 Hz, 2H, SO_2Ph-*p*-**H**), 7.63 (app t, *J* = 7.5 Hz, 4H, SO_2Ph-*m*-**H**), 7.38 (d, *J* = 8.5 Hz, 2H, C_4**H**), 7.19 (app t, *J* = 8.5 Hz, 2H, C_6**H**), 7.03 (br d, *J* = 7.5 Hz, 2H, C_7**H**), 6.87 (t, *J* = 7.5 Hz, 2H, C_5**H**), 6.28 (s, 2H, C_{8a}**H**), 3.74 (dd, *J* = 11.5, 8.0 Hz, 2H, C_2**H**), 3.56 (s, 6H, NCO_2C**H**$_3$),

	2.57 (td, J = 11.8, 5.5 Hz, 2H, C_2**H**), 1.97 (td, J = 12.0, 8.0 Hz, 2H, C_3**H**), 1.85 (dd, J = 12.5, 5.5 Hz, 2H, C_3**H**).
^{13}C NMR (125.8 MHz, DMSO-d_6, 100 ºC):	153.11 (**C**=O), 141.71 ($\mathbf{C}_{7a}$), 139.65 (SO_2Ph-*i*-**C**), 132.89 ($\mathbf{C}_{4a}$), 130.21 (SO_2Ph-*p*-**C**), 128.89 (SO_2Ph-*m*-**C**), 128.63 (SO_2Ph-*o*-**C**), 125.56 ($\mathbf{C}_6$), 123.75 ($\mathbf{C}_5$), 122.97 ($\mathbf{C}_4$), 112.95 ($\mathbf{C}_7$), 80.72 ($\mathbf{C}_{8a}$), 61.99 ($\mathbf{C}_{3a}$), 51.89 (**C**H$_3$), 43.92 ($\mathbf{C}_2$), 35.13 ($\mathbf{C}_3$).
FTIR (thin film):	2955 (m), 1713 (s), 1599 (w), 1476 (m), 1447 (s).
HRMS-ESI (m/z):	calc'd for $C_{36}H_{34}N_4NaO_8S_2$ $[M+Na]^+$: 737.1716, found: 737.1720.
$[\alpha]_D^{22}$:	+161 (c = 1.00, CH_2Cl_2).
TLC (50 % EtOAc in hexanes), Rf:	0.53 (UV, I_2).



Hexacycle (+)-16:

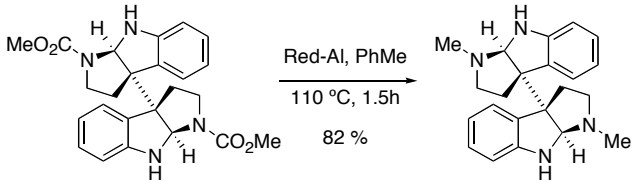
Anhydrous sodium phosphate dibasic (Na_2HPO_4, 170 mg, 1.20 mmol, 8.00 equiv) followed by freshly prepared 5% Na(Hg)[6] (590 mg, 1.28 mmol, 8.50 equiv) were added to a solution of hexacycle (+)-**15** (107 mg, 0.150 mmol, 1 equiv) in methanol (2.0 mL). The resulting suspension was stirred and an additional sample of Na(Hg) (400 mg) was added approximately every hour until the completion of the reaction as judged by TLC analysis (total time 3.5 h). The reaction mixture was diluted with water (30 mL) and the aqueous layer was separated from the mercury. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford a white gel. The residue was purified by flash chromatography (20% ethyl acetate in CH_2Cl_2) to afford the product (+)-**16** (64.6 mg, 99%) as white foam.[7] This hexacycle (+)-**16** was determined to be >99% ee by chiral HPLC analysis (Chirapak AD-H, 10% isopropanol in hexanes, 3.0 mL/min, 254 nm, t_R (minor, not observed) = 7.6 min, t_R (major) = 11.7 min).

^{1}H NMR (500 MHz, DMSO-d_6, 100 ºC):	7.23 (d, J = 7.5 Hz, 2H, C_4**H**), 7.02 (td, J = 7.8, 1.2 Hz, 2H, C_6**H**), 6.64 (td, J = 7.5, 1.0 Hz, 2H, C_5**H**), 6.59 (d, J

[6] The reagent was prepared according to R. N. McDonald, C. E. Reineke, *Org. Synth.*, *Coll. Vol. VI* **1988**, 461.

[7] For the synthesis of **16** in racemic form, see: a) M. Nakagawa, H. Sugumi, S. Kodato, H. Hino, *Tetrahedron*, **1981**, *22*, 5323. b) L. Verotta, F. Orsini, M. Sbacchi, M. A. Scheildler, T. A. Amador, E. Elisabetsky, *Bioorg. Med. Chem.* **2002**, *10*, 2133.

	= 7.5 Hz, 2H, C_7**H**), 6.11 (s, 2H, N**H**), 4.91 (s, 2H, C_{8a}**H**), 3.54–3.58 (m, 8H, C_2**H**, NCO_2C**H**$_3$), 2.75 (td, *J* = 10.8, 6.0 Hz, 2H, C_2**H**), 2.52 (td, *J* = 12.0, 8.0 Hz, 2H, C_3**H**), 2.12 (dd, *J* = 12.5, 6.0 Hz, 2H, C_3**H**).
^{13}C NMR (125.8 MHz, DMSO-d_6, 100 ºC):	153.41 (**C**=O), 150.38 (**C**$_{7a}$), 128.06 (**C**$_6$), 127.97 (**C**$_{4a}$), 123.96 (**C**$_4$), 116.90 (**C**$_5$), 108.21 (**C**$_7$), 77.43 (**C**$_{8a}$), 60.92 (**C**$_{3a}$), 51.25 (**C**H$_3$), 44.20 (**C**$_2$), 31.75 (**C**$_3$).
FTIR (thin film):	3365 (br m), 2954 (m), 1695 (s), 1607 (m), 1451 (s).
HRMS-ESI (*m*/*z*):	calc'd for $C_{24}H_{26}N_4NaO_4$ $[M+Na]^+$: 457.1846, found: 457.1830.
$[\alpha]_D^{22}$:	+474 (*c* = 1.00, CH_2Cl_2).
TLC (20% EtOAc in CH_2Cl_2), R*f*:	0.38 (UV, CAM).



(+)-**16** (+)-**Chimonanthine (1)**

(+)-Chimonanthine (1):

Hexacycle (+)-**16** (64 mg, 0.147 mmol, 1 equiv) was concentrated from anhydrous benzene (2.5 ml) and the residue was dissolved in anhydrous toluene (14.7 mL) and placed under an argon atmosphere. A solution of Red-Al (65% wt, 450 μL, 1.47 mmol, 10.0 equiv) in toluene was added via syringe and the reaction mixture was heated to reflux. After 1.5 h, the mixture was cooled to 23 ºC and excess reducing agent was quenched by the slow addition of methanol (5:95) in dichloromethane saturated with ammonia. The resulting mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (5% methanol in dichloromethane saturated with ammonia) to afford (+)-chimonanthine (**1**) as a white solid (41.7 mg, 82 %). X-ray quality crystals were grown by slow evaporation of a benzene solution of (+)-**1**. All spectral data were in agreement with the literature.[8c]

^{1}H NMR (500 MHz, $CDCl_3$, 50 ºC):	7.19 (d, J = 7.5 Hz, 2H, C_4**H**), 6.98 (t, J = 7.3 Hz, 2H, C_6**H**), 6.66 (t, J = 7.3 Hz, 2H, C_5**H**), 6.53 (d, J = 7.5 Hz, 2H, C_7**H**), 4.40 (br-s, 2H, C_{8a}**H**), 4.23 (s, 2H, N**H**), 2.51-2.57 (m, 6H, C_2**H**, C_2**H**, C_3**H**), 2.33 (s, 6H, C**H**$_3$), 2.05 (app dd, J = 10.5, 5.0 Hz, 2H, C_3**H**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 50 ºC):	151.08 (**C**$_{7a}$), 133.79 (**C**$_{4a}$), 128.22 (**C**$_6$), 124.64 (**C**$_4$), 118.78 (**C**$_5$), 109.39 (**C**$_7$), 85.52 (**C**$_{8a}$), 63.81 (**C**$_{3a}$), 52.94 (**C**$_2$), 37.40 (**C**H$_3$), 36.06 (**C**$_3$).
FTIR (thin film):	3406 (m), 2934 (m), 1603 (m), 1484 (m), 1361 (s).
HRMS-ESI (*m*/*z*):	calc'd for $C_{22}H_{27}N_4$ $[M+H]^+$: 347.2230, found: 347.2222.
$[\alpha]_D^{22}$:	+254 (c = 1.00, EtOH).[8]
M.p. (C_6H_6):	176-178 ºC.

TLC (5% CH_3OH in CH_2Cl_2 saturated with NH_3), R*f*: 0.26 (UV, CAM).

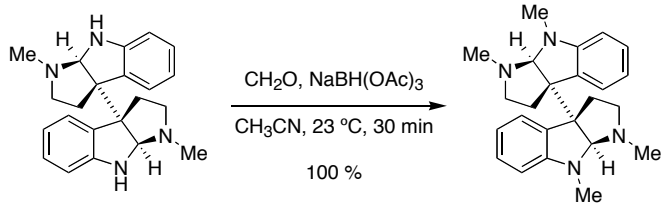
---

[8] a) $[\alpha]_D^{25}$: +280 (MeOH, concentration not reported), T. Tokuyama, J. W. Daly, *Tetrahedron*, **1983**, *39*, 41. b) $[\alpha]_D$: +224 (conditions not reported), N. H. Lajis, Z. Mahmud, R. F. Toia, *Planta Med*. **1993**, *59*, 383. c) $[\alpha]_D^{20}$: +264.5 (c = 1, EtOH), L. Verotta, T. Pilati, M. Tatò, E. Elisabetsky, T. A. Amador, D. S. Nunes, *J. Nat. Prod*. **1998**, *61*, 392. d) $[\alpha]_D^{23}$: +274 (c = 0.5, EtOH), L. E. Overman, J. F. Larrow, B. A. Stearns, J. M. Vance, *Angew. Chem. Int. Ed*. **2000**, *39*, 213. Data related to (–)-chimonanthine: e) $[\alpha]_D$: –329 (EtOH, conditions not reported), H. F. Hodson, B. Robinson, G. F. Smith, *Proc. Chem. Soc.* **1961**, 465. f) $[\alpha]_D^{25}$: –328 (c = 1.0, EtOH), R. K. Duke, R. D. Allan, G. A. R. Johnston, K. N. Mewett, A. D. Mitrovic, C. C. Duke, T. W. Hambley, *J. Nat. Prod*. **1995**, *58*, 1200. g) $[\alpha]_D^{23}$: –310 (c = 0.5, EtOH), L. E. Overman, D. V. Paone, B. A. Stearns, *J. Am. Chem. Soc*. **1999**, *121*, 7702.

Comparison of our data for (+)-chimonanthine (1) with literature:

Assignment	**Verotta's report**[8c] (+)-chimonanthine (**1**) (^{1}H NMR, 200 MHz, $CDCl_3$)	**This report** (+)-chimonanthine (**1**) (^{1}H NMR, 500 MHz, $CDCl_3$, 50 ºC)
C2	2.50 (m)	2.57, (m)
C3	2.50 (m), 2.07 (dt, *J* = 12.0, 6.4 Hz)	2.57 (m), 2.05 (app dd, *J* = 10.5, 5.0 Hz)
C3a		
C4a		
C4	7.20, (d, *J* = 7.4 Hz)	7.19, (d, *J* = 7.5 Hz)
C5	6.67 (t, *J* = 7.3 Hz)	6.66 (t, *J* = 7.3 Hz)
C6	7.00 (t, *J* = 7.6 Hz)	6.98 (t, *J* = 7.3 Hz)
C7	6.55, (d, *J* = 7.7 Hz)	6.53, (d, *J* = 7.5 Hz)
C7a		
N8	–	4.23 (s)
C8a	4.35 (br s)	4.40 (br s)
N1-CH_3	2.31 (s)	2.33 (s)

Tokuyama's report[8a] (+)-chimonanthine (**1**) (^{13}C NMR, 25.05 MHz, $CDCl_3$)	**This report** (+)-chimonanthine (**1**) (^{13}C NMR, 125.8 MHz, $CDCl_3$, 50 ºC)
150.6 (s)	151.08 (C7a)
133.1 (s)	133.79 (C4a)
128.1 (d)	128.22 (C6)
124.4 (d)	124.64 (C4)
118.7 (d)	118.78 (C5)
109.4 (d)	109.39 (C7)
85.2 (d)	85.52 (C8a)
63.2 (s)	63.81 (C3a)
52.7 (t)	52.94 (C2)
37.2 (q)	37.40 (Me)
36.5 (t)	36.06 (C3)



(+)-Chimonanthine (1) **(+)-Folicanthine (2)**

(+)-Folicanthine (2):

Formalin (37%, 5.5 μL, 0.0734 mmol, 5.2 equiv) followed by solid sodium triacetoxyborohydride (15.6 mg, 0.0734 mmol, 5.2 equiv) were added to a solution of (+)-chimonanthine (**1**, 5.0 mg, 0.0141 mmol, 1 equiv) in acetonitrile (700 μL) at 23 °C and placed under an argon atmosphere. After 30 min, a solution of methanol (5:95) in dichloromethane saturated with ammonia was added slowly. After 5 min, the resulting slurry was concentrated under reduced pressure and the residue was purified by flash column chromatography (1% methanol in dichloromethane saturated with ammonia) to afford (+)-folicanthine (**2**)[9] as a white solid (5.3 mg, 100 %). All spectral data were in agreement with the literature.

^{1}H NMR (500 MHz, $CDCl_3$, 50 ºC):	6.98 (t, *J* = 7.5 Hz, 2H, C_6**H**), 6.94 (d, *J* = 6.5 Hz, 2H, C_4**H**), 6.51 (t, *J* = 7.0 Hz, 2H, C_5**H**), 6.27 (d, *J* = 7.5 Hz, 2H, C_7**H**), 4.37 (s, 2H, C_{8a}**H**), 3.00 (s, 6H, N_8C**H$_3$**), 2.62-2.64 (m, 2H, C_2**H**), 2.41-2.50 (m, 10H, C_2**H**, C_3**H**, N_1C**H$_3$**), 1.95-1.99 (m, 2H, C_3**H**).
^{13}C NMR (125.8 MHz, $CDCl_3$, 50 ºC):	153.21 (**C**$_{7a}$), 133.16 (**C**$_{4a}$), 128.29 (**C**$_6$), 123.95 (**C**$_4$), 116.85 (**C**$_5$), 106.05 (**C**$_7$), 92.34 (**C**$_{8a}$), 63.00 (**C**$_{3a}$), 52.94 (**C**$_2$), 38.25 (N_8**C**H_3), 35.58 (**C**$_3$), 35.52 (N_1**C**H_3).
FTIR (thin film):	3047 (w), 2931 (m), 1603 (s), 1493 (s), 1155 (m).
HRMS-ESI (*m*/*z*):	calc'd for $C_{24}H_{31}N_4$ $[M+H]^+$: 375.2549, found: 375.2547.
$[\alpha]_D^{22}$:	+207 (*c* = 0.75, MeOH).[10]
M.p. (methanol-dichloromethane):	184-189 ºC.

TLC (5 % MeOH in CH_2Cl_2 saturated with NH_3), R*f*: 0.40 (UV, CAM).

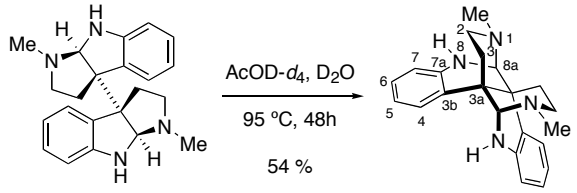
[9] For a synthesis of folicanthine in racemic form, see: C.-l. Fang, S. Horne, N. Taylor, R. Rodrigo, *J. Am. Chem. Soc.* **1994**, *116*, 9480.

[10] Data for (–)-folicanthine is available: a) $[\alpha]_D^{21.5}$: –364.4 (*c* = 2.043, MeOH), K. Eiter, O. Svierak, *Monatsh. Chem.* **1952**, *83*, 1453. b) $[\alpha]_D$: –364 (EtOH, concentration not reported), see ref. 8e. c) $[\alpha]_D$: –364 (EtOH, concentration not reported), J. E. Saxton, W. G. Bardsley, G. F. Smith, *Proc. Chem. Soc.* **1962**, 148.

Comparison of our data for (+)-folicanthine (2) with literature for (±)-2:

Assignment	**Rodrigo's report**[9] (±)-folicanthine (**2**) (^{1}H NMR, 250 MHz, $CDCl_3$)	**This report** (+)-folicanthine (**2**) (^{1}H NMR , 500 MHz, $CDCl_3$, 50 ºC)
C2	2.58-2.67 (m), 2.30-2.49 (m)	2.62-2.64, (m), 2.41-2.50 (m)
C3	2.30- 2.49 (m), 1.92-1.98 (m)	2.41-2.50 (m), 1.95-1.99 (m)
C3a		
C4a		
C4	6.89-6.99 (m)	6.94 (d, *J* = 6.5 Hz)
C5	6.49 (t, *J* = 7.3 Hz)	6.51 (t, *J* = 7.0 Hz)
C6	6.89-6.99 (m)	6.98 (t, *J* = 7.5 Hz)
C7	6.25, (d, *J* = 7.8 Hz)	6.27, (d, *J* = 7.5 Hz)
C7a		
N8-CH_3	3.00 (s)	3.00 (s)
C8a	4.38 (s)	4.37 (s)
N1-CH_3	2.40 (s)	2.41-2.50 (m)

Assignment	**Rodrigo's report**[9] (±)-folicanthine (**2**) (^{13}C NMR, 62.86 MHz, $CDCl_3$)	**This report** (+)-folicanthine (**2**) (^{13}C NMR, 125.8 MHz, $CDCl_3$, 50 ºC)
C2	52.61	52.94
C3	35.28	35.58
C3a	62.65	63.00
C4a	132.78	133.16
C4	123.60	123.95
C5	116.60	116.85
C6	128.02	128.29
C7	105.78	106.05
C7a	152.87	153.21
N8-CH_3	37.90	38.25
C8a	92.95	92.34
N1-CH_3	35.38	35.52



(+)-Chimonanthine (1) **(–)-Calycanthine (3)**

(–)-Calycanthine (3):

A solution of (+)-chimonanthine (**1**, 10.0 mg, 0.0289 mmol, 1 equiv) in a mixture of acetic acid-d_4 (0.43 M) in deuterium oxide (700 μL) was placed in a J-Young tube and the contents were sealed under an atmosphere of argon and heated to 95 °C. Equilibrium was reached within 24 h, affording a ~85:15 ratio in favor of (–)-calycanthine (**3**). After 48 h, the reaction mixture was cooled to 23 °C and partitioned between dichloromethane (10 mL) and saturated aqueous sodium bicarbonate (10 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (4 × 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford a brown residue. The residue was purified by flash column chromatography (1% methanol in dichloromethane saturated with ammonia) to afford (–)-calycanthine (**3**, 5.4 mg, 54%) as a white solid along with recovered (+)-chimonanthine (**1**, 0.5 mg, 5%).

