Total Synthesis of (–)-Himandrine

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Supporting Information

Contents:

General procedure. All reactions were performed in oven-dried or flame-dried round-bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. 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, 40-63 µm, 4-6% H_2O content, Zeochem).[1] Where necessary (so noted), silica gel was neutralized by treatment of the silica gel prior to chromatography with the eluent containing 1% triethylamine or 1% ammonium hydroxide. 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). Where necessary (so noted), silica gel plates were neutralized by treatment with a solution of 1% triethylamine or 1% ammonium hydroxide in dichloromethane followed by heating on a hot plate (~250 °C). 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 ~20 Torr at 25–35 °C unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, and toluene were purchased from J.T. Baker (Cycletainer^{TM}) and were purified by the method of Grubbs et al. under positive argon pressure.[2] Triethylamine, diisopropylethylamine, and benzene were distilled over calcium hydride immediately before use. Acrolein was distilled over calcium sulfate immediately before use. Methyl vinyl ketone was distilled over potassium carbonate and calcium chloride immediately prior to use. Martin sulfurane was purchased from Aldrich and stored in a glove box under nitrogen atmosphere. *N*-Chlorosuccinimide (NCS) was recrystallized from benzene prior to use. Phosphorus oxychloride was distilled under reduced pressure before use. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).[3] Ammonia saturated dichloromethane was obtained by agitation of dichloromethane in the presence of ammonium hydroxide followed by drying over anhydrous sodium sulfate. Where necessary (so noted) solutions were deoxygenated by alternate freeze (liquid nitrogen)/evacuation/argon-flush/thaw cycles (FPT, three iterations) or degassed by purging with argon for several minutes.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian 300 Mercury or a Varian inverse probe 500 INOVA spectrometer or a Bruker 400 spectrometer or a Bruker inverse probe 600 Avance spectrometer. Chemical shifts are recorded in parts per million on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, C_6D_5H: δ7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Bruker 600 Avance spectrometer, a Varian 500 INOVA spectrometer or a Bruker 400 spectrometer with a Magnex Scientific superconducting magnet and are recorded in parts per million on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.2, benzene-d_6: δ 128.4). Infrared data were obtained with a Perkin-Elmer 2000 FT-IR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Optical rotations were measured on a Jasco-1010 polarimeter. 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) or electronspray (ES). The structure of (–)-himandrine was obtained with the assistance

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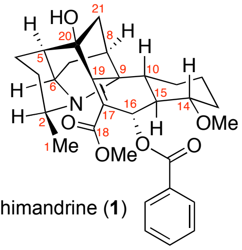
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
[3] Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

of Dr. Peter Muller at the X-ray diffraction facility of Department of Chemistry, Massachusetts Institute of Technology, and Justin Kim of the Movassaghi group.

Additional Notes. Positional numbering system: For ease of direct comparison, particularly from *trans*-decalin (–)-**14** to himandrine (–)-**1** , the numbering scheme used by Taylor and coworkers in the isolation paper[4] is used in this supporting document. In key instances the products are accompanied by the numbering system as shown below for this document.



(–)-himandrine (**1**)

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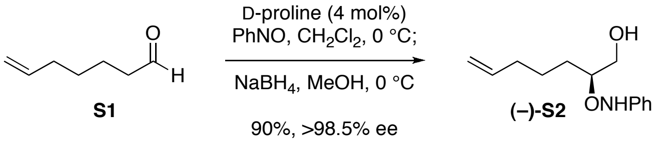
[4] Ritchie, E.; Taylor, W. C. *In the Alkaloids*; Manske, R. H. F., Ed.; Academic Press; New York, 1967; Vol. 9, Chapter 14.



<u>(–)-(*S*)-2-(*N*-Phenyl-aminooxy)-hept-6-en-1-ol (S2):</u>

Nitrosobenzene (9.7 g, 0.090 mmol, 1 equiv) was added as a solid to a suspension of D-proline (0.46 g, 4.0 mmol, 4.0 mol%) in chloroform (50 mL) at 0 °C, and the resulting mixture was sealed under an argon atmosphere. After 15 min, hept-6-enal[5] (11.2 g, 10.0 mmol, 1.10 equiv) was added drop-wise via additional funnel to the bright green solution. After 3 h, the resulting brown reaction mixture was added dropwise via additional funnel to a suspension of sodium borohydride (14.2 g, 0.375 mol, 4.17 equiv) in methanol (50 mL) at 0 °C. After 30 min, saturated aqueous sodium bicarbonate solution (100 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed with brine (200 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was purified by flash column chromatography (silica gel: diam. 7 cm, ht. 7 cm; eluent: 33% EtOAc in hexanes) to afford alcohol (–)-**S2** (18.1 g, 91%) as a yellow oil ($[\alpha]^{22}_{D}$ = –26.4 (*c* 1.0, CH_2Cl_2)). This compound was determined to be of >98.5% ee by chiral HPLC analysis (Chirapak AD-H, 95% hexanes / 5% *iso*-propanol, 3 mL/min, 215 nm t_R (major) = 18.03 min; t_R (minor) = 22.15 min).

The corresponding enantiomer, (+)-(*R*)-2-(*N*-Phenyl-aminooxy)-hept-6-en-1-ol (3.22 g, 80%, $[\alpha]^{22}_{D}$ = +26 (*c* 0.90, CH_2Cl_2)), was prepared according to the same procedure using L-proline as the catalyst. This compound was determined to be of >98.5% ee by chiral HPLC analysis (Chirapak AD-H, 95% hexanes / 5% *iso*-propanol, 3 mL/min, 215 nm t_R (minor) = 18.12 min; t_R (major) = 22.02 min). Structural assignment utilized additional information from gCOSY and HSQC.

^1H NMR (400 MHz, $CDCl_3$, 20 ˚C):	7.29-7.23 (m, 2H, Ar**H**), 7.03 (br-s, 1H, N**H**Ph), 7.00-6.94 (m, 3H, Ar**H**), 5.90-5.72 (m, 1H, C**H**=CH_2), 5.07-4.90 (m, 2H, CH=C**H_2**), 4.00-3.91 (m, 1H, C**H**ONHPh), 3.88-3.71 (m, 2H, C**H_2**OH), 2.60 (br-s, 1H, CH_2O**H**), 2.13-2.02 (m, 2H, CH_2=CHC**H_2**), 1.72-1.43 (m, 4H, C**H_2**C**H_2**).
^{13}C NMR (100 MHz, $CDCl_3$, 20 ˚C):	148.5 (Ar**C**), 138.5 (CH_2=**C**H), 129.3 (Ar**C**H), 122.8 (Ar**C**H), 115.1 (**C**H_2=CH), 115.0 (Ar**C**H), 84.0 (**C**HNHPh), 65.7 (**C**H_2OH), 34.0 (**C**H_2CH=CH_2), 29.6 (**C**H_2CHNHPh), 25.2 (**C**$H_2$$CH_2$CH=$CH_2$).
FTIR (thin film) cm^{-1}:	3385 (br, s), 3273 (s), 3076 (w), 2939 (s), 1641 (m), 1602 (s), 1494 (s), 1460 (w), 1241 (m), 1028 (s), 997 (m), 911 (s), 767 (m), 693 (m).
HRMS (ESI)	calc'd for $C_{13}H_{19}NNaO_2$ $[M+Na]^+$: 244.1308, found: 244.1308.
TLC (17% EtOAc in hexanes), *Rf*:	0.20 (UV, CAM).

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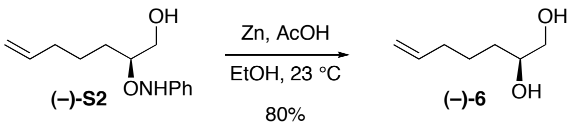
[5] 6-Heptenal was prepared from 7-octene-1,2-diol (commercially available), sodium metaperiodate, diethyl ether, water, 1h, 93%. Spectroscopic data matched those in the literature; see: Taylor, R. E.; Galvin, G. M.; Hilfiker, K. A.; Chen, Y. *J. Org. Chem.* **1998**, *63*, 9580.



(–)-(*S*)-Hept-6-ene-1,2-diol (6):

Zinc powder (8.89 g, 136 mmol, 2.00 equiv) was added as a solid to a solution of alcohol (–)-**S2** (15.1 g, 68.0 mmol, 1 equiv) in a mixture of ethanol and acetic acid (3:1, 340 mL) at 23 °C. After 2 h, the resulting mixture was filtered through a plug of celite (diam. 8.5 cm, ht. 2 cm), and the residue was washed with ethanol (3 × 150 mL). The filtrate was concentrated under reduced pressure at 30 °C. The residue was dissolved in ethyl acetate (400 mL), was washed with saturated aqueous sodium bicarbonate solution (100 mL), was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The resulting light yellow oil was purified via flash column chromatography (silica gel: diam. 5 cm, ht. 25 cm; eluent: 5% EtOAc in hexanes to 75% EtOAc in hexanes) to afford diol (–)-**6** (7.1 g, 80%) as a yellow oil ($[\alpha]^{22}_{D}$ = –21 (*c* 0.44, EtOH)). The spectroscopic data was consistent with the literature.[6] Structural assignment utilized additional information from gCOSY and HSQC.

^{1}H NMR (500 MHz, CDCl$_3$, 20 ˚C):	5.83-5.71 (m, 1H, CH$_2$=C**H**), 5.04-4.87 (m, 2H, C**H**$_2$=CH), 3.65 (br-s, 1H, C**H**OH), 3.59 (app-d, *J* = 11.0Hz, 1H, C**H**H'OH), 3.43-3.34 (m, 1H, CH**H**'OH), 3.33-3.12 (br-s, 2H, O**H**, O**H**), 2.08-1.99 (m, 2H, C**H**$_2$CH=CH$_2$), 1.57-1.34 (m. 4H, C**H**$_2$C**H**$_2$).
^{13}C NMR (100 MHz, CDCl$_3$, 20 ˚C):	138.6 (CH$_2$=**C**H), 115.0 (**C**H$_2$=CH), 72.4 (**C**HOH), 66.9 (**C**H$_2$OH), 33.8 (CH$_2$=CH**C**H$_2$), 32.6 (CH$_2$=CHCH$_2$-CH$_2$**C**H$_2$), 25.0 (CH$_2$=CHCH$_2$**C**H$_2$CH$_2$).
FTIR (thin film) cm^{-1}:	3364 (br, s), 1641 (m), 1064 (m), 908 (m), 666 (w).
HRMS (ESI)	calc'd for $C_7H_{14}NaO_2$ [M+Na]$^+$: 153.0886, found: 153.0892.
TLC (75% EtOAc in hexanes), *Rf*:	0.40 (KMnO$_4$, CAM).

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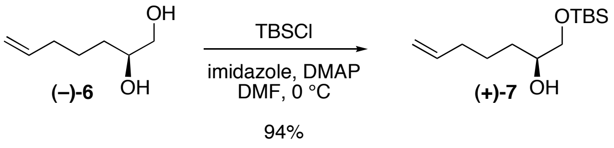
[6] Takahata, H.; Takahashi, S.; Kouno, S.; Momose, T. *J. Org. Chem.* **1998**, *63*, 2224.

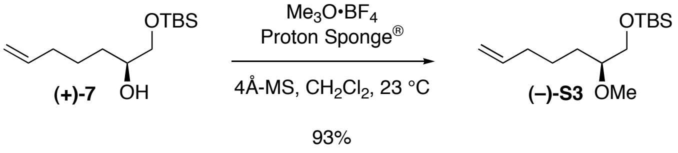


(–)-6 → **(+)-7**

(+)-(*S*)-1-(*tert*-Butyl-dimethyl-silanyloxy)-hept-6-en-2-ol (7):

tert-Butylchlorodimethylsilane (6.4 g, 42 mmol, 1 equiv) was added as a solid to a solution of diol (–)-**6** (6.10 g, 47.0 mmol. 1.05 equiv), 4-dimethylaminopyridine (229 mg, 1.90 mmol, 4.00 mol%), and imidazole (4.1 g, 60 mmol, 1.5 equiv) in *N,N*-dimethylformamide (230 mL) at 0 ºC, and the reaction mixture was sealed under an argon atmosphere. After 3 h, the reaction mixture was diluted with diethyl ether (300 mL) and brine (150 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 150 mL). The combined organic layers were washed with brine (250 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was purified via flash column chromatography (silica gel: diam. 5 cm, ht. 17 cm; eluent: 10% EtOAc in hexanes) to provide silyl ether (+)-**7** (9.6 g, 94%) as a pale yellow oil ($[\alpha]^{22}_{D}$ = +3.5 (*c* 1.4, CH_2Cl_2)).

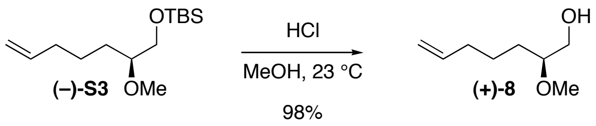
^{1}H NMR (600 MHz, $CDCl_3$, 20 ˚C):	5.82-5.72 (m, 1H, CH$_2$=C**H**), 4.99-4.91 (m, 2H, C**H**$_2$=CH), 3.61-3.57 (m, 2H, C**H**OH, C**H**H'OTBS), 3.37-3.34 (m, 1H, CH**H'**OTBS), 2.45 (br-s, 1H, CHO**H**), 2.08-2.03 (m, 2H, CH$_2$=CHC**H**$_2$), 1.58-1.49 (m, 1H, C**H**H'CH$_2$), 1.44-1.33 (m, 3H, CH**H'**C**H**$_2$), 0.87 (s, 9H, SiC(C**H**$_3$)$_3$), 0.04 (s, 6H, Si(C**H**$_3$)$_2$).
^{13}C NMR (100 MHz, $CDCl_3$, 20 ˚C):	138.9 (CH$_2$=**C**H), 114.8 (**C**H=CH), 71.8, 67.4, 34.1, 32.3, 26.1 (SiC(**C**H$_3$)$_3$), 25.1, 18.6, –5.2 (Si(**C**H$_3$)$_2$).
FTIR (thin film) cm^{-1}:	3446 (br, s), 3078 (m), 2859 (s), 1642 (m), 1463 (m), 1472 (m), 1362 (w), 1257 (m).
HRMS (ESI)	calc'd for $C_{13}H_{28}NaO_2Si$ $[M+Na]^+$: 267.1751, found: 267.1750.
TLC (10% EtOAc in hexanes), *Rf*:	0.55 ($KMnO_4$).



(–)-(*S*)-*tert*-Butyl-(2-methoxy-hept-6-enyloxy)-dimethyl-silane (S3):

Oven-dried 4Å molecular sieves (19.6 g, 2:1, wt/wt), Proton Sponge® (25.5 g, 118 mmol, 3.00 equiv), and trimethoxyl oxonium tetrafluoroborate (14.5 g, 98.0 mmol, 2.51 equiv) were added sequentially to a solution of alcohol (+)-**7** (9.6 g, 39 mmol, 1 equiv) in dichloromethane (392 mL) at 23 °C, and the reaction mixture was sealed under an argon atmosphere. After 3 h, the reaction mixture was filtered through a plug of celite (diam. 8.5 cm, ht. 3 cm), and the residue was washed with dichloromethane (3 × 100 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in a mixture of hexanes and ethyl acetate (1 : 1, 400 mL), and the residual insoluble light brown solid was removed by filtration, and was washed with a mixture of hexanes and ethyl acetate (1 : 1, 2 × 100 mL). The filtrate was washed with saturated aqueous copper sulfate solution (150 mL) and brine (150 mL), was dried over anhydrous sodium sulfate, was filtered, and was concentrated under reduced pressure. The resulting oil was purified via flash column chromatography (silica gel: diam. 5 cm, ht. 17 cm; eluent: 3% EtOAc in hexanes) to afford methyl ether (–)-**S3** (9.3 g, 93%) as a colorless oil ($[\alpha]^{22}_{D} = -11$ (*c* 1.4, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY and HSQC.

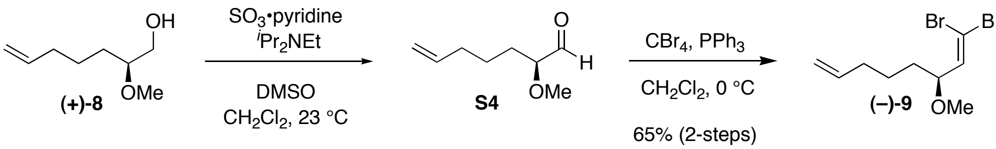
^{1}H NMR (600 MHz, $CDCl_3$, 20 ˚C):	5.83-5.73 (m, 1H, $CH_2=C\mathbf{H}$), 5.01-4.88 (m, 2H, $C\mathbf{H}_2=CH$), 3.60 (dd, *J* = 6.0, 10.2 Hz, 1H, C**H**H'OTBS), 3.52 (dd, *J* = 4.8, 10.2 Hz, 1H, CH**H'**OTBS), 3.38 (s, 3H, $OC\mathbf{H}_3$), 3.19-3.16 (m, 1H, $C\mathbf{H}OCH_3$), 2.04-2.03 (m, 2H, $CH_2=CHC\mathbf{H}_2$), 1.53-1.46 (m, 2H, $C\mathbf{H}_2CH_2$), 1.45-1.36 (m, 2H, $CH_2C\mathbf{H}_2$), 0.87 (s, 9H, $SiC(C\mathbf{H}_3)_3$), 0.03 (s, 6H, $Si(C\mathbf{H}_3)_2$).
^{13}C NMR (100 MHz, $CDCl_3$, 20 ˚C):	139.0 ($CH_2=\mathbf{C}H$), 114.8 ($\mathbf{C}H=CH$), 82.1 ($O\mathbf{C}H_3$), 65.4, 58.2, 34.1, 31.0, 26.2 ($SiC(\mathbf{C}H_3)_3$), 24.9, 18.4, –5.1 ($Si(\mathbf{C}H_3)_2$).
FTIR (thin film) cm^{-1}:	2929 (s), 2859 (s), 1642 (w), 1472 (m), 1463 (m), 1256 (s), 1107 (s), 837 (s), 776 (s).
HRMS (ESI)	calc'd for $C_{14}H_{30}NaO_2Si$ $[M+Na]^+$: 281.1907, found: 281.1918.
TLC (3% EtOAc in hexanes), *Rf*:	0.63 ($KMnO_4$).



(+)-(*S*)-2-Methoxy-hept-6-en-1-ol (8):

Thionyl chloride (0.495 mL, 13.6 mmol, 0.400 equiv) was added dropwise to methanol (340 mL) at 23 °C. After 5 min, the resulting methanolic hydrochloric acid solution (0.04 M) was added to a solution of silyl ether (–)-**S3** (8.6 g, 34 mmol, 1 equiv) in methanol (340 mL) at 23 °C. After 15 min, the reaction solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 10 cm; eluent: 33% EtOAc in hexanes) to afford alcohol (+)-**8** (4.9 g, 98%) as a pale yellow oil ($[\alpha]^{22}_{D} = +22$ (*c* 0.70, CH_2Cl_2)).

^{1}H NMR (400 MHz, $CDCl_3$, 20 ˚C):	5.80-5.67 (m, 1H, $CH_2=C\mathbf{H}$), 5.00-4.87 (m, 2H, $C\mathbf{H}_2=CH$), 3.64-3.57 (m, 1H, $C\mathbf{H}_2OH$), 3.45-3.39 (m, 1H, $C\mathbf{H}_2OH$), 3.34 (s, 3H, $OC\mathbf{H}_3$), 3.23-3.16 (m, 1H, $C\mathbf{H}OCH_3$), 2.56-2.53 (m, 1H, $CH_2O\mathbf{H}$), 2.05-1.98 (m, 2H, $CH_2=CHC\mathbf{H}_2$), 1.55-1.44 (m, 1H, $C\mathbf{H}H'CH_2$), 1.44-1.32 (m, 3H, $CH\mathbf{H}'C\mathbf{H}_2$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 ˚C):	138.5 ($CH_2=\mathbf{C}H$), 114.9 ($\mathbf{C}H=CH$), 81.7 ($O\mathbf{C}H_3$), 63.9, 57.2, 33.9 ($CH_2=CH\mathbf{C}H_2$), 29.8, 24.7.
FTIR (thin film) cm^{-1}:	3421 (br, s), 2935 (s), 1641 (w), 1458 (w), 1093 (s), 910 (m).
HRMS (ESI)	calc'd for $C_8H_{16}NaO_2$ $[M+Na]^+$: 167.1043, found: 167.1040.
TLC (33% EtOAc in hexanes), *Rf*:	0.60 ($KMnO_4$).



(–)-1,1-Dibromo-3-methoxy-octa-1,7-diene (9):

Dimethyl sulfoxide (24.2 mL, 340 mmol, 10.0 equiv), diisopropylethylamine (30.5 mL, 170 mmol, 5.00 equiv) and sulfur trioxide pyridine complex (16.2 g, 102 mmol, 3.00 equiv) were added sequentially to a solution of alcohol (+)-**8** (4.9 g, 34 mmol, 1 equiv) in dichloromethane (170 mL) at 23 °C, and the reaction mixture was sealed under an argon atmosphere. After 15 min, the reaction mixture was diluted with diethyl ether (250 mL) and water (100 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 150 mL). The combined organic layers were washed sequentially with aqueous hydrochloric acid solution (1M, 100 mL), saturated aqueous sodium bicarbonate solution (100 mL), and brine (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was purified via flash column chromatography (silica gel: diam. 3 cm, ht. 10 cm; eluent: 33% diethyl ether in hexanes) to afford aldehyde **S4** as a colorless oil.[7]

Triphenylphosphine (21.4 g, 81.6 mmol, 2.40 equiv) was added as a solid to a solution of carbon tetrabromide (13.5 g, 40.8 mmol, 1.20 equiv) in dichloromethane at 0 ºC, and the reaction mixture was sealed under an argon atmosphere. After 15 min, the solution of aldehyde **S4** in dichloromethane (10 mL) was added dropwise via cannula to the resulting orange reaction mixture. After 15 min, excess dibromophosphorane was quenched by sequential addition of triethylamine (11.5 mL, 81.6 mmol, 2.40 equiv) and methanol (3.5 mL, 81.6 mmol, 2.40 equiv). The reaction mixture was added dropwise to a mixture of hexanes and ethyl acetate (5:1, 400 mL). The resulting light brown solid was removed by filtration, and was washed with a mixture of hexanes and ethyl acetate (5:1, 100 mL). The filtrate was concentrated, and the residue was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 17 cm; eluent: 10% diethyl ether in hexanes) to provide dibromide (–)-**9** (6.1 g, 65% 2-steps) as a colorless oil ($[\alpha]^{22}_{D}$ = –19 (*c* 2.8, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY.

^1H NMR (500 MHz, $CDCl_3$, 20 ˚C):	6.30 (d, *J* = 8.5 Hz, 1H, $CBr_2=C\mathbf{H}$), 5.83-5.72 (m, 1H, $CH_2=C\mathbf{H}$), 5.03-4.91 (m, 2H, $C\mathbf{H}_2=CH$), 3.89-3.84 (m, 1H, $C\mathbf{H}CH=CBr_2$), 3.28 (s, 3H, $OC\mathbf{H}_3$), 2.08-2.03 (m, 2H, $CH_2=CHC\mathbf{H}_2$), 1.65-1.57 (m, 1H, $C\mathbf{H}H'CH_2$), 1.53-1.37 (m, 3H, $CH\mathbf{H}'C\mathbf{H}_2$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 ˚C):	140.1 ($CH_2=\mathbf{C}H$), 138.7, 115.1 ($\mathbf{C}H_2=CH$), 91.4, 81.5 ($O\mathbf{C}H_3$), 57.2, 33.9, 33.8, 24.3.
FTIR (thin film) cm^{-1}:	2931 (s), 2822 (w), 1641 (m), 1617 (m), 1458 (m), 1105 (s), 912 (s), 782 (s).
Elemental Analysis:	calc'd for $C_9H_{14}Br_2O$: C, 36.27; H, 4.74, found: C, 35.98; H, 4.70.
TLC (10% Et_2O in hexanes), *Rf*:	0.78 (UV, CAM).

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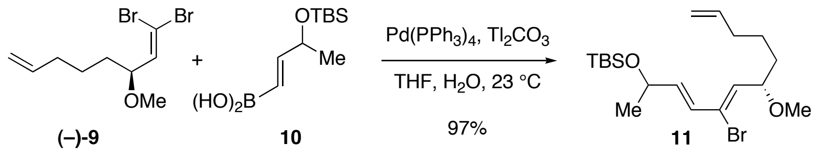
[7] Reduction of a sample of aldehyde **S4** ($NaBH_4$) returned the alcohol (+)-**8** with the same optical activity as compared to the starting alcohol (+)-**8**.



(4-Bromo-6-methoxy-1-methyl-undeca-2,4,10-trienyloxy)-*tert*-butyl-dimethyl-silane (11):

Tetrakis(triphenylphosphine)palladium (1.54 g, 1.30 mmol, 8.00 mol%) and thallium carbonate (15.7 g, 33.0 mmol, 2.00 equiv) were added sequentially to a degassed solution of dibromide (–)-**9** (4.99 g, 17.0 mmol, 1 equiv) and boronic acid **10**[8] (4.04 g, 17.6 mmol, 1.10 equiv) in a mixture of tetrahydrofuran and water (2:1, 68 mL) at 23 °C in the dark, and the reaction mixture was sealed under an argon atmosphere. After 10 h, the pale yellow heterogeneous reaction mixture was diluted with ethyl acetate, was filtered through a plug of silica gel (diam. 5 cm, ht. 3 cm), and the residue was washed with ethyl acetate (3 × 100 mL). The filtrate was washed with saturated aqueous sodium bicarbonate solution (100 mL) and brine (100 mL), was dried over anhydrous sodium sulfate, was filtered and was concentrated under reduced pressure. The resulting oil was purified by flash column chromatography (silica gel: diam. 5 cm, ht. 10 cm; eluent: 33% EtOAc in hexanes) to afford vinyl bromide **11** (6.7 g, 97%) as a 1:1 mixture of two diastereomers. Structural assignment utilized additional information from gCOSY.

^{1}H NMR (500 MHz, CDCl$_3$, 20 ˚C, one diastereomer noted by *):	6.23-6.19 (m, 1H, CH=C**H**–CBr; 1H, CH=C**H**–CBr*), 6.12-6.08 (m, 1H, C**H**=CH–CBr; 1H, C**H**=CH–CBr*), 5.83-5.73 (m, 2H, CBr=C**H**, CH$_2$=C**H**; 2H, CBr=C**H***, CH$_2$=C**H***), 5.03-4.90 (m, 2H, C**H**$_2$=CH; 2H, C**H**$_2$=CH*), 4.47-4.40 (m, 1H, C**H**OTBS; 1H, C**H**OTBS*), 4.22-4.15 (m, 1H, C**H**OCH$_3$; 1H, C**H**OCH$_3$*), 3.29 (s, 3H, OC**H**$_3$), 3.28 (s, 3H, OC**H**$_3$*), 2.06 (app-q, *J* = 7.0 Hz, 2H, C**H**$_2$CH=CH$_2$; 2H, C**H**$_2$CH=CH$_2$*), 1.67-1.40 (m, 4H, C**H**$_2$C**H**$_2$; 4H, C**H**$_2$C**H**$_2$*), 1.24 (d, *J* = 6.0 Hz, 3H, C**H**$_3$CHOTBS; 3H, C**H**$_3$CHOTBS*), 0.89 (s, 9H, SiC(C**H**$_3$)$_3$; 9H, SiC(C**H**$_3$)$_3$*), 0.05 (s, 6H, Si(C**H**$_3$)$_2$), 0.05 (s, 6H, Si(C**H**$_3$)$_2$*).
^{13}C NMR (100 MHz, CDCl$_3$, 20 ˚C):	140.5, 140.4, 138.8, 138.8, 134.2, 134.1, 127.0, 126.9, 126.9, 126.8, 114.9, 80.5, 77.4, 68.3, 56.9, 34.4, 33.9, 26.1, 24.6, 18.5, –4.5.
FTIR (thin film) cm^{-1}:	2929 (s), 1470 (m), 1368 (w), 1253 (s), 1147 (s), 1093 (s), 835 (m), 776 (m).
HRMS (ESI)	calc'd for $C_{19}H_{35}BrNaO_2Si$ [M+Na]$^+$: 425.1482, found: 425.1491.
TLC (10% EtOAc in hexanes), *Rf*:	0.65(UV, CAM).