^{1}H NMR (500 MHz, $CDCl_3$, 20 °C):	7.01 (d, J = 7.5 Hz, 2H, C_4**H**), 6.82 (app t, J = 7.5 Hz, 2H, C_6**H**), 6.55 (t, J = 7.5 Hz, 2H, C_5**H**), 6.27 (d, J = 8.0 Hz, 2H, C_7**H**), 4.58 (br s, 2H, N**H**), 4.32 (s, 2H, C_{8a}**H**), 3.13 (td, J = 13.3, 5.3 Hz, 2H, C_3**H**), 2.62 (dd, J = 11.3, 5.3 Hz, 2H, C_2**H**), 2.42 (s, 6H, C**H**$_3$), 2.27 (dt, J = 12.5, 3.6 Hz, 2H, C_2**H**), 1.29 (dd, J = 13.3, 3.8 Hz, 2H, C_3**H**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C):	145.56 (**C**$_{7a}$), 126.72 (**C**$_6$), 125.21 (**C**$_{4a}$), 124.61 (**C**$_4$), 116.51 (**C**$_5$), 112.18 (**C**$_7$), 71.20 (**C**$_{8a}$), 46.72 (**C**$_2$), 42.78 (**C**H$_3$), 36.13 (**C**$_{3a}$), 31.90 (**C**$_3$).
FTIR (thin film):	3418 (m), 2929 (m), 1678 (w), 1605 (m), 1487 (s).
HRMS-ESI (m/z):	calc'd for $C_{22}H_{27}N_4$ $[M+H]^+$: 347.2230, found: 347.2217.
$[\alpha]_D^{22}$:	–612 (c = 0.18, EtOH).[11]
M.p. (EtOH):	230-232 °C.

TLC (5 % CH_3OH in CH_2Cl_2 saturated with NH_3), Rf: 0.53 (UV, CAM).

[11] For data on (–)-calycanthine, see: a) $[\alpha]_D^{25}$: –570 (MeOH, concentration not reported), see ref. 8a. b) $[\alpha]_D$: –633 (MeOH, concentration not reported), see ref. 8b. c) $[\alpha]_D^{20}$: –463 (c = 1, EtOH), see ref. 8c. For data on (+)-calycanthine, see: d) $[\alpha]_D^{18}$: +684.3 (EtOH, concentration not reported), E. Späth, W. Stroh, *Chem. Ber.* **1925**, *58*, 2131. e) $[\alpha]_D^{25}$: +675 (c = 1.0, $CHCl_3$), see ref. 8f. f) $[\alpha]_D^{25}$: +664 (c = 0.7, EtOH), see ref. 8g.

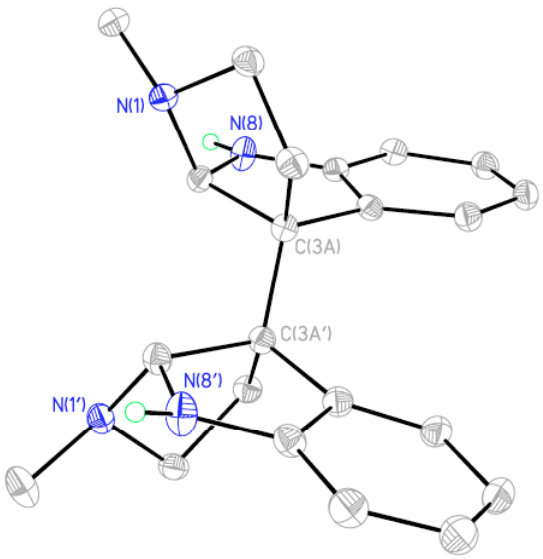
Comparison of our data for (–)-calycanthine (3) with literature:

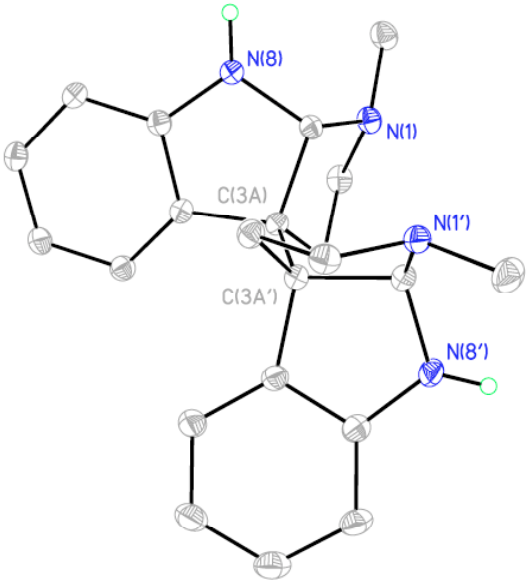
Assignment	**Verotta's report**[8c] (–)-calycanthine (**3**) (^{1}H NMR, 200 MHz, $CDCl_3$)	**This report** (–)-calycanthine (**3**) (^{1}H NMR, 500 MHz, $CDCl_3$,20 ºC)
C2	2.63 (ddd, *J* = 12.0, 5.6, 1.4 Hz), 2.26 (ddd, *J* = 12.0. 4.1, 1.4 Hz)	2.62 (dd, *J* = 11.3, 5.3 Hz), 2.27 (dt, *J* = 12.5, 3.6 Hz)
C3	3.15 (dt, *J* = 13.2, 5.5 Hz), 1.30 (ddd, *J* = 13.2, 4.1, 1.4 Hz)	3.13 (app-td, *J* = 13.3, 5.3 Hz), 1.29 (dd, *J* = 13.3, 3.8 Hz)
C3a		
C4a		
C4	6.28, (dd, *J* = 8.0, 1.0 Hz)	7.01, (d, *J* = 7.5 Hz)[12]
C5	6.55 (td, *J* = 7.5, 1.0 Hz)	6.55 (t, *J* = 7.5 Hz)
C6	6.83 (dt, *J* = 7.5, 1.0 Hz)	6.82 (app t, *J* = 7.5 Hz)
C7	7.02, (dd, *J* = 8.0, 1.0 Hz)	6.27, (d, *J* = 8.0 Hz)[12]
C7a		
N8	1.63 (br s)	4.58 (br s)
C8a	4.33 (s)	4.32 (s)
N1-CH_3	2.42 (s)	2.42 (s)

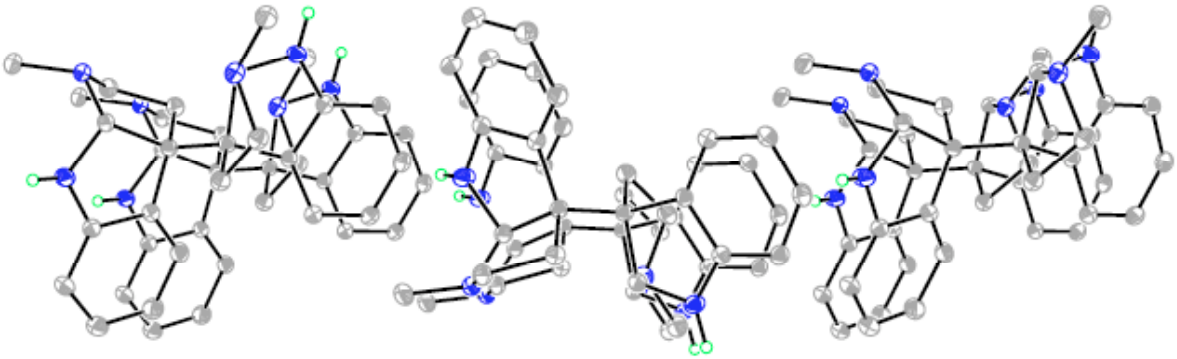
Tokuyama's report[8a] (–)-calycanthine (**3**) (^{13}C NMR, 25.05 MHz, $CDCl_3$)	**This report** (–)-calycanthine (**3**) (^{13}C NMR, 125.8 MHz, $CDCl_3$, 20 ºC)
145.3 (s)	145.56 (C7a)
126.5 (d)	126.72 (C6)
125.0 (s)	125.21 (C4a)
124.4 (d)	124.61 (C4)
116.4 (d)	116.51 (C5)
112.0 (d)	112.18 (C7)
71.0 (d)	71.20 (C8a)
46.6 (t)	46.72 (C2)
42.6 (q)	42.78 (Me)
36.0 (s)	36.13 (C3a)
31.7 (t)	31.90 (C3)

[12] Our assignment of C4 and C7 methines is supported by HMBC data.

Crystal Structure of (+)-Chimonanthine (3).







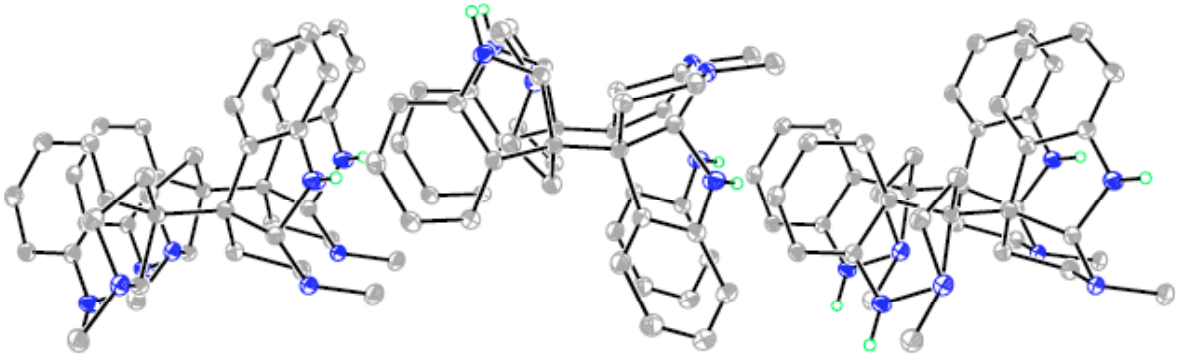


Table S1. Crystal data and structure refinement for (+)-chimonanthine.

Identification code	07003	
Empirical formula	C22 H26 N4	
Formula weight	346.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 15.692(2) Å	α= 90°.
	b = 16.844(2) Å	β= 90°.
	c = 7.1828(9) Å	γ = 90°.
Volume	1898.5(4) $Å^3$	
Z	4	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	744	
Crystal size	0.30 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.77 to 29.58°.	
Index ranges	-21<=h<=21, -23<=k<=23, -9<=l<=9	
Reflections collected	42252	
Independent reflections	3024 [R(int) = 0.0586]	
Completeness to theta = 29.58°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9855 and 0.9784	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3024 / 2 / 243	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0970	
R indices (all data)	R1 = 0.0407, wR2 = 0.1010	
Absolute structure parameter	No anomalous signal	
Largest diff. peak and hole	0.495 and -0.193 e.$Å^{-3}$	

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

	x	y	z	U(eq)
N(1')	6023(1)	6635(1)	1369(2)	16(1)
N(1)	6202(1)	4492(1)	-2152(2)	16(1)
C(2)	7067(1)	4195(1)	-2448(2)	18(1)
C(2')	6140(1)	6461(1)	3352(2)	17(1)
C(3A)	7016(1)	4752(1)	612(2)	14(1)
C(3)	7580(1)	4725(1)	-1151(2)	17(1)
C(3A')	7032(1)	5556(1)	1678(2)	14(1)
C(3')	6400(1)	5590(1)	3330(2)	16(1)
C(4A)	7179(1)	4029(1)	1825(2)	14(1)
C(4)	7927(1)	3755(1)	2610(2)	16(1)
C(4')	8435(1)	5559(1)	3720(2)	20(1)
C(4A')	7914(1)	5830(1)	2299(2)	16(1)
C(5)	7915(1)	3066(1)	3706(2)	18(1)
C(5')	9220(1)	5930(1)	4038(3)	24(1)
C(6)	7151(1)	2657(1)	3976(2)	18(1)
C(6')	9467(1)	6572(1)	2947(3)	25(1)
C(7)	6403(1)	2902(1)	3101(2)	16(1)
C(7A')	8147(1)	6508(1)	1294(2)	17(1)
C(7A)	6427(1)	3580(1)	1986(2)	14(1)
C(7')	8934(1)	6877(1)	1569(3)	22(1)
N(8)	5795(1)	3890(1)	880(2)	18(1)
C(8A)	6093(1)	4589(1)	-145(2)	14(1)
C(8A')	6741(1)	6256(1)	373(2)	16(1)
N(8')	7495(1)	6753(1)	152(2)	20(1)
C(9')	5920(1)	7477(1)	956(3)	24(1)
C(9)	5531(1)	4058(1)	-3101(2)	20(1)

Table S3. Bond lengths [Å] and angles [°] for (+)-chimonanthine.

N(1')-C(9')	1.458(2)	C(4')-C(5')	1.399(2)
N(1')-C(2')	1.466(2)	C(4A')-C(7A')	1.400(2)
N(1')-C(8A')	1.4792(19)	C(5)-C(6)	1.396(2)
N(1)-C(9)	1.4513(19)	C(5')-C(6')	1.391(3)
N(1)-C(8A)	1.4610(19)	C(6)-C(7)	1.393(2)
N(1)-C(2)	1.4624(19)	C(6')-C(7')	1.393(2)
C(2)-C(3)	1.521(2)	C(7)-C(7A)	1.396(2)
C(2')-C(3')	1.524(2)	C(7A')-N(8')	1.375(2)
C(3A)-C(4A)	1.519(2)	C(7A')-C(7')	1.396(2)
C(3A)-C(3)	1.546(2)	C(7A)-N(8)	1.3737(19)
C(3A)-C(3A')	1.556(2)	N(8)-C(8A)	1.4659(19)
C(3A)-C(8A)	1.571(2)	C(8A')-N(8')	1.458(2)
C(3A')-C(4A')	1.525(2)		
C(3A')-C(3')	1.547(2)	C(9')-N(1')-C(2')	113.99(13)
C(3A')-C(8A')	1.574(2)	C(9')-N(1')-C(8A')	114.02(13)
C(4A)-C(4)	1.380(2)	C(2')-N(1')-C(8A')	106.75(12)
C(4A)-C(7A)	1.4066(19)	C(9)-N(1)-C(8A)	115.79(13)
C(4)-C(5)	1.402(2)	C(9)-N(1)-C(2)	115.68(12)
C(4')-C(4A')	1.385(2)	C(8A)-N(1)-C(2)	106.87(12)
		N(1)-C(2)-C(3)	101.63(12)
		N(1')-C(2')-C(3')	102.50(12)
		C(4A)-C(3A)-C(3)	110.45(12)

C(4A)-C(3A)-C(3A')	114.36(11)
C(3)-C(3A)-C(3A')	114.79(12)
C(4A)-C(3A)-C(8A)	102.36(11)
C(3)-C(3A)-C(8A)	103.86(12)
C(3A')-C(3A)-C(8A)	109.75(12)
C(2)-C(3)-C(3A)	102.45(12)
C(4A')-C(3A')-C(3')	110.26(12)
C(4A')-C(3A')-C(3A)	114.96(12)
C(3')-C(3A')-C(3A)	113.49(11)
C(4A')-C(3A')-C(8A')	102.22(11)
C(3')-C(3A')-C(8A')	104.06(12)
C(3A)-C(3A')-C(8A')	110.71(12)
C(2')-C(3')-C(3A')	102.42(12)
C(4)-C(4A)-C(7A)	119.99(13)
C(4)-C(4A)-C(3A)	130.21(13)
C(7A)-C(4A)-C(3A)	109.63(12)
C(4A)-C(4)-C(5)	119.67(14)
C(4A')-C(4')-C(5')	119.61(15)
C(4')-C(4A')-C(7A')	119.58(14)
C(4')-C(4A')-C(3A')	130.71(14)
C(7A')-C(4A')-C(3A')	109.45(13)
C(6)-C(5)-C(4)	119.80(14)
C(6')-C(5')-C(4')	119.94(16)
C(7)-C(6)-C(5)	121.01(13)
C(5')-C(6')-C(7')	121.34(15)
C(6)-C(7)-C(7A)	118.55(13)
N(8')-C(7A')-C(7')	127.54(15)
N(8')-C(7A')-C(4A')	110.96(13)
C(7')-C(7A')-C(4A')	121.41(15)
N(8)-C(7A)-C(7)	128.53(13)
N(8)-C(7A)-C(4A)	110.80(13)
C(7)-C(7A)-C(4A)	120.61(13)
C(6')-C(7')-C(7A')	117.85(15)
C(7A)-N(8)-C(8A)	111.36(12)
N(1)-C(8A)-N(8)	116.29(13)
N(1)-C(8A)-C(3A)	104.67(12)
N(8)-C(8A)-C(3A)	105.15(11)
N(8')-C(8A')-N(1')	114.95(13)
N(8')-C(8A')-C(3A')	105.02(12)
N(1')-C(8A')-C(3A')	104.91(12)
C(7A')-N(8')-C(8A')	111.50(12)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1')	15(1)	14(1)	20(1)	2(1)	-1(1)	0(1)
N(1)	18(1)	16(1)	14(1)	-1(1)	-1(1)	1(1)
C(2)	19(1)	19(1)	16(1)	-1(1)	3(1)	3(1)
C(2')	18(1)	16(1)	18(1)	-3(1)	0(1)	0(1)
C(3A)	13(1)	14(1)	13(1)	1(1)	1(1)	-1(1)
C(3)	17(1)	18(1)	16(1)	1(1)	3(1)	1(1)
C(3A')	14(1)	14(1)	14(1)	1(1)	0(1)	0(1)
C(3')	17(1)	16(1)	14(1)	0(1)	1(1)	0(1)
C(4A)	14(1)	13(1)	14(1)	0(1)	2(1)	1(1)
C(4)	16(1)	16(1)	18(1)	0(1)	0(1)	0(1)
C(4')	21(1)	16(1)	22(1)	1(1)	-5(1)	-1(1)
C(4A')	16(1)	15(1)	18(1)	0(1)	0(1)	-1(1)
C(5)	17(1)	18(1)	18(1)	2(1)	-2(1)	3(1)
C(5')	22(1)	22(1)	30(1)	-1(1)	-10(1)	0(1)
C(6)	22(1)	15(1)	17(1)	2(1)	0(1)	2(1)
C(6')	18(1)	22(1)	36(1)	-3(1)	-3(1)	-2(1)
C(7)	17(1)	15(1)	16(1)	1(1)	2(1)	-1(1)
C(7A')	16(1)	16(1)	21(1)	0(1)	2(1)	1(1)
C(7A)	16(1)	15(1)	13(1)	-1(1)	0(1)	0(1)
C(7')	17(1)	19(1)	29(1)	1(1)	2(1)	-4(1)
N(8)	14(1)	20(1)	20(1)	6(1)	-2(1)	-2(1)
C(8A)	14(1)	15(1)	13(1)	0(1)	-1(1)	0(1)
C(8A')	16(1)	15(1)	17(1)	3(1)	0(1)	-1(1)
N(8')	15(1)	22(1)	24(1)	10(1)	1(1)	-2(1)
C(9')	20(1)	16(1)	36(1)	5(1)	2(1)	3(1)
C(9)	22(1)	20(1)	17(1)	-2(1)	-4(1)	0(1)

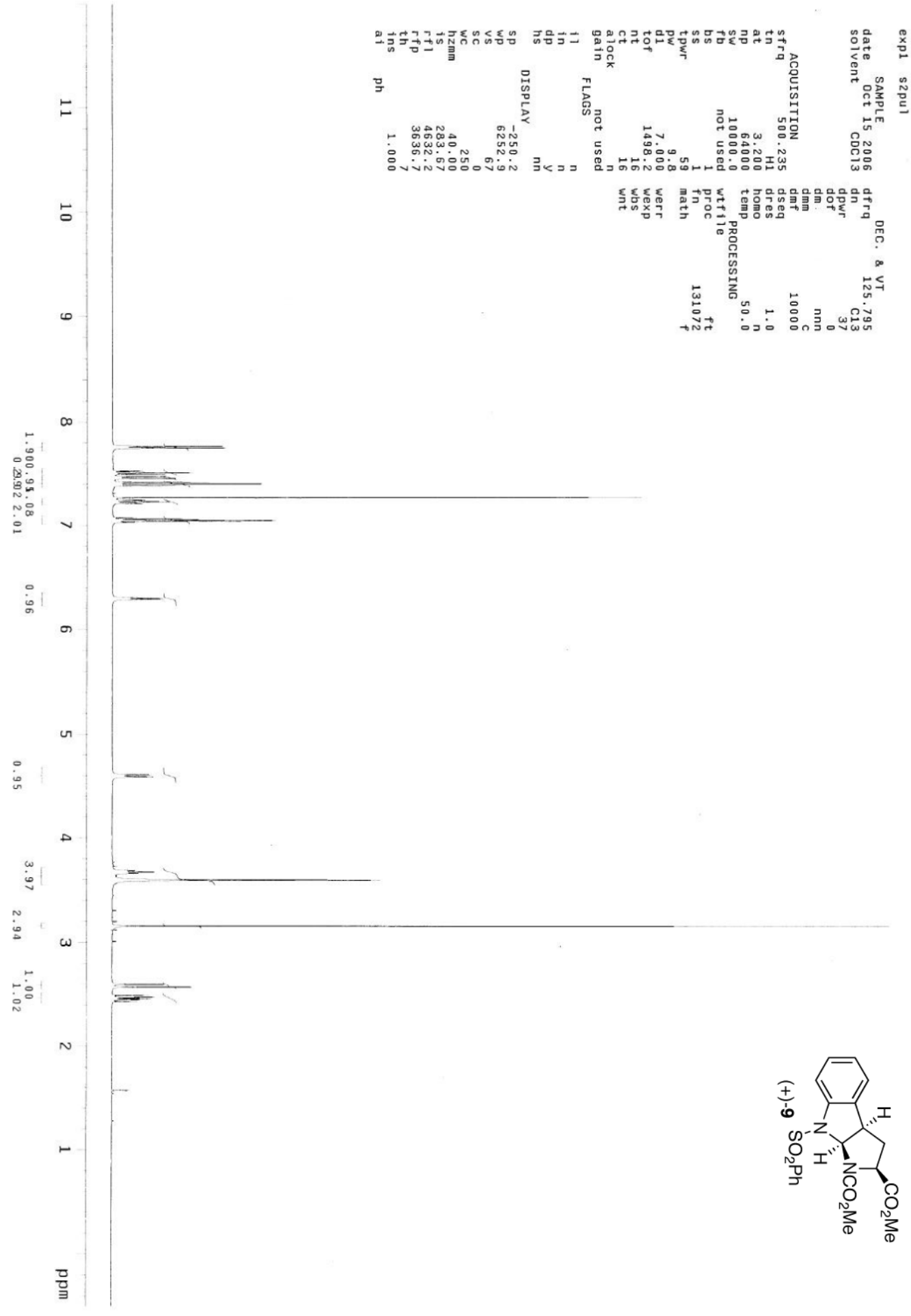
Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (+)-chimonanthine.

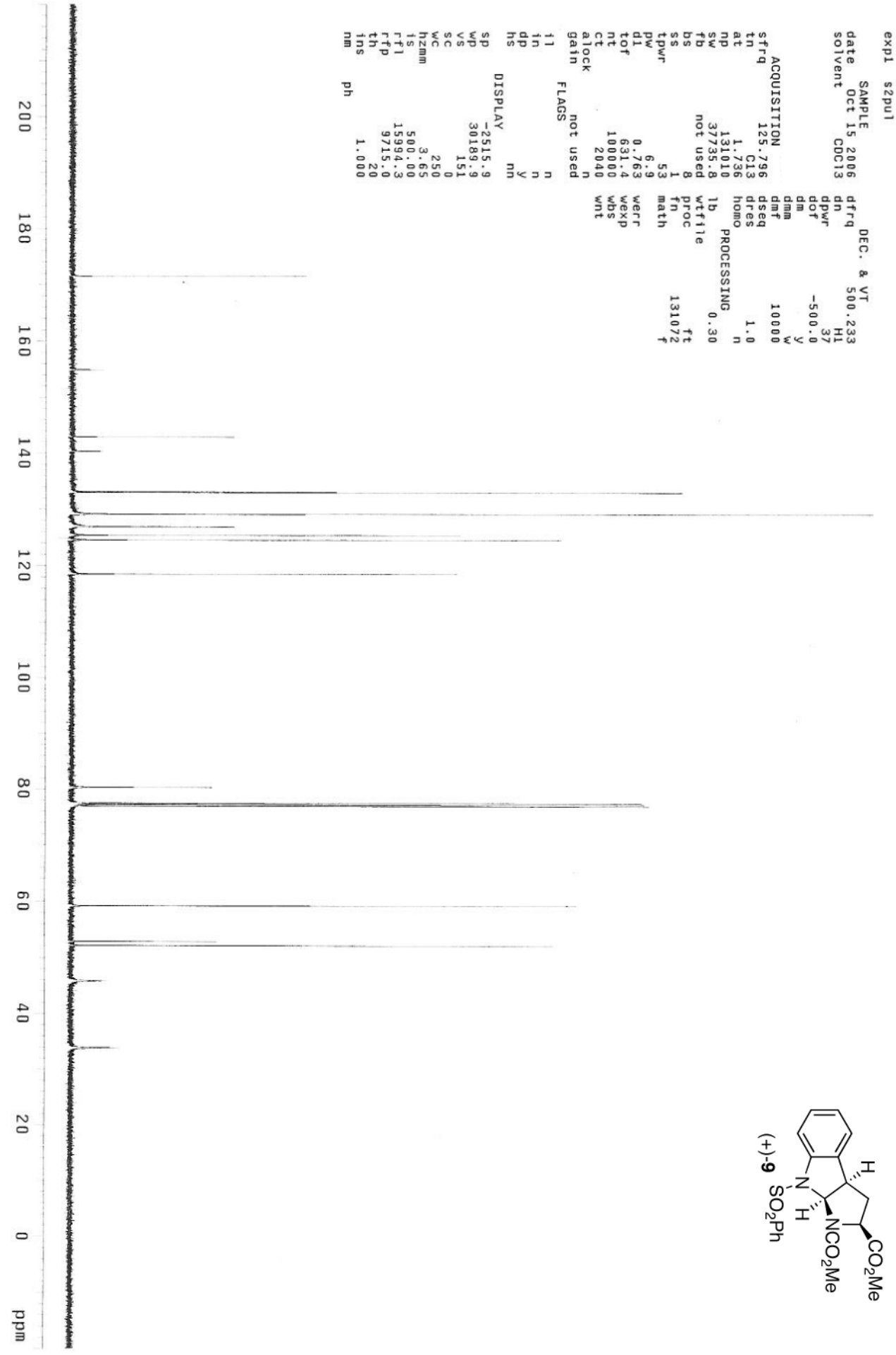
	x	y	z	U(eq)
H(2A)	7248	4260	-3759	21
H(2B)	7117	3629	-2093	21
H(2'1)	5604	6540	4055	21
H(2'2)	6592	6797	3902	21
H(3A)	7658	5261	-1688	20
H(3B)	8146	4491	-878	20
H(3'1)	5903	5240	3113	19
H(3'2)	6680	5435	4511	19
H(4)	8446	4031	2408	20
H(4')	8261	5125	4474	24
H(5)	8426	2878	4264	21
H(5')	9584	5742	4999	29
H(6)	7141	2206	4768	22
H(6')	10009	6808	3145	30
H(7)	5888	2613	3260	19
H(7')	9101	7321	841	26
H(8)	5231(10)	3745(12)	960(30)	21
H(8A)	5715	5053	119	17
H(8A')	6548	6046	-860	19
H(8')	7563(14)	7063(11)	-860(20)	24
H(9'1)	5406	7677	1572	36
H(9'2)	5867	7551	-393	36
H(9'3)	6418	7770	1410	36
H(9A)	5542	3501	-2709	30
H(9B)	5620	4090	-4450	30
H(9C)	4977	4292	-2786	30

Table S6. Hydrogen bonds for (+)-chimonanthine [Å and °].

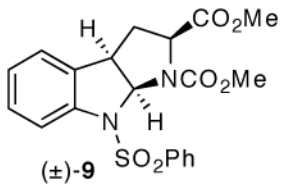
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8)...N(1')#1	0.918(15)	2.091(15)	3.0072(19)	174.8(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,z

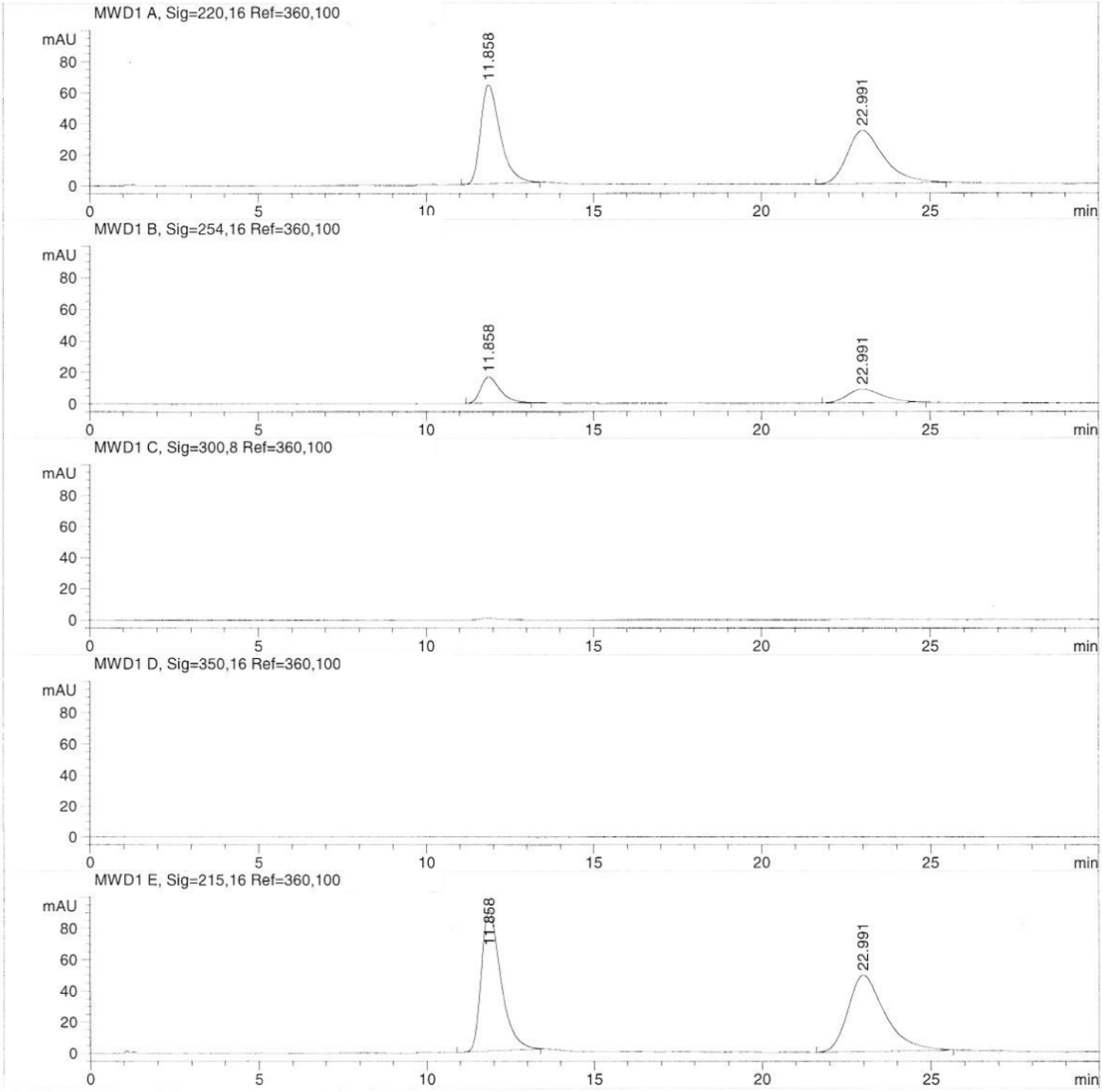

exp1 s2pul
SAMPLE
date Oct 15 2006
solvent CDCl3
DEC. & VT
dfrq 125.795
dn C13
dpwr 37
dof 0
dm nnn
dmm c
dmf 10000
ACQUISITION
sfrq 500.235
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 59
pw 9.8
d1 7.000
tof 1498.2
nt 16
ct 16
alock n
gain not used
PROCESSING
dseq 1.0
dres 1.0
homo n
temp 50.0
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6252.9
vs 67
sc 0
wc 250
hzmm 40.00
is 283.67
rfl 4632.2
rfp 3636.7
th 7
ins 1.000
ai ph
1.90 0.92
0.95 2.01
0.96
0.95
3.97
2.94
1.00
1.02
11
10
9
8
7
6
5
4
3
2
1
ppm
(+)-9
H
N
H
SO2Ph
NCO2Me
CO2Me


expt s2pul
SAMPLE
date Oct 15 2006
solvent CDCl3
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb
bs not used
ss 8
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 100000
ct 2040
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30189.9
vs 151
sc 0
wc 250
hzmm 3.65
is 500.00
rfl 15994.3
rfp 9715.0
th 20
ins 1.000
nm 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
fn 131072
math f
werr
wexp
wbs
wnt
(+)-9
CO2Me
NCO2Me
SO2Ph
200
180
160
140
120
100
80
60
40
20
0
ppm

```
Injection Date  : 8/8/2006 9:10:38 AM          Seq. Line :   1
Sample Name     :                              Location : Vial 1
Acq. Operator   :                                  Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 8/8/2006 9:11:05 AM
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:07:41 AM
                  (modified after loading)
```