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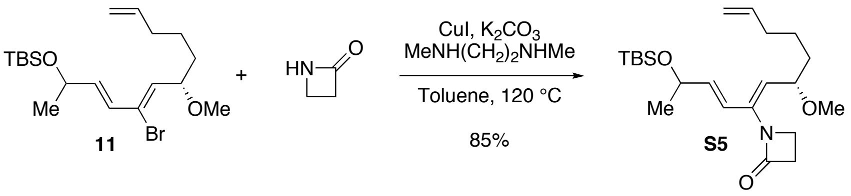
[8] The boronic acid was prepared as described previously; see Movassaghi, M.; Hunt, D. K.; Tjandra, M. *J. Am. Chem. Soc.* **2006**, *128*, 8126.



1-{1-[3-(*tert*-Butyl-dimethyl-silanyloxy)-but-1-enyl]-3-methoxy-octa-1,7-dienyl}-azetidin-2-one (S5): 2-Azetidinone (1.16 g, 16.3 mmol, 2.50 equiv), copper iodide (1.58 g, 8.30 mmol, 50.0 mol%), potassium carbonate (5.74 g, 41.5 mmol, 2.50 equiv) and *N,N*-dimethyl ethylene diamine (4.50 mL, 41.5 mmol, 2.50 equiv) were added sequentially to a solution of vinyl bromide **11** (6.72 g, 16.6 mmol, 1 equiv) in anhydrous toluene (16 mL) at 23 °C in a 50-mL schlenk flask. The reaction vessel was sealed under an argon atmosphere, and it was heated to 120 °C. After 16 h, the reaction mixture was cooled to 23 °C and filtered through a plug of silica gel (diam. 3 cm, ht. 3 cm), and the residue was washed with ethyl acetate (3 × 200 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 15 cm; eluent: 33% EtOAc in hexanes) to afford triene **S5** (5.4 g, 85%) as a 1:1 mixture of two diastereomers. Structural assignment utilized additional information from gCOSY.

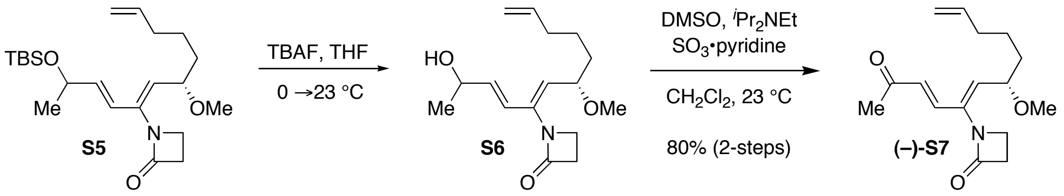
^{1}H NMR (400 MHz, CDCl$_3$, 20 ˚C, one diastereomer noted by *): 6.02 (app-dt, *J* = 4.0, 15.6 Hz, 1H, CH=C**H**–CN; 1H, CH=C**H**–CN*), 5.83-5.65 (m, 2H, CH$_2$=C**H**, C**H**=CHCN; 2H, CH$_2$=C**H***, C**H**=CHCN*), 5.30 (app-dd, *J* = 2.0, 8.8 Hz, 1H, NC=C**H**; 1H, NC=C**H***), 5.00-4.89 (m, 2H, C**H**$_2$=CH; 2H, C**H**$_2$=CH*), 4.40-4.31 (m, 1H, C**H**OTBS; 1H, C**H**OTBS*), 3.95-3.85 (m, 1H, C**H**OCH$_3$; 1H, C**H**OCH$_3$*), 3.50-3.39 (m, 2H, C**H**$_2$C=O; 2H, C**H**$_2$C=O*), 3.25 (s, 3H, OC**H**$_3$), 3.24 (s, 3H, OC**H**$_3$*), 3.11-3.05 (app-t, *J* = 4.4 Hz, 2H, C**H**$_2$N; 2H, C**H**$_2$N*), 2.06 (app-q, *J* = 6.8 Hz, 2H, C**H**$_2$CH=CH$_2$; 2H, C**H**$_2$CH=CH$_2$*), 1.65-1.33 (m, 4H, C**H**$_2$C**H**$_2$; 4H, C**H**$_2$C**H**$_2$*), 1.23 (d, *J* = 6.5 Hz, 3H, C**H**$_3$CHOTBS; 3H, C**H**$_3$CHOTBS*), 0.87 (s, 9H, SiC(C**H**$_3$)$_3$; 9H, SiC(C**H**$_3$)$_3$*), 0.04 (s, 6H, Si(C**H**$_3$)$_2$), 0.03 (s, 6H, Si(C**H**$_3$)$_2$*).

^{13}C NMR (100 MHz, CDCl$_3$, 20 ˚C): 166.1, 166.0, 138.9, 138.8, 136.9, 136.9, 135.1, 135.0, 130.1, 130.1, 124.1, 124.1, 114.8, 114.7, 77.1, 77.1, 68.6, 68.5, 56.7, 56.7, 41.7, 41.7, 36.7, 34.8, 34.7, 33.9, 26.1, 24.8, 24.6, 18.4, –4.5.

FTIR (thin film) cm^{-1}: 2929 (s), 1761 (s), 1640 (w), 1472 (w), 1396 (m), 1252 (w), 1093 (s), 966 (m), 909 (m), 834 (m), 777 (m).

HRMS (ESI) calc'd for $C_{22}H_{39}NNaO_3Si$ [M+Na]$^+$: 416.2591, found: 416.2599.

TLC (33% EtOAc in hexanes), *Rf*: 0.50 (UV, CAM).

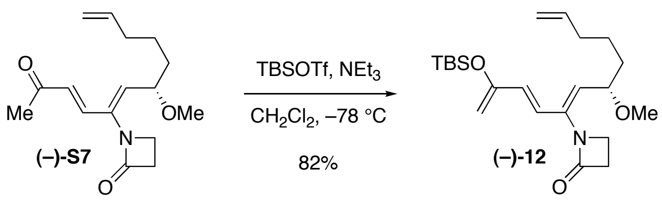


(–)-(*S*)-1-[3-Methoxy-1-(3-oxo-but-1-enyl)-octa-1,7-dienyl]-azetidin-2-one (S7):

Tetrabutylammonium fluoride solution in tetrahydrofuran (1.0 M, 21 mL, 21 mmol, 1.5 equiv) was added via syringe to a solution of triene **S5** (6.9g, 17.6 mmol) in tetrahydrofuran (176 mL) at 0 °C under an argon atmosphere, and the reaction mixture was allowed to warm to 23 °C. After 2 h, the reaction mixture was diluted with diethyl ether (400 mL) and brine (150 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 150 mL). The combined organic layers were washed with brine (100 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 8 cm; eluent: 75% EtOAc in hexanes) to afford alcohol **S6** (4.6 g, 95%) as a pale yellow oil, which was used directly in the following oxidation step.

Dimethyl sulfoxide (12.5 mL, 175 mmol, 10.0 equiv), diisopropylethylamine (15.7 mL, 87.5 mmol, 5.00 equiv), and sulfur trioxide pyridine complex (8.40 g, 52.5 mmol, 3.00 equiv) were added sequentially to a solution of alcohol **S6** (4.62 g, 16.6 mmol, 1 equiv) in dichloromethane (176 mL) at 23 °C, and the reaction mixture was sealed under an argon atmosphere. After 15 min, the reaction mixture was diluted with diethyl ether (250 mL) and brine (100 mL), and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine (200 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was purified by flash column chromatagraphy (silica gel: diam. 3 cm, ht. 10 cm; eluent: 75% EtOAc in hexanes) to afford ketone (–)-**S7** (3.9 g, 83%) as a pale yellow oil ($[\alpha]^{22}_{D} = -29$ (*c* 0.27, CH$_2$Cl$_2$)). Structural assignment utilized additional information from gCOSY and HSQC.

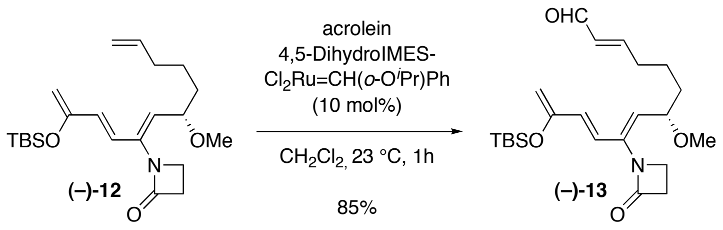
^{1}H NMR (600 MHz, CDCl$_3$, 20 ˚C):	6.94 (d, *J* = 15.6 Hz, 1H, CH=C**H**CN), 6.08 (d, *J* = 16.2 Hz, 1H, C**H**=CHCN), 5.80 (d, *J* = 9.0 Hz, 1H, CN=C**H**), 5.78-5.71 (m, 1H, CH$_2$=C**H**), 4.97-4.90 (m, 2H, C**H**$_2$=CH), 3.95-3.90 (m, 1H, C**H**OCH$_3$), 3.51-3.44 (m, 2H, C**H**$_2$C=ON), 3.24 (s, 3H, OC**H**$_3$), 3.09 (t, *J* = 10.2 Hz, 2H, C**H**$_2$N), 2.26 (s, 3H, C**H**$_3$C=O), 2.01 (app-q, *J* = 7.2 Hz, 2H, C**H**$_2$CH=CH$_2$), 1.64-1.36 (m, 4H, C**H**$_2$C**H**$_2$).
^{13}C NMR (100 MHz, CDCl$_3$, 20 ˚C):	197.7 (**C**=O), 166.0 (**C**=ON), 140.1 (CN=**C**H), 139.5 (CH=**C**HCN), 138.5 (CH$_2$=**C**H), 134.1 (**C**N=CH), 128.5 (**C**H=CHCN), 115.0 (**C**H$_2$=CH), 77.1 (**C**HOCH$_3$), 57.1 (O**C**H$_3$), 42.1 (**C**H$_2$C=O), 37.2 (**C**H$_2$NC=O), 34.3 (**C**H$_2$CHOTBS), 33.7 (**C**H$_2$CH=CH$_2$), 27.8 (**C**H$_3$C=O), 24.6 (**C**H$_2$CH$_2$CH=CH$_2$).
FTIR (thin film) cm^{-1}:	2932 (s), 1756 (s), 1692 (w), 1673 (m), 1603 (m), 1401 (m), 1361 (w), 1256 (m), 1101 (m), 977 (w), 911 (w), 779 (w).
HRMS (ESI)	calc'd for C$_{16}$H$_{32}$NNaO$_3$ [M + Na]$^+$: 300.1570, found: 300.1579.
TLC (75% EtOAc-hexanes), *Rf*:	0.65 (UV, CAM).



(–)-(*S*)1-{1-[3-(*tert*-Butyl-dimethyl-silanyloxy)-buta-1,3-dienyl]-3-methoxy-octa-1,7-dienyl}-azetidin-2-one (12): Triethylamine (2.1 mL, 15 mmol, 1.5 equiv) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (2.9 mL, 12 mmol, 1.2 equiv) were added sequentially to a solution of ketone (–)-**S7** (2.77g, 10.0 mmol, 1 equiv) in dichloromethane (100 mL) at –78 °C under an argon atmosphere. After 2 h, saturated aqueous sodium bicarbonate solution (40 mL) was added, and the reaction mixture was allowed to warm to 23 °C. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with brine, were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The resulting oil was then purified by flash column chromatography (silica gel, treated with 1% NEt_3 in [49% EtOAc in hexanes], diam. 3 cm, ht. 10 cm; eluent: 1% of NEt_3 in [49% EtOAc in hexanes]) to afford silyl enol ether (–)-**12** (3.4 g, 86%) as a pale yellow oil ($[\alpha]^{22}_{D}$ = –28 (*c* 0.27, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY and HSQC.

^{1}H NMR (600 MHz, C_6D_6, 20 ˚C):	6.67 (d, *J* = 15 Hz, 1H, CH=C**H**CN), 6.19 (d, *J* = 15.6 Hz, 1H, C**H**=CHCN), 5.81-5.72 (m, 1H, CH_2=C**H**), 5.48 (d, *J* = 9.0 Hz, 1H, NC=C**H**), 5.04-4.95 (m, 2H, C**H**$_2$=CH), 4.42 (s, 1H, C**H**H'=COTBS), 4.38 (s, 1H, CH**H'**=COTBS), 4.09-4.04 (m, 1H, C**H**OCH_3), 3.21 (s, 3H, OC**H**$_3$), 2.87 (app-q, *J* = 4.8 Hz, 1H, C**H**$_2$C(=O)N), 2.80 (app-q, *J* = 4.8 Hz, 1H, C**H**$_2$C(=O)N), 2.45 (t, *J* = 4.2 Hz, 2H, C**H**$_2$NC=O), 2.00 (app-t, *J* = 6.6 Hz, 2H, CH**H'**CH=CH_2), 1.74-1.49 (m, 4H, C**H**$_2$C**H**$_2$), 0.98 (s, 9H, SiC(C**H**$_3$)$_3$), 0.14 (s, 6H, Si(C**H**$_3$)$_2$).
^{13}C NMR (100 MHz, C_6D_6, 20 ˚C):	165.3, 155.4, 139.4, 135.9, 131.5, 129.2, 126.6, 115.1, 98.0, 77.6, 56.8, 41.8, 37.1, 35.5, 34.4, 26.3, 25.6, 18.8, –4.2, –4.2.
FTIR (thin film) cm^{-1}:	2930 (m), 1760 (s), 1622 (w), 1583 (w), 1396 (m), 1318 (m), 1254 (m), 1102 (m), 1028 (m), 840 (m), 782 (m).
HRMS (ESI)	calc'd for $C_{22}H_{37}NNaO_3Si$ $[M+Na]^+$: 414.2435, found: 414.2436.

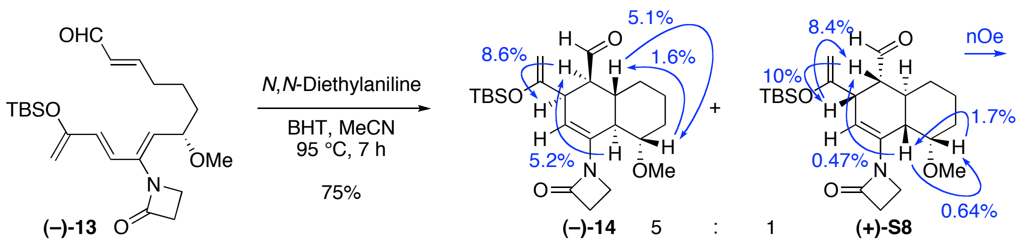
TLC (1% NEt_3 in [32% EtOAc in hexanes]), *Rf*: 0.55 (UV, CAM).



(–)-(*S*,2*E*,8*Z*,10*E*)-12-(*tert*-Butyl-dimethyl-silanyloxy)-7-methoxy-9-(2-oxo-azetidin-1-yl)-trideca-2,8,10,12-tetraenal (13): Acrolein (0.80 mL, 12 mmol, 5.0 equiv) and the Grubbs-Hoveyda catalyst (150 mg, 0.240 mmol, 10.0 mol%) were added sequentially to a solution of silyl enol ether (–)-**12** (0.95 g, 2.4 mmol, 1 equiv) in dichloromethane (8 mL) at 23 °C, and the reaction vessel was sealed under an argon atmosphere. After 1 h, the reaction mixture was directly loaded onto and purified by flash column chromatography (silica gel, treated with 1% NEt_3 in [32% EtOAc in hexanes], diam. 5 cm, ht. 15 cm; eluent: 1% NEt_3 in [32% EtOAc in hexanes]) to afford tetraenal (–)-**13** (855 mg, 85%) as a pale yellow oil ($[\alpha]^{22}_D = -70$ (*c* 0.20, benzene)). The starting material (–)-**12** (140 mg, 15%) was also recovered.

^{1}H NMR (500 MHz, C_6D_6, 20 ˚C):	9.32 (d, *J* = 7.5 Hz, 1H, HC=O), 6.68 (d, *J* = 15.0 Hz, 1H, CH=C**H**CN), 6.19 (d, *J* = 15.5 Hz, 1H, C**H**=CHCN), 6.14-6.06 (m, 1H, CHOCH=C**H**), 5.99-5.92 (m, 1H, CHOC**H**=CH), 5.47 (d, *J* = 9.5 Hz, 1H, N–C=C**H**), 4.44 (s, 1H, C**H**H'=COTBS), 4.37 (s, 1H, CH**H'**=COTBS), 4.08-4.02 (m, 1H, C**H**OCH$_3$), 3.18 (s, 3H, OC**H**$_3$), 2.92-2.89 (m, 1H, C**H**H'C=ON), 2.76-2.73 (m, 1H, CH**H'**C=ON), 2.43 (t, *J* = 4.8 Hz, 2H, C**H**$_2$NC=O), 1.87-1.80 (m, 2H, CH$_2$=CHC**H**$_2$), 1.61-1.57 (m, 2H, C**H**$_2$), 1.53-1.38 (m, 2H), 0.99 (s, 9H SiC(C**H**$_3$)$_3$), 0.15 (s, 6H, Si(C**H**$_3$)$_2$).
^{13}C NMR (125 MHz, C_6D_6, 20 ˚C):	193.1, 165.3, 157.6, 155.3, 135.9, 133.8, 130.7, 129.5, 128.9, 128.7, 126.3, 98.2, 77.5, 56.8, 41.5, 37.0, 35.3, 32.8, 26.3, 24.3, 18.6, –4.2, –4.2.
FTIR (thin film) cm^{-1}:	2931 (s), 1756 (s), 1694 (s), 1628 (m), 1466 (m), 1398 (m), 1097 (m), 840 (m), 782 (m).
HRMS (ESI)	calc'd for $C_{23}H_{37}NNaO_4Si$ $[M+Na]^+$: 442.2384, found: 442.2381.

TLC (1% NEt_3 in [32% EtOAc in hexanes]), *Rf*: 0.33 (UV, CAM).



trans-Decalin aldehyde (–)-14:

2,6-Di-*tert*-butyl-4-methylphenol (10 mg, 45 µmol, 0.56 mol%) and *N,N*-diethyl aniline (0.13 mL, 0.81 mmol, 10 mol%) were added sequentially to a solution of tetraenal (–)-**13** (3.4 g, 8.1 mmol, 1 equiv) in acetonitrile (800 mL). The resulting solution was degassed thoroughly by passage of a stream of argon. The resulting pale yellow solution was partitioned into two 500-mL pressure vessels. The vessels were sealed under an argon atmosphere and heated to 95 °C. After 7 h, the reaction vessels were allowed to cool to 23 °C, and the combined mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, treated with 1% NEt_3 in [32% EtOAc in hexanes], diam. 5 cm, ht. 10 cm; 1% NEt_3 in [32% EtOAc in hexanes]) to afford the desired *trans*-decalin aldehyde (–)-**14** (2.1 g, 63%) as a pale yellow oil ($[\alpha]^{22}_D = -39$ (*c* 1.5, CH_2Cl_2)). The minor diastereomer (+)-**S8** (420 mg, 13%) was also isolated ($[\alpha]^{22}_D = +66$ (*c* 0.45, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY, HSQC, and HMBC.

Data for the major and desired diastereomer (–)-**14**:

^{1}H NMR (400 MHz, C_6D_6, 20 ˚C):	9.62 (d, J = 5.2 Hz, 1H, $C_8\mathbf{H}$), 5.70 (dd, J = 2.0, 5.2 Hz, 1H, $C_{17}\mathbf{H}$), 4.63 (d, J = 1.6 Hz, 1H, $C_{21}\mathbf{H}H'$), 4.39 (d, J = 1.2 Hz, 1H, $C_{21}H\mathbf{H'}$), 3.36-3.31 (m, 1H, C**H**H'C=ON), 3.05 (s, 3H, $OC\mathbf{H}_3$), 2.92 (dt, J = 2.0, 6.0 Hz, 1H, $C_{14}\mathbf{H}$), 2.71-2.65 (m, 1H, CH**H'**C=ON), 2.58-2.43 (m, 2H, $C\mathbf{H}_2NC{=}O$), 2.17-2.08 (m, 1H, $C_9\mathbf{H}$), 2.05-1.94 (m, $C_{10}\mathbf{H}$), 1.90-1.83 (m, 1H, $C_{13}\mathbf{H}H'$), 1.73 (app-tt, J = 2.4, 12.4 Hz, 1H, $C_{15}\mathbf{H}$), 1.50-1.36 (m, 2H, $C_{11}\mathbf{H}H'$, $C_{12}\mathbf{H}H'$), 1.05-0.90 (m, 2H, $C_{12}H\mathbf{H'}$, $C_{13}H\mathbf{H'}$), 0.97 (s, 9H, $SiC(C\mathbf{H}_3)_3$), 0.64 (app-dq, J = 6.6, 18.0 Hz, 1H, $C_{11}H\mathbf{H'}$), 0.15 (s, 3H, $SiC\mathbf{H}_3$), 0.10 (s, 3H, $SiC\mathbf{H}_3$).
^{13}C NMR (125 MHz, C_6D_6, 20 ˚C):	202.8 ($\mathbf{C}_8$), 165.8, 157.1, 137.6, 124.8 ($\mathbf{C}_{17}$), 96.2 ($\mathbf{C}_{21}$), 82.3 ($\mathbf{C}_{14}$), 56.3 ($CHO\mathbf{C}H_3$), 53.4 ($\mathbf{C}_9$), 47.4 ($\mathbf{C}_{15}$), 44.4 ($\mathbf{C}_{19}$), 42.1 ($\mathbf{C}H_2C{=}ON$), 37.3 ($\mathbf{C}H_2CH_2C{=}ON$), 35.2 ($\mathbf{C}_{10}$), 32.1 ($\mathbf{C}_{13}$), 29.8 ($\mathbf{C}_{11}$), 26.2 ($SiC(\mathbf{C}H_3)_3$), 24.0 ($\mathbf{C}_{12}$), 18.6 ($Si\mathbf{C}(CH_3)_3$), 4.0 ($Si\mathbf{C}H_3$), 4.6 ($Si\mathbf{C}H_3$).
FTIR (thin film) cm^{-1}:	2929 (s), 2863 (m), 1750 (s), 1723 (m), 1628 (w), 1383 (m), 1093 (m), 832 (m).
HRMS (ESI)	calc'd for $C_{23}H_{37}NNaO_4Si$ $[M+Na]^+$: 442.2384, found: 442.2361.

TLC (1% NEt_3 in [32% EtOAc in hexanes]), *Rf*: 0.25 (UV, CAM).

Data for the minor diastereomer (+)-**S8**:

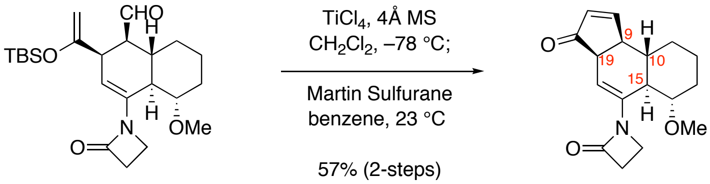
^{1}H NMR (600 MHz, C_6D_6, 20 ˚C): 9.69 (d, *J* = 5.4 Hz, 1H, $C_8\mathbf{H}$), 4.74 (dd, *J* = 1.8, 5.4 Hz, 1H, $C_{17}\mathbf{H}$), 4.54 (s, 1H, $C_{21}\mathbf{H}H'$), 4.41 (s, 1H, $C_{21}H\mathbf{H'}$), 4.23 (br-s, 1H, $C_{14}\mathbf{H}$), 3.10 (s, 3H, $OC\mathbf{H}_3$), 3.04-3.01 (m, 1H, $C_{19}\mathbf{H}$), 2.75 (app-dq, *J* = 2.4, 12.0 Hz, $C_{10}\mathbf{H}$), 2.67-2.65 (m, 1H, $C\mathbf{H}H'C{=}ON$), 2.49-2.43 (m, 2H, $CH\mathbf{H'}C{=}ON$, $C_{15}\mathbf{H}$), 2.37-2.32 (m, 1H, $C\mathbf{H}H'NC{=}O$), 2.23-2.19 (m, 1H, $C_9\mathbf{H}$), 2.16-2.13 (m, 1H, $CH\mathbf{H'}NC{=}O$), 1.89-1.87 (m, 1H, $C_{13}\mathbf{H}H'$), 1.65-1.53 (m, 2H, $C_{11}\mathbf{H}H'$, $C_{12}\mathbf{H}H'$), 1.32-1.27 (m, 2H, $C_{13}H\mathbf{H'}$, $C_{12}H\mathbf{H'}$), 0.98 (s, 9H, $SiC(C\mathbf{H}_3)_3$), 0.84 (app-dq, *J* = 3.0, 12.6 Hz, 1H, $C_{11}H\mathbf{H'}$), 0.14 (s, 6H, $Si(C\mathbf{H}_3)_2$).

^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 203.6 ($\mathbf{C}_8$), 164.1, 158.3, 139.8, 109.4 ($\mathbf{C}_{17}$), 95.4 ($\mathbf{C}_{21}$), 76.6 ($\mathbf{C}_{14}$), 56.8 ($O\mathbf{C}H_3$), 53.9 ($\mathbf{C}_9$), 47.0 ($\mathbf{C}_{15}$), 44.1 ($\mathbf{C}_{19}$), 37.6 ($\mathbf{C}H_2C{=}ON$), 35.1 ($\mathbf{C}H_2CH_2C{=}ON$), 30.4 ($\mathbf{C}_{11}$), 29.7 ($\mathbf{C}_{10}$), 28.4 ($\mathbf{C}_{13}$), 26.1 ($SiC(\mathbf{C}H_3)_3$), 21.2 ($\mathbf{C}_{12}$), 18.6 ($Si\mathbf{C}(CH_3)_3$), –4.1 ($Si\mathbf{C}H_3$), –4.6 ($Si\mathbf{C}H_3$).

FTIR (thin film) cm^{-1}: 2931 (s), 2858 (m), 1750 (s), 1723 (m), 1629 (w), 1363 (m), 1254 (m), 1224 (s), 1094 (m), 1002 (w), 837 (m), 781 (m).

HRMS (ESI) calc'd for $C_{23}H_{37}NNaO_4Si$ $[M+Na]^+$: 442.2384, found: 442.2383.

TLC (1% NEt_3 in [32% EtOAc in hexanes]), *Rf*: 0.40 (UV, CAM).



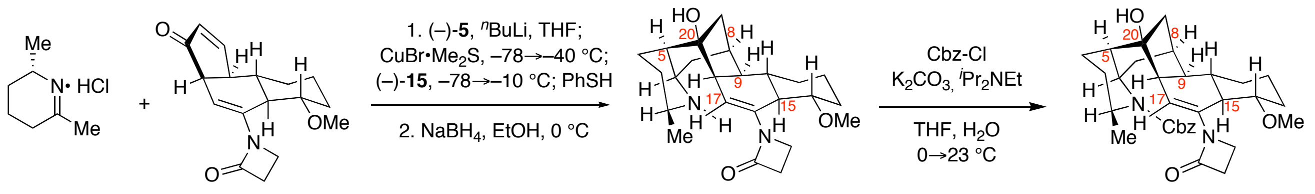
(–)-14 (–)-15

Tricyclic Enone (–)-15:

A freshly prepared solution of titanium tetrachloride in dichloromethane (1.0 M, 0.36 mL, 0.36 mmol, 2.0 equiv) was added in one portion via syringe to a suspension of *trans*-decalin aldehyde (–)-**14** (75 mg, 0.18 mmol, 1 equiv) and oven-dried 4Å-molecular sieves (100 mg) in dichloromethane (8.9 mL) at −78 °C under an argon atmosphere. After 2 min, saturated aqueous sodium chloride solution (10 mL) was added in one portion via syringe. The resulting mixture was allowed to warm to 23 °C, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (25 mL), were dried over anhydrous sodium sulfate, were filtered and were concentrated under reduced pressure to afford the desired crude intramolecular aldol addition product as an oil. The residue was dried by concentration from anhydrous benzene (2 × 5 mL) and was directly used in the following dehydration step.

A solution of the Martin sulfurane reagent (133 mg, 0.198 mmol, 1.10 equiv) in anhydrous benzene (3.6 mL) was added via cannula to the crude solution of aldol product in anhydrous benzene (3.6 mL) at 23 °C. After 30 min, the reaction mixture was directly loaded onto and purified via flash column chromatography (silica gel: diam. 1.5 cm, ht. 4 cm; eluent: 75% EtOAc in hexanes) to afford enone **(–)-15** (30 mg, 57%) as an oil ($[\alpha]^{22}_{D} = -18$ (*c* 0.65, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY, and HSQC.