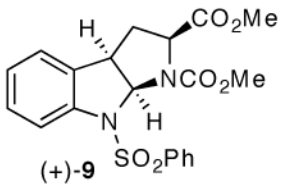


(±)-**9**

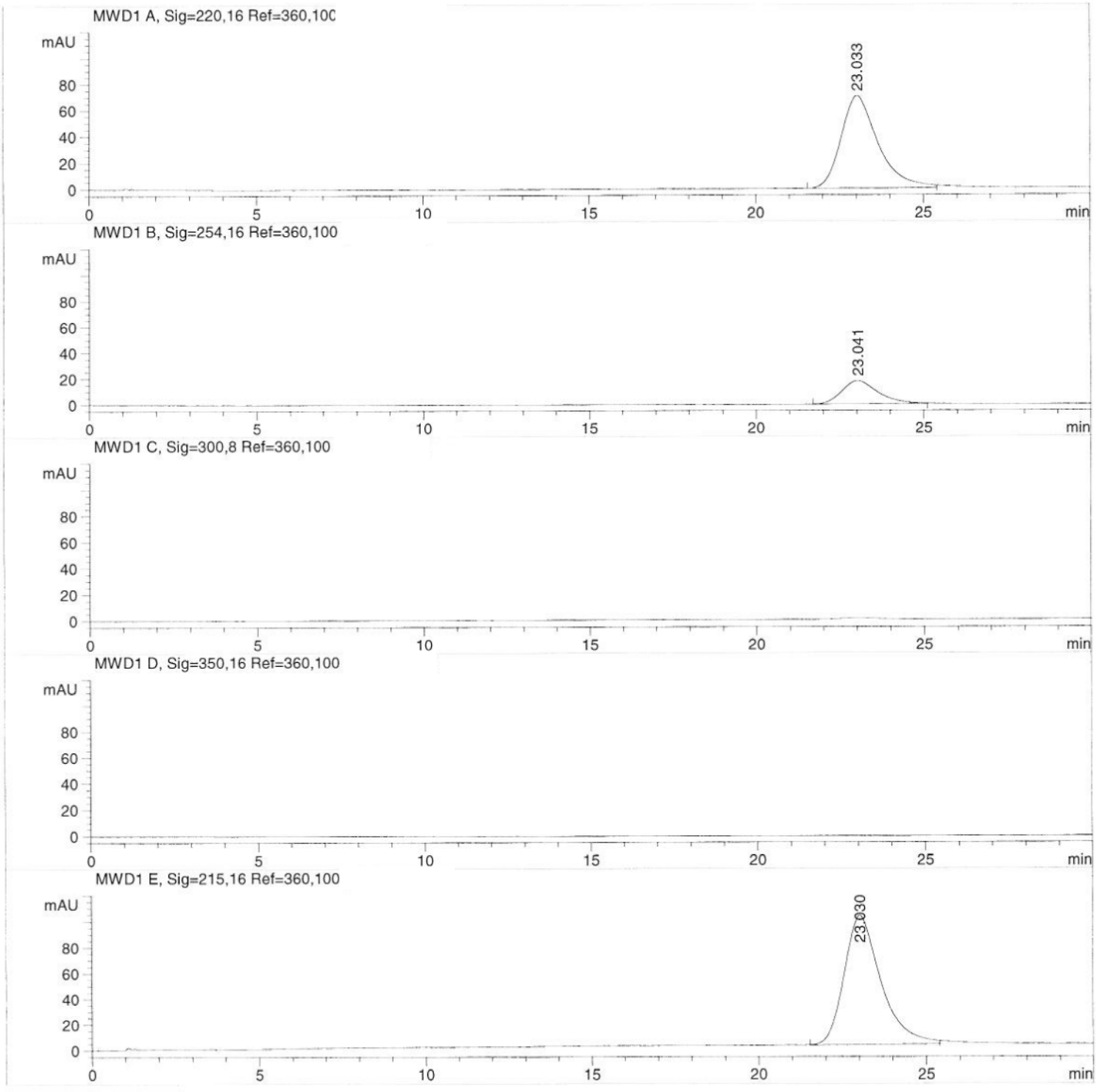


```
================================================================================
                          Area Percent Report
================================================================================

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  11.858 PB    0.6182 2585.91675   63.62169  50.0545
   2  22.991 PB    1.0919 2580.28857   34.28851  49.9455

Totals :                  5166.20532   97.91020

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.858 BB    0.6104  663.39410   16.52487  51.1690
   2  22.991 BB    0.9137  633.08154    8.77511  48.8310

Totals :                  1296.47565   25.29999

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100


Signal 4: MWD1 D, Sig=350,16 Ref=360,100


Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.858 PB    0.6178 3665.81055   90.27012  49.6775
   2  22.991 PB    1.1018 3713.41357   48.90760  50.3225

Totals :                  7379.22412  139.17772

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

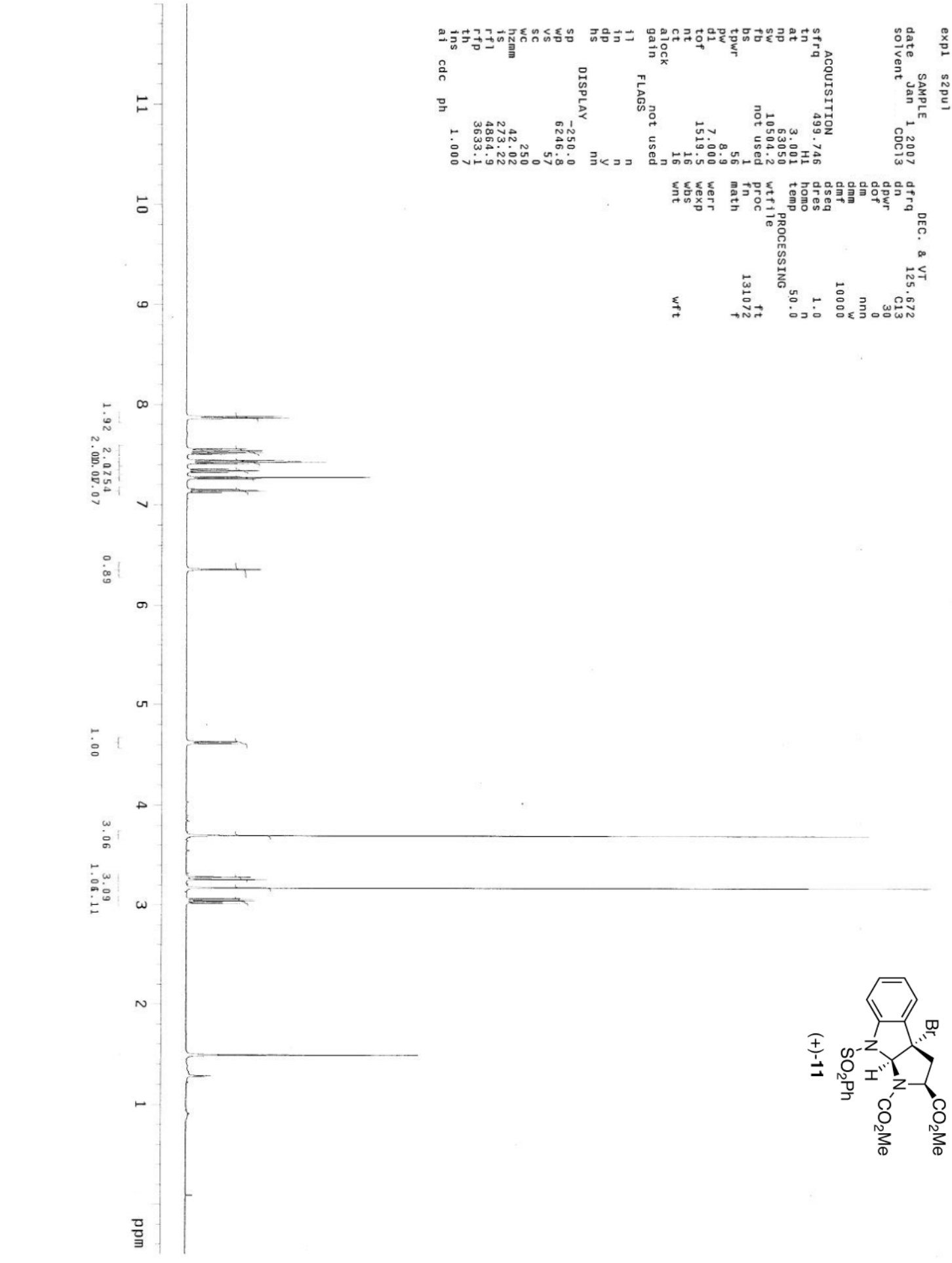
```
==========================================================================
Injection Date  : 8/8/2006 4:42:15 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 2
Acq. Operator   :                                   Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 8/8/2006 10:21:36 AM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:08:14 AM
                  (modified after loading)
```

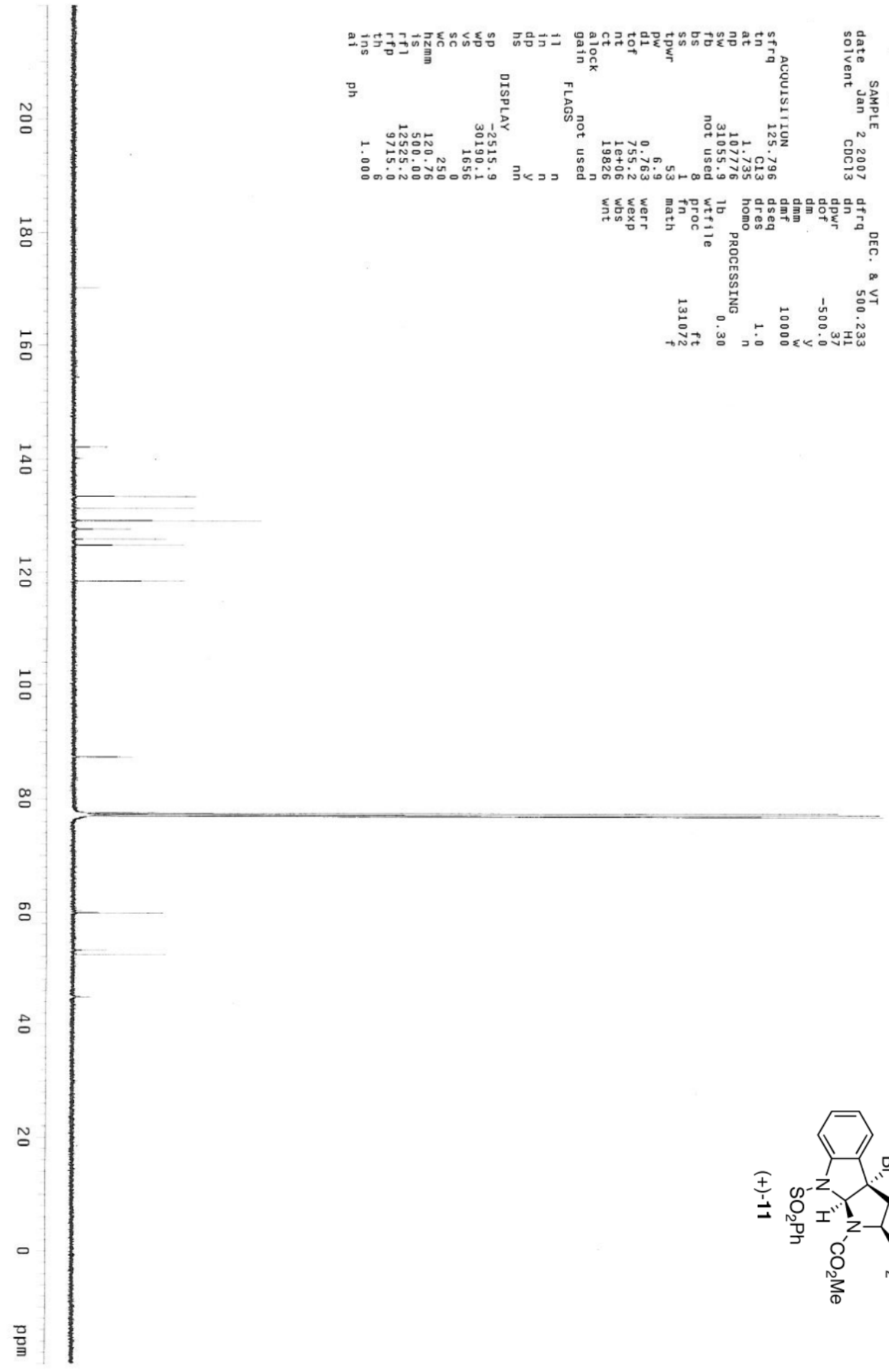


(+)-**9**

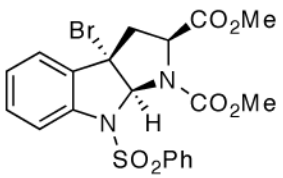


```
=====================================================================
                        Area Percent Report
=====================================================================

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  23.033 VV    0.9641 5360.91748   70.42066 100.0000

Totals :                  5360.91748   70.42066

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.041 VB    0.8716 1318.07544   18.05686 100.0000

Totals :                  1318.07544   18.05686

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100


Signal 4: MWD1 D, Sig=350,16 Ref=360,100


Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.030 VV    1.0140 7638.75244  100.13385 100.0000

Totals :                  7638.75244  100.13385

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

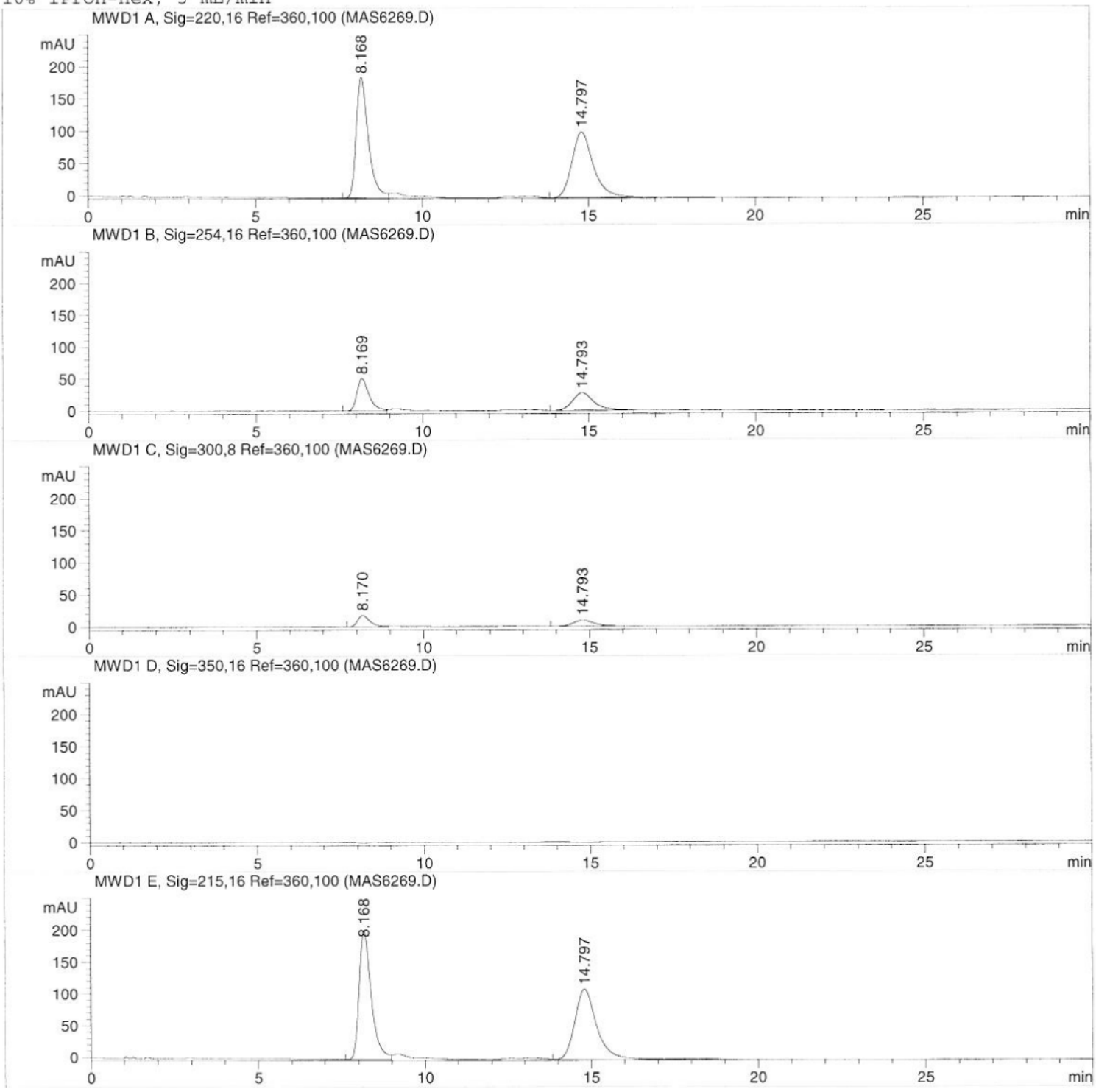

expl s2pul
SAMPLE
date Jan 1 2007
solvent CDCl3
DEC. & VT
dfrq 125.672
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
ACQUISITION
sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.9
d1 7.000
tof 1519.5
nt 16
ct 16
alock n
gain not used
PROCESSING
dseq 1.0
dres n
homo 50.0
temp
wtfile
proc ft
fn 131072
math f
wexp
wbs
wnt wft
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.8
vs 57
sc 0
wc 250
hzmm 42.02
is 273.22
rfl 4864.9
rfp 3633.1
th 7
ins 1.000
ai cdc ph
11
10
9
8
7
6
5
4
3
2
1
ppm
1.92
2.00
2.07
2.07
0.89
1.00
3.06
3.09
1.06
1.11
Br
CO2Me
N
H
N
CO2Me
SO2Ph
(+)-11


expl s2pul
SAMPLE
date Jan 2 2007
solvent CDCl3
DEC. & VT
dfrq 500.233
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
ACQUISITION
sfrq 125.796
tn C13
at 1.735
np 107776
sw 31055.9
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 755.2
nt 1e+06
ct 19826
alock n
gain not used
PROCESSING
dseq 1.0
dres n
homo
lb 0.30
wtfile
proc
fn ft
math 131072 f
werr
wexp
wbs
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30190.1
vs 1656
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 12525.2
rfp 9715.0
th 6
ins 1.000
ai ph
200
180
160
140
120
100
80
60
40
20
0
ppm
Br
N
H
N
SO2Ph
CO2Me
CO2Me
(+)-11

```
==========================================================================
Injection Date  : 8/25/2006 4:36:58 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 1
Acq. Operator   :                                   Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 8/10/2006 9:12:26 AM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:09:43 AM
                  (modified after loading)
10% iPrOH-hex; 3 mL/min
```



(±)-**11**



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	8.168	VV	0.3799	4729.16699	186.43048	51.1452
2	14.797	VB	0.6735	4517.38184	101.44996	48.8548
Totals :				9246.54883	287.88044	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.169	VV	0.3825	1285.78845	50.59615	50.8871
2	14.793	VV	0.6615	1240.95898	27.54830	49.1129
Totals :				2526.74744	78.14444	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.170	BB	0.3812	441.07721	17.42985	52.1192
2	14.793	VB	0.5962	405.20792	9.37651	47.8808
Totals :				846.28513	26.80636	

Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=350,16 Ref=360,100

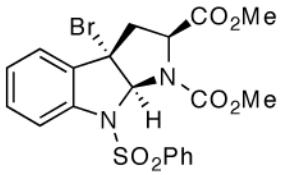
Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.168	VV	0.3797	5157.93701	203.47020	50.0545
2	14.797	VB	0.6910	5146.70264	111.82165	49.9455
Totals :				1.03046e4	315.29185	

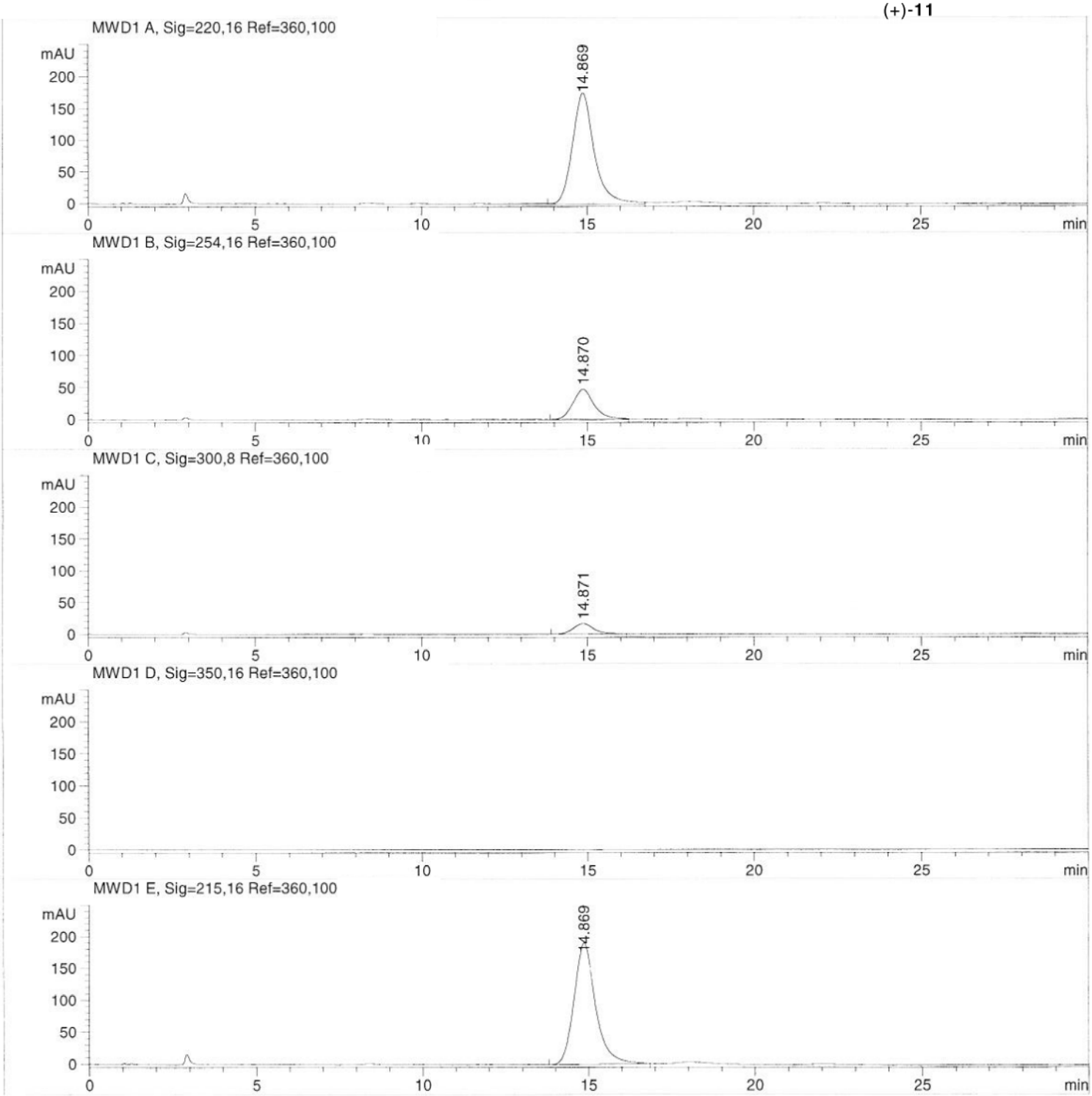
Results obtained with enhanced integrator!

*** End of Report ***

```
==========================================================================
Injection Date  : 8/25/2006 5:09:48 PM          Seq. Line :   1
Sample Name     :                                Location : Vial 1
Acq. Operator   :                                    Inj :   1
                                                 Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 8/10/2006 9:12:26 AM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:09:43 AM
                  (modified after loading)
```



(+)-**11**



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	14.869	VV	0.6733	7974.86328	175.11238	100.0000
Totals :				7974.86328	175.11238	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.870	VV	0.6657	2145.04810	47.42588	100.0000
Totals :				2145.04810	47.42588	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.871	PB	0.6027	704.74915	16.16243	100.0000
Totals :				704.74915	16.16243	

Results obtained with enhanced integrator!

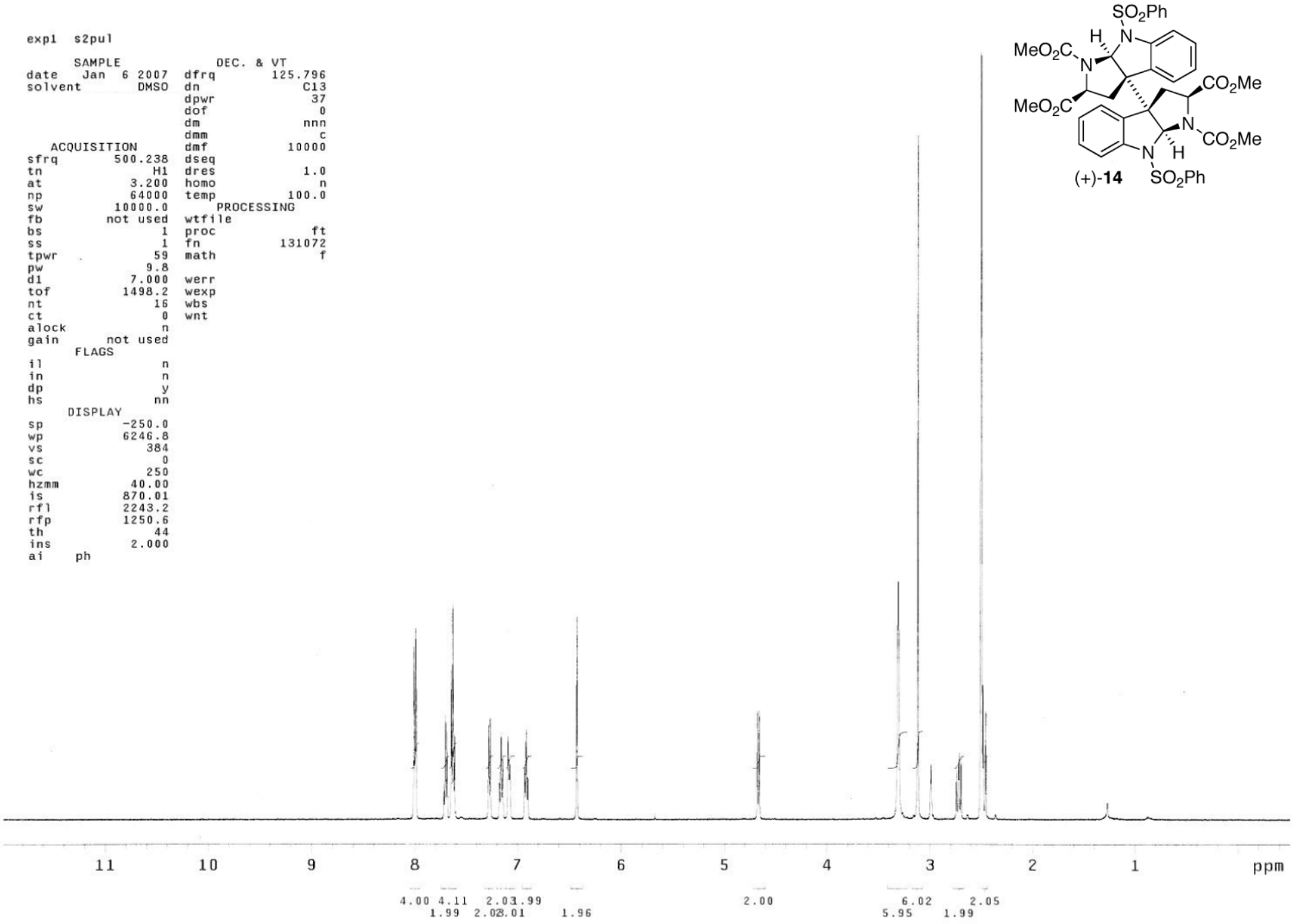
Signal 4: MWD1 D, Sig=350,16 Ref=360,100

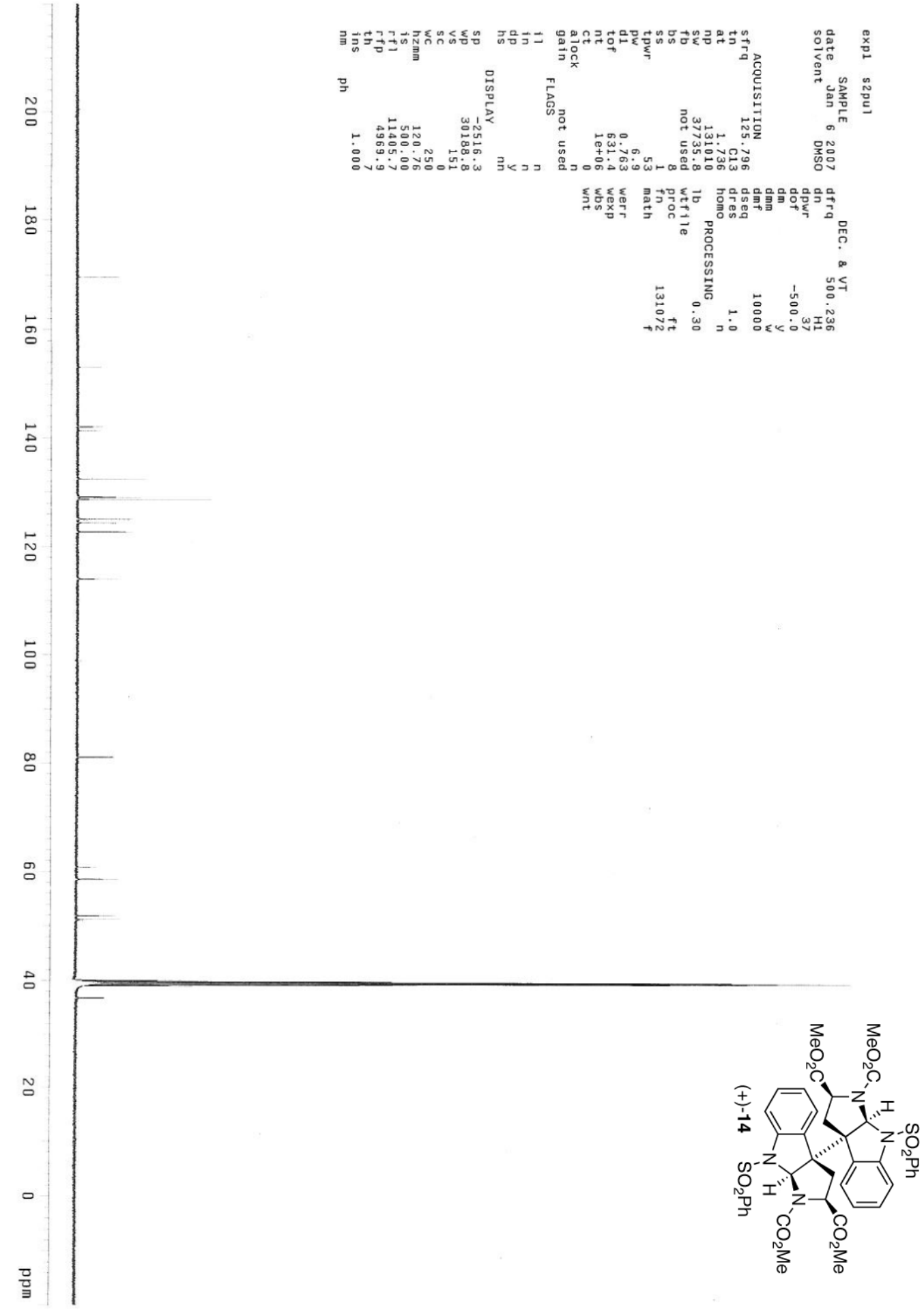
Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.869	VB	0.6633	8502.20898	190.29601	100.0000
Totals :				8502.20898	190.29601	

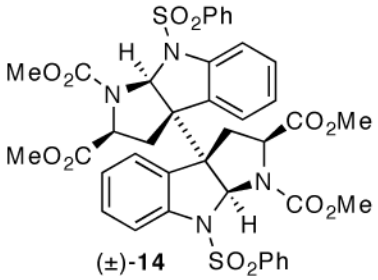
Results obtained with enhanced integrator!

*** End of Report ***

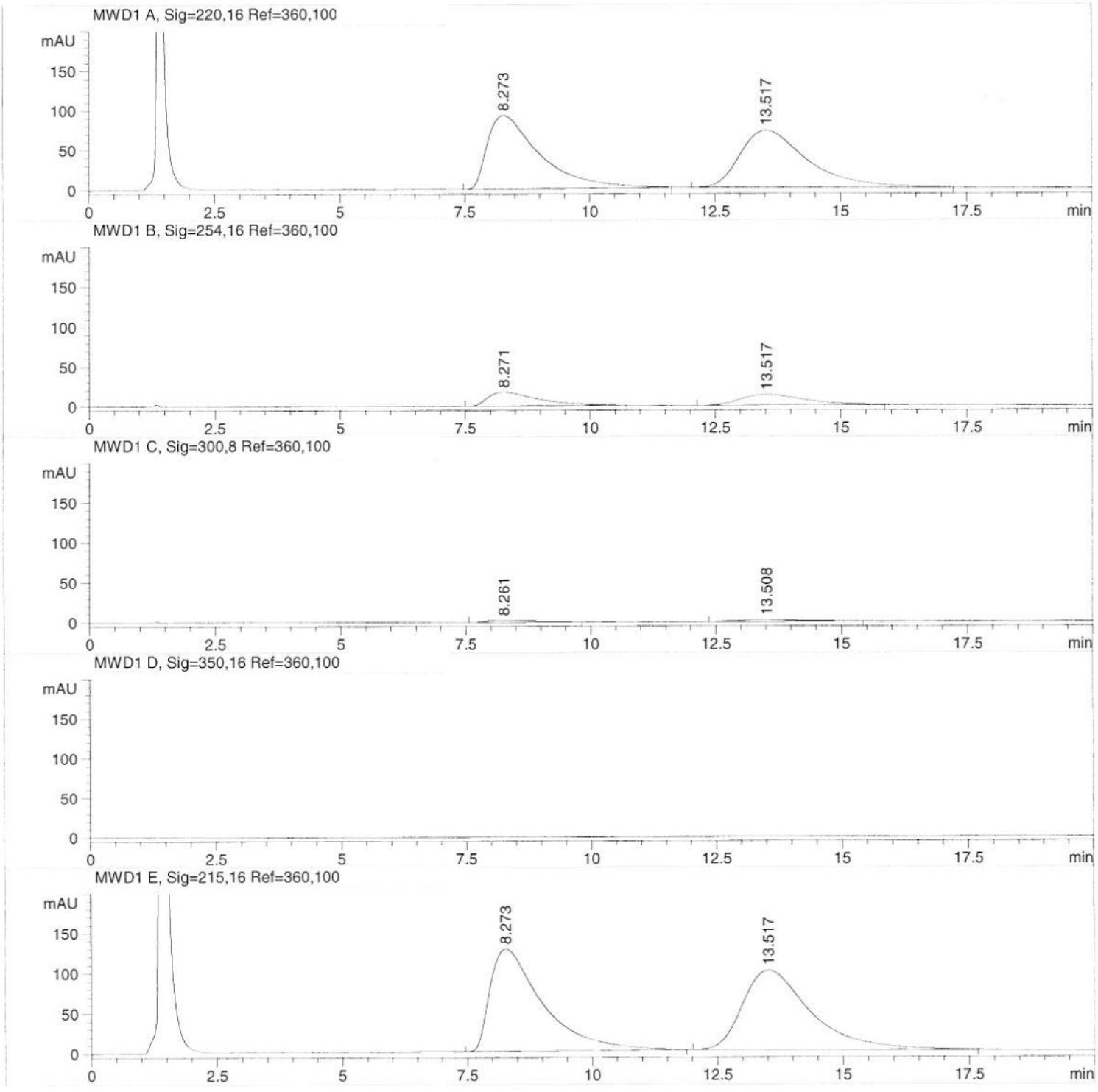

expl s2pul
SAMPLE
date Jan 6 2007
solvent DMSO
ACQUISITION
sfrq 500.238
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 59
pw 9.8
d1 7.000
tof 1498.2
nt 16
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.8
vs 384
sc 0
wc 250
hzmm 40.00
is 870.01
rfl 2243.2
rfp 1250.6
th 44
ins 2.000
ai ph
DEC. & VT
dfrq 125.796
dn C13
dpwr 37
dof 0
dm nnn
dmm c
dmf 10000
dseq
dres 1.0
homo n
temp 100.0
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
SO2Ph
MeO2C
CO2Me
(+)-14
11
10
9
8
7
6
5
4
3
2
1
ppm
4.00 4.11 2.03 1.99
1.99 2.02 3.01 1.96
2.00
6.02 2.05
5.95 1.99


expl s2pul
SAMPLE
date Jan 6 2007
solvent DMSO
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 0
alock wnt
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -2516.3
wp 30188.8
vs 151
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 11405.7
rfp 4969.9
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 500.236
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq 1.0
dres n
homo
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
200
180
160
140
120
100
80
60
40
20
0
ppm
MeO2C
MeO2C
N
H
N
SO2Ph
MeO2C
N
H
N
CO2Me
CO2Me
N
SO2Ph
(+)-14

```
==========================================================================
Injection Date  : 2/4/2007 2:02:53 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 1
Acq. Operator   :                                   Inj :   1
                                               Inj Volume : 10 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 2/4/2007 2:18:18 PM
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/4/2007 3:52:41 PM
                  (modified after loading)
```



(±)-14



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	8.273	PB	1.0746	6723.83008	92.22232	50.2531
2	13.517	BB	1.3247	6656.10840	71.72623	49.7469
Totals :				1.33799e4	163.94855	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.271	PB	0.9890	1210.04333	17.32205	50.9955
2	13.517	BB	1.1372	1162.79785	13.31084	49.0045
Totals :				2372.84119	30.63289	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.261	PB	0.7330	150.77000	2.41303	49.2840
2	13.508	BB	0.9804	155.15099	1.87301	50.7160
Totals :				305.92099	4.28603	

Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=350,16 Ref=360,100

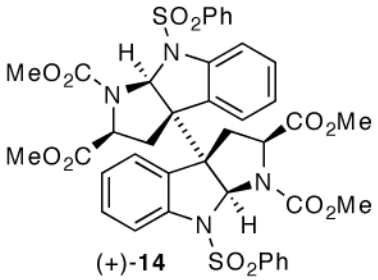
Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.273	PB	1.0785	9358.08594	127.77487	50.1776
2	13.517	BB	1.3478	9291.83203	99.46951	49.8224
Totals :				1.86499e4	227.24438	