^{1}H NMR (600 MHz, C_6D_6, 20 ˚C):	6.89 (dd, *J*= 3.0, 6.0 Hz, 1H, C_8**H**), 6.13, (app-t, *J* = 3.0 Hz, 1H, C_{17}**H**), 5.84 (dd, *J* = 1.8, 6.0 Hz, 1H, C_{21}**H**), 3.47-3.42 (m, 1H, C_{14}**H**), 3.14 (s, 3H, OC**H**$_3$), 3.11-3.08 (m, 1H, C**H**H'C=ON), 2.76-2.74 (m, 1H, CH**H**'C=ON), 2.52-2.41 (m, 3H, C_{19}**H**, C**H**H'NC=O, CH**H**'NC=O), 2.07-2.01 (m, 1H, C_{13}**H**H'), 1.99-1.93 (m, 1H, C_9**H**), 1.79-1.73 (m, 1H, C_{15}**H**), 1.43-1.35 (m, 2H, C_{12}**H**H', C_{11}**H**H'), 0.89-0.76 (m, 3H, C_{13}H**H'**, C_{10}H, C_{12}H**H'**), 0.48 (m, 1H, C_{11}H**H'**).
^{13}C NMR (150 MHz, C_6D_6, 20 ˚C):	205.7 (**C**$_{20}$), 166.1, 164.5 (**C**$_8$), 139.9, 132.7 (**C**$_{21}$), 125.2 (**C**$_{17}$), 78.6 (**C**$_{14}$), 55.4 (O**C**H$_3$), 48.1 (**C**$_{15}$), 47.4 (**C**$_9$), 46.7 (**C**$_{19}$), 43.8 (**C**$_{10}$), 42.9 (**C**H$_2$C=ON), 36.7 (**C**H$_2$NC=O), 30.8 (**C**$_{11}$), 30.7 (**C**$_{13}$), 23.0 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	2931 (s), 1741 (s), 1710 (s), 1384 (m), 1083 (m).
HRMS (ESI)	calc'd for $C_{17}H_{21}NaNO_3$ [M+Na]$^+$: 310.1414, found: 310.1421.
TLC (75% EtOAc in hexanes), *Rf*:	0.35 (UV, CAM).



(–)-5 **(–)-15** **(–)-19** **(–)-20**

Hydroxycarbamate (–)-20:

A solution of *n*-butyl lithium in hexanes (2.5 M, 0.80 mL, 2.0 mmol, 4.0 equiv) was added dropwise via syringe to a degassed suspension of the iminium chloride (–)-**5**[9] (145 mg, 0.980 mmol, 2.00 equiv) in tetrahydrofuran (1.4 mL) at –78 °C under an argon atmosphere. After 15 min, the reaction mixture was allowed to warm to 0 °C. Complete dissolution of the iminium chloride was detected after 15 min at which time the reaction mixture was cooled to –78 °C. The brown solution of the lithioenamine was transferred via cannula under positive argon pressure to a degassed suspension of copper bromide dimethyl sulfide (101 mg, 0.490 mmol, 1 equiv) in tetrahydrofuran (0.7 mL) at –78 °C. The reaction mixture was allowed to gradually warm to –40 °C over 1 h. The resulting brown reaction mixture was cooled to –78 °C, and a degassed solution of enone (–)-**15** (150 mg, 0.520 mmol, 1.05 equiv) in tetrahydrofuran (0.5 mL) was added via cannula. The resulting reaction mixture was allowed to warm to –10 °C over 1.5 h. A solution of degassed thiophenol (0.11 mL, 1.0 mmol, 2.2 equiv) in absolute ethanol (200 proof, 1 mL) was added to the reaction mixture. The resulting mixture was diluted with a degassed aqueous ammonium hydroxide in a saturated aqueous ammonium chloride solution (1:5, 2.4 mL), and the reaction was allowed to warm to 23 °C. After 1.5 h of vigorous stirring, the reaction mixture was diluted with degassed dichloromethane (8 mL), and the layers were separated under an argon atmosphere. The organic layer and the aqueous layer were partitioned, and the aqueous layer was extracted with degassed dichloromethane (3 × 8 mL) under an argon atmosphere. The combined organic layers were concentrated under reduced pressure, and the residue was dried by concentration from degassed anhydrous benzene (2 × 5 mL) and was directly used in the following reduction step.

Sodium borohydride (59 mg, 1.6 mmol 3.2 equiv) was added as a solid to a degassed solution of the crude pentacylic imine in ethanol (8 mL) at 0 °C under an argon atmosphere. After 30 min, aqueous sodium carbonate solution (1.0 M, 10 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with aqueous sodium carbonate solution (1.0 M, 15 mL), and were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was filtered through a plug of silica gel (silica gel, treated with 1% NH_3 in [3% MeOH in CH_2Cl_2], diam. 1.5 cm, ht. 3 cm; eluent: 1% NH_3 in [3% methanol in dichloromethane]) to afford crude pentacyclic compound (–)-**19** and was directly used in the following step.

Benzyl chloroformate (0.32 mL, 2.2 mmol, 4.5 equiv) was added via syringe to a heterogeneous mixture of crude pentacyclic amine (–)-**19,** a solution of potassium carbonate (1.3 g, 9.4 mmol, 19 equiv) in water (9.2 mL), and diisopropylethyl amine (1.3 mL, 7.4 mmol, 15 equiv) in tetrahydrofuran (9.2 mL) at 0 °C. The reaction vessel was sealed under an argon atmosphere, and the reaction mixture was allowed to warm to 23 °C. Additional portions of benzyl chloroformate (2 × 0.32 mL) were added at 0 °C at 30 min intervals. Morpholine (0.58 mL, 6.7 mmol, 14 equiv) was added to quench excess benzyl chloroformate. The reaction mixture was diluted with dichloromethane (50 mL), and the layers were separated. The aqueous layer was extracted with

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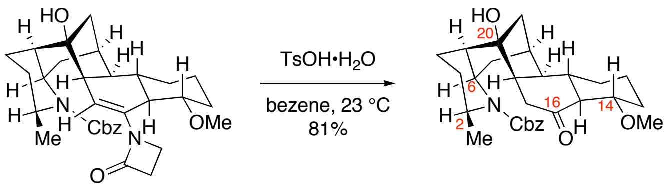
[9] Movassaghi, M.; Hunt, D. K.; Tjandra, M. *J. Am. Chem. Soc.* **2006**, *128*, 8126

dichloromethane (2 × 35 mL). The combined organic layers were washed with aqueous sodium carbonate solution (1.0 M, 20 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, treated with 1% NEt$_3$ in [5% acetone in hexanes], diam. 1.5 cm, ht. 4 cm; eluent: 1% NEt$_3$ in [5% acetone in hexanes] to 1% NEt$_3$ in [35% acetone in hexanes]) to afford hydroxy carbamate (–)-**20** (132 mg, 50%) as a white solid ($[\alpha]^{22}_{D}$ = –22 (*c* 1.0, CH$_2$Cl$_2$)). Structural assignment utilized additional information from gCOSY, HSQC, HMBC, and NOESY.

^{1}H NMR (600 MHz, C$_6$D$_6$, 20 ˚C):	7.33-7.28 (m, 2H, Ar**H**), 7.16-7.12 (m, 2H, Ar**H**), 7.08-7.04 (m, 1H, Ar**H**), 6.18 (app-t, *J* = 2.4 Hz, 1H, C$_{17}$**H**), 5.24 (d, *J* = 12 Hz, 1H, PhC**H**H'OC=ON), 5.21 (d, *J* = 12 Hz, 1H, PhCH**H'**OC=ON), 4.57-4.50 (m, 1H, C$_6$**H**), 4.44-4.37 (m, 1H, C$_2$**H**), 3.50-3.41 (m, 1H, C$_{14}$**H**), 3.29-3.22 (m, 1H, C**H**H'C=ON), 3.14 (s, 3H, OC**H$_3$**), 2.84-2.77 (CH**H'**C=ON), 2.55-2.34 (m, 4H, C**H$_2$**NC=O, C$_{19}$**H**, C$_7$**H**H'), 2.16-2.05 (m, 1H, C$_{13}$**H**H'), 2.03-1.98 (m, 1H, C$_5$**H**), 1.78-1.72 (m, 1H, C$_{15}$**H**), 1.66-1.23 (m, 9H, C$_8$**H**, C$_4$**H**H', C$_{12}$**H**H', C$_{11}$**H**H', C$_3$**H**H', C$_3$**H**H', C$_{21}$**H**H', C$_4$H**H'**, C$_{21}$H**H'**), 1.17 (t, *J* = 9.8 Hz, 1H, C$_9$**H**), 1.06 (d, *J* = 6.6 Hz, 3H, C$_1$**H**), 1.02-0.81 (m, 4H, **C**$_7$H**H'**, C$_{10}$**H**, C$_{12}$H**H'**, C$_{13}$H**H'**), 0.68 (app-q, *J* = 11.6 Hz, 1H, C$_{11}$H**H'**).
^{13}C NMR (125 MHz, C$_6$D$_6$, 20 ˚C):	166.7 (**C**$_{\text{amide}}$), 155.9 (**C**$_{\text{carbamate}}$), 139.4 (**C**$_{16}$), 138.3 (Ar**C**), 129.5 (**C**$_{17}$), 129.0 (Ar**C**H), 128.9 (Ar**C**H), 128.6 (Ar**C**H), 80.2 (**C**$_{20}$), 79.5 (**C**$_{14}$), 67.4 (Ph**C**H$_2$), 55.4 (O**C**H$_3$), 54.8 (**C**$_9$), 48.3 (**C**$_5$), 47.8 (**C**$_6$), 47.0 (**C**$_{15}$), 46.4 (**C**$_2$), 44.6 (**C**$_{10}$), 43.5 (**C**H$_2$C=ON), 39.7 (**C**$_{19}$), 36.7 (**C**H$_2$NC=O), 34.7 (**C**$_4$), 34.4 (**C**$_7$), 34.6 (**C**$_{13}$), 32.5 (**C**$_8$), 31.2 (**C**$_{11}$), 30.3 (**C**$_{21}$), 23.6 (**C**$_{12}$), 20.5 (**C**$_1$), 17.8 (**C**$_3$).
FTIR (thin film) cm^{-1}:	3414 (br, s), 2932 (s), 1742 (s), 1722 (s), 1689 (s), 1454 (m), 1391 (s), 1315 (s), 1084 (s), 978 (w), 666 (m).
HRMS (ESI)	calc'd for C$_{32}$H$_{43}$N$_2$O$_5$ [M+H]$^+$: 535.3166, found: 535.3175.
TLC (40% acetone in hexanes), *Rf*:	0.50 (UV, KMnO$_4$, CAM).



(–)-20 **(–)-21**

Ketoalcohol (–)-21:

p-Toluenesulfonic acid monohydrate (8.3 mg, 0.043 mmol, 30 mol%) was added as a solid to a solution of hydroxy carbamate (–)-**20** (77 mg, 0.14 mmol, 1 equiv) in benzene (15 mL) at 23 °C, and the reaction mixture was sealed under an argon atmosphere. Because of the sensitivity of the product to acid, aqueous work-up was avoided. After 1.5 h, the reaction mixture was directly loaded onto and purified via flash column chromatography (silica gel, treated with 1% NEt$_3$ in [35% acetone in hexanes]: diam. 1.5 cm, ht. 4 cm; eluent: 1% NEt$_3$ in [35% acetone in hexanes]) to afford ketone (–)-**21** (54.8 mg, 81%) as a white solid ($[\alpha]^{22}_{D}$ = –62 (*c* 1.1, CH$_2$Cl$_2$)). Structural assignment utilized additional information from gCOSY, HSQC, HMBC, and NOESY.

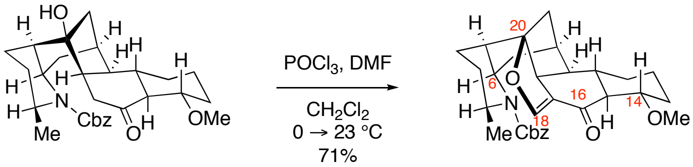
^{1}H NMR (600 MHz, C$_6$D$_6$, 20 ˚C): 7.32-7.29 (m, 2H, Ar**H**), 7.16-7.13 (m, 2H, Ar**H**), 7.07-7.04 (m, 1H, Ar**H**), 5.23 (br-s, 2H, PhC**H$_2$**OC=ON), 4.54 (br-s, 1H, C$_6$**H**), 4.43 (br-s, 1H, C$_2$**H**), 3.53 (s, 3H, OC**H$_3$**), 3.25-3.18 (m, 1H, C$_{14}$**H**), 2.45-2.36 (m, 2H, C$_{17}$**H**H', C$_7$**H**H'), 2.13-1.98 (m, 4H, C$_{17}$H**H'**, C$_8$**H**, C$_{13}$**H**H', C$_{19}$**H**), 1.82 (dd, *J* = 9.1, 12.5 Hz, 1H, C$_{15}$**H**), 1.61-1.56 (m, 1H, C$_5$**H**), 1.47-1.36 (m, 3H, C$_{11}$**H**H', C$_{21}$**H**H', C$_{21}$H**H'**), 1.35-1.20 (m, 3H, C$_{12}$**H**H', C$_3$**H**H', C$_3$H**H'**), 1.16-1.09 (m, 2H, C$_{13}$H**H'**, C$_4$**H**H'), 1.07 (d, *J* = 7.2 Hz, 3H, C$_1$**H**), 1.02 (app-t, *J* = 10.8 Hz, 1H, C$_9$**H**), 1.00-0.94 (m, 2H, C$_4$H**H'**, C$_7$H**H'**), 0.80-0.71 (m, 1H, C$_{12}$H**H'**), 0.67 (app-dq, *J* = 3.6, 12.0 Hz, 1H, C$_{10}$**H**), 0.52-0.45 (m, 1H, C$_{11}$H**H'**).

^{13}C NMR (125 MHz, C$_6$D$_6$, 20 ˚C): 210.8 (**C**$_{16}$), 156.0 (**C**$_{\text{carbamate}}$), 138.1 (Ar**C**), 133.3 (Ar**C**H), 130.4 (Ar**C**H), 129.9 (Ar**C**H), 80.6 (**C**$_{20}$), 78.0 (**C**$_{14}$), 67.5 (Ph**C**H$_2$), 57.2 (O**C**H$_3$), 56.7 (**C**$_{15}$), 56.0 (**C**$_9$), 48.9 (**C**$_5$), 47.8 (**C**$_6$), 46.4 (**C**$_2$), 41.1 (**C**$_{10}$), 39.3 (**C**$_{17}$), 39.2 (**C**$_8$), 37.1 (**C**$_{19}$), 34.9 (**C**$_7$, **C**$_{21}$), 32.5 (**C**$_{11}$), 31.7 (**C**$_{13}$), 30.4 (**C**$_3$), 23.3 (**C**$_{12}$), 20.4 (**C**$_1$), 18.4 (**C**$_4$).

FTIR (thin film) cm^{-1}: 3429 (br, s), 2933 (s), 1739 (s), 1690 (s), 1440 (m), 1347 (m), 1317 (s), 1245 (w), 1188 (w), 1114 (m), 1088 (s), 741 (w), 697 (m).

HRMS (ESI) calc'd for C$_{29}$H$_{39}$NNaO$_5$ [M+Na]$^+$: 504.2720,
found: 504.2721.

TLC (50% acetone in hexanes), *Rf*: 0.63 (UV, CAM).

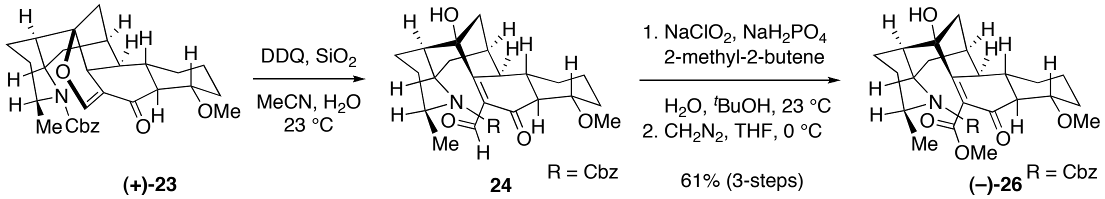


(–)-21 **(+)-23**

Vinyl ether (+)-23:

Freshly distilled phosphorus oxychloride (13 µL, 0.14 mmol, 2.0 equiv) was added dropwise via syringe to *N,N*-dimethylformamide (450 µL, 5.61 mmol, 81.0 equiv) at 0 °C under an argon atmosphere. After 30 min, a solution of ketone (–)-**21** (33.3 mg, 69.0 µmol, 1 equiv) in dichloromethane (1.4 mL) was added dropwise via cannula to the reaction mixture at 0 °C, and the resulting yellow solution was allowed to warm to 23 °C. After 30 min, saturated aqueous sodium bicarbonate solution (4 mL) was added to quench excess acid, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the resulting yellow oil via flash column chromatography (silica gel: diam. 1.5 cm, ht. 3 cm; eluent: 40% EtOAc in hexanes then 50% acetone in hexanes afforded the vinyl ether (+)-**23** (24 mg, 71%) as a white film ($[\alpha]^{22}_{D}$ = +19 (*c* 0.50, CH$_2$Cl$_2$)). Structural assignment utilized additional information from gCOSY, HSQC, HMBC, and NOESY.

^{1}H NMR (600 MHz, C$_6$D$_6$, 20 ˚C):	7.29 (app-d, *J* = 7.2 Hz, 2H, Ar**H**), 7.16-7.13 (m, 2H, Ar**H**), 7.07 (app-t, *J* = 7.2 Hz, 1H, Ar**H**), 6.89 (app-d, *J* = 1.8 Hz, 1H, C$_{18}$**H**), 5.20 (br-s, 2H, PhC**H**$_2$OC=ON), 4.52 (br-s, 1H, C$_6$**H**), 4.26 (br-s, 1H, C$_2$**H**), 3.64 (s, 3H, OC**H**$_3$), 3.55-3.49 (m, 1H, C$_{14}$**H**), 3.00 (d, *J* = 9.0 Hz, 1H, C$_{19}$**H**), 2.33 (br-s, 1H, C$_5$**H**), 2.27 (br-s, 1H, C$_7$**H**H'), 2.11 (app-d, *J* = 15.0 Hz, 1H, C$_{13}$**H**H'), 1.89 (app-dd, 1H, *J* = 9.0, 12.0 Hz, C$_{15}$**H**), 1.49-1.44 (m, 4H, C$_8$**H**, C$_{21}$**H**H', C$_{11}$**H**H', C$_{12}$**H**H'), 1.30 (app-dd, *J* = 3.6, 11.4 Hz, 1H, C$_{21}$H**H'**), 1.27-1.07 (m, 6H, C$_3$**H**H', C$_3$H**H'**, C$_4$**H**H', C$_4$H**H'**, C$_{13}$H**H'**, C$_9$**H**), 1.05 (d, *J* = 6.6 Hz, 3H, C$_1$**H**), 0.82-0.70 (m, 3H, C$_7$H**H'**, C$_{12}$H**H'**, C$_{10}$**H**), 0.59 (app-q, *J* = 13.8 Hz, 1H, C$_{11}$H**H'**).
^{13}C NMR (125 MHz, C$_6$D$_6$, 20 ˚C):	194.7 (**C**$_{16}$), 155.7 (**C**$_{carbamate}$), 151.0 (**C**$_{18}$), 138.0 (Ar**C**), 129.1 (Ar**C**H), 128.9 (Ar**C**H), 128.7 (Ar**C**H), 119.4 (**C**$_{17}$), 102.7 (**C**$_{20}$), 77.1 (**C**$_{14}$), 67.5 (Ph**C**H$_2$OC=ON), 57.4 (O**C**H$_3$), 56.9 (**C**$_{15}$), 55.6 (**C**$_9$), 47.6 (**C**$_6$), 46.9 (**C**$_2$), 42.0 (**C**$_{19}$), 41.1 (**C**$_{10}$), 40.1 (**C**$_5$), 35.4 (**C**$_7$), 34.5 (**C**$_8$), 32.4 (**C**$_{11}$), 32.0 (**C**$_{21}$), 31.3 (**C**$_{13}$), 29.1 (**C**$_4$), 23.1 (**C**$_{12}$), 20.8 (**C**$_1$H), 18.0 (**C**$_3$).
FTIR (thin film) cm^{-1}:	2932 (s), 1693 (s, C=O), 1596 (s), 1312 (w), 1120 (m).
HRMS (ESI)	calc'd for C$_{30}$H$_{38}$NO$_5$ [M+H]$^+$: 492.2744, found: 492.2745.
TLC (50% EtOAc in hexanes), *Rf*:	0.49 (UV, CAM).



Ketoester (–)-26:

A solution of vinyl ether (+)-**23** (7.5 mg, 15 μmol, 1 equiv) in mixture of acetonitrile and water (5:1, 150 μL) was treated sequentially with silica gel (1.7 mg) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 3.5 mg, 16 μmol, 1.1 equiv) at 23 °C, and the reaction vessel was sealed under an argon atmosphere. After 6 h, the reaction mixture was filtered through a plug of cotton to remove the silica gel and the filtrate was partitioned between water (1 mL) and dichloromethane (8 mL). The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford the crude ketoaldehyde **24**. The ketoaldehyde was directly used in the following oxidation step.

To a solution of the crude ketoaldehyde **24** in *tert*-butanol (380 μL) at 23 °C was added 2-methyl-2-butene (16 μL, 0.15 mmol 10 equiv) and a solution of sodium phosphate monohydrate monobasic (21 mg, 0.15 mmol, 10 equiv) in water (150 μL) followed by a solution of sodium chlorite (14 mg, 0.15 mmol, 10 equiv) in water (150 μL) via syringe. After 1 h, saturated aqueous sodium thiosulfate solution (1 mL) was added to quench excess oxidant, and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure to afford the crude ketoacid that was directly used in the following methylation step.

Freshly prepared diazomethane solution in ether (1.50 mL, 1.60 mmol, 100 equiv) was added to a solution of the crude sample and acetic acid (31 μL, 61 μmol, 4.0 equiv) in THF (100 μL) at 0 °C. After 30 min, a tetrahydrofuran solution of acetic acid (2 M, 0.5 mL) was added to quench excess diazomethane and the volatiles were removed under reduced pressure. Purification of the resulting yellow oil via flash column chromatography (silica gel: diam. 1.5 cm, ht. 2 cm; eluent: 50% EtOAc in hexanes to 75% EtOAc in hexanes then 50% acetone in hexanes afforded the ketoester (–)-**26** (5 mg, 61%) as a clear film ($[\alpha]^{22}_D = -64$ (*c* 0.42, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY, HSQC, and HMBC.

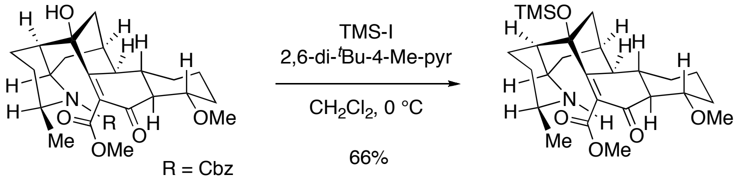
^1H NMR (500 MHz, C_6D_6, 20 ˚C): 7.29 (app-d, *J* = 7.2 Hz, 2H, Ar**H**), 7.16-7.14 (m, 2H, Ar**H**), 7.10-7.05 (m, 1H, Ar**H**), 5.22 (d, *J* = 12.5 Hz, 1H, PhC**H**H'OC=ON), 5.18 (d, *J* = 12.5 Hz, 1H, PhCH**H**'OC=ON), 4.66 (br-s, 1H, C_6**H**), 4.38 (br-s, 1H, C_2**H**), 3.57 (s, 3H, $OC\mathbf{H}_3$), 3.55 (s, 3H, $COOC\mathbf{H}_3$), 3.15 (dt, *J* = 5.5, 10.5 Hz, 1H, C_{14}**H**), 2.58-2.40 (m, 2H, C_7**H**H', O**H**), 2.10-1.94 (m, 3H, C_5**H**, C_{13}**H**H', C_{15}**H**), 1.94-1.86 (m, 1H, C_4**H**H'), 1.78 (app-d, *J* = 12.0 Hz, 1H, C_9**H**), 1.72 (br-s, 1H, C_{21}**H**H'), 1.57 (br-s, 1H, C_8**H**), 1.39-1.20 (m, 4H, C_3**H**H', C_{12}**H**H', C_{11}**H**H', C_3H**H'**), 1.13-0.87 (m, 5H, C_{13}H**H'**, C_4H**H'**, C_7H**H'**, C_{21}H**H'**, C_{10}**H**), 1.02 (d, *J* = 7.0 Hz, 3H, $C_1\mathbf{H}_3$), 0.75-0.64 (m, 1H, C_{12}H**H'**), 0.48-0.38 (m, 1H, C_{11}H**H'**).

^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 195.1 ($\mathbf{C}_{16}$), 168.4 ($\mathbf{C}_{18}$), 167.9 ($\mathbf{C}_{19}$), 155.8 ($\mathbf{C}_{\text{carbamate}}$), 138.1 (Ar**C**), 129.1 (Ar**C**H), 128.9 (Ar**C**H), 128.7 (Ar**C**H), 128.3 ($\mathbf{C}_{17}$), 82.5 ($\mathbf{C}_{20}$), 77.1 ($\mathbf{C}_{14}$), 67.6 (Ph$\mathbf{C}H_2$OC=ON), 58.3 ($\mathbf{C}_{9}$), 58.1 ($\mathbf{C}_{15}$), 57.6 (O$\mathbf{C}H_3$), 52.4 (COO$\mathbf{C}H_3$), 47.0 ($\mathbf{C}_{6}$), 46.4 ($\mathbf{C}_{5}$), 46.2 ($\mathbf{C}_{2}$), 46.1 ($\mathbf{C}_{10}$), 35.8 ($\mathbf{C}_{7}$, $\mathbf{C}_{21}$), 31.8 ($\mathbf{C}_{13}$), 30.2 ($\mathbf{C}_{8}$), 30.1 ($\mathbf{C}_{3}$, $\mathbf{C}_{11}$), 22.6 ($\mathbf{C}_{12}$), 20.3 ($\mathbf{C}_{1}$), 19.1 ($\mathbf{C}_{4}$).

FTIR (thin film) cm^{-1}: 3440 (br, s, OH), 2928 (s), 2856 (m), 1733 (COOMe), 1675 (C=O), 1316 (w), 1111 (w).

HRMS (ESI) calc'd for $C_{31}H_{40}NO_7$ [M+H]$^+$: 538.2799,
found: 538.2803.

TLC (50% acetone in hexanes), *Rf*: 0.75 (UV, CAM).

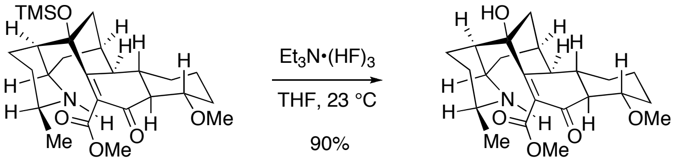


(–)-26 **(–)-S9**

Amino Ketoester (–)-S9:

Iodotrimethylsilane (26 µL, 0.18 mmol, 14 equiv) was added via syringe to a solution of keto ester (–)-**26** (7.1 mg, 13 mmol, 1 equiv) and 2,6-di-*tert*-butyl-4-methyl-pyridine (670 mg, 3.25 mmol, 250 equiv) in dichloromethane (500 µL) at 0 °C under an argon atmosphere. Additional portions of iodotrimethylsilane (8 × 26 µL) were added at 1 h intervals until complete consumption of (–)-**26** was observed by TLC analysis (~8 h). Isopropanol (300 µL) and aqueous sodium carbonate solution (1 M, 6 mL) were added, and the biphasic reaction mixture was stirred vigorously at 23°C. After 2 h, the organic layer and the aqueous layer were separated. The aqueous layer was extracted with dichloromethane (4 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the resulting yellow oil via flash column chromatography (silica gel, treated with 1% NEt_3 in [35% EtOAc in hexanes], diam. 1.5 cm, ht. 4 cm; eluent: 1% NEt_3 in [5% EtOAc in hexanes] to 1% NEt_3 in [35% EtOAc in hexanes] then 5% methanol in CH_2Cl_2) afforded the pentacyclic amino ketoester (–)-**S9** (4.1 mg, 66%) as a clear film ($[\alpha]^{22}_D$ = –4.7 (*c* 0.15, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY, HSQC, and HMBC.