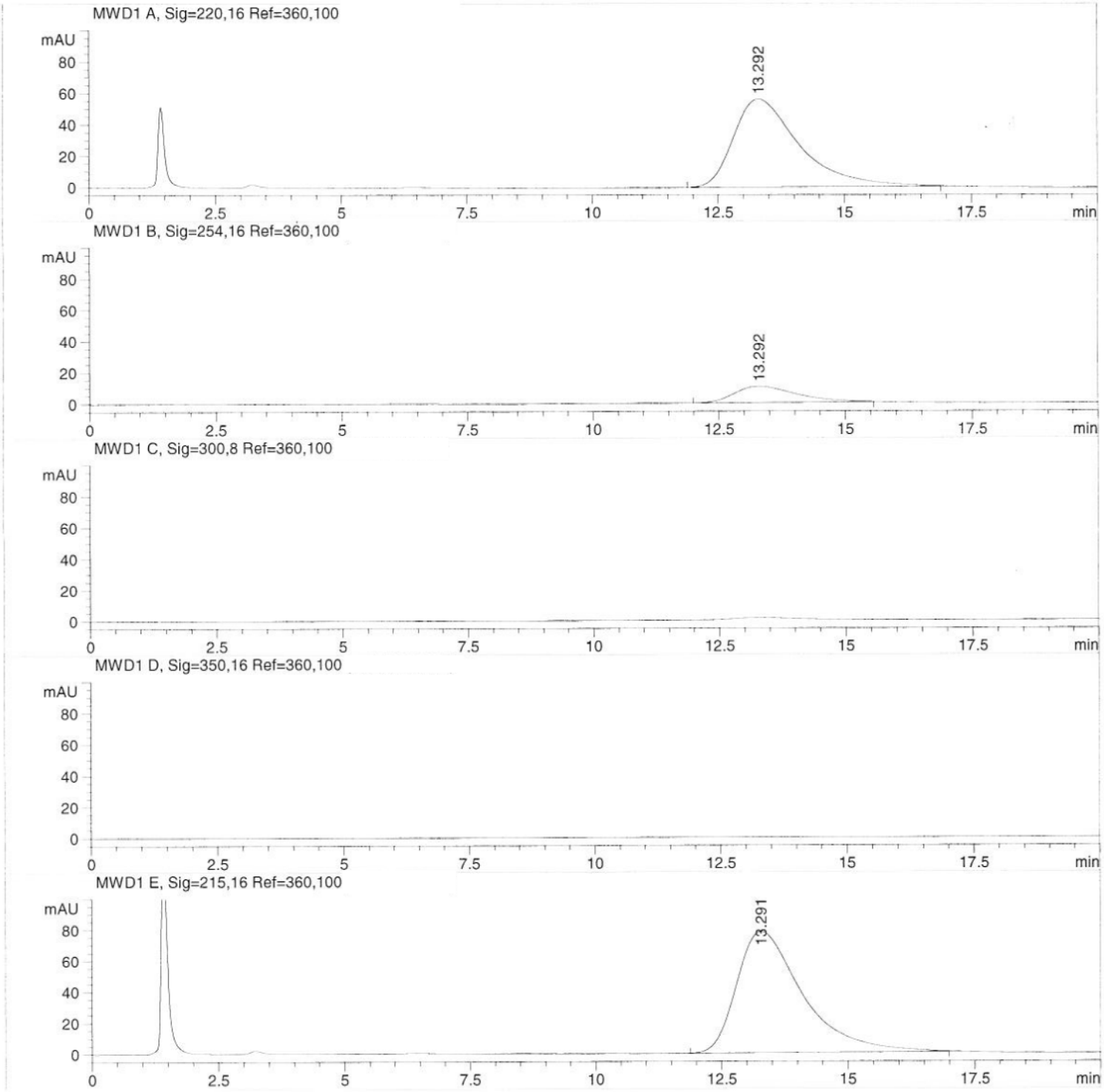
Results obtained with enhanced integrator!

*** End of Report ***

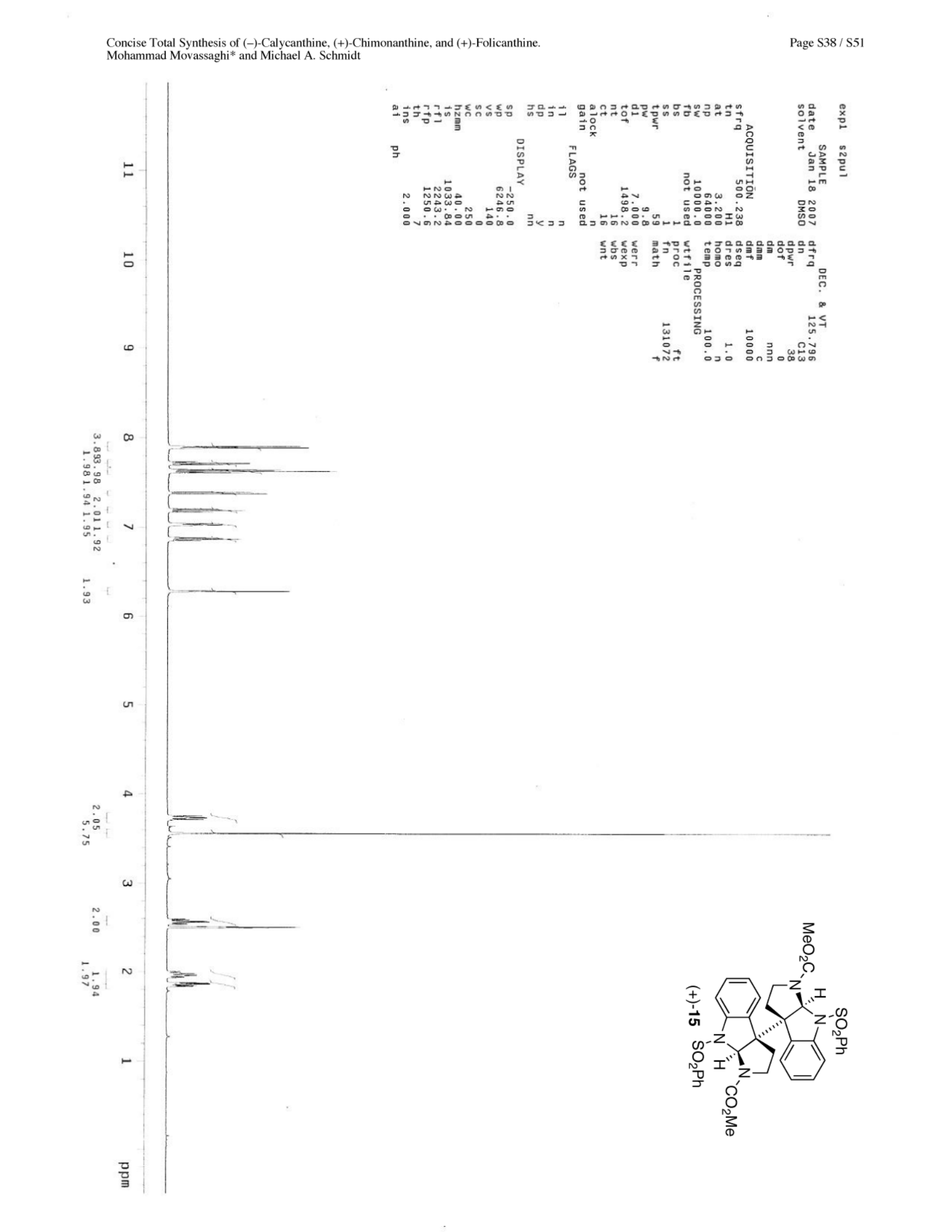
```
==========================================================================
Injection Date  : 2/4/2007 2:44:38 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 2
Acq. Operator   :                                   Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 2/4/2007 2:24:09 PM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/4/2007 3:53:08 PM
                  (modified after loading)
```

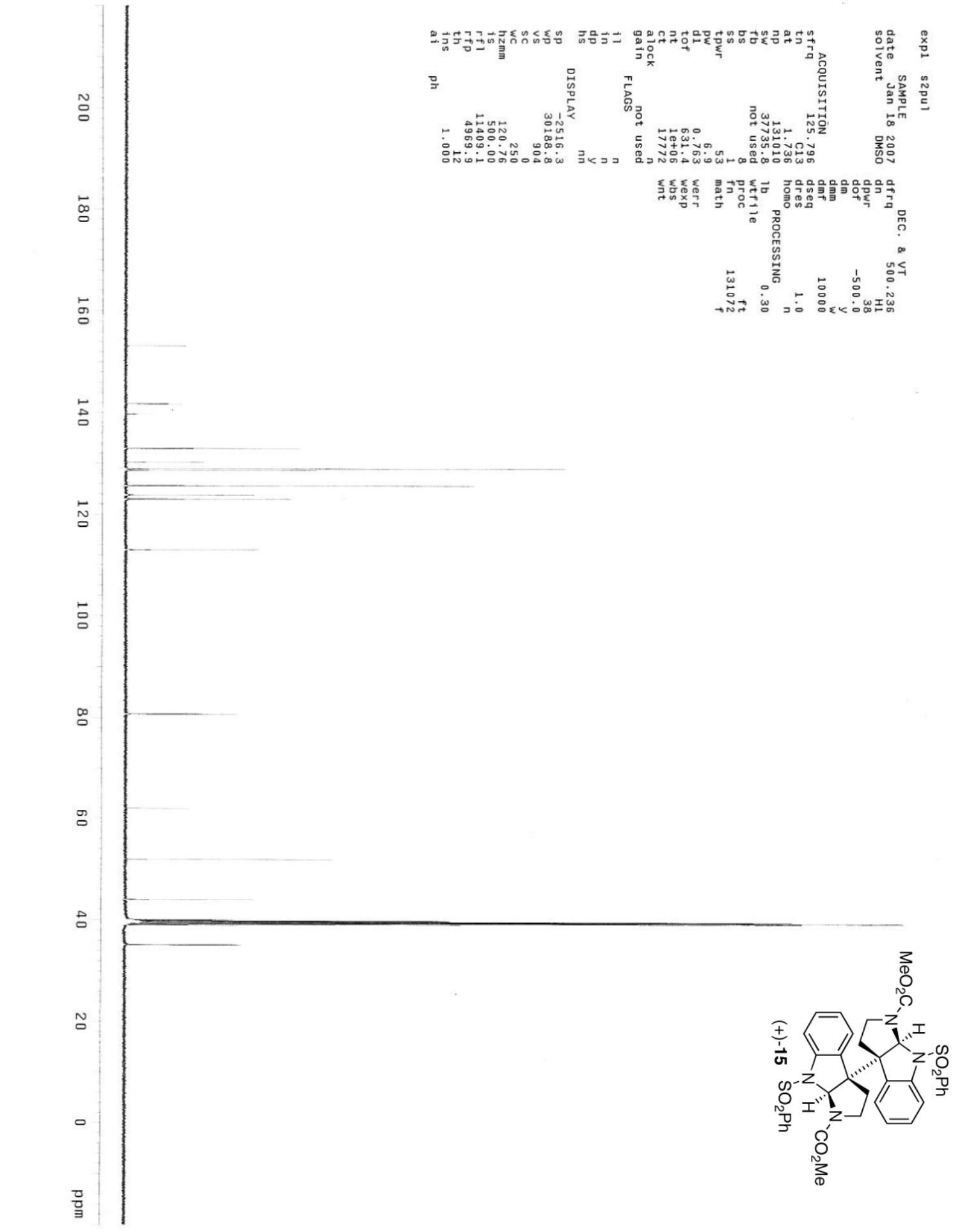


(+)-**14**



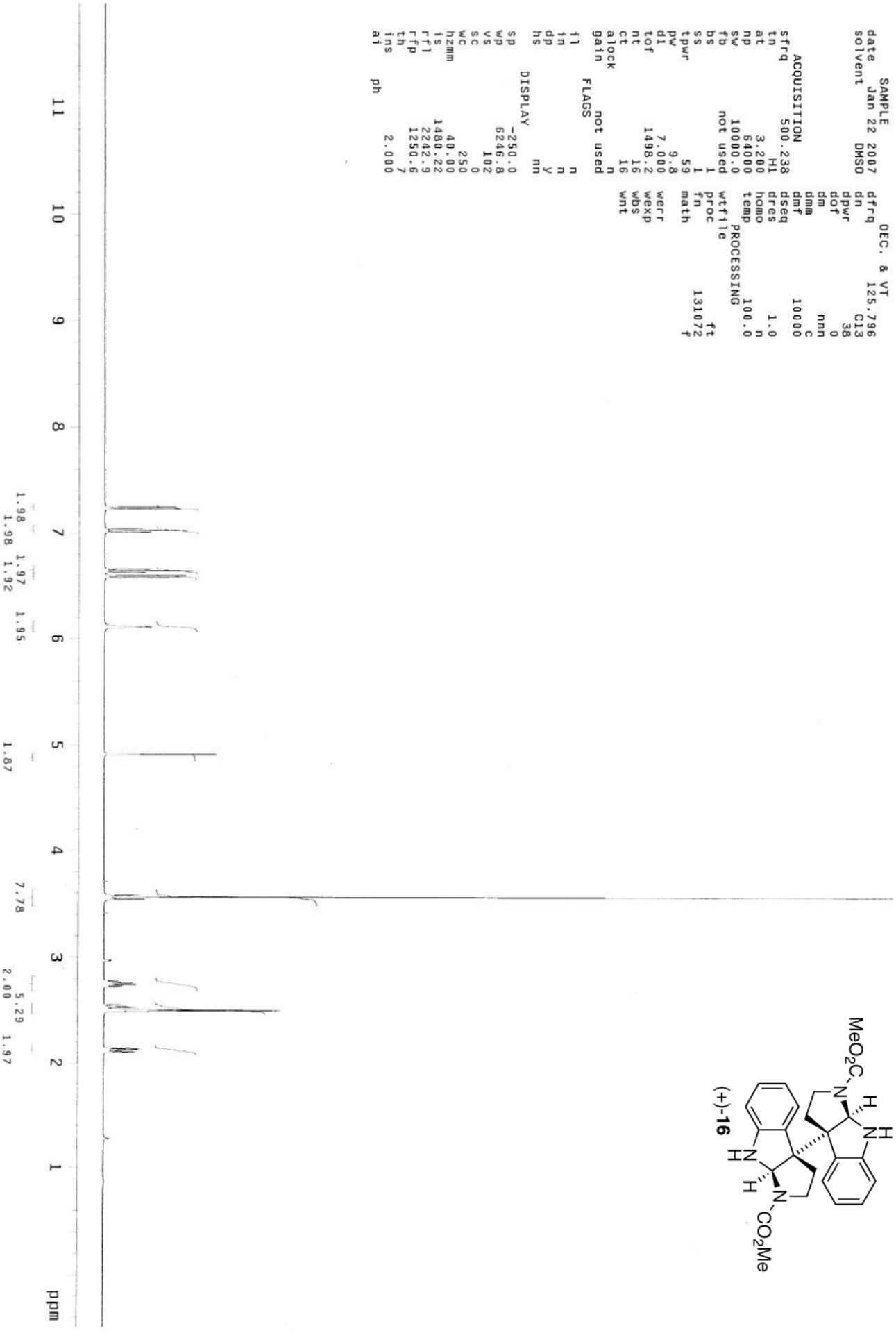
```
=====================================================================
                      Area Percent Report
=====================================================================

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  13.292 BB    1.3205 5109.18359   56.41901 100.0000

Totals :                  5109.18359   56.41901

 Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.292 BB    1.0247  884.91693   10.46322 100.0000

Totals :                   884.91693   10.46322

 Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100


Signal 4: MWD1 D, Sig=350,16 Ref=360,100


Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.291 BB    1.3380 7069.39355   78.10255 100.0000

Totals :                  7069.39355   78.10255

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

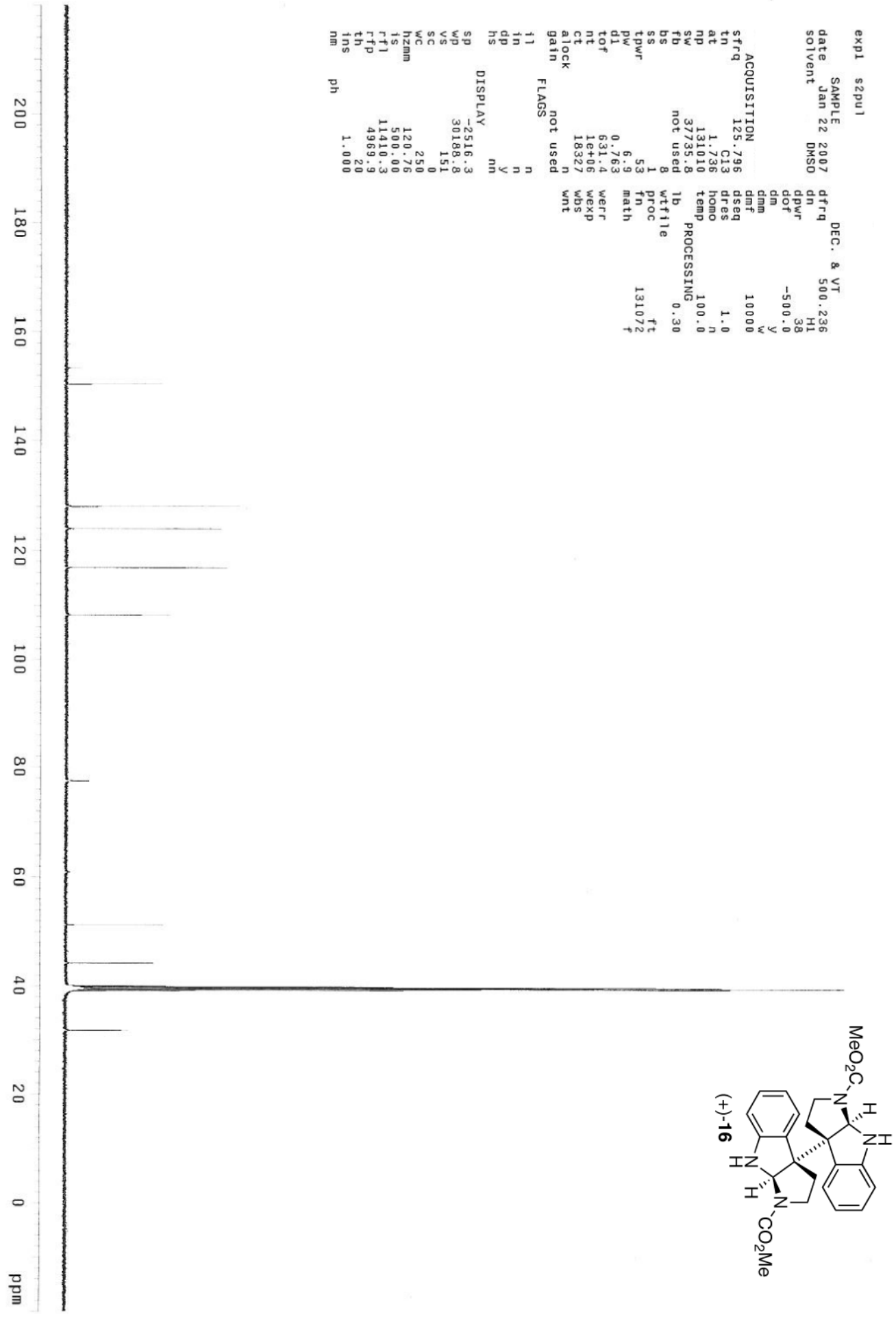

exp1 s2pul
SAMPLE
date Jan 18 2007
solvent DMSO
DEC. & VT
dfrq 125.796
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10000
dres 1.0
dseq n
homo n
temp 100.0
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
ACQUISITION
sfrq 500.238
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 59
pw 9.8
d1 7.000
tof 1498.2
nt 16
ct 16
alock n
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.8
vs 140
sc 0
wc 250
hzmm 40.00
is 1033.84
rfl 2243.2
rfp 1250.6
th 7
ins 2.000
ai ph
3.89 3.98 2.01 1.92
1.98 1.94 1.95
1.93
2.05
5.75
2.00
1.94
1.97
11 10 9 8 7 6 5 4 3 2 1 ppm
MeO2C
N
H
N
SO2Ph
N
H
N
CO2Me
SO2Ph
(+)-15


exp1 s2pul
SAMPLE
date Jan 18 2007
solvent DMSO
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 17772
alock wnt
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -2516.3
wp 30188.8
vs 904
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 11409.1
rfp 4969.9
th 12
ins 1.000
ai ph
dfrq DEC. & VT
dn 500.236
dpwr H1
dof 38
dm -500.0
dmm y
dmf w
dseq 10000
dres
homo 1.0
PROCESSING n
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
200
180
160
140
120
100
80
60
40
20
0
ppm

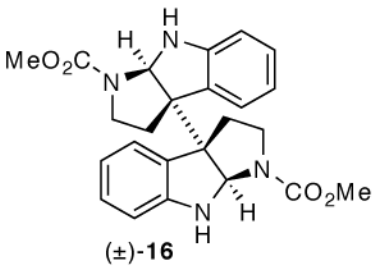
MeO2C
N
H
N
SO2Ph
N
H
N
CO2Me
SO2Ph

(+)-**15**

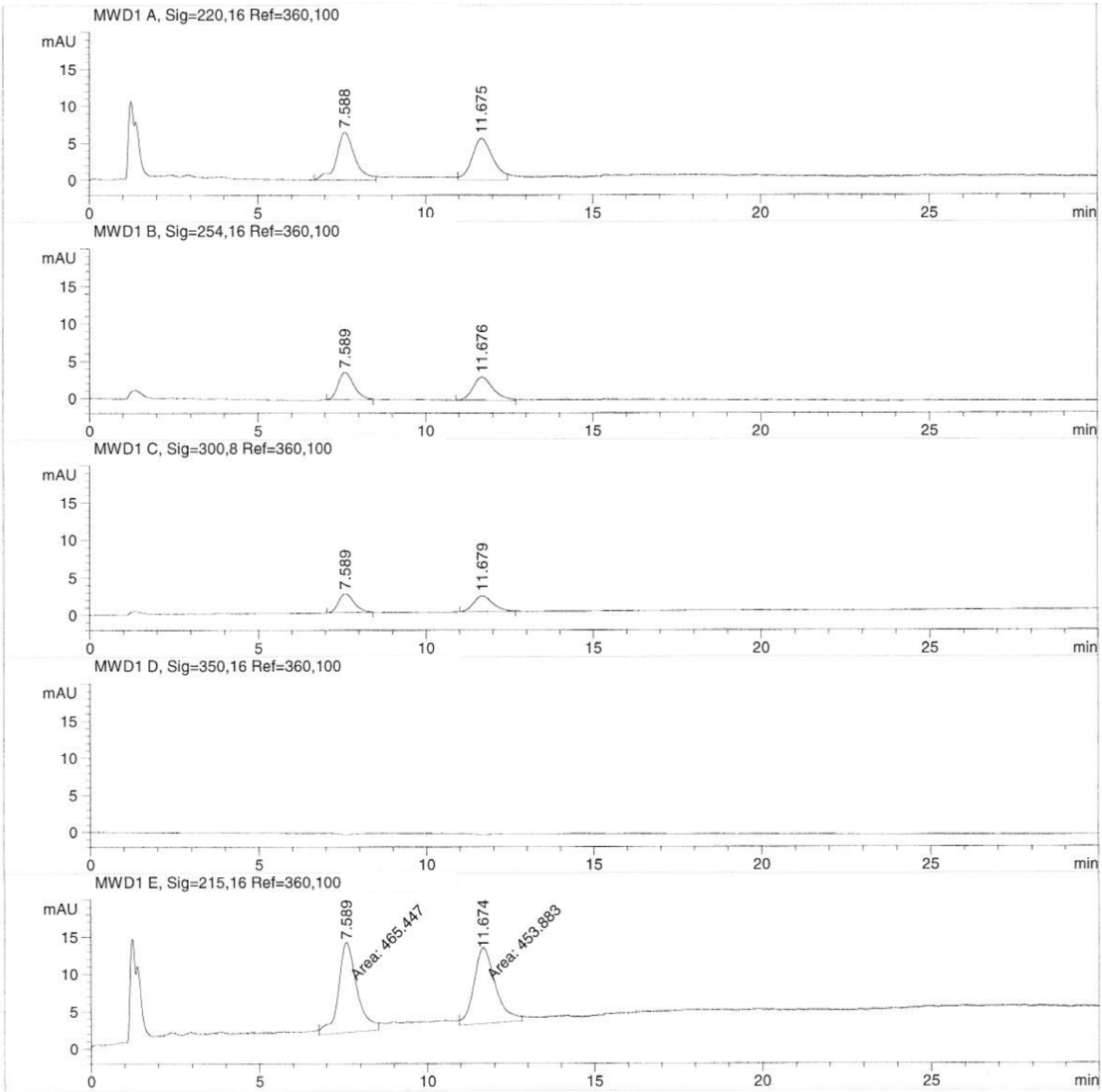

expl s2pul
SAMPLE
date Jan 22 2007
solvent DMSO
DEC. & VT
dfrq 125.796
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10000
ACQUISITION
sfrq 500.238
tn H1
at 3.200
np 64000
sw 10000.0
fb not used
bs 1
ss 1
tpwr 59
pw 9.8
d1 7.000
tof 1498.2
nt 16
ct 16
alock n
gain n
PROCESSING
dseq 1.0
dres 1.0
homo n
temp 100.0
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 6246.8
vs 102
sc 0
wc 250
hzmm 40.00
is 1480.22
rfl 2242.9
rfp 1250.6
th 7
ins 2.000
al ph
1.98
1.98 1.97 1.92
1.95
1.87
7.78
5.29
2.00
1.97
11 10 9 8 7 6 5 4 3 2 1 ppm
MeO2C
N
H
H
N
H
N
CO2Me
(+)-16


expl s2pul
SAMPLE
date Jan 22 2007
solvent DMSO
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 18327
alock n
gain n
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.3
wp 30188.8
vs 151
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 11410.3
rfp 4969.9
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 500.236
dn H1
dpwr 38
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 100.0
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
200
180
160
140
120
100
80
60
40
20
0
ppm
MeO2C
CO2Me
(+)-16

```
==========================================================================
Injection Date  : 10/8/2006 11:14:12 AM          Seq. Line :   1
Sample Name     :                                 Location : Vial 1
Acq. Operator   :                                     Inj :   1
                                                  Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 10/5/2006 8:02:15 PM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:23:43 AM
                  (modified after loading)
```



(±)-**16**



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	7.588	BV	0.4916	245.93385	6.46734	50.4826
2	11.675	VV	0.5146	241.23187	5.64461	49.5174
Totals :				487.16573	12.11195	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.589	BB	0.4437	118.53646	3.68065	47.6941
2	11.676	BV	0.4996	129.99820	3.13637	52.3059
Totals :				248.53466	6.81702	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.589	BB	0.4477	81.09453	2.51831	49.1445
2	11.679	BB	0.4839	83.91788	2.09222	50.8555
Totals :				165.01241	4.61052	

Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=350,16 Ref=360,100

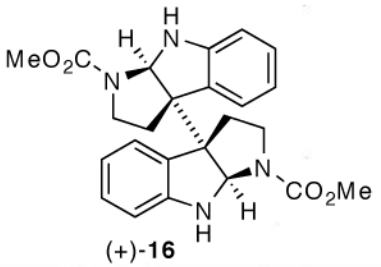
Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.589	MM	0.6417	465.44702	12.08867	50.6290
2	11.674	MM	0.7397	453.88260	10.22663	49.3710
Totals :				919.32962	22.31530	

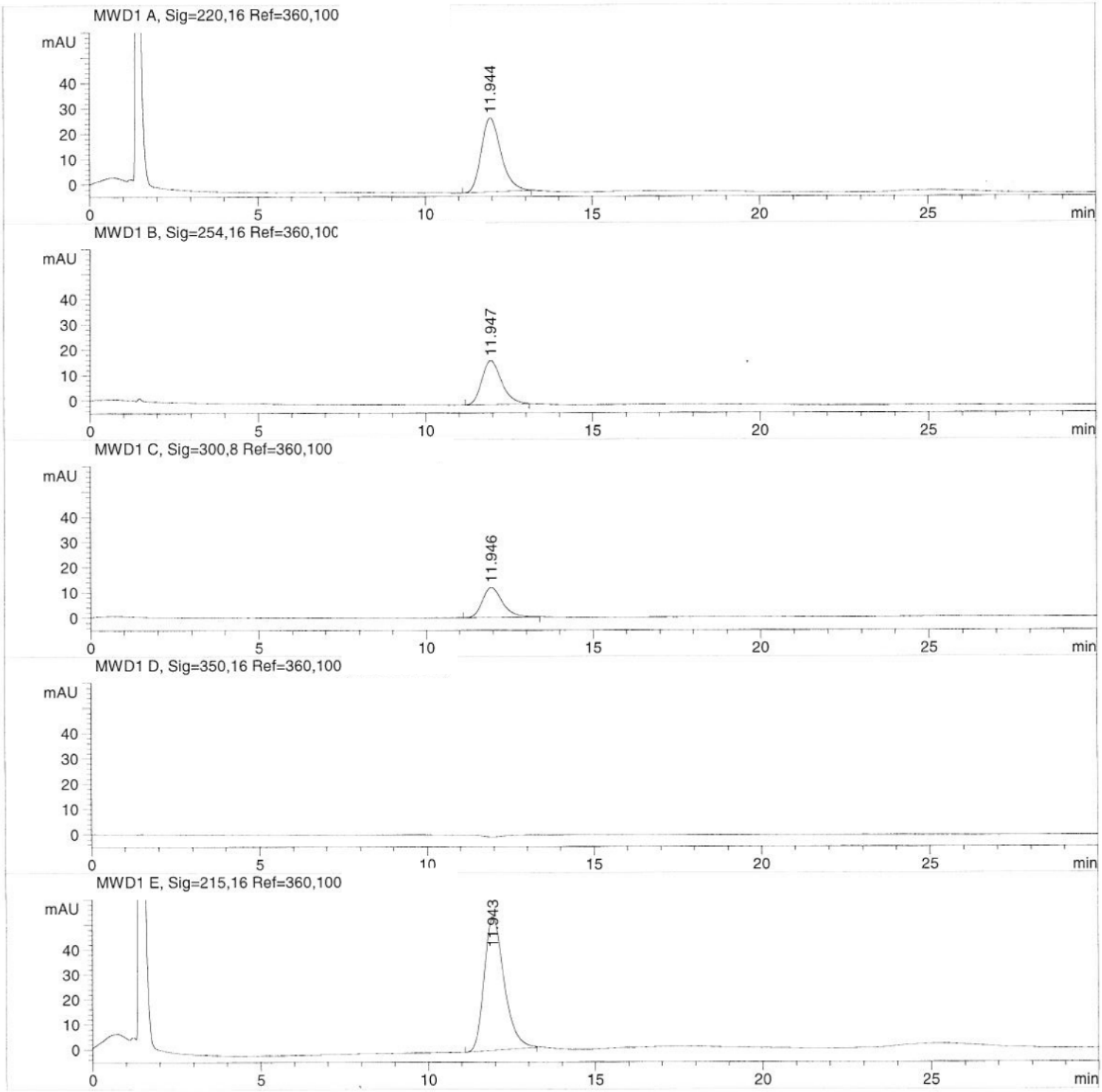
Results obtained with enhanced integrator!

*** End of Report ***

```
==========================================================================
Injection Date  : 10/5/2006 8:03:13 PM          Seq. Line :   1
Sample Name     :                                Location : Vial 1
Acq. Operator   :                                    Inj :   1
                                                 Inj Volume : 1 µl