^{1}H NMR (500 MHz, C_6D_6, 20 ˚C):	3.75 (app-d, *J* = 11.0 Hz, 1H, C_9**H**), 3.64 (s, 3H, COOC**H**$_3$), 3.57 (s, 3H, OC**H**$_3$), 3.19-3.11 (m, 1H, C_{14}**H**), 2.93 (app-t, *J* = 5.0 Hz, 1H, C_6**H**), 2.50 (app-d, *J* = 14.0 Hz, 1H, C_4**H**'), 2.22-2.13 (m, 2H, C_{15}**H**, C_2**H**), 2.00-1.91 (m, 2H, C_{21}**H**H', C_{13}**H**H'), 1.88-1.81 (m, 2H, C_8**H**, C_5**H**), 1.75-1.63 (m, 1H, C_3**H**H'), 1.57-1.49 (m, 1H, C_7**H**), 1.46-0.97 (m, 8H, C_{12}**H**H', C_{11}**H**H', C_{21}H**H**', C_3H**H**', C_{10}**H**, C_4H**H**', C_{13}H**H**', C_7H**H**'), 0.72 (d, *J* = 6.5 Hz, 3H, C_1**H**), 0.77-0.62 (m, 2H, C_{12}H**H**', C_{11}H**H**'), 0.21 (br-s, 9H, Si(C**H**$_3$)$_3$).
^{13}C NMR (125 MHz, C_6D_6, 20 ˚C):	195.6 (**C**$_{16}$), 171.7 (**C**$_{19}$), 167.1 (**C**$_{18}$), 127.9 (**C**$_{17}$), 82.8 (**C**$_{20}$), 77.5 (**C**$_{14}$), 58.7 (**C**$_2$), 57.7 (O**C**H$_3$), 55.4 (**C**$_6$), 53.3 (**C**$_{15}$), 51.4 (COO**C**H$_3$), 50.6 (**C**$_9$), 48.2 (**C**$_5$), 47.2 (**C**$_{21}$), 46.2 (**C**$_{10}$), 41.0 (**C**$_7$), 33.6 (**C**$_8$), 32.2 (**C**$_{13}$), 31.0 (**C**$_3$), 30.4 (**C**$_{11}$), 24.8 (**C**$_4$), 23.7 (**C**$_1$), 22.7 (**C**$_{12}$), 2.6 (Si(**C**H$_3$)$_3$).
FTIR (thin film) cm^{-1}:	2927 (s), 2855 (m), 1741 (s, COOMe), 1673 (s, C=O), 1251 (w), 1113 (w), 842 (m).
HRMS (ESI)	calc'd for $C_{26}H_{42}NO_5Si$ $[M+H]^+$: 476.2827, found: 476.2820.
TLC (5% Methanol in CH_2Cl_2), *Rf*:	0.33 (UV, CAM).

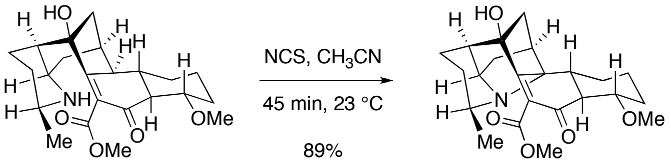


(–)-S9 **(–)-3**

Pentacyclic amino alcohol (–)-3:

Triethylamine trihydrogen fluoride (0.114 mL, 0.700 mmol, 82.0 equiv) was added via syringe to a solution of pentacyclic amine (–)-**S9** (4.0 mg, 8.4 μmol, 1 equiv) in tetrahydrofuran (100 μL) at 23°C under an argon atmosphere. After 4 h, aqueous sodium carbonate solution (1 M, 5 mL) was added to quench excess acid. The reaction mixture was diluted with dichloromethane (5 mL), and the layers were separated. The aqueous layer was extracted with dichloromethane (4 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the resulting residue via flash column chromatography (silica gel: diam. 1.5 cm, ht. 3 cm; eluent: 2% to 5% to 10% methanol in CH_2Cl_2) afforded the pentacyclic amino alcohol (–)-**3** (3 mg, 90%) as a clear film ($[\alpha]^{22}_{D}$ = –24 (*c* 0.080, CH_2Cl_2). Structural assignment utilized additional information from gCOSY, HSQC, and HMBC.

^{1}H NMR (600 MHz, C_6D_6, 20 ˚C):	3.69 (dd, *J* = 1.8, 11.4 Hz, 1H, C$_9$**H**), 3.55 (s, 6H, COOC**H**$_3$, OC**H**$_3$), 3.28-3.19 (m, 1H, C$_{14}$**H**), 2.93-2.83 (m, 2H, C$_6$**H**, O**H**), 2.57 (app-d, *J* = 12.6 Hz, 1H, C$_4$**H**H'), 2.21-2.13 (m, 2H, C$_{15}$**H**, C$_2$**H**), 1.97 (app-dd, *J* = 4.2, 13.2 Hz, 1H, C$_{13}$**H**H'), 1.89 (app-t, *J* = 5.4 Hz, 1H, C$_5$**H**), 1.76 (br-s, 1H, C$_8$**H**), 1.73-1.68 (m, 1H, C$_{21}$**H**H'), 1.57 (app-dd, *J* = 3.8, 11.2 Hz, 1H, C$_3$H**H'**), 1.50 (ddd, *J* = 3.2, 6.1, 14.3 Hz, 1H, C$_7$**H**H'), 1.45-1.17 (m, 6H, C$_{11}$**H**H', C$_{12}$**H**H', C$_3$H**H'**, C$_{21}$H**H'**, C$_4$H**H'**, C$_{10}$**H**), 1.17-1.08 (m, 1H, C$_{13}$H**H'**), 0.97 (app-d, *J* = 16.2 Hz, 1H, C$_7$H**H'**), 0.85-0.74 (m, 1H, C$_{12}$H**H'**), 0.71 (d, *J* = 6.0 Hz, 3H, C$_1$**H**$_3$), 0.62 (app-dq, *J* = 3.4, 11.9 Hz, 1H, C$_{11}$H**H'**).
^{13}C NMR (125 MHz, C_6D_6, 20 ˚C):	195.7 (**C**$_{16}$), 174.9 (**C**$_{19}$), 169.1 (**C**$_{18}$), 127.3 (**C**$_{17}$), 80.4 (**C**$_{20}$), 77.6 (**C**$_{14}$), 58.8 (**C**$_2$), 57.6 (O**C**H$_3$), 55.2 (**C**$_6$), 53.2 (**C**$_{15}$), 52.3 (**C**$_9$), 52.1 (COO**C**H$_3$), 48.1 (**C**$_{21}$), 47.8 (**C**$_5$), 46.3 (**C**$_{10}$), 40.9 (**C**$_7$), 32.7 (**C**$_8$), 32.1 (**C**$_{13}$), 30.9 (**C**$_3$), 30.3 (**C**$_{11}$), 24.9 (**C**$_4$), 23.6 (**C**$_1$), 22.9 (**C**$_{12}$).
FTIR (thin film) cm^{-1}:	2921 (s), 2850 (m), 1734 (m, COOMe), 1671 (m, C=O), 1460 (m), 1261 (w), 1111 (w).
HRMS (ESI)	calc'd for $C_{23}H_{34}NO_5$ $[M+H]^+$: 404.2431, found: 404.2432.
TLC (8% MeOH in CH_2Cl_2), *Rf*:	0.38 (UV, CAM).

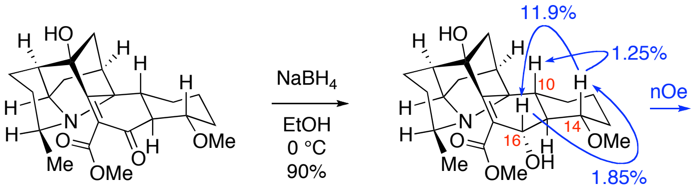


(–)-3 (+)-28

(+)-Hexacyclic ketoester (28):

Freshly recrystallized *N*-chlorosuccinimide (1.6 mg, 12 μmol, 2.0 equiv) was added as a solid to a solution of amino alcohol (–)-**3** (2.5 mg, 6.2 μmol, 1 equiv) in acetonitrile (0.3 mL) at 23 °C, and the reaction mixture sealed under an argon atmosphere. After 45 min, the reaction solvent was removed under reduced pressure. The residue was immediately purified by flash column chromatography (silica gel: diam. 1.25 cm, ht. 2 cm; eluent: 3% methanol in dichloromethane) to afford hexacyclic ketoester (+)-**28** (2.2 mg, 89%) as a white solid ($[\alpha]^{22}_{D}$ = +20 (*c* 0.11, CH_2Cl_2)). Structural assignment utilized additional information from gCOSY, HSQC, HMBC, ROESY, and NOESY.

^{1}H NMR (600 MHz, C_6D_6, 20 ˚C):	3.56 (s, 3H, $OC\mathbf{H}_3$), 3.48 (s, 3H, $COOC\mathbf{H}_3$), 3.37 (br-s, 1H, O**H**), 3.24-3.18 (m, 1H, $C_{14}\mathbf{H}$), 3.13-3.04 (m, 2H, $C_2\mathbf{H}$, $C_{15}\mathbf{H}$), 2.88 (br-s, 1H, $C_6\mathbf{H}$), 2.39-2.33 (m, 1H, $C_4\mathbf{H}H'$), 2.07-1.96 (m, 2H, $C_3\mathbf{H}H'$, $C_{13}\mathbf{H}H'$), 1.80 (br-s, 1H, $C_5\mathbf{H}$), 1.77-1.73 (m, 1H, $C_{21}\mathbf{H}H'$), 1.65-1.58 (m, 2H, $C_8\mathbf{H}$, $C_7\mathbf{H}H'$), 1.55-1.46 (m, 2H, $C_{11}\mathbf{H}H'$, $C_{12}\mathbf{H}H'$), 1.40-1.24 (m, 4H, $C_{10}\mathbf{H}$, $C_{11}H\mathbf{H'}$, $C_4H\mathbf{H'}$, $C_{21}H\mathbf{H'}$), 1.23-1.14 (m, 1H, $C_{13}H\mathbf{H'}$), 1.11 (d, *J* = 7.2 Hz, 3H, $C_1\mathbf{H}$), 1.07 (app-d, *J* = 9.6 Hz, 1H, $C_7H\mathbf{H'}$), 0.97-0.78 (m, 2H, $C_3H\mathbf{H'}$, $C_{12}H\mathbf{H'}$).
^{13}C NMR (125 MHz, C_6D_6, 20 ˚C):	195.8 ($\mathbf{C}_{16}$), 171.9 ($\mathbf{C}_{19}$), 169.5 ($\mathbf{C}_{18}$), 123.0 ($\mathbf{C}_{17}$), 81.0 ($\mathbf{C}_{20}$), 78.2 ($\mathbf{C}_{14}$), 69.9 ($\mathbf{C}_6$), 66.0 ($\mathbf{C}_9$), 57.6 ($O\mathbf{C}H_3$), 56.3 ($\mathbf{C}_2$), 52.7 ($COO\mathbf{C}H_3$), 52.6 ($\mathbf{C}_{15}$), 49.9 ($\mathbf{C}_5$), 49.9 ($\mathbf{C}_8$), 46.2 ($\mathbf{C}_{10}$), 45.0 ($\mathbf{C}_{21}$), 37.5 ($\mathbf{C}_7$), 32.1 ($\mathbf{C}_{13}$), 27.9 ($\mathbf{C}_3$), 27.3 ($\mathbf{C}_{11}$), 26.4 ($\mathbf{C}_4$), 25.0 ($\mathbf{C}_1$), 23.8 ($\mathbf{C}_{12}$).
FTIR (thin film) cm^{-1}:	3373 (br, s), 2923 (s), 1771 (m), 1712 (s), 1664 (s), 1461 (m), 1348 (m), 1269 (m), 1180 (m), 1091 (w), 802 (w).
HRMS (ESI)	calc'd for $C_{23}H_{32}NO_5$ $[M+H]^+$: 402.2275, found: 402.2290.
TLC (15% MeOH in CH_2Cl_2), *Rf*:	0.56 (CAM).



(+)-28 (+)-29

(+)-16-Debenzoyl-himandrine (29):

Sodium borohyride (4.0 mg, 0.11 mmol, 10 equiv) was added as a solid to a solution of hexacyclic ketoester (+)-**28** (4.0 mg, 9.9 mmol, 1 equiv) in ethanol (150 µL) at 0 °C, and the reaction mixture was sealed under an argon atmosphere. After 30 min, aqueous sodium carbonate solution (1 M, 0.5 mL) was added, and the layers were separated. The aqueous layer was extracted with dichloromethane (4 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. Purification of the resulting residue via flash column chromatography (silica gel: diam. 1.25 cm, ht. 1.5 cm; eluent: 5% methanol in CH_2Cl_2) afforded the hexacyclic diol (+)-**29** (3.6 mg, 90%) as a single diastereomer ($[\alpha]^{22}_{D} = +28$ (*c* 0.035, $CHCl_3$). Structural assignment utilized additional information from gCOSY, HSQC, and HMBC.

^{1}H NMR (600 MHz, $CDCl_3$, 20 ˚C):	4.53 (app-d, *J* = 7.2 Hz, 1H, C_{16}**H**), 4.22 (br-s, 1H, C_{20}O**H**), 3.84 (s, 3H, COOC**H$_3$**), 3.86-3.80 (br-s, 1H, C_{16}O**H**), 3.43-3.37 (m, 1H, C_2**H**), 3.40 (s, 3H, OC**H**$_3$), 3.31 (br-s, 1H, C_6**H**), 3.08 (dt, *J* = 4.2, 10.2 Hz, 1H, C_{14}**H**), 2.27-2.12 (m, 5H, C_4**H**H', C_{13}**H**H', C_{15}**H**, C_3**H**H', C_8**H**), 1.94 (br-s, 1H, C_5**H**), 1.90-1.68 (m, 4H, C_{12}**H**H', C_7**H**H', C_{21}**H**H', C_4H**H'**), 1.65-1.56 (m, 2H, C_{11}**H**H', C_{21}H**H'**), 1.52 (app-d, *J* = 10.2 Hz, 1H, C_7H**H'**), 1.46 (app-dq, *J* = 3.6, 12.6 Hz, 1H, C_{11}H**H'**), 1.34 (d, *J* = 7.2 Hz, 3H, C_1**H**), 1.38-1.30 (m, 1H, C_{10}**H**), 1.29-1.08 (m, C_3H**H'**, C_{12}H**H'**, C_{13}H**H'**).
^{13}C NMR (125 MHz, $CDCl_3$, 20 ˚C):	170.7 (**C**$_{18}$), 158.8 (**C**$_{19}$), 118.2 (**C**$_{17}$), 87.5 (**C**$_{14}$), 80.7 (**C**$_{20}$), 72.3 (**C**$_{16}$), 69.5 (**C**$_6$), 67.6 (**C**$_9$), 56.4 (O**C**H_3), 55.9 (**C**$_2$), 52.5 (COO**C**H_3), 49.6 (**C**$_5$), 49.3 (**C**$_8$), 48.4 (**C**$_{15}$), 44.9 (**C**$_{21}$), 42.9 (**C**$_{10}$), 37.6 (**C**$_7$), 30.4 (**C**$_{13}$), 27.3 (**C**$_3$), 27.0 (**C**$_{11}$), 25.7 (**C**$_4$), 24.3 (**C**$_{12}$), 24.0 (**C**$_1$).
FTIR (thin film) cm^{-1}:	3496 (br, s), 2930 (s), 2858 (m), 1733 (m), 1689 (m), 1459 (m), 1281 (m), 1262 (m), 1080 (m).
HRMS (ESI)	calc'd for $C_{23}H_{34}NO_5$ $[M+H]^+$: 404.2431, found: 404.2428.
TLC (10% Methanol in CH_2Cl_2), *Rf*:	0.19 (UV, CAM).

Comparison of our assignments for (+)-16-debenzoyl-himandrine (29) with literature data:

Assignment	**Original report**[10] (+)-16-Debenzoyl-himandrine (**29**) (^{1}H, 60 MHz, $CDCl_3$)	**This report** (+)-16-Debenzoyl-himandrine (**29**) (^{1}H, 600 MHz, $CDCl_3$)	**This report** (+)-16-Debenzoyl-himandrine (**29**) (^{13}C, 125 MHz, $CDCl_3$)
C1	1.33 (d, *J* = 7 Hz)	1.34 (d, *J* = 7.2 Hz)	24.0
C2	3.30 (br)	3.43-3.37 (m)[11]	55.9
C3, C4, C8, C13, C15	–	2.27-2.12 (m)	27.3 (C3), 25.7 (C4), 49.3 (C8), 30.4 (C13), 48.4 (C15)
C5	–	1.94 (br-s)	49.6
C6	3.30 (br)	3.31 (br-s)	69.5
C4, C7, C12, C21	–	1.90-1.68 (m)	25.7 (C4), 44.9 (C21), 24.3 (C12)
C7	–	1.52 (app-d, *J* = 10.2 Hz)	37.6
C9	–	–	67.6
C10	–	1.38-1.30 (m)	42.9
C11, C21		1.65-1.56 (m)	27.0 (C11), 44.9 (C21)
C11	–	1.46 (app-dq, *J* = 3.6, 12.6 Hz)	27.0
C3, C12, C13	–	1.29-1.08 (m)	27.3 (C3), 24.3 (C12), 30.4 (C13)
C14	3.10 (br)	3.08 (dt, *J* = 4.2, 10.2 Hz)	87.5
C1	4.60 (d, *J* = 8.0 Hz)	4.53 (app-d, *J* = 7.2 Hz)	72.3
C17	–	–	118.2
C18	–	–	170.7
C19	–	–	158.8
C20	–	–	80.7
C20-OH	4.20 (s)	4.22 (br-s)	–
C16-OH	3.80 (s)	3.86-3.80 (br-s)	–
$COOCH_3$	3.88 (s)	3.84 (s)	52.5
OCH_3	3.43 (s)	3.40 (s)	56.4

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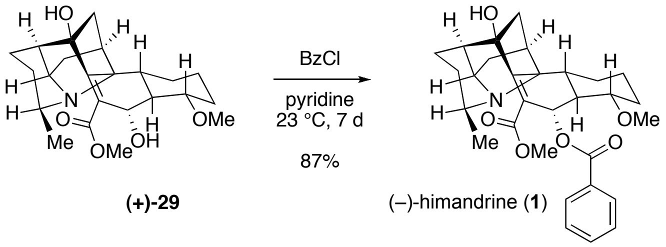
[10] Chemical degradation of himandrine (**1**) gave (+)-16-debenzoyl-himandrine (**29**); see Mander, L. N.; Prager, R. H.; Rasmussen, M.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.*, **1967**, *20*, 1473.

[11] Our assignment of the C2 methine is supported by our gCOSY, HSQC and HMBC data. The original paper (ref. 10) listed both C2 and C6 methines at 3.30 ppm (br). Our 2D data reveals the C2 methine is actually obscured by the methyl ether signal (3.40 ppm), while C6 methine alone corresponds to the signal at 3.31 ppm (br).



(+)-29

(–)-himandrine (**1**)

(–)-Himandrine (1):

Freshly distilled benzoyl chloride (0.1 mL) was added to a solution of alcohol (+)-**29** (2.0 mg, 4.9 µmol, 1 equiv) in pyridine (0.12 mL) at 23 °C under an argon atmosphere. After 7 d, the reaction mixture was diluted with dichloromethane (5 mL) and aqueous sodium carbonate solution (1.0 M, 2 mL). After 30 min, the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel: diam. 0.5 cm, ht. 5 cm; eluent: 3% methanol in CH_2Cl_2) to afford (–)-himandrine (**1**, 2.0 mg, 87%) ($[\alpha]^{22}_{D} = -21$ (*c* 0.12, $CHCl_3$)).[12] Structural assignment utilized additional information from gCOSY, HSQC, HMBC, and ROESY. Crystals suitable for X-ray diffraction were obtained from dichloromethane–hexanes (5:1). For a thermal ellipsoid representation of (–)-himandrine (**1**) see page S31.

^{1}H NMR (600 MHz, $CDCl_3$, 20 °C):	7.94 (app-d, *J* = 7.8 Hz, 2H, Ar**H**), 7.49 (app-t, *J* = 7.2 Hz, 1H, Ar**H**), 7.39 (app-t, *J* = 7.2 Hz, 2H, Ar**H**), 6.18 (d, *J* = 7.8 Hz, 1H, $C_{16}\mathbf{H}$), 4.54 (br-s, 1H, $C_{20}O\mathbf{H}$), 3.58 (s, 3H, $COOC\mathbf{H}_3$), 3.53-3.44 (m, 1H, $C_2\mathbf{H}$), 3.35 (br-s, 1H, $C_6\mathbf{H}$), 3.12 (s, 3H, $OC\mathbf{H}_3$), 3.05 (dt, *J* = 4.2, 10.8 Hz, 1H, $C_{14}\mathbf{H}$), 2.44-2.37 (m, 1H, $C_{15}\mathbf{H}$), 2.34-2.27 (m, 1H, $C_4\mathbf{H}H'$), 2.23-2.08 (m, 3H, $C_8\mathbf{H}$, $C_{13}\mathbf{H}H'$, $C_3\mathbf{H}H'$), 2.03 (br-s, 1H, $C_5\mathbf{H}$), 1.91-1.75 (m, 4H, $C_7\mathbf{H}H'$, $C_{12}\mathbf{H}H'$, $C_4H\mathbf{H}'$, $C_{21}\mathbf{H}H'$), 1.68-1.62 (m, 2H, $C_{11}\mathbf{H}H'$, $C_{21}H\mathbf{H}'$), 1.57 (app-d, *J* = 11.4 Hz, 1H, $C_7H\mathbf{H}'$), 1.45 (d, *J* = 6.6 Hz, 3H, $C_1\mathbf{H}$), 1.45-1.42 (m, 2H, $C_{10}\mathbf{H}$, $C_{11}H\mathbf{H}'$), 1.41-1.33 (m, 1H, $C_3H\mathbf{H}'$), 1.33-1.27 (m, 1H, $C_{12}H\mathbf{H}'$), 1.13-1.04 (m, 1H, $C_{13}H\mathbf{H}'$).
^{13}C NMR (125 MHz, $CDCl_3$, 20 °C):	169.6 ($\mathbf{C}_{18}$), 165.7 (Ar**C**=O), 163.2 ($\mathbf{C}_{19}$), 132.7 (Ar**C**H), 131.4 (Ar**C**H), 129.6 (Ar**C**H), 128.6 (Ar**C**H), 116.6 ($\mathbf{C}_{17}$), 85.5 ($\mathbf{C}_{14}$), 81.1 ($\mathbf{C}_{20}$), 72.9 ($\mathbf{C}_{16}$), 69.5 ($\mathbf{C}_6$), 67.7 ($\mathbf{C}_9$), 56.7 ($O\mathbf{C}H_3$), 55.8 ($\mathbf{C}_2$), 52.3 ($COO\mathbf{C}H_3$), 50.2 ($\mathbf{C}_5$), 49.4 ($\mathbf{C}_8$), 45.9 ($\mathbf{C}_{15}$), 44.8 ($\mathbf{C}_{21}$), 43.4 ($\mathbf{C}_{10}$), 37.4 ($\mathbf{C}_7$), 30.8 ($\mathbf{C}_{13}$), 27.7 ($\mathbf{C}_3$), 27.3 ($\mathbf{C}_{11}$), 25.7 ($\mathbf{C}_4$), 24.6 ($\mathbf{C}_1$), 23.8 ($\mathbf{C}_{12}$).
FTIR (thin film) cm^{-1}:	3429 (br, s), 2919 (s), 2852 (s), 1727 (s), 1687 (m), 1450 (w), 1276 (m), 1268 (s), 1097 (m), 1066 (w), 709 (w).
HRMS (ESI)	calc'd for $C_{30}H_{38}NO_6$ $[M+H]^+$: 508.2694, found: 508.2694.
TLC (15% MeOH in CH_2Cl_2), *Rf*:	0.60 (UV, CAM)

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[12] The magnitude of the optical rotation of (–)-himandrine (**1**) is sensitive to concentration: $[\alpha]^{22}_{D} = -12$ (*c* 0.060, $CHCl_3$).

Comparison of our assignments for (–)-himandrine (1) with literature:

Assignment	**Isolation paper**[13] (–)-Himandrine (**1**) (^{1}H, 60 MHz, CDCl$_3$)	**This report** (–)-Himandrine (**1**) (^{1}H, 600 MHz, CDCl$_3$)	**This report**[14] (–)-Himandrine (**1**) (^{13}C, 125 MHz, CDCl$_3$)
C1	1.48 (d, J = 7 Hz)	1.45 (d, J = 6.6 Hz)	24.6
C2	3.38(br)	3.53-3.44 (m)[15]	55.8
C3	–	1.41-1.33 (m)	27.7 (C3), 23.8 (C12), 30.8 (C13)
C3, C8, C13	–	2.23-2.08 (m)	27.7 (C3), 49.4 (C8), 30.8 (C13)
C4		2.34-2.27 (m)	25.7
C5	–	2.03 (br-s)	50.2
C6	3.38 (br)	3.35 (br-s)	69.5
C4, C7, C12, C21	–	1.91-1.75 (m)	25.7 (C4), 44.8 (C21), 23.8 (C12)
C7	–	1.57 (app-d, J = 11.4 Hz)	37.4
C9	–	–	67.7
C10, C11	–	1.45-1.42 (m)	43.4 (C10), 27.3 (C11)
C11, C21		1.68-1.62 (m)	27.3 (C11), 44.8 (C21)
C12		1.33-1.27 (m)	23.8 (C12)
C13		1.13-1.04 (m)	30.8 (C13)
C14	3.10 (br)	3.05 (dt, J = 4.2, 10.8 Hz)	85.5
C15		2.44-2.37 (m)	45.9
C16	6.20 (d, J = 8 Hz)	6.18 (d, J = 7.8 Hz)	72.9
C17	–	–	116.6
C18	–	–	169.6
C19	–	–	163.2
C20	–	–	81.1
C20-OH	4.50	4.54 (br-s)	–
COOCH$_3$	–	3.58 (s)	52.3
OCH$_3$	3.15 (s)	3.12 (s)	56.7
Bz	7.5 (m), 8.0 (m)	7.94 (app-d, J = 7.8 Hz), 7.49 (app-t, J = 7.2 Hz), 7.39 (app-t, J = 7.2 Hz)	165.7 (ArC=O), 163.2, 132.7, 131.4, 129.6, 128.6 (ArCH)

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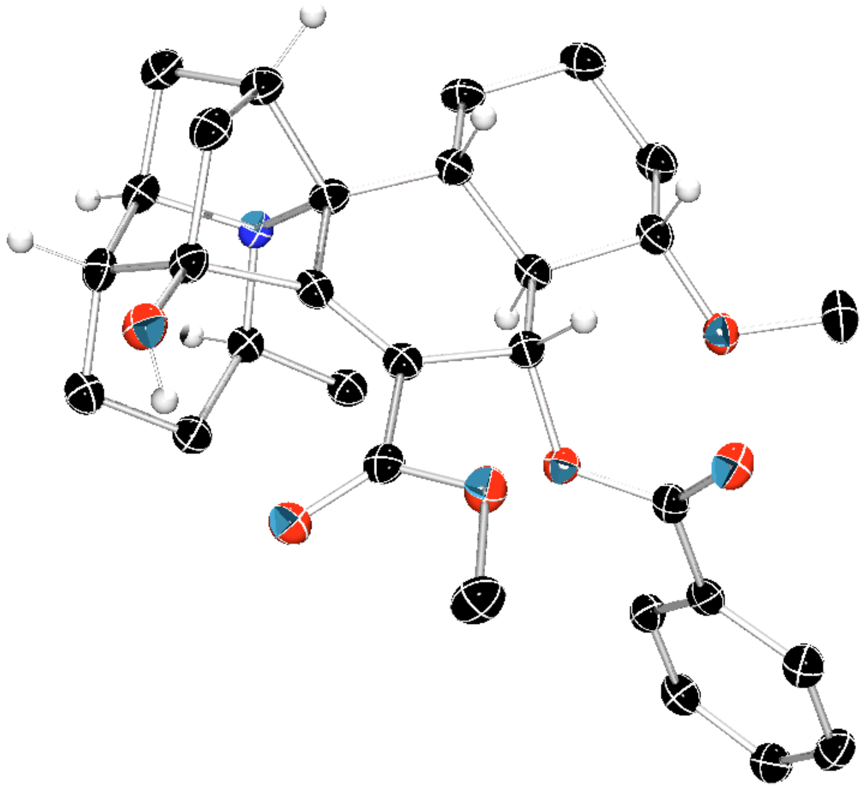
[13] The original structure of himandrine was based on X-ray crystallographic analysis of the corresponding hydrobromide salt of **1**; see (a) Guise, G. B.; Mander, L. N.; Prager, R. H.; Rasmussen, M.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.*, **1967**, *20*, 1029, and (b) Willis, A. C.; O'Connor, P. D.; Taylor, W. C.; Mander, L. N. *Aust. J. Chem.*, **2006**, *59*, 629.

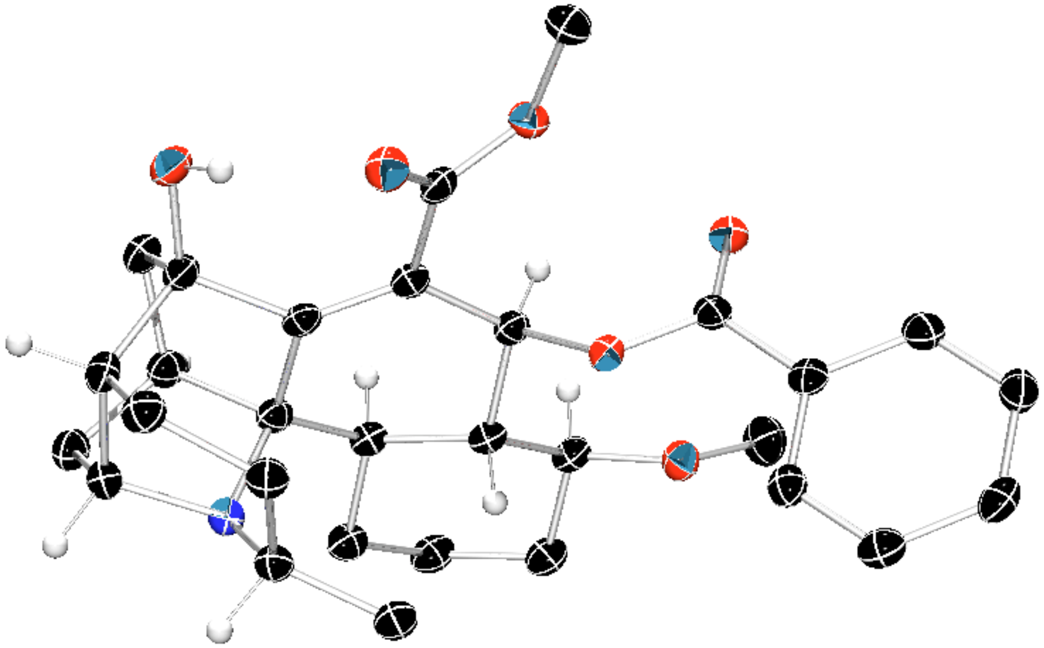
[14] We confirmed the structure of our synthetic (–)-himandrine (**1**) by both X-ray crystallographic analysis and extensive 2D NMR data,

[15] Our assignment of the C2 methine is supported by our gCOSY, HSQC, HMBC, and ROESY data. The isolation paper (ref. 13) listed both C2 and C6 methines at 3.38 ppm (br). Our 2D data reveals the C2 methine is actually at 3.53-3.44 ppm (m), while C6 methine alone corresponds to the signal at 3.35 ppm (br-s).

Crystal Structure of (–)-Himandrine (1).



View 1:



View 2:

Table S1. Crystal data and structure refinement for (–)-himandrine (**1**).

Identification code	d8_09005	
Empirical formula	C30 H37 N O6	
Formula weight	507.61	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.3136(2) Å	a= 78.8230(10)°.
	b = 8.7575(2) Å	b= 67.4340(10)°.
	c = 10.6508(3) Å	g = 62.0950(10)°.
Volume	632.72(3) Å^3	
Z	1	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.746 mm^{-1}	
F(000)	272	
Crystal size	0.30 x 0.25 x 0.03 mm^3	
Theta range for data collection	4.50 to 68.74°.	
Index ranges	-10<=h<=10, -8<=k<=10, -12<=l<=12	
Reflections collected	11853	
Independent reflections	3819 [R(int) = 0.0157]	
Completeness to theta = 68.74°	95.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9780 and 0.8072	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3819 / 374 / 340	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0704	
R indices (all data)	R1 = 0.0273, wR2 = 0.0707	
Absolute structure parameter	0.12(12)	
Largest diff. peak and hole	0.160 and -0.149 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (–)-himandrine (**1**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9286(2)	-3433(2)	-3435(1)	24(1)
O(2)	6909(2)	3613(2)	906(1)	25(1)
O(3)	10744(1)	-1800(1)	-2501(1)	19(1)
O(4)	10437(2)	1690(2)	-759(1)	25(1)
O(5)	10469(2)	1605(2)	-2855(1)	24(1)
O(6)	11133(2)	-1066(2)	-4733(1)	25(1)
N(1)	5882(2)	-875(2)	1922(1)	20(1)
C(1)	9013(2)	-3652(2)	1181(2)	23(1)
C(2)	7830(2)	-2051(2)	2058(2)	21(1)
C(3)	9083(2)	-1168(2)	1986(2)	22(1)
C(4)	7936(2)	497(2)	2808(2)	25(1)
C(5)	5954(2)	1601(2)	2634(2)	23(1)
C(6)	4864(2)	465(2)	2972(2)	23(1)
C(7)	2890(2)	1421(2)	2799(2)	25(1)
C(8)	3544(2)	1824(2)	1278(2)	23(1)
C(9)	5574(2)	207(2)	662(2)	20(1)
C(10)	5535(2)	-649(2)	-444(2)	20(1)
C(11)	4371(2)	-1710(2)	141(2)	24(1)
C(12)	4213(2)	-2404(2)	-996(2)	26(1)
C(13)	6223(2)	-3455(2)	-1982(2)	25(1)
C(14)	7374(2)	-2392(2)	-2581(2)	21(1)
C(15)	7549(2)	-1665(2)	-1466(2)	19(1)
C(16)	8698(2)	-584(2)	-2059(2)	18(1)
C(17)	8412(2)	634(2)	-1068(2)	19(1)
C(18)	9843(2)	1376(2)	-1511(2)	20(1)
C(19)	6985(2)	1007(2)	139(2)	19(1)
C(20)	6117(2)	2420(2)	1172(2)	21(1)
C(21)	4089(2)	3327(2)	1048(2)	24(1)
C(22)	11947(2)	2234(2)	-3369(2)	28(1)
C(23)	9405(3)	-3736(3)	-4732(2)	34(1)
C(24)	11671(2)	-2049(2)	-3856(2)	20(1)
C(25)	13481(2)	-3698(2)	-4122(2)	20(1)

C(26)	14848(2)	-4000(2)	-5428(2)	24(1)
C(27)	16546(2)	-5528(2)	-5694(2)	26(1)
C(28)	16881(2)	-6760(2)	-4668(2)	25(1)
C(29)	15491(2)	-6478(2)	-3377(2)	25(1)
C(30)	13799(2)	-4961(2)	-3103(2)	22(1)

Table S3. Bond lengths [Å] and angles [°] for (–)-himandrine (**1**).

O(1)-C(23)	1.4142(19)	C(13)-C(14)	1.525(2)
O(1)-C(14)	1.4284(19)	C(14)-C(15)	1.533(2)
O(2)-C(20)	1.412(2)	C(15)-C(16)	1.535(2)
O(3)-C(24)	1.3541(17)	C(16)-C(17)	1.522(2)
O(3)-C(16)	1.4605(16)	C(17)-C(19)	1.340(2)
O(4)-C(18)	1.2153(19)	C(17)-C(18)	1.495(2)
O(5)-C(18)	1.3318(19)	C(19)-C(20)	1.531(2)
O(5)-C(22)	1.453(2)	C(20)-C(21)	1.539(2)
O(6)-C(24)	1.2094(19)	C(24)-C(25)	1.493(2)
N(1)-C(6)	1.482(2)	C(25)-C(26)	1.395(2)
N(1)-C(2)	1.5048(19)	C(25)-C(30)	1.397(2)
N(1)-C(9)	1.5195(19)	C(26)-C(27)	1.391(2)
C(1)-C(2)	1.523(2)	C(27)-C(28)	1.390(2)
C(2)-C(3)	1.535(2)	C(28)-C(29)	1.390(2)
C(3)-C(4)	1.534(2)	C(29)-C(30)	1.383(2)
C(4)-C(5)	1.536(2)		
C(5)-C(6)	1.547(2)	C(23)-O(1)-C(14)	114.26(13)
C(5)-C(20)	1.566(2)	C(24)-O(3)-C(16)	117.11(11)
C(6)-C(7)	1.521(2)	C(18)-O(5)-C(22)	115.22(12)
C(7)-C(8)	1.525(2)	C(6)-N(1)-C(2)	107.31(12)
C(8)-C(21)	1.532(2)	C(6)-N(1)-C(9)	101.81(12)
C(8)-C(9)	1.599(2)	C(2)-N(1)-C(9)	124.53(11)
C(9)-C(19)	1.515(2)	N(1)-C(2)-C(1)	115.50(13)
C(9)-C(10)	1.533(2)	N(1)-C(2)-C(3)	115.94(13)
C(10)-C(11)	1.530(2)	C(1)-C(2)-C(3)	111.01(13)
C(10)-C(15)	1.537(2)	C(4)-C(3)-C(2)	113.00(13)
C(11)-C(12)	1.528(2)	C(3)-C(4)-C(5)	112.15(14)
C(12)-C(13)	1.526(2)	C(4)-C(5)-C(6)	108.71(13)

C(4)-C(5)-C(20)	112.62(13)
C(6)-C(5)-C(20)	110.63(13)
N(1)-C(6)-C(7)	100.94(13)
N(1)-C(6)-C(5)	108.84(12)
C(7)-C(6)-C(5)	113.24(14)
C(6)-C(7)-C(8)	98.68(12)
C(7)-C(8)-C(21)	108.84(14)
C(7)-C(8)-C(9)	104.54(12)
C(21)-C(8)-C(9)	103.48(12)
C(19)-C(9)-N(1)	108.05(12)
C(19)-C(9)-C(10)	113.70(12)
N(1)-C(9)-C(10)	117.25(13)
C(19)-C(9)-C(8)	102.83(13)
N(1)-C(9)-C(8)	102.66(11)
C(10)-C(9)-C(8)	110.85(12)
C(11)-C(10)-C(9)	112.54(13)
C(11)-C(10)-C(15)	112.64(13)
C(9)-C(10)-C(15)	113.45(12)
C(12)-C(11)-C(10)	110.84(13)
C(13)-C(12)-C(11)	110.31(13)
C(14)-C(13)-C(12)	111.64(14)
O(1)-C(14)-C(13)	110.51(13)
O(1)-C(14)-C(15)	107.72(12)
C(13)-C(14)-C(15)	111.57(13)
C(14)-C(15)-C(16)	111.97(12)
C(14)-C(15)-C(10)	110.17(12)
C(16)-C(15)-C(10)	112.27(13)
O(3)-C(16)-C(17)	107.10(12)
O(3)-C(16)-C(15)	106.85(12)
C(17)-C(16)-C(15)	115.20(12)
C(19)-C(17)-C(18)	121.64(15)
C(19)-C(17)-C(16)	122.44(14)
C(18)-C(17)-C(16)	115.91(13)
O(4)-C(18)-O(5)	122.83(15)
O(4)-C(18)-C(17)	125.03(14)
O(5)-C(18)-C(17)	112.10(13)
C(17)-C(19)-C(9)	123.37(15)
C(17)-C(19)-C(20)	132.98(15)
C(9)-C(19)-C(20)	102.82(12)
O(2)-C(20)-C(19)	118.91(13)
O(2)-C(20)-C(21)	110.00(13)
C(19)-C(20)-C(21)	96.65(12)
O(2)-C(20)-C(5)	111.34(13)
C(19)-C(20)-C(5)	109.96(12)
C(21)-C(20)-C(5)	108.76(12)
C(8)-C(21)-C(20)	102.03(12)
O(6)-C(24)-O(3)	125.12(14)
O(6)-C(24)-C(25)	124.37(14)
O(3)-C(24)-C(25)	110.49(12)
C(26)-C(25)-C(30)	119.63(15)
C(26)-C(25)-C(24)	118.99(14)
C(30)-C(25)-C(24)	121.35(14)
C(27)-C(26)-C(25)	119.79(15)
C(28)-C(27)-C(26)	120.36(15)
C(29)-C(28)-C(27)	119.70(15)
C(30)-C(29)-C(28)	120.32(15)
C(29)-C(30)-C(25)	120.15(15)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3) for (–)-himandrine (**1**). The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	27(1)	25(1)	22(1)	-4(1)	-8(1)	-12(1)
O(2)	26(1)	19(1)	30(1)	-4(1)	-7(1)	-10(1)
O(3)	18(1)	17(1)	21(1)	-2(1)	-6(1)	-7(1)
O(4)	24(1)	27(1)	27(1)	-3(1)	-9(1)	-13(1)
O(5)	28(1)	24(1)	22(1)	-1(1)	-5(1)	-16(1)
O(6)	28(1)	21(1)	22(1)	1(1)	-6(1)	-9(1)
N(1)	21(1)	20(1)	20(1)	-1(1)	-6(1)	-9(1)
C(1)	23(1)	20(1)	26(1)	1(1)	-11(1)	-7(1)
C(2)	21(1)	20(1)	20(1)	1(1)	-7(1)	-8(1)
C(3)	22(1)	22(1)	23(1)	1(1)	-9(1)	-10(1)
C(4)	28(1)	23(1)	26(1)	-1(1)	-11(1)	-11(1)
C(5)	25(1)	21(1)	22(1)	-6(1)	-6(1)	-8(1)
C(6)	23(1)	22(1)	18(1)	-2(1)	-3(1)	-9(1)
C(7)	22(1)	23(1)	26(1)	-4(1)	-4(1)	-8(1)
C(8)	20(1)	20(1)	26(1)	-1(1)	-7(1)	-6(1)
C(9)	18(1)	17(1)	22(1)	0(1)	-6(1)	-7(1)
C(10)	20(1)	18(1)	23(1)	0(1)	-8(1)	-8(1)
C(11)	20(1)	23(1)	30(1)	0(1)	-8(1)	-10(1)
C(12)	25(1)	22(1)	37(1)	-1(1)	-13(1)	-12(1)
C(13)	27(1)	22(1)	32(1)	-3(1)	-12(1)	-12(1)
C(14)	25(1)	17(1)	24(1)	-1(1)	-12(1)	-8(1)
C(15)	20(1)	16(1)	22(1)	0(1)	-10(1)	-8(1)
C(16)	19(1)	16(1)	20(1)	0(1)	-7(1)	-6(1)
C(17)	19(1)	16(1)	22(1)	0(1)	-9(1)	-6(1)
C(18)	19(1)	13(1)	25(1)	-3(1)	-7(1)	-4(1)
C(19)	22(1)	14(1)	22(1)	1(1)	-12(1)	-6(1)
C(20)	21(1)	16(1)	24(1)	-4(1)	-5(1)	-8(1)
C(21)	22(1)	18(1)	26(1)	-3(1)	-7(1)	-5(1)
C(22)	26(1)	28(1)	30(1)	1(1)	-3(1)	-16(1)
C(23)	43(1)	38(1)	24(1)	-5(1)	-13(1)	-17(1)
C(24)	23(1)	20(1)	20(1)	-1(1)	-7(1)	-13(1)
C(25)	22(1)	20(1)	24(1)	-3(1)	-8(1)	-12(1)

C(26)	28(1)	22(1)	24(1)	0(1)	-7(1)	-14(1)
C(27)	25(1)	26(1)	25(1)	-6(1)	-2(1)	-13(1)
C(28)	24(1)	19(1)	33(1)	-8(1)	-9(1)	-7(1)
C(29)	29(1)	21(1)	28(1)	1(1)	-14(1)	-12(1)
C(30)	23(1)	23(1)	23(1)	-4(1)	-6(1)	-12(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for (–)-himandrine (**1**).

	x	y	z	U(eq)
H(2O)	8110(20)	3030(30)	640(20)	30
H(1A)	8143	-4058	1096	35
H(1B)	9910	-4563	1606	35
H(1C)	9746	-3367	277	35
H(2)	7524	-2517	3011	25
H(3A)	10141	-1984	2333	27
H(3B)	9677	-892	1024	27
H(4A)	8691	1182	2511	29
H(4B)	7748	194	3783	29
H(5)	5198	2559	3302	28
H(6)	4761	-69	3902	27
H(7A)	2059	2484	3344	31
H(7B)	2211	677	3027	31
H(8)	2579	2029	848	28
H(10)	4816	319	-979	24
H(11A)	5010	-2688	693	28
H(11B)	3059	-977	743	28
H(12A)	3524	-3143	-599	32
H(12B)	3459	-1428	-1491	32
H(13A)	6933	-4483	-1499	30
H(13B)	6095	-3862	-2728	30
H(14)	6709	-1411	-3134	26
H(15)	8282	-2670	-962	23
H(16)	8361	97	-2865	22

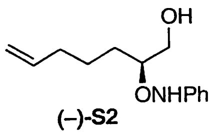
H(21A)	3174	4219	1749	29
H(21B)	4127	3867	136	29
H(22A)	11418	3381	-3004	43
H(22B)	12362	2309	-4364	43
H(22C)	13058	1435	-3086	43
H(23A)	8788	-4491	-4635	51
H(23B)	10767	-4294	-5306	51
H(23C)	8744	-2634	-5154	51
H(26)	14619	-3166	-6134	29
H(27)	17482	-5729	-6582	31
H(28)	18055	-7790	-4847	31
H(29)	15703	-7331	-2680	30
H(30)	12852	-4778	-2220	27

Table S6. Hydrogen bonds for (–)-himandrine (**1**) [Å and °].

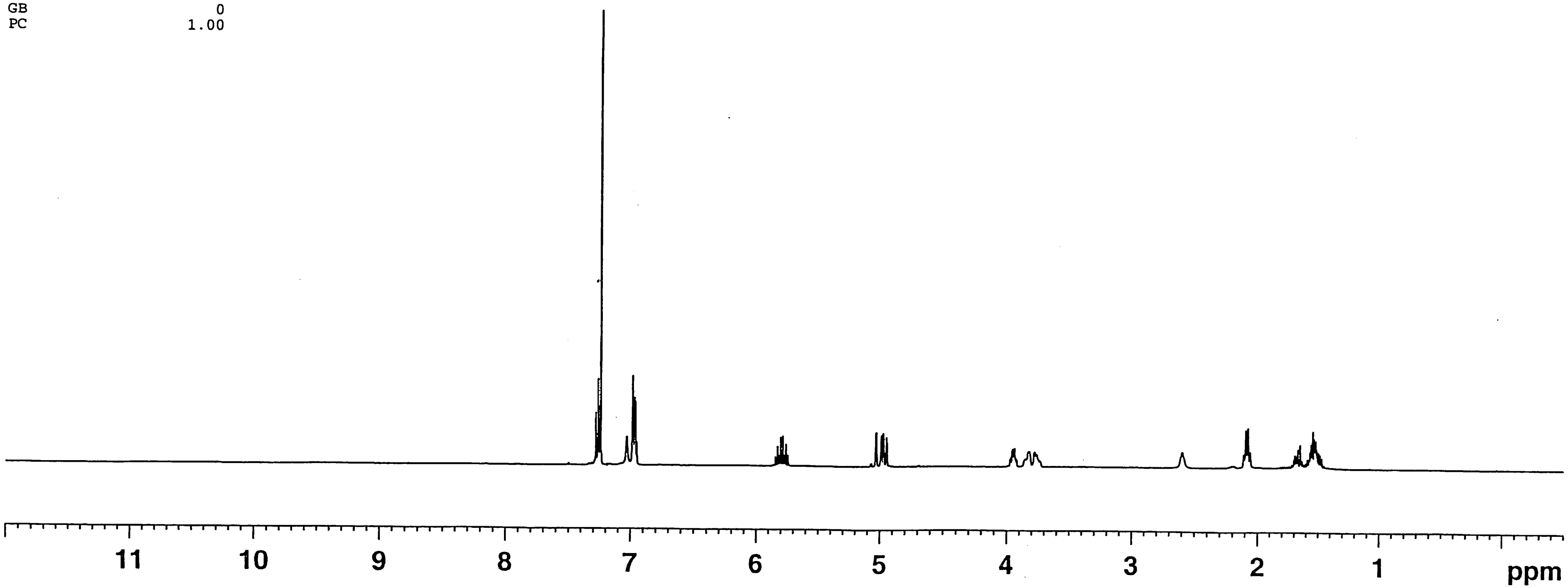
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2O)...O(4)	0.834(15)	1.922(17)	2.6693(16)	148.7(19)

Symmetry transformations used to generate equivalent atoms:

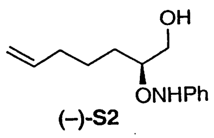
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 203.2
DW                60.400 usec
DE                  6.00 usec
TE                 293.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.00 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300178 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



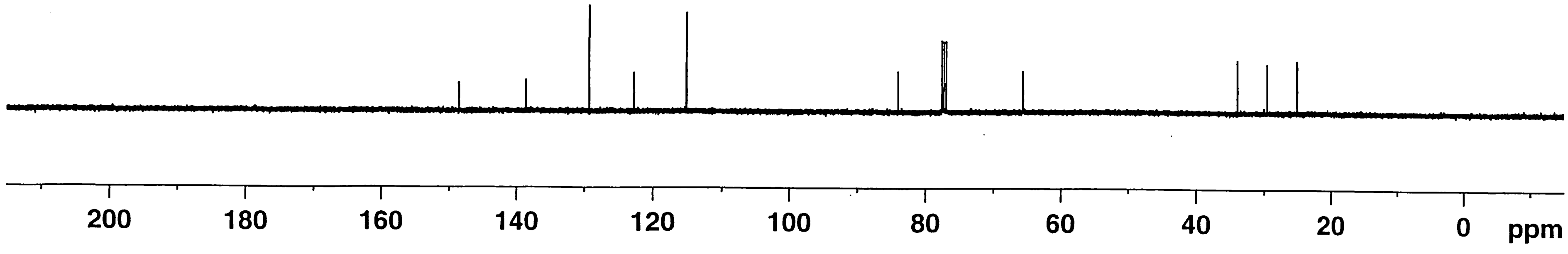
(–)-S2

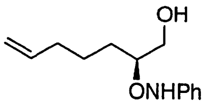


```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  2580.3
DW                  20.850 usec
DE                    6.00 usec
TE                   294.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.38 usec
PL1                   0.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 16.10 dB
PL13                 19.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127509 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```

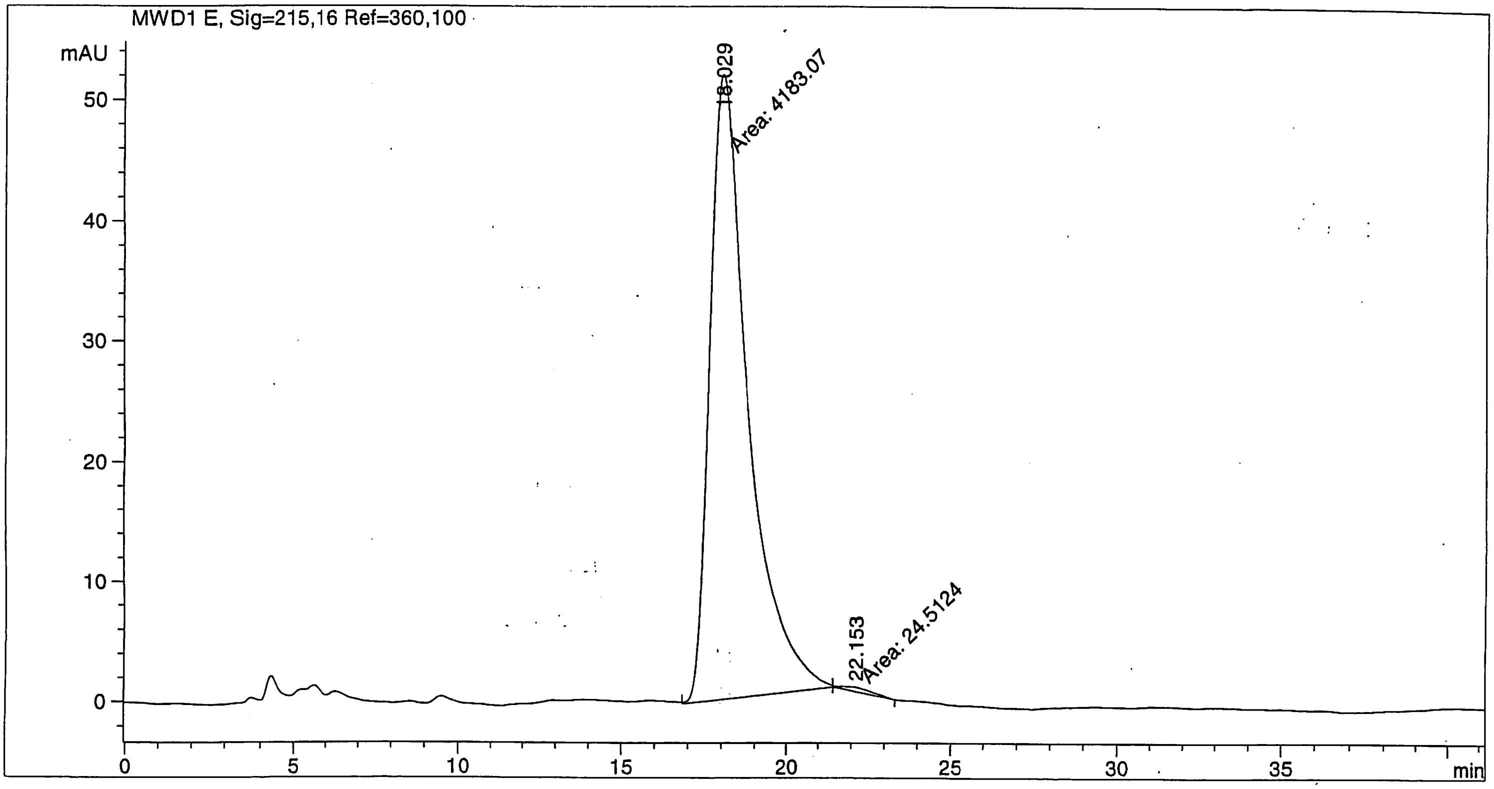


(–)-S2

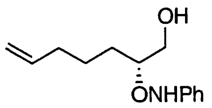




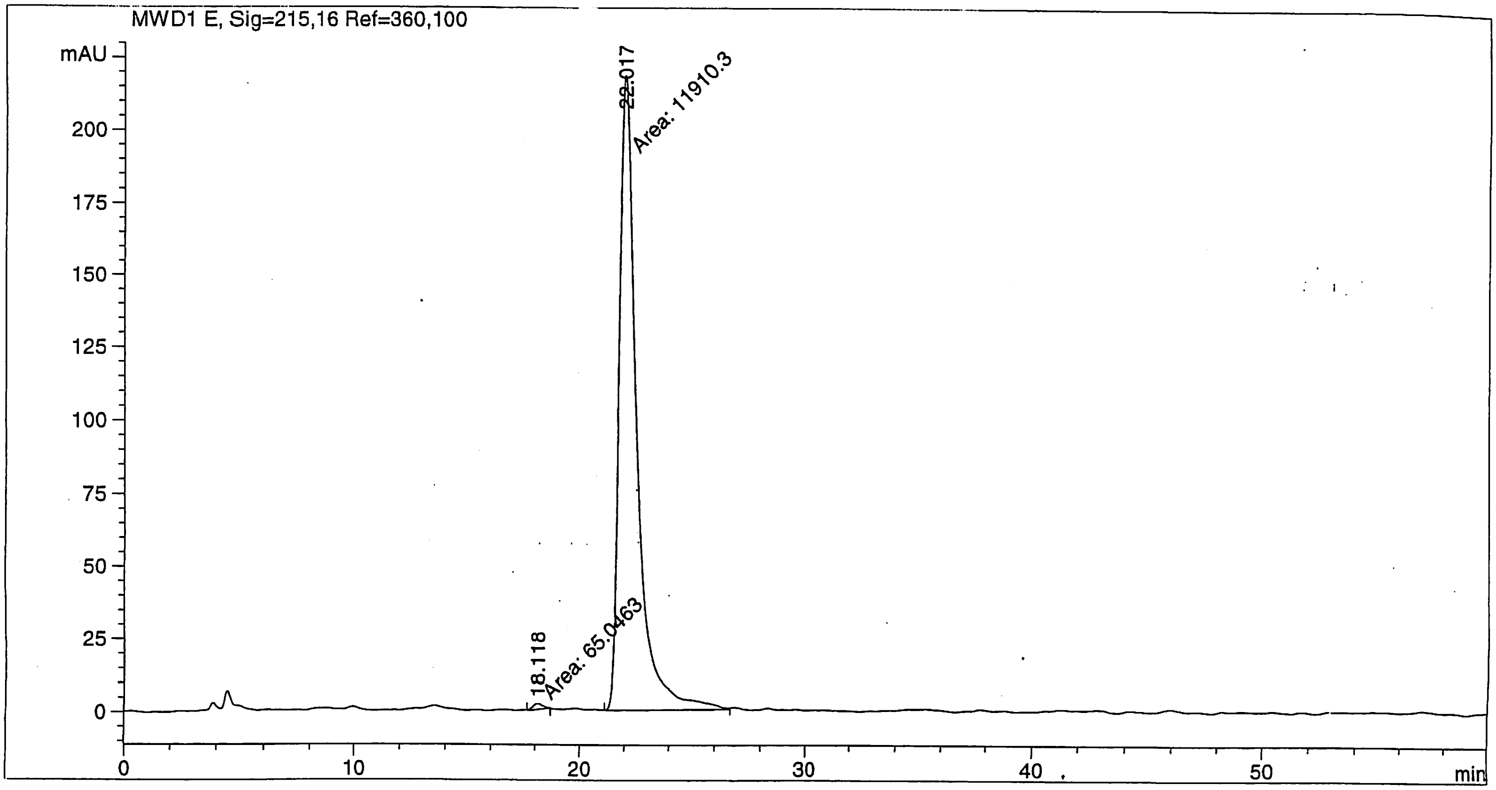
(−)-(*S*)-S2



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

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


Signal 1: MWD1 E, Sig=215,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  18.029 MM     1.3433 4183.07324   51.89904 99.4174
   2  22.153 MM     1.0577   24.51239 3.86262e-1  0.5826

Totals :                   4207.58564   52.28530

 Results obtained with enhanced integrator!
=====================================================================
                          Summed Peaks Report
=====================================================================

Signal 1: MWD1 E, Sig=215,16 Ref=360,100
```

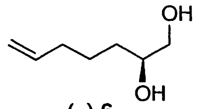


(+)-(*R*)-S2

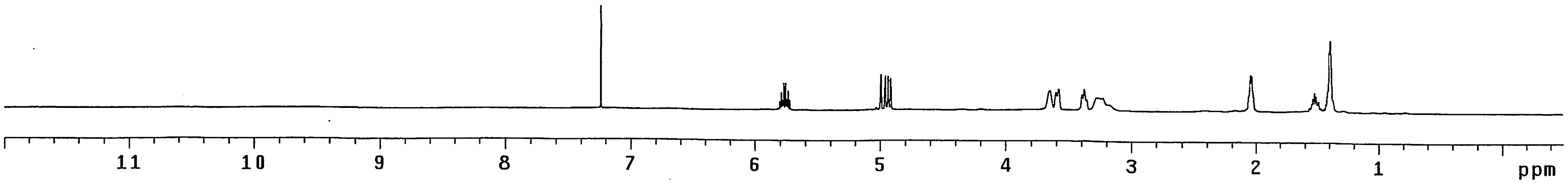


```
==================================================================
                      Area Percent Report
==================================================================

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


Signal 1: MWD1 E, Sig=215,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.118 MM    0.5225   65.04629    2.07490   0.5432
   2  22.017 MM    0.9094 1.19103e4  218.27008  99.4568

Totals :                  1.19753e4  220.34498

 Results obtained with enhanced integrator!
==================================================================
                      Summed Peaks Report
==================================================================

Signal 1: MWD1 E, Sig=215,16 Ref=360,100
```

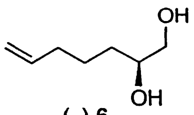
```
exp1  s2pul

                            DEC. & VT
date                      dfrq         125.845
solvent        CDCl3      dn               C13
                          dpwr              30
                          dof                0
                          dm               nnn
                          dmm                c
     ACQUISITION          dmf              200
sfrq         500.435      dseq
tn                H1      dres             1.0
at             4.999      homo               n
np            120102         PROCESSING
sw           12012.0      wtfile
fb          not used      proc              ft
bs                 2      fn            262144
tpwr              56      math               f
pw               8.0
d1             0.100      werr
tof           3003.2      wexp
nt                16      wbs
ct                10      wnt              wft
alock              n
gain        not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp            -250.2
wp            6255.3
vs                16
sc                 0
wc               250
hzmm           25.02
is             33.57
rfl           4139.5
rfp           3623.1
th                 7
ins          100.000
ai   cdc   ph
```



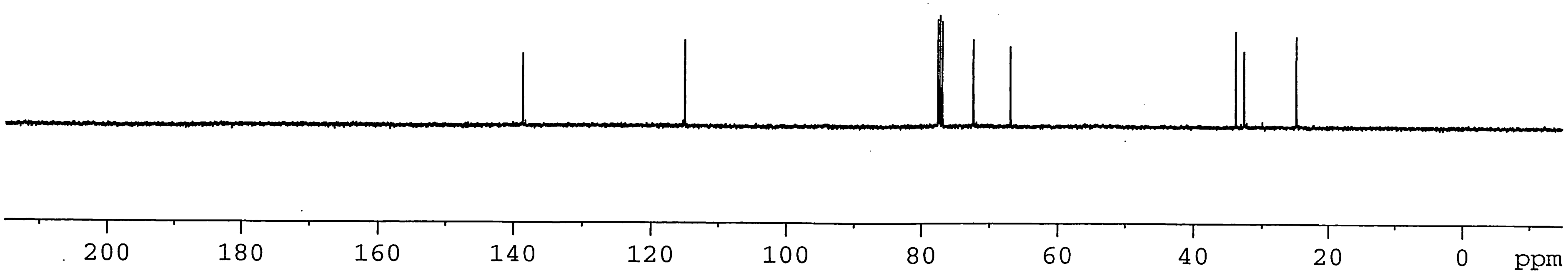
(−)-6



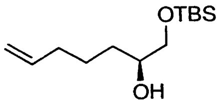
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDC13
NS                     64
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                 1824.6
DW                 20.850 usec
DE                   6.00 usec
TE                  292.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.38 usec
PL1                  0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                16.10 dB
PL13                19.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127520 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```



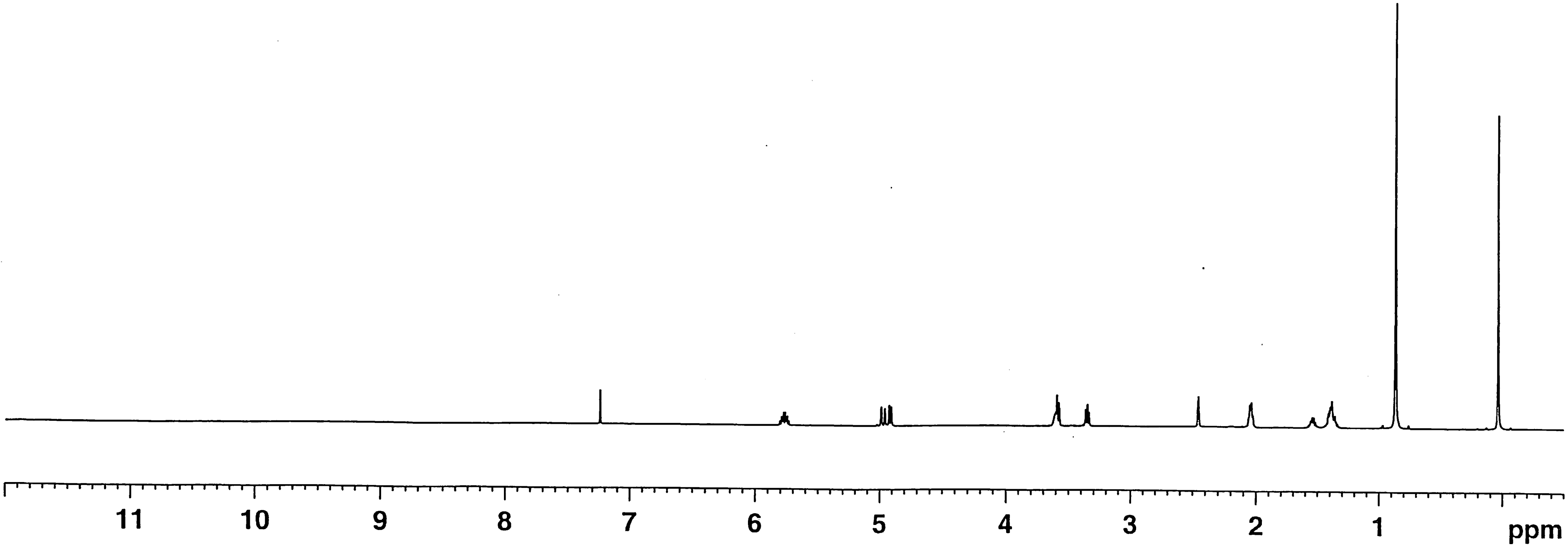
(−)-6



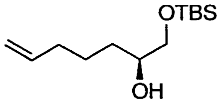
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM           spect
PROBHD   5 mm CPTXI 1H-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12376.237 Hz
FIDRES         0.188846 Hz
AQ            2.6477044 sec
RG                    4
DW               40.400 usec
DE                 6.00 usec
TE                293.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.00 usec
PL1                4.00 dB
SFO1        600.1337060 MHz

F2 - Processing parameters
SI                65536
SF          600.1300281 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



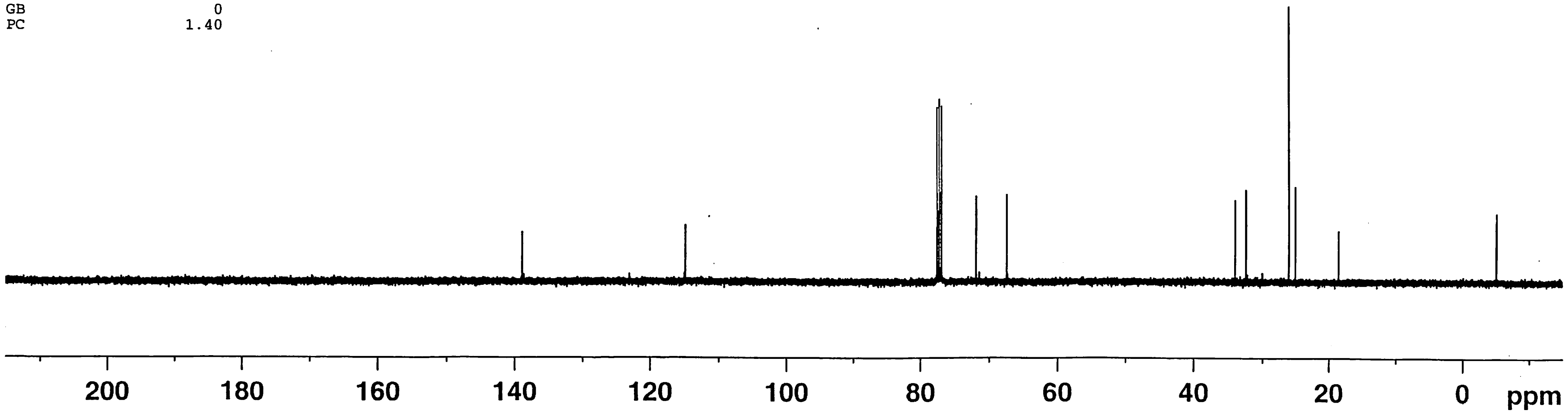
(+)-7



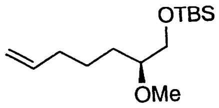
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   615
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                  6.00 usec
TE                 294.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127478 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```



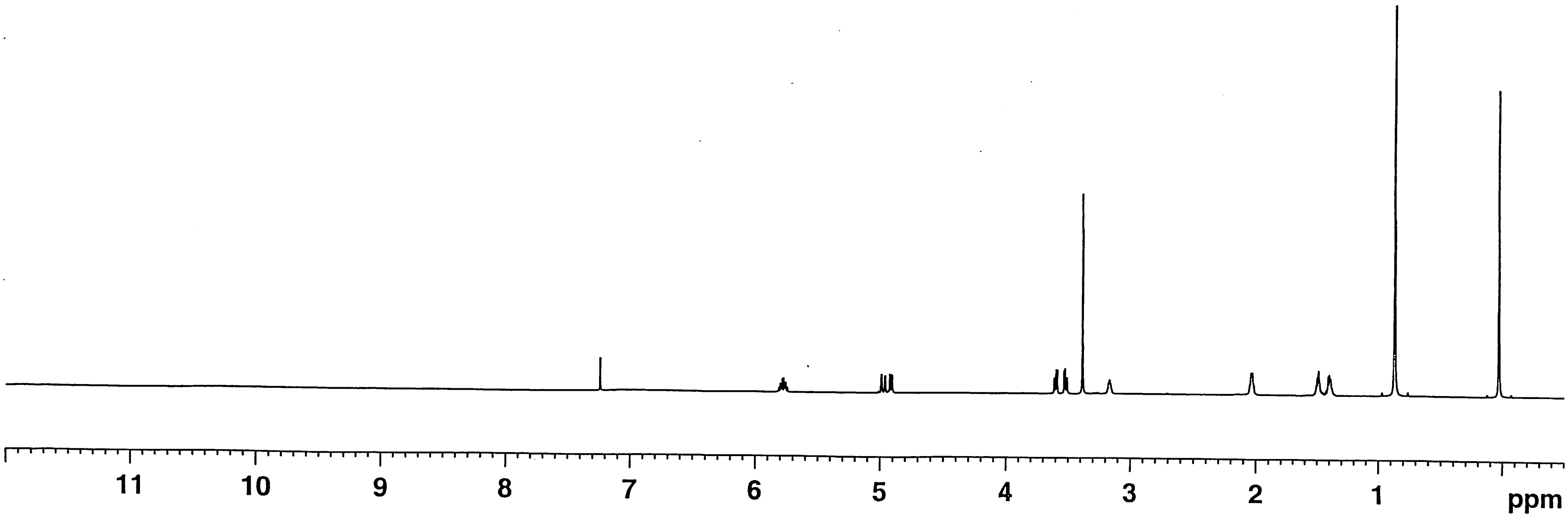
(+)-7



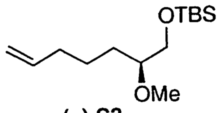
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD   5 mm CPTXI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    13
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                   5.7
DW                40.400 usec
DE                  6.00 usec
TE                 304.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300278 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



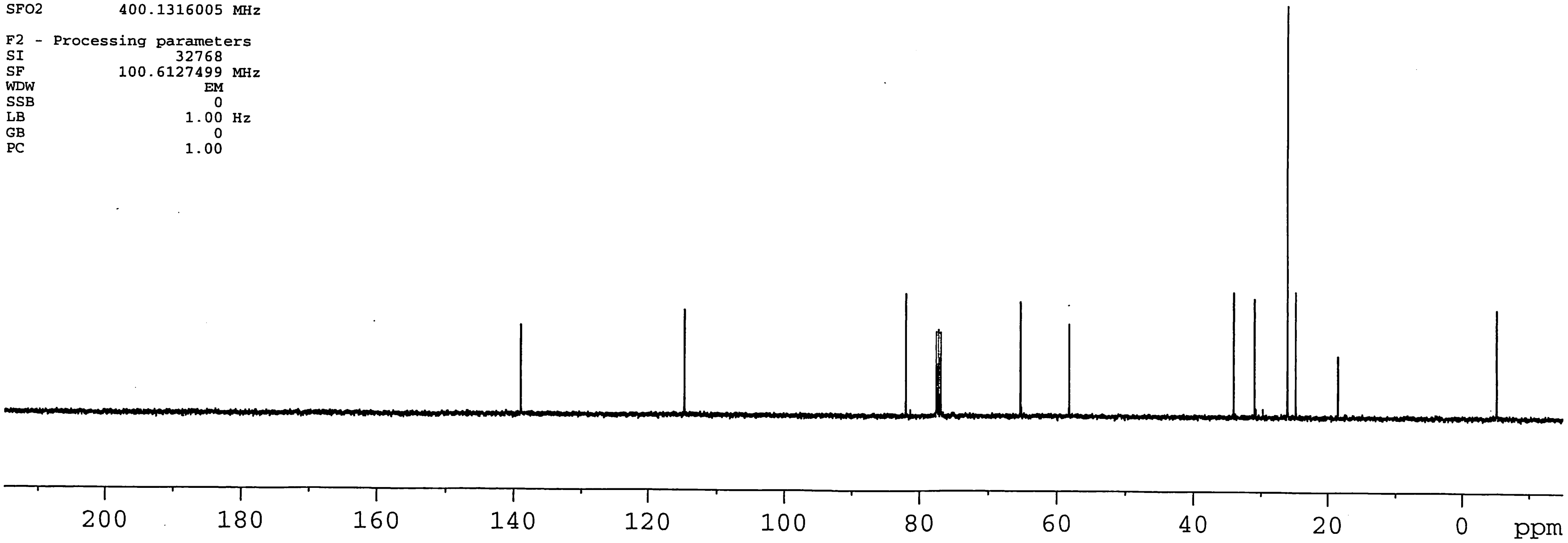
(–)-S3



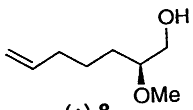
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      30
DS                       4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ           1.3664756 sec
RG                  2580.3
DW              20.850 usec
DE                6.00 usec
TE               291.2 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                9.38 usec
PL1               0.00 dB
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            90.00 usec
PL2               0.00 dB
PL12             16.10 dB
PL13             19.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF         100.6127499 MHz
WDW                     EM
SSB                      0
LB                1.00 Hz
GB                       0
PC                    1.00
```



(–)-S3



```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      13
DS                       2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                    45.3
DW                 60.400 usec
DE                   6.00 usec
TE                  291.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300175 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



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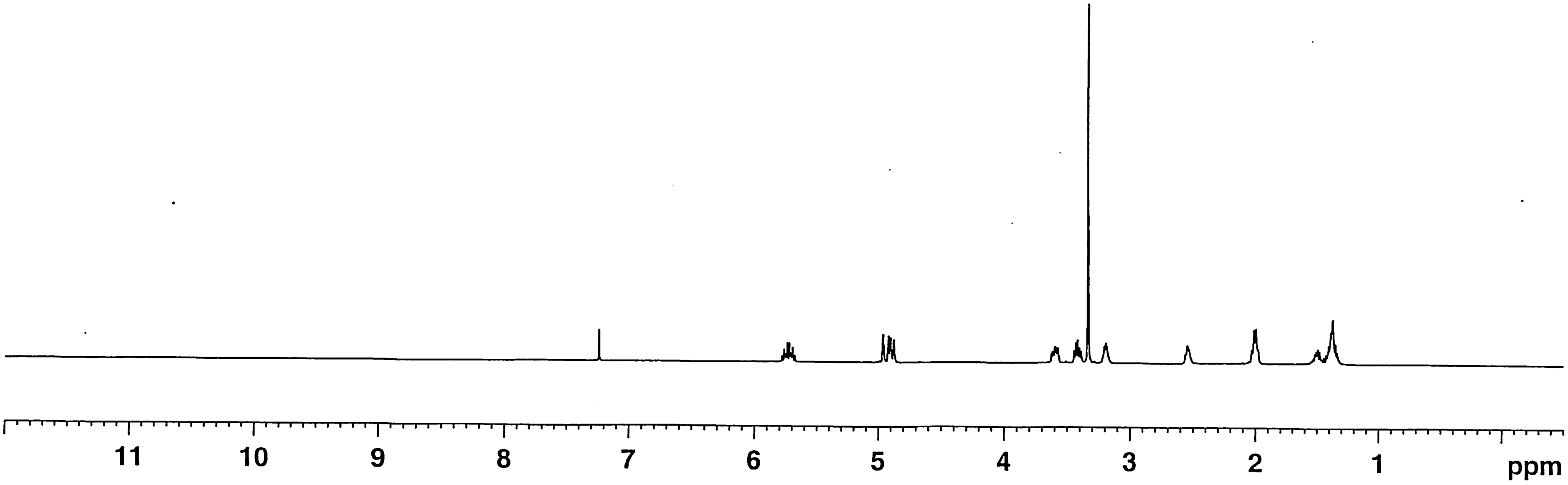


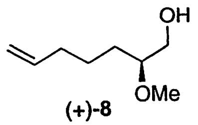
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      21
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  1824.6
DW                  20.850 usec
DE                    6.00 usec
TE                   291.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.38 usec
PL1                   0.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 16.10 dB
PL13                 19.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF             100.6127571 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```



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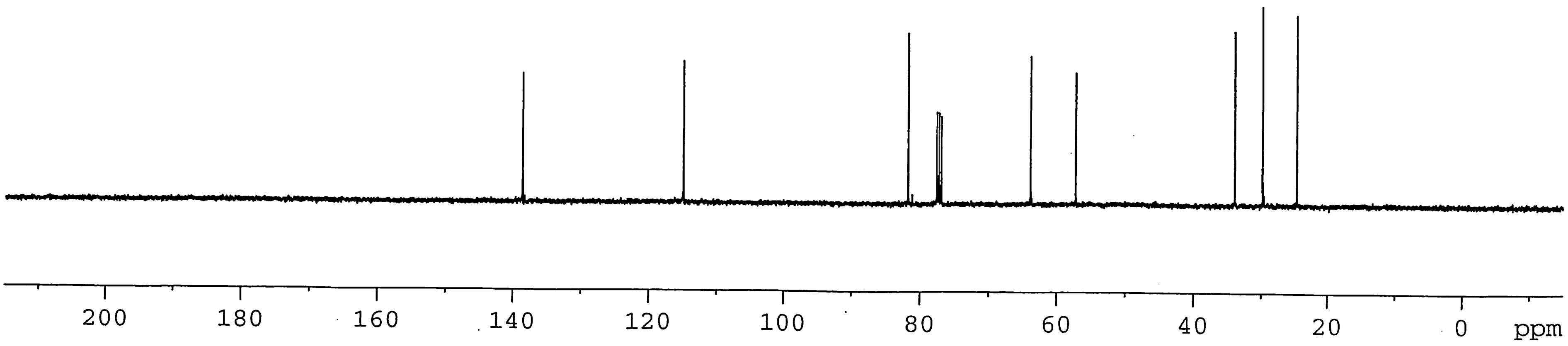
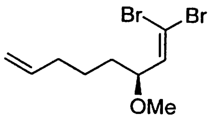
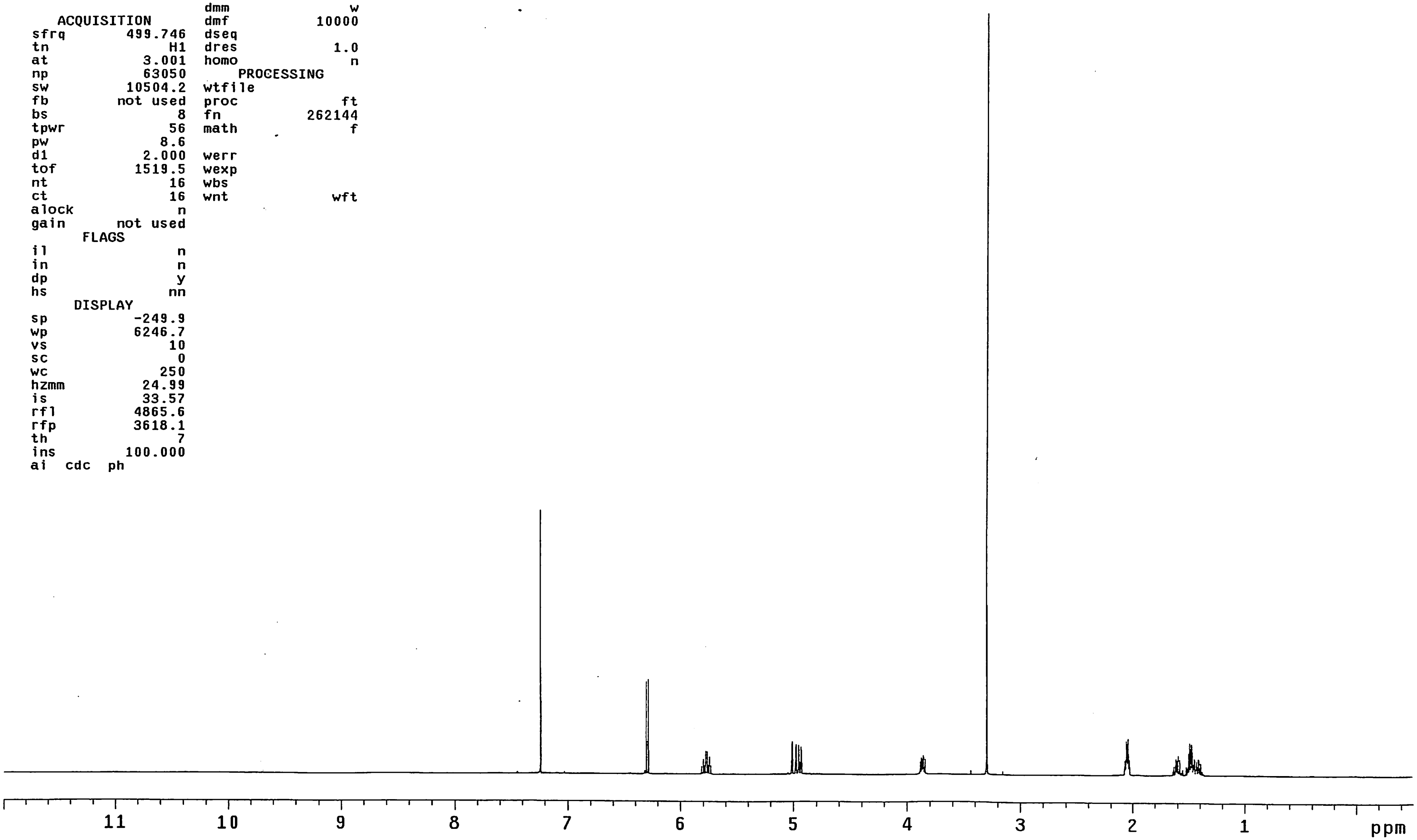


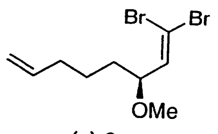


(–)-9

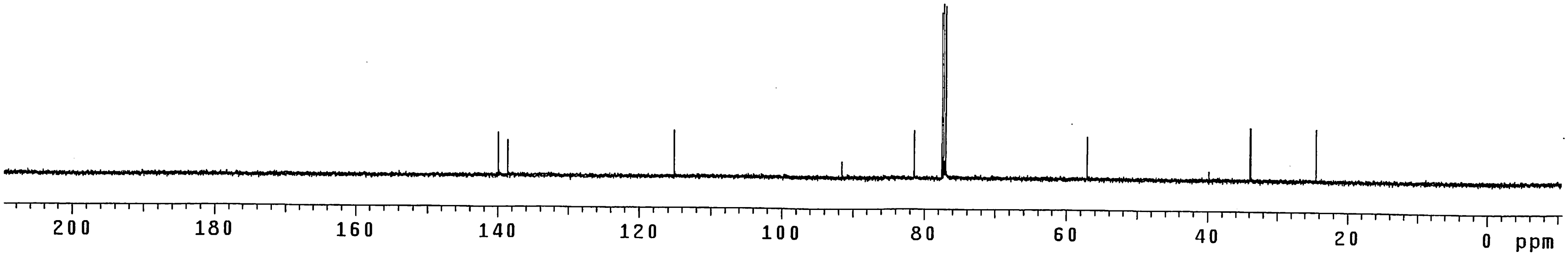
```
                              DEC. & VT
                        dfrq        125.672
solvent         CDCl3   dn              C13
                        dpwr             30
                        dof               0
                        dm              nnn
                        dmm               w
   ACQUISITION          dmf           10000
sfrq          499.746   dseq
tn                 H1   dres            1.0
at              3.001   homo              n
np              63050         PROCESSING
sw            10504.2   wtfile
fb           not used   proc             ft
bs                  8   fn           262144
tpwr               56   math              f
pw                8.6
d1              2.000   werr
tof            1519.5   wexp
nt                 16   wbs
ct                 16   wnt             wft
alock               n
gain         not used
      FLAGS
il                  n
in                  n
dp                  y
hs                 nn
      DISPLAY
sp             -249.9
wp             6246.7
vs                 10
sc                  0
wc                250
hzmm            24.99
is              33.57
rfl            4865.6
rfp            3618.1
th                  7
ins           100.000
ai  cdc  ph
```

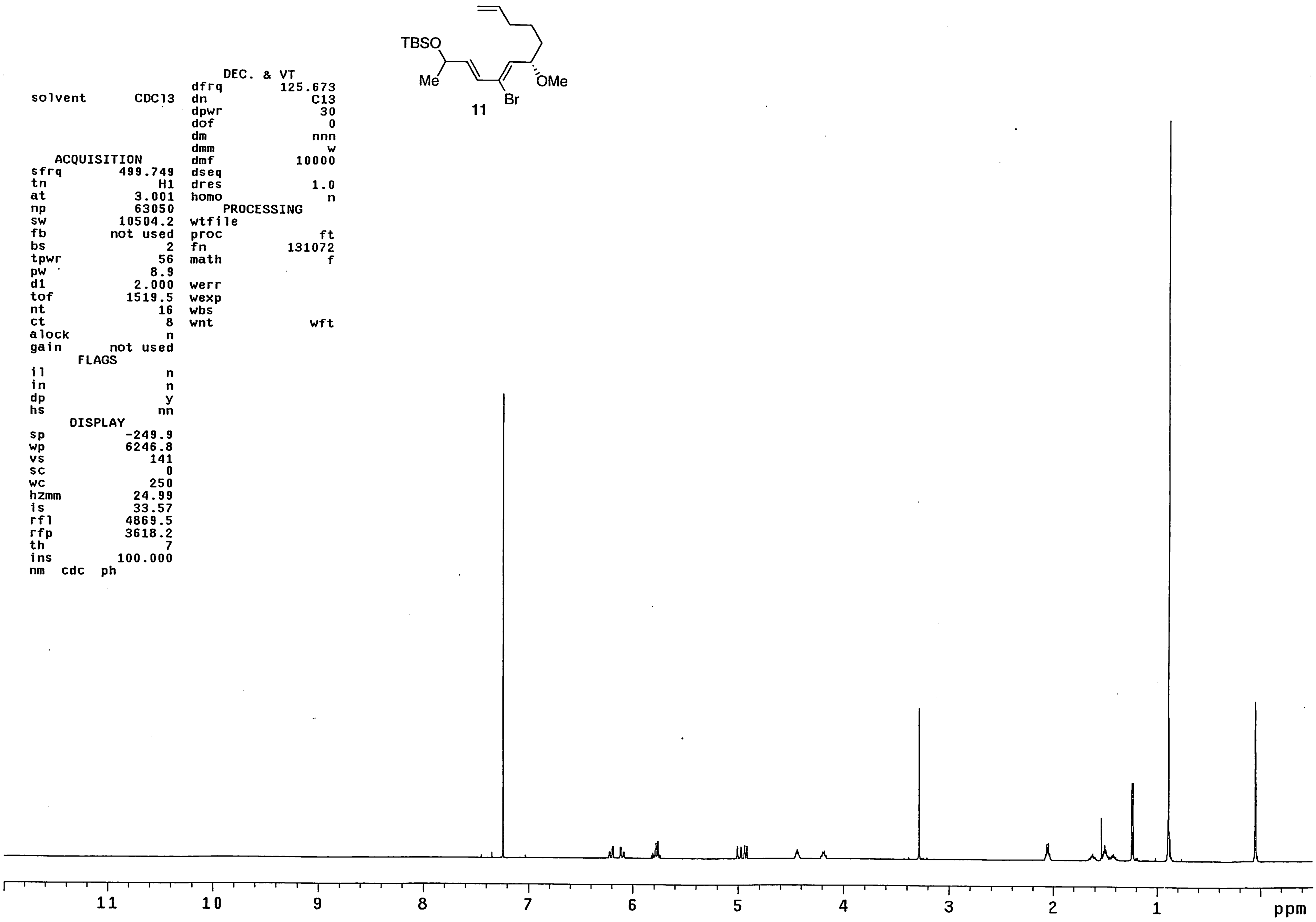


```
                                   DEC. & VT
date                         dfrq        499.744
solvent         CDCl3        dn               H1
                             dpwr             34
                             dof               0
                             dm              yyy
                             dmm               w
     ACQUISITION             dmf           10000
sfrq          125.672        dseq
tn                C13        dres            1.0
at              2.000        homo              n
np             125588            PROCESSING
sw            31397.2        lb             1.00
fb           not used        wtfile
bs                  8        proc             ft
tpwr               58        fn           131072
pw                6.7        math              f
d1              3.000
tof                 0        werr
nt                256        wexp
ct                160        wbs
alock               n        wnt
gain         not used
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp            -1329.0
wp            27683.3
vs                172
sc                  0
wc                250
hzmm           110.73
is             500.00
rfl           13468.0
rfp            9704.7
th                 68
ins           100.000
ai   cdc   ph
```



(–)-9





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```
                        DEC. & VT
                 dfrq          125.673
solvent    CDCl3 dn                C13
                 dpwr               30
                 dof                 0
                 dm                nnn
                 dmm                 w
   ACQUISITION   dmf             10000
sfrq     499.749 dseq
tn            H1 dres              1.0
at         3.001 homo                n
np         63050       PROCESSING
sw       10504.2 wtfile
fb      not used proc               ft
bs             2 fn             131072
tpwr          56 math                f
pw           8.9
d1         2.000 werr
tof       1519.5 wexp
nt            16 wbs
ct             8 wnt               wft
alock          n
gain    not used
      FLAGS
il             n
in             n
dp             y
hs            nn
     DISPLAY
sp        -249.9
wp        6246.8
vs           141
sc             0
wc           250
hzmm       24.99
is         33.57
rfl       4869.5
rfp       3618.2
th             7
ins      100.000
nm  cdc  ph
```

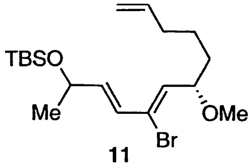
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                    8192
DW                  20.850 usec
DE                    6.00 usec
TE                   293.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127514 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```



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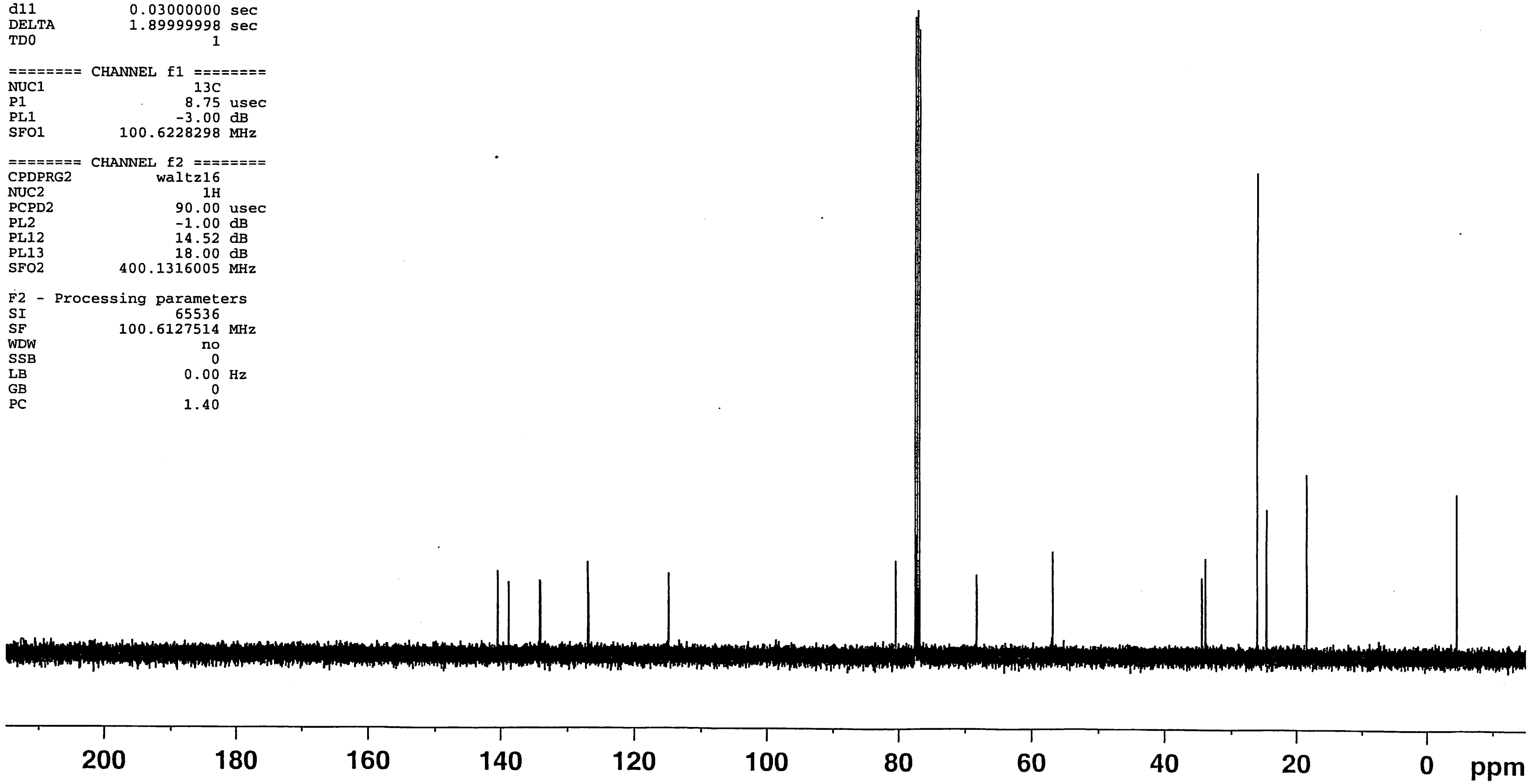
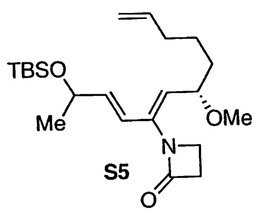
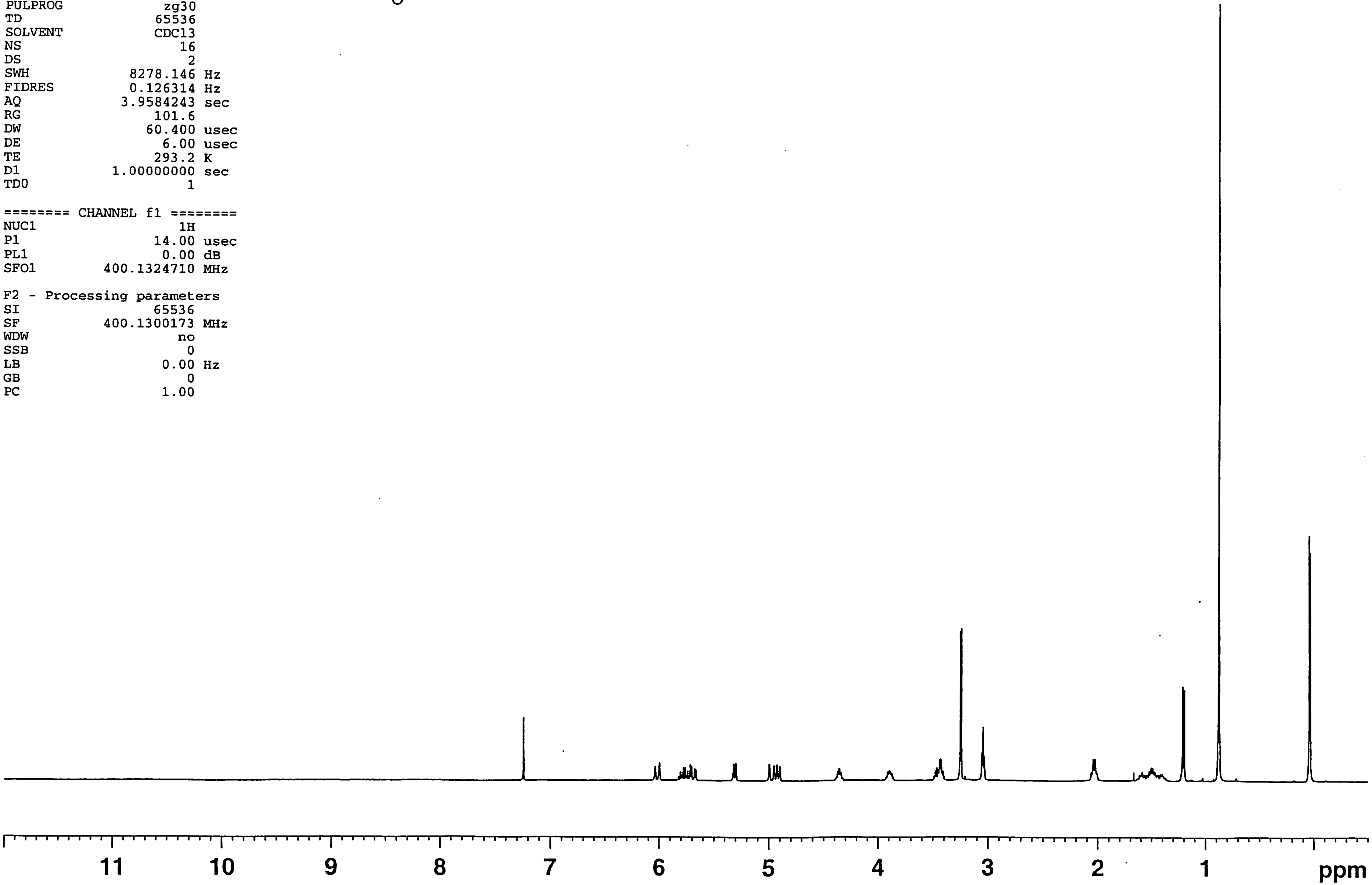


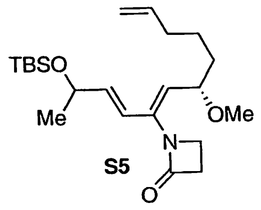
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                   101.6
DW                  60.400 usec
DE                    6.00 usec
TE                   293.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300173 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```



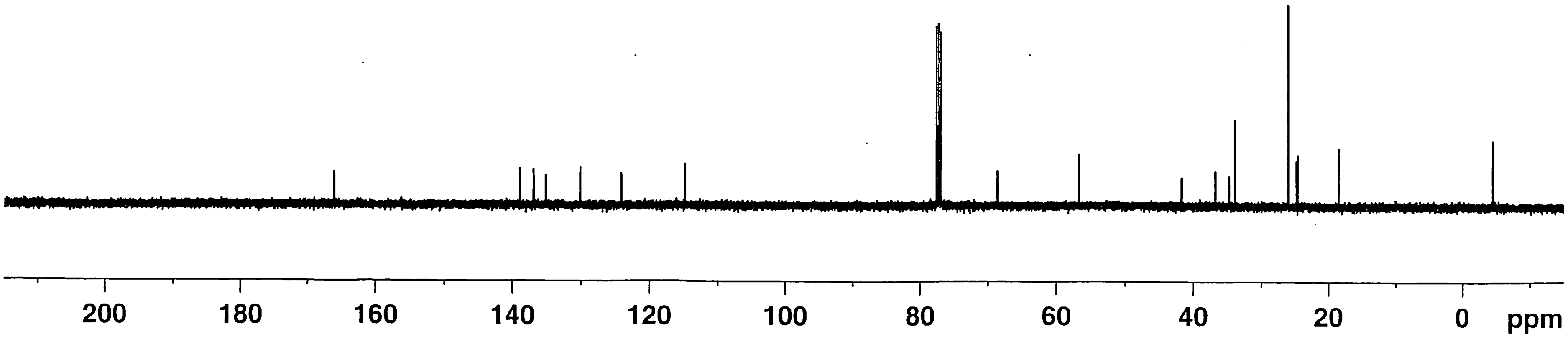
S5



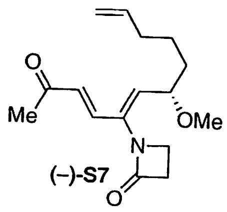
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    2
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 8192
DW               20.850 usec
DE                 6.00 usec
TE                293.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.38 usec
PL1                0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              16.10 dB
PL13              19.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                65536
SF          100.6127511 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```



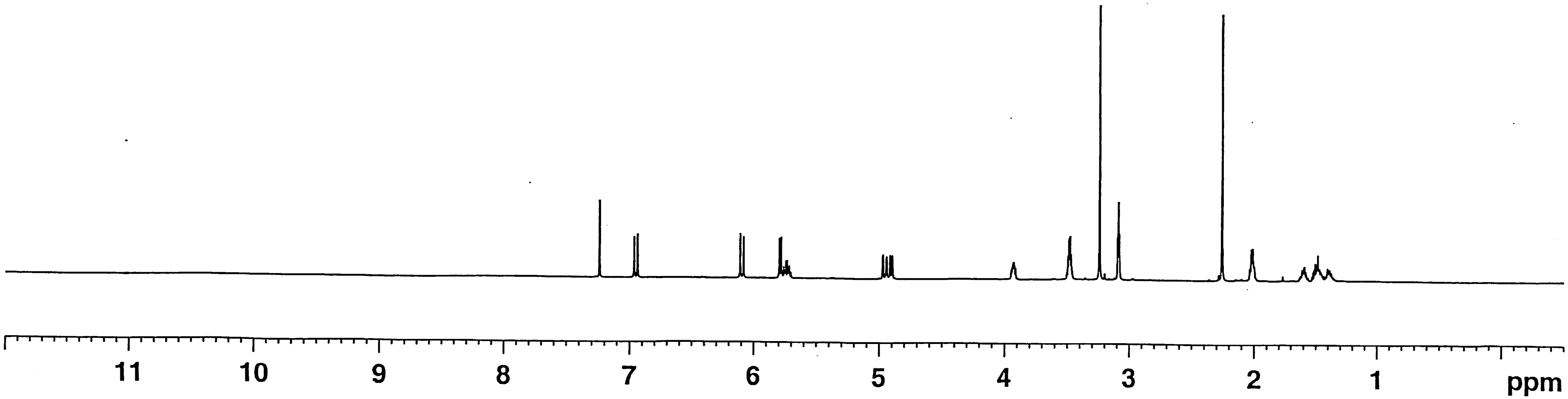
S5



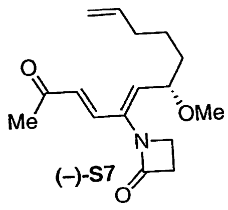
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM             spect
PROBHD    5 mm CPTXI 1H-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     11
DS                      2
SWH             12376.237 Hz
FIDRES           0.188846 Hz
AQ              2.6477044 sec
RG                   12.7
DW                 40.400 usec
DE                   6.00 usec
TE                  304.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                  65536
SF            600.1300277 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



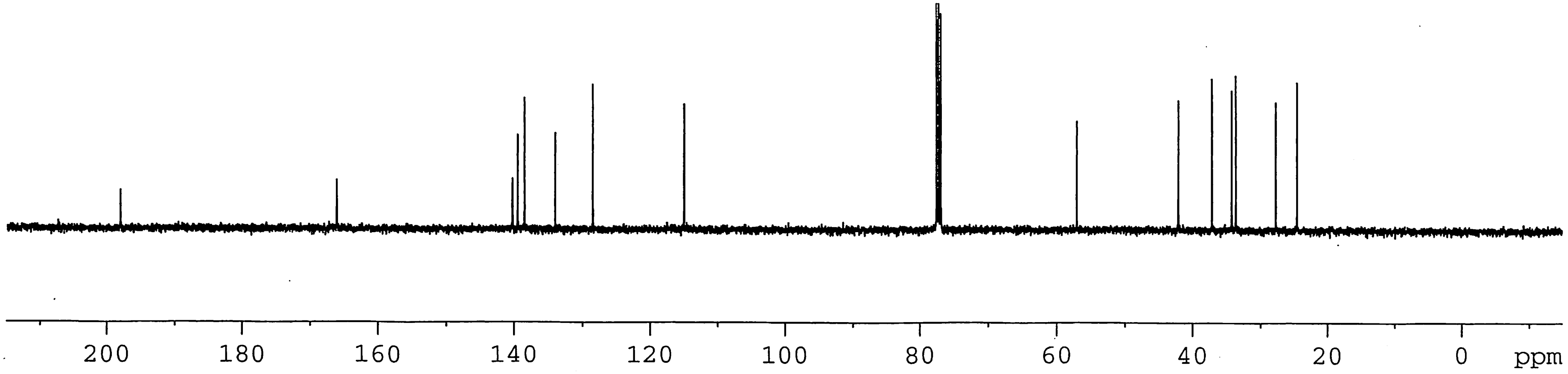
(−)-S7



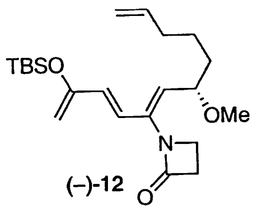
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      85
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  1824.6
DW                  20.850 usec
DE                    6.00 usec
TE                   291.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.38 usec
PL1                   0.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 16.10 dB
PL13                 19.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127562 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```



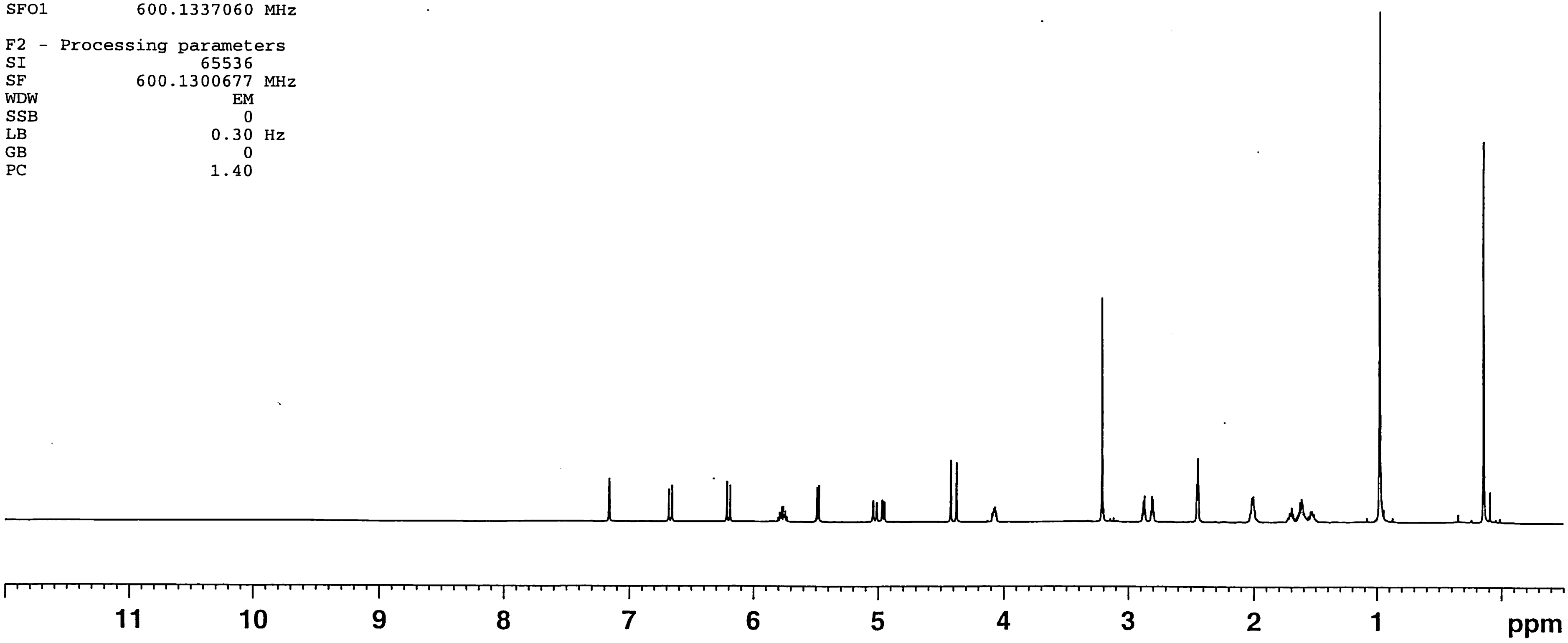
(–)-S7



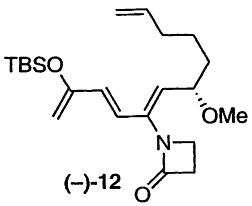
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm CPTXI 1H-
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                      15
DS                       2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ               2.6477044 sec
RG                     6.3
DW                  40.400 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1           600.1337060 MHz

F2 - Processing parameters
SI                   65536
SF             600.1300677 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.40
```



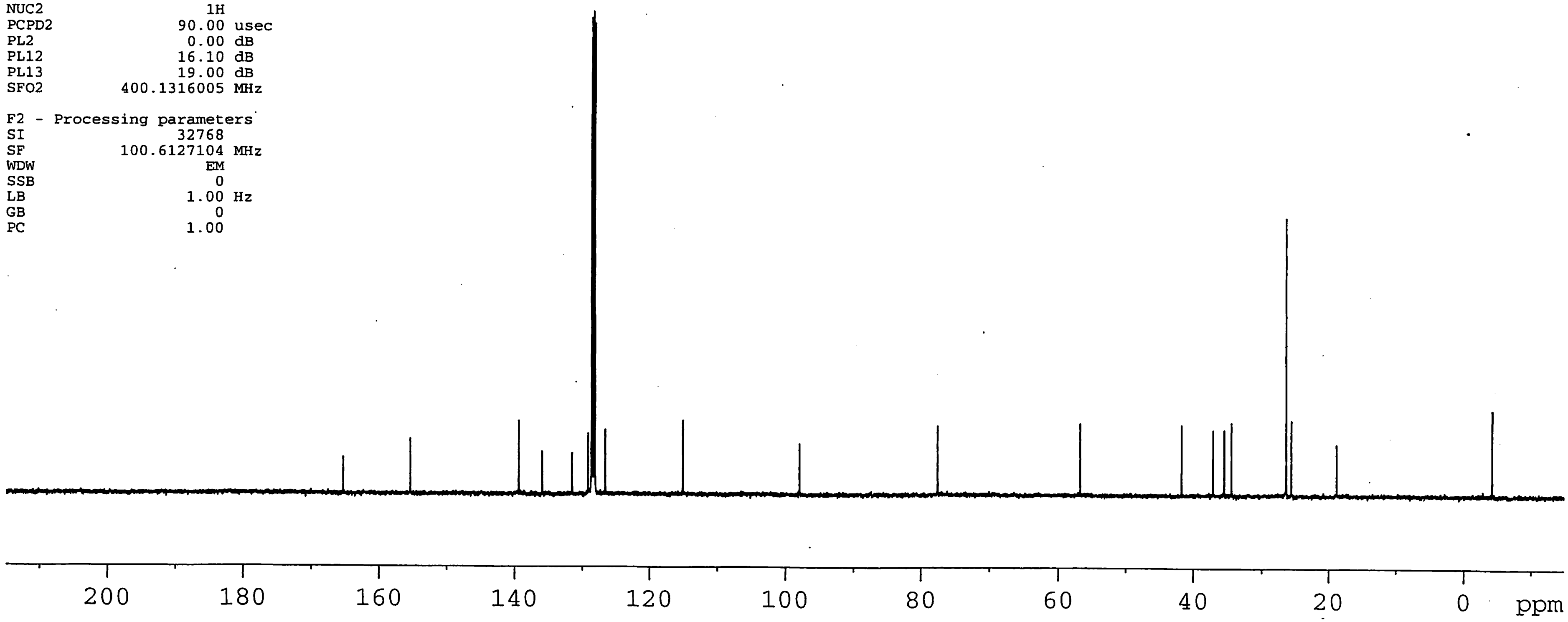
(–)-12



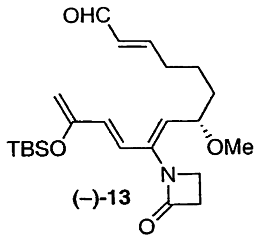
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD    5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      40
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  1625.5
DW                  20.850 usec
DE                    6.00 usec
TE                   291.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.38 usec
PL1                   0.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 16.10 dB
PL13                 19.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF          100.6127104 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```



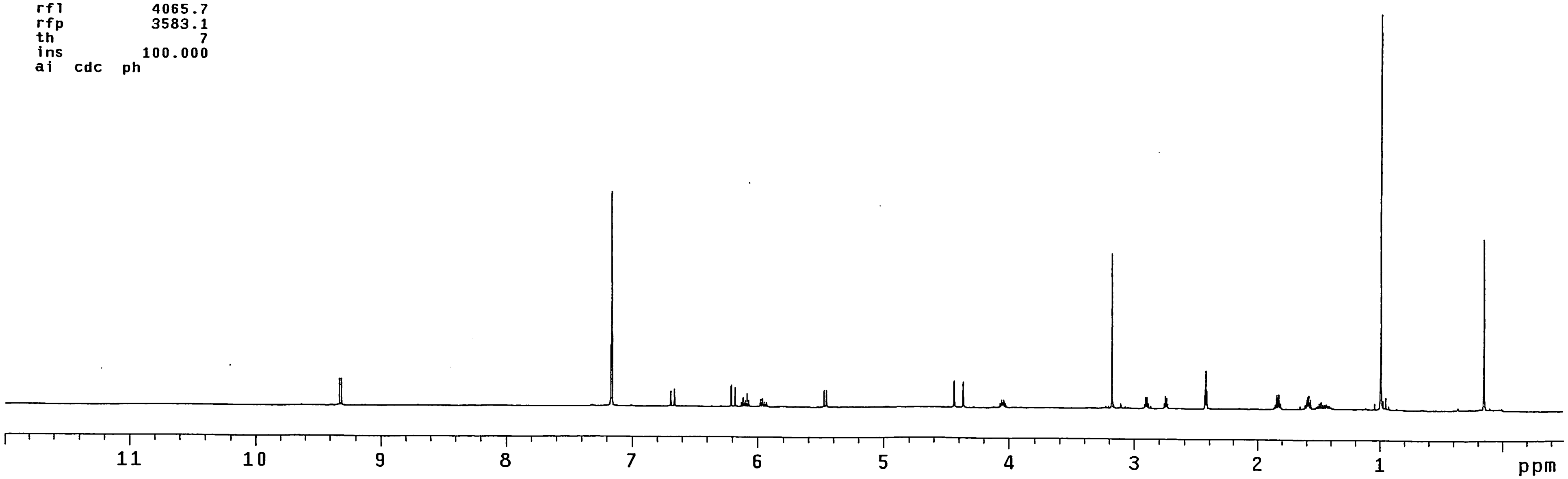
(–)-12

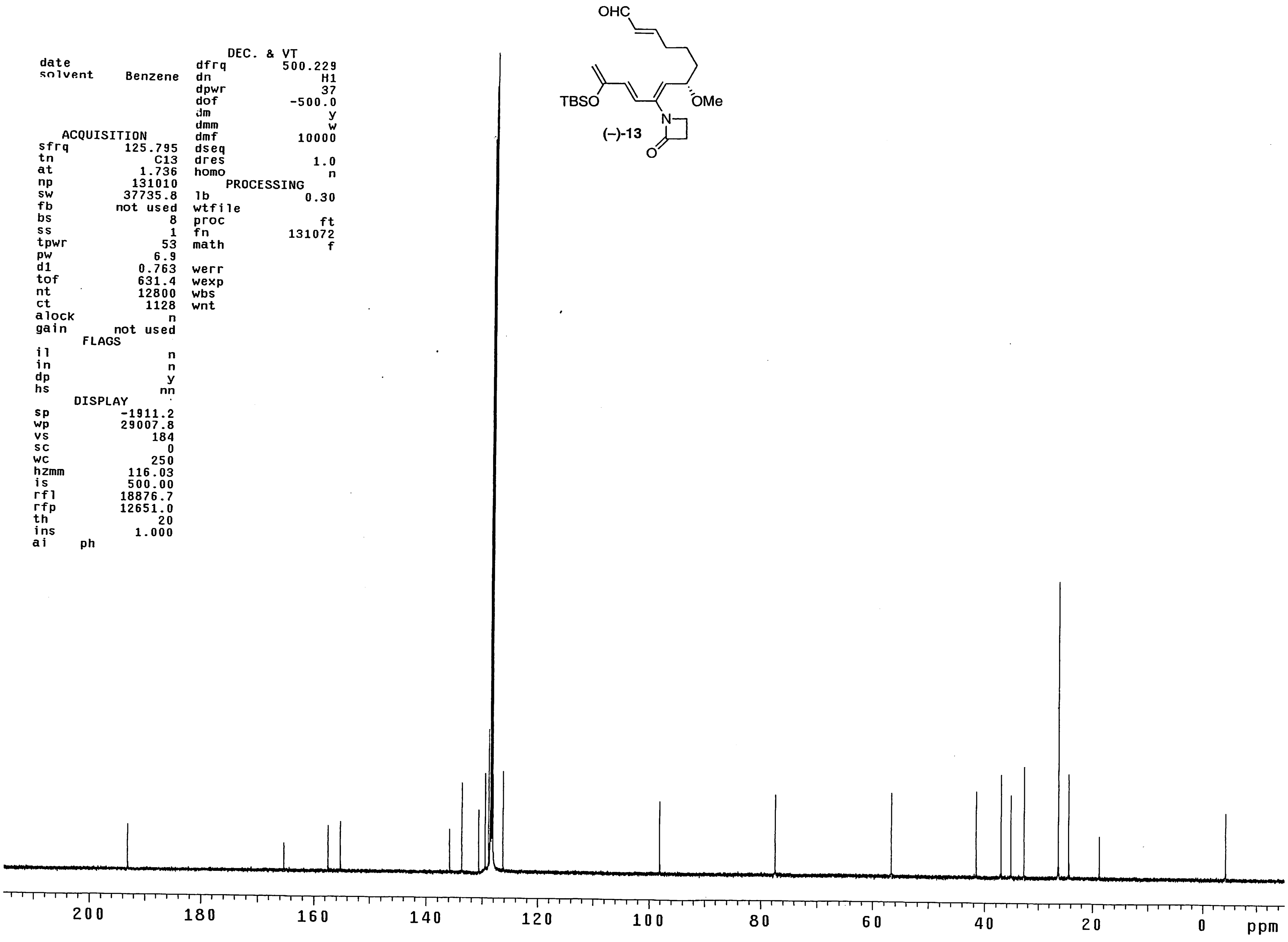


```
                             DEC. & VT
date                    dfrq       125.845
solvent       Benzene   dn             C13
                        dpwr            30
                        dof              0
                        dm             nnn
                        dmm              c
   ACQUISITION          dmf            200
sfrq          500.435   dseq
tn                 H1   dres           1.0
at              4.999   homo             n
np             120102      PROCESSING
sw            12012.0   wtfile
fb           not used   proc            ft
bs                  8   fn          262144
tpwr               56   math             f
pw                8.0
d1              0.100   werr
tof            3003.2   wexp
nt                 16   wbs
ct                 16   wnt            wft
alock               n
gain         not used
      FLAGS
il                  n
in                  n
dp                  y
hs                 nn
     DISPLAY
sp             -250.2
wp             6255.3
vs                 14
sc                  0
wc                250
hzmm            25.02
is              33.57
rfl            4065.7
rfp            3583.1
th                  7
ins           100.000
ai   cdc  ph
```



(–)-13

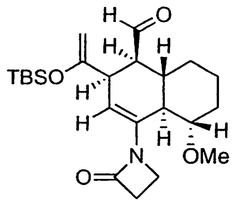




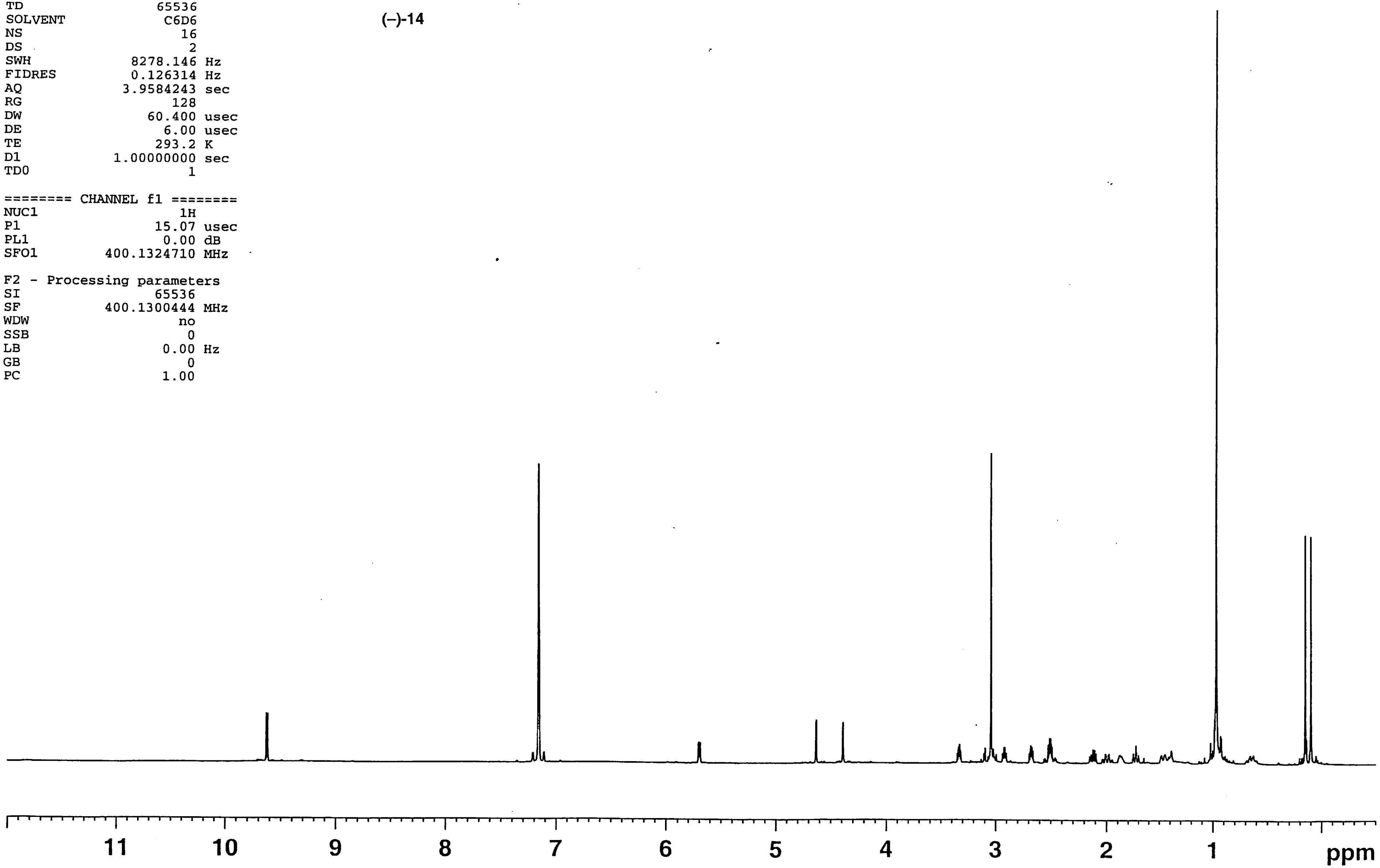
(−)-13

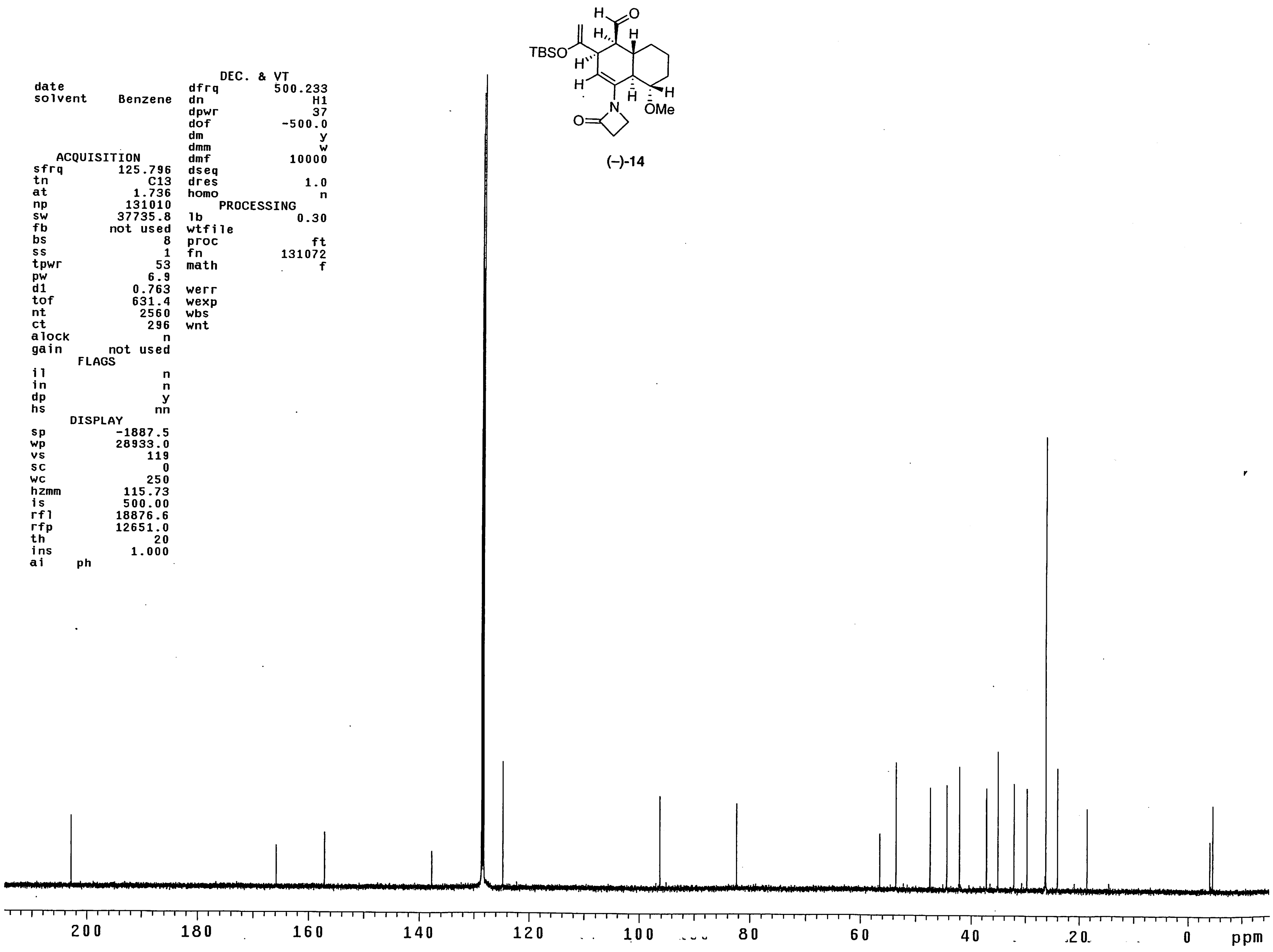
```
date                      DEC. & VT
solvent   Benzene  dfrq      500.229
                   dn             H1
                   dpwr           37
                   dof        -500.0
                   dm              y
                   dmm             w
  ACQUISITION      dmf         10000
sfrq      125.795  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              8  proc           ft
ss              1  fn         131072
tpwr           53  math            f
pw            6.9
d1          0.763  werr
tof         631.4  wexp
nt          12800  wbs
ct           1128  wnt
alock           n
gain     not used
     FLAGS
il              n
in              n
dp              y
hs             nn
    DISPLAY
sp        -1911.2
wp        29007.8
vs            184
sc              0
wc            250
hzmm       116.03
is         500.00
rfl       18876.7
rfp       12651.0
th             20
ins         1.000
ai    ph
```

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT            C6D6
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  128
DW               60.400 usec
DE                 6.00 usec
TE                293.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.07 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                65536
SF          400.1300444 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```



(–)-14

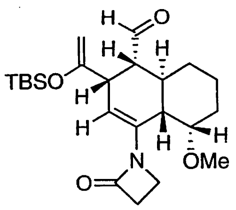




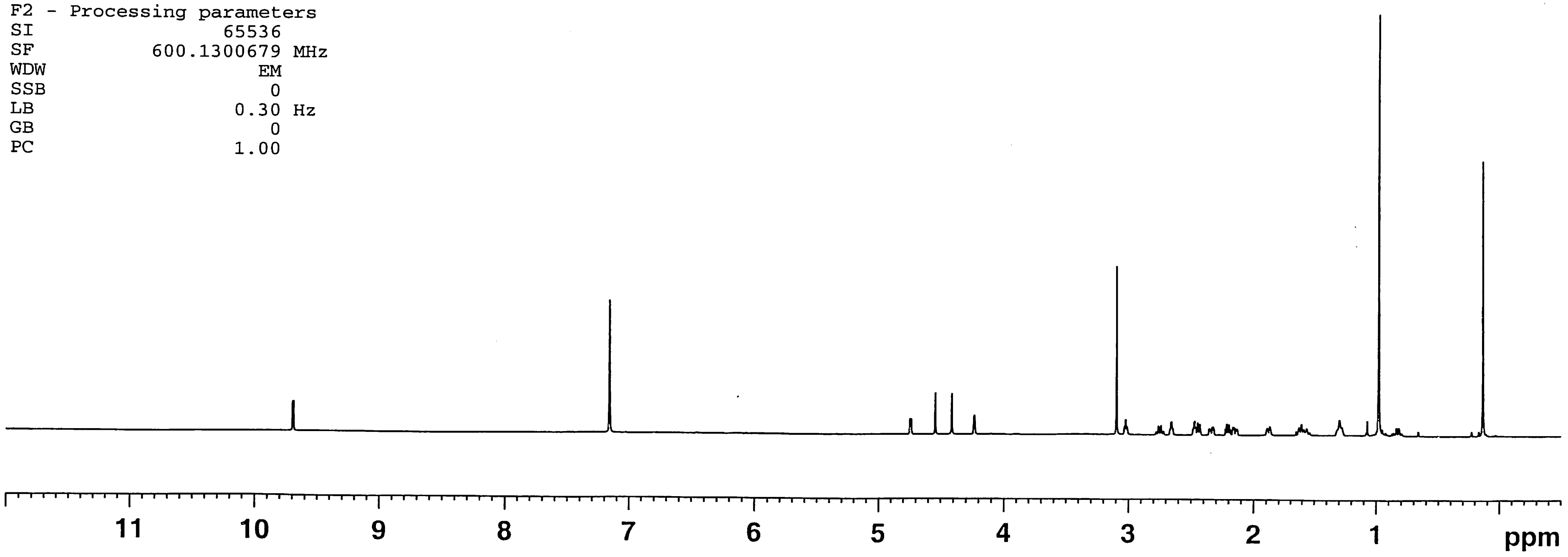
(–)-14

```
date                         DEC. & VT
solvent     Benzene  dfrq          500.233
                     dn                 H1
                     dpwr               37
                     dof            -500.0
                     dm                  y
   ACQUISITION       dmm                 w
sfrq        125.796  dmf             10000
tn              C13  dseq
at            1.736  dres              1.0
np           131010  homo                n
sw          37735.8     PROCESSING
fb         not used  lb               0.30
bs                8  wtfile
ss                1  proc               ft
tpwr             53  fn             131072
pw              6.9  math                f
d1            0.763
tof           631.4  werr
nt             2560  wexp
ct              296  wbs
alock             n  wnt
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -1887.5
wp          28933.0
vs              119
sc                0
wc              250
hzmm         115.73
is           500.00
rfl         18876.6
rfp         12651.0
th               20
ins           1.000
ai    ph
```

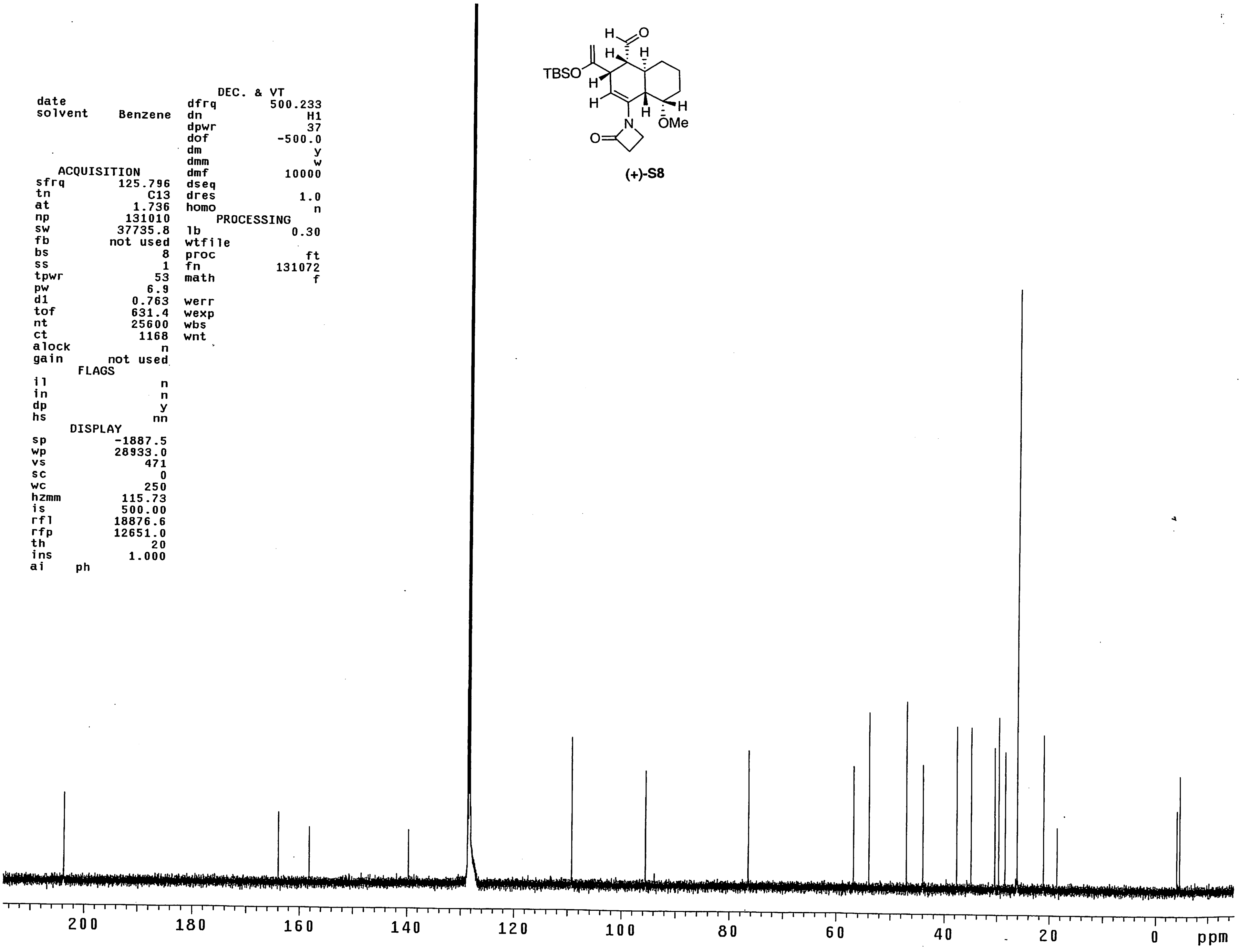
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm CPTXI 1H-
PULPROG               zg30
TD                   65536
SOLVENT               C6D6
NS                      16
DS                       2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ               2.6477044 sec
RG                      18
DW                  40.400 usec
DE                    6.00 usec
TE                   304.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1        600.1337060 MHz

F2 - Processing parameters
SI                   65536
SF          600.1300679 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



(+)-S8



```
date                         DEC. & VT
solvent    Benzene   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               8   proc             ft
ss               1   fn           131072
tpwr            53   math              f
pw             6.9
d1           0.763   werr
tof          631.4   wexp
nt           25600   wbs
ct            1168   wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp         -1887.5
wp         28933.0
vs             471
sc               0
wc             250
hzmm        115.73
is          500.00
rfl        18876.6
rfp        12651.0
th              20
ins          1.000
ai     ph
```



(+)-S8

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD   5 mm CPTXI 1H-
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                  22.6
DW                40.400 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300667 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

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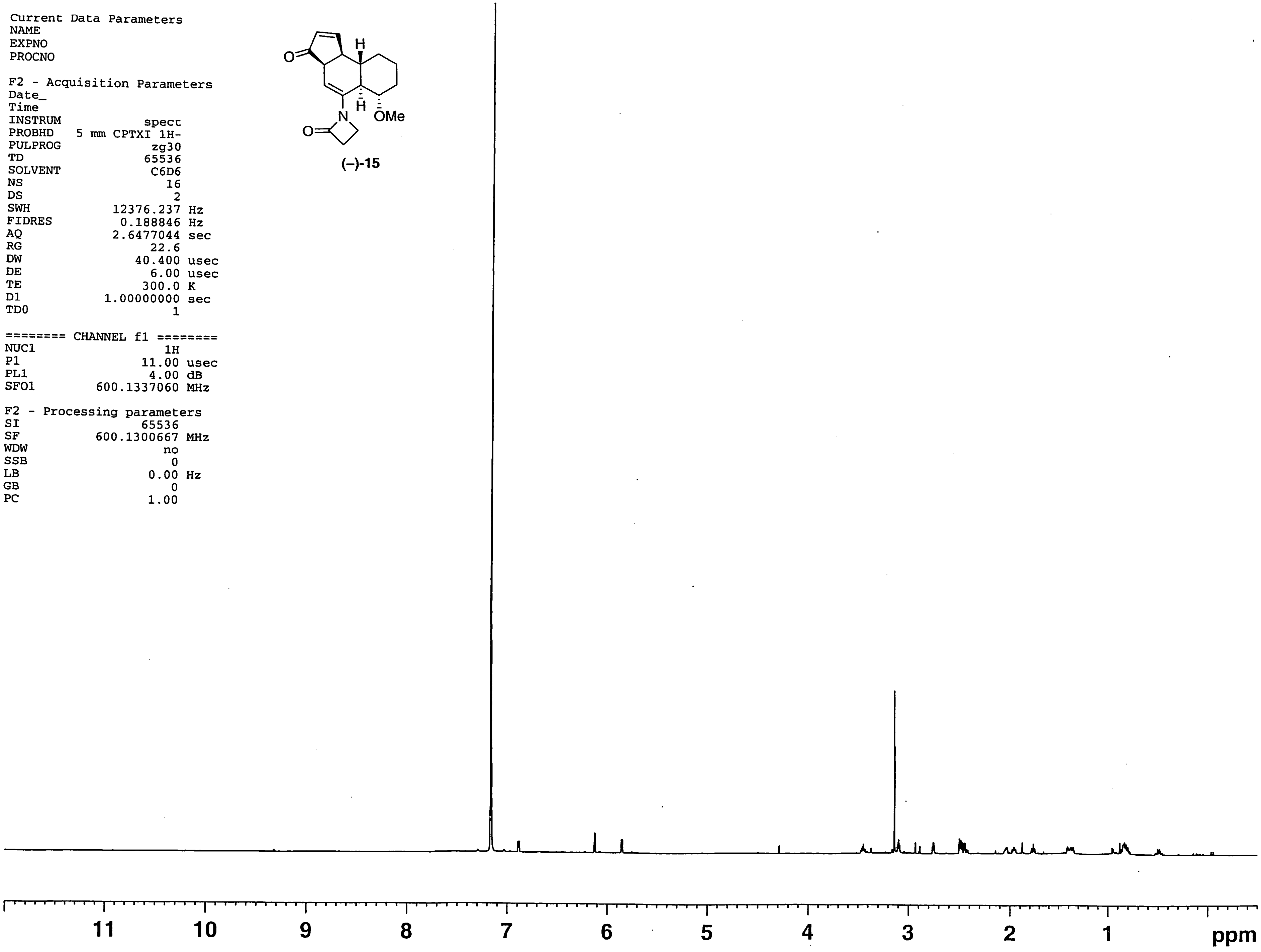
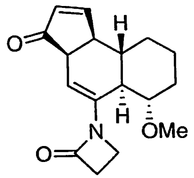
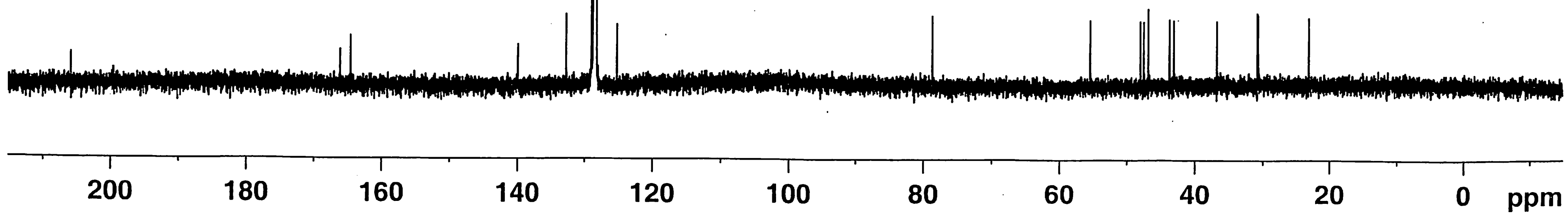