Acq. Method     : C:\HPCHEM\2\METHODS\DIAST1.M
Last changed    : 10/5/2006 8:02:15 PM
Analysis Method : C:\HPCHEM\2\METHODS\BCEE.M
Last changed    : 2/2/2007 10:21:44 AM
                  (modified after loading)
```



(+)-**16**



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	11.944	VB	0.6221	1205.06702	29.16266	100.0000
Totals :				1205.06702	29.16266	

Results obtained with enhanced integrator!

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.947	VB	0.5942	712.70563	17.31634	100.0000
Totals :				712.70563	17.31634	

Results obtained with enhanced integrator!

Signal 3: MWD1 C, Sig=300,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.946	VV	0.6064	502.43103	11.95302	100.0000
Totals :				502.43103	11.95302	

Results obtained with enhanced integrator!

Signal 4: MWD1 D, Sig=350,16 Ref=360,100

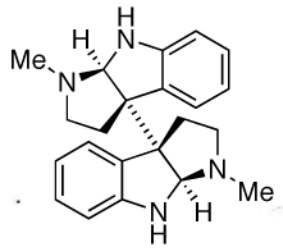
Signal 5: MWD1 E, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.943	VB	0.6284	2234.56982	53.59673	100.0000
Totals :				2234.56982	53.59673	

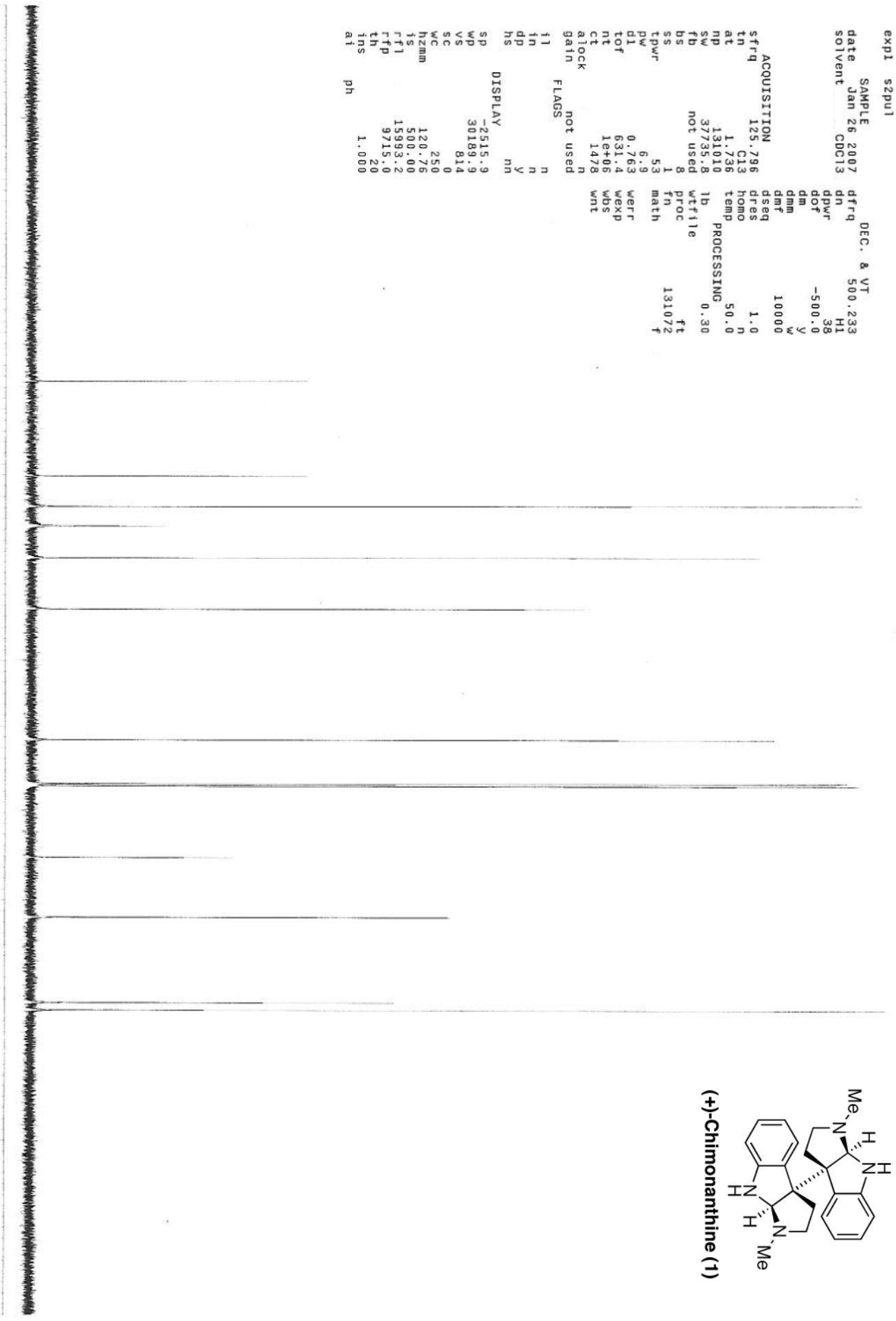
Results obtained with enhanced integrator!

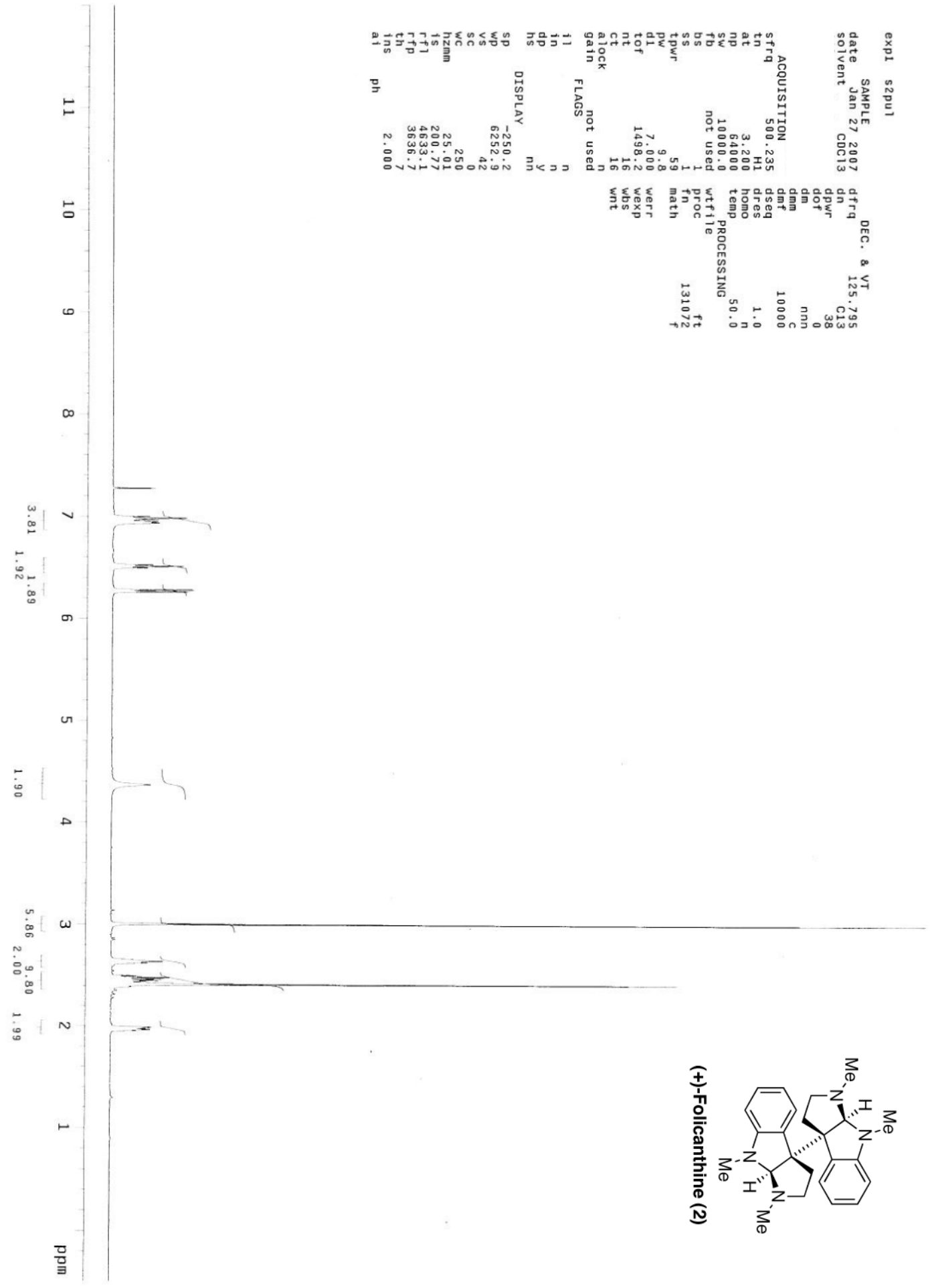
*** End of Report ***

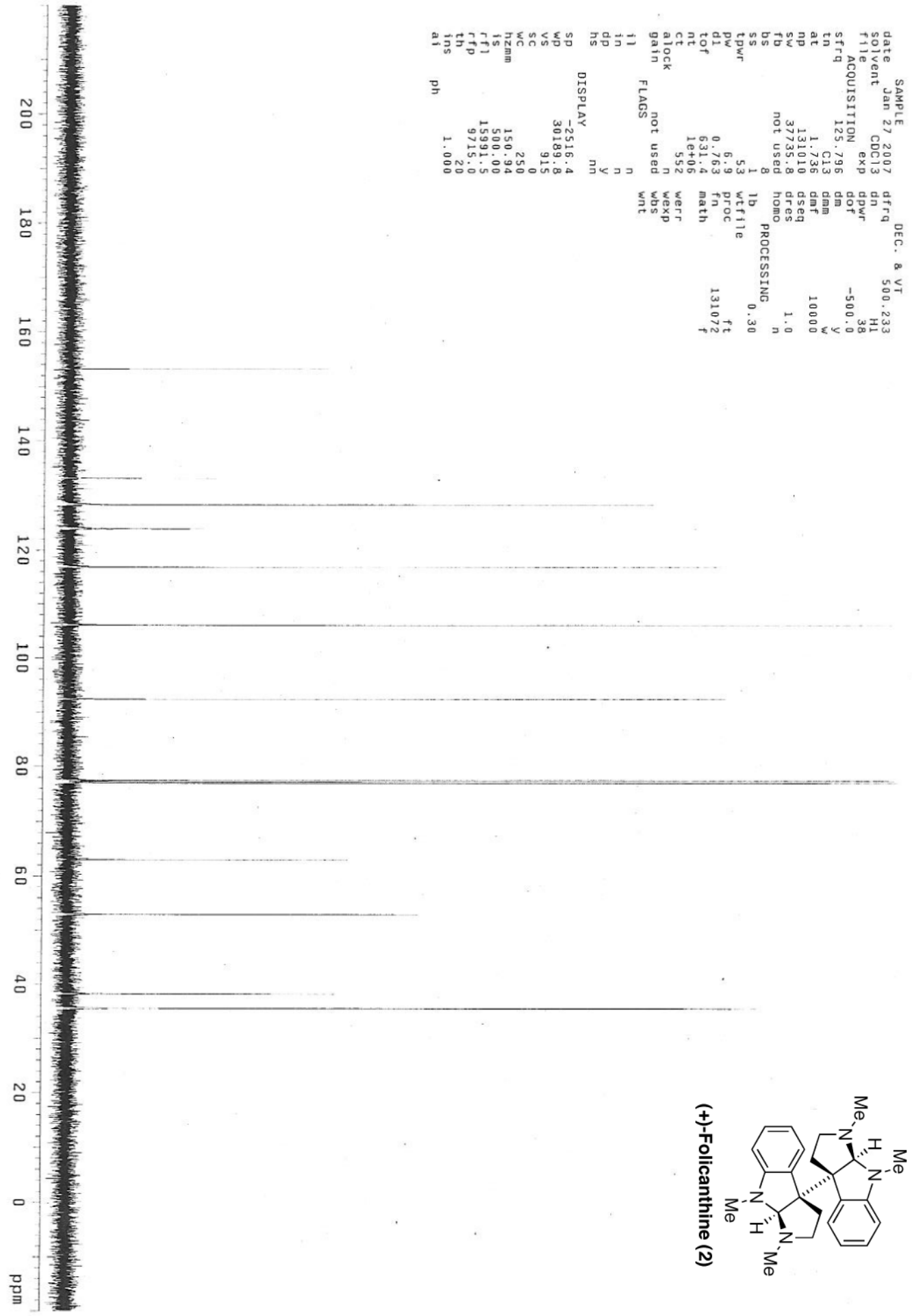
```
exp1  s2pul

      SAMPLE
date    Jan 26 2007
solvent       CDCl3

   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             7.000
tof           1498.2
nt                16
ct                16
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp            -249.9
wp            6246.8
vs                91
sc                 0
wc               250
hzmm           40.00
is            616.67
rfl           4633.2
rfp           3636.7
th                 7
ins            2.000
ai     ph

      DEC. & VT
dfrq         125.795
dn               C13
dpwr              38
dof                0
dm               nnn
dmm                c
dmf            10000
dseq
dres             1.0
homo               n
temp            50.0
     PROCESSING
wtfile
proc              ft
fn            131072
math               f

werr
wexp
wbs
wnt
```

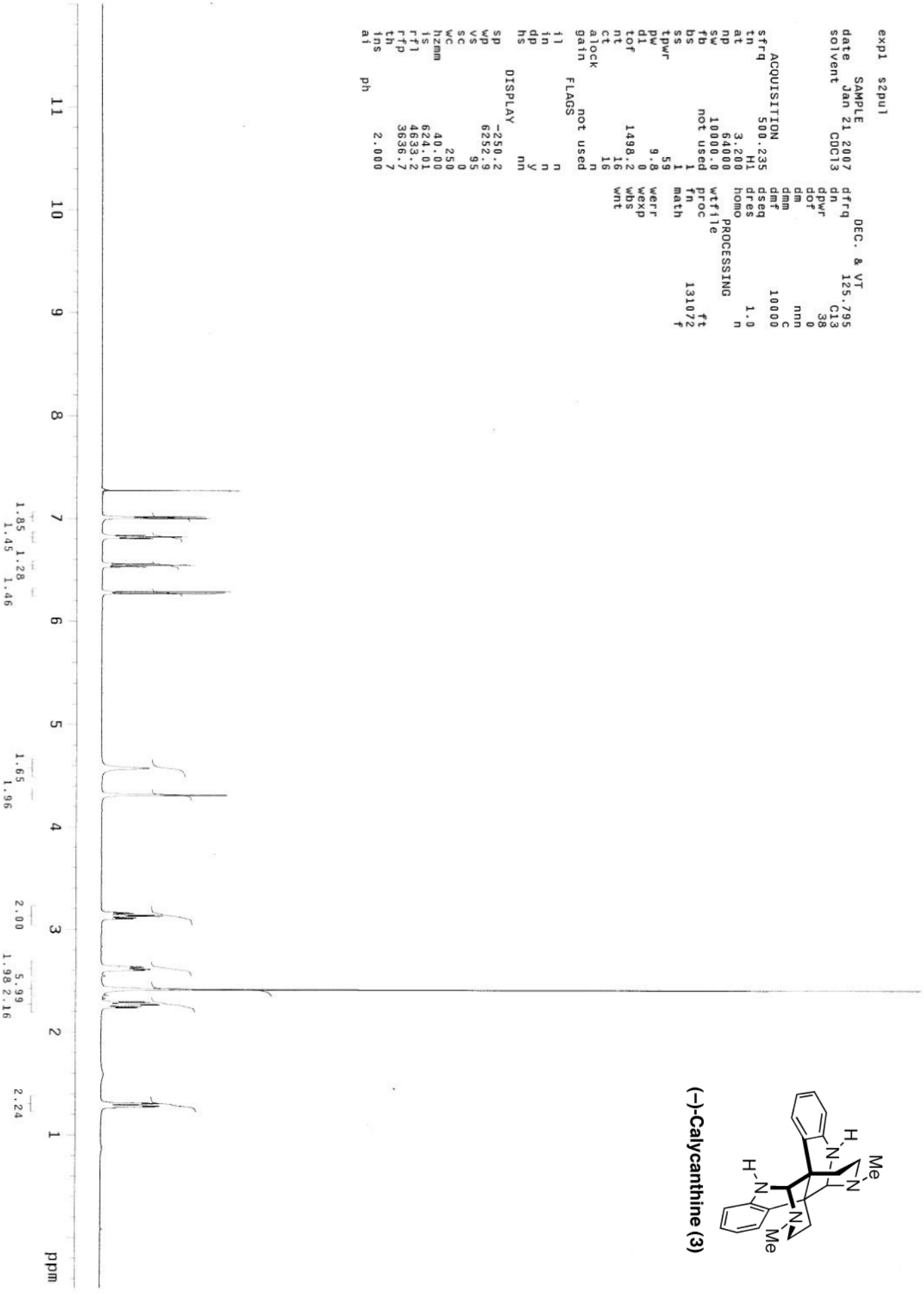


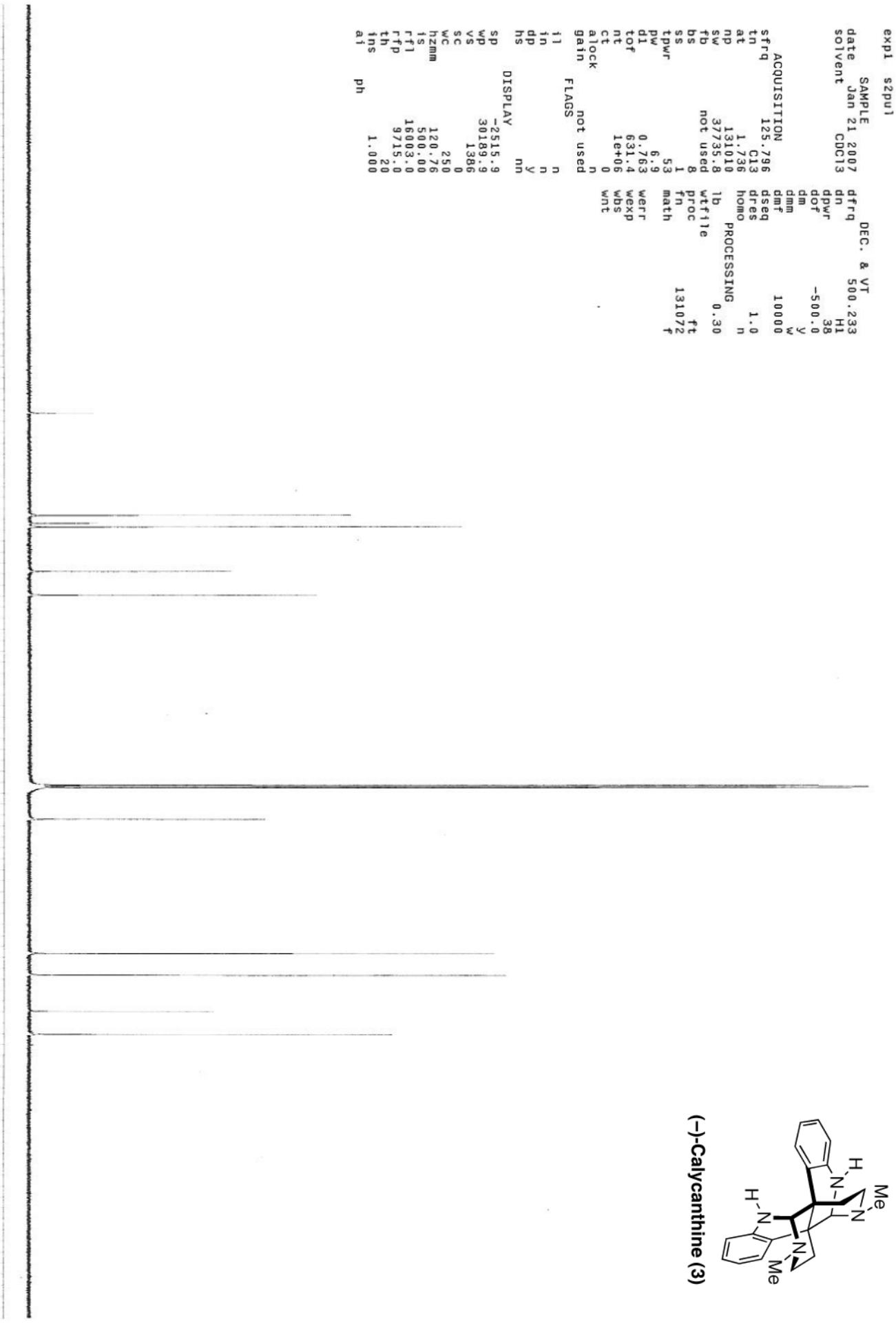
(+)-Chimonanthine (1)


expl s2pul
SAMPLE
date Jan 26 2007
solvent CDCl3
DEC. & VT
dfrq 500.233
dn H1
dpwr 38
dof -500.0
dm y
dmm w
dmf 10000
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 1478
alock n
gain not used
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2515.9
wp 30189.9
vs 814
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 1593.2
rfp 9715.0
th 20
ins 1.000
ai ph
200
180
160
140
120
100
80
60
40
20
0
ppm
Me
N
H
N
H
N
H
N
Me
(+)-Chimonanthine (1)


expl s2pul
SAMPLE
date Jan 27 2007
solvent CDCl3
DEC. & VT
dfrq 125.795
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10000
dseq
dres 1.0
homo n
temp 50.0
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 7.000
tof 1498.2
nt 16
ct 16
alock n
gain n
FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 6252.9
vs 42
sc 0
wc 250
hzmm 25.01
is 200.77
rfl 4633.1
rfp 3636.7
th 2.000
ins
ph
ai
3.81
1.89
1.92
1.90
5.86
9.80
2.00
1.99
11
10
9
8
7
6
5
4
3
2
1
ppm
(+)-Folicanthine (2)


exp3 s2pul
SAMPLE
date Jan 27 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 125.796
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 1e+06
ct 552
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.4
wp 30189.8
vs 915
sc 0
wc 250
hzmm 150.94
is 500.00
rfl 15991.5
rfp 9715.0
th 20
ins 1.000
ai ph
DEC. & VT
dfrq 500.233
dn H1
dpwr 38
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
200
180
160
140
120
100
80
60
40
20
0
ppm
Me
N
H
N
Me
N
H
N
Me
Me
(+)-Folicanthine (2)


expl s2pul
SAMPLE
date Jan 21 2007
solvent CDCl3
DEC. & VT
dfrq 125.795
dn C13
dpwr 38
dof 0
dm nnn
dmm c
dmf 10000
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 131072
math f
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 6252.9
vs 95
sc 0
wc 250
hzmm 40.00
is 624.01
rfl 4633.2
rfp 3636.7
th 7
ins 2.000
al ph
11
10
9
8
7
6
5
4
3
2
1
ppm
1.85
1.45
1.28
1.46
1.65
1.96
2.00
5.99
1.98
2.16
2.24
Me
H
N
N
H
N
N
Me
(–)-Calycanthine (3)



(–)-Calycanthine (3)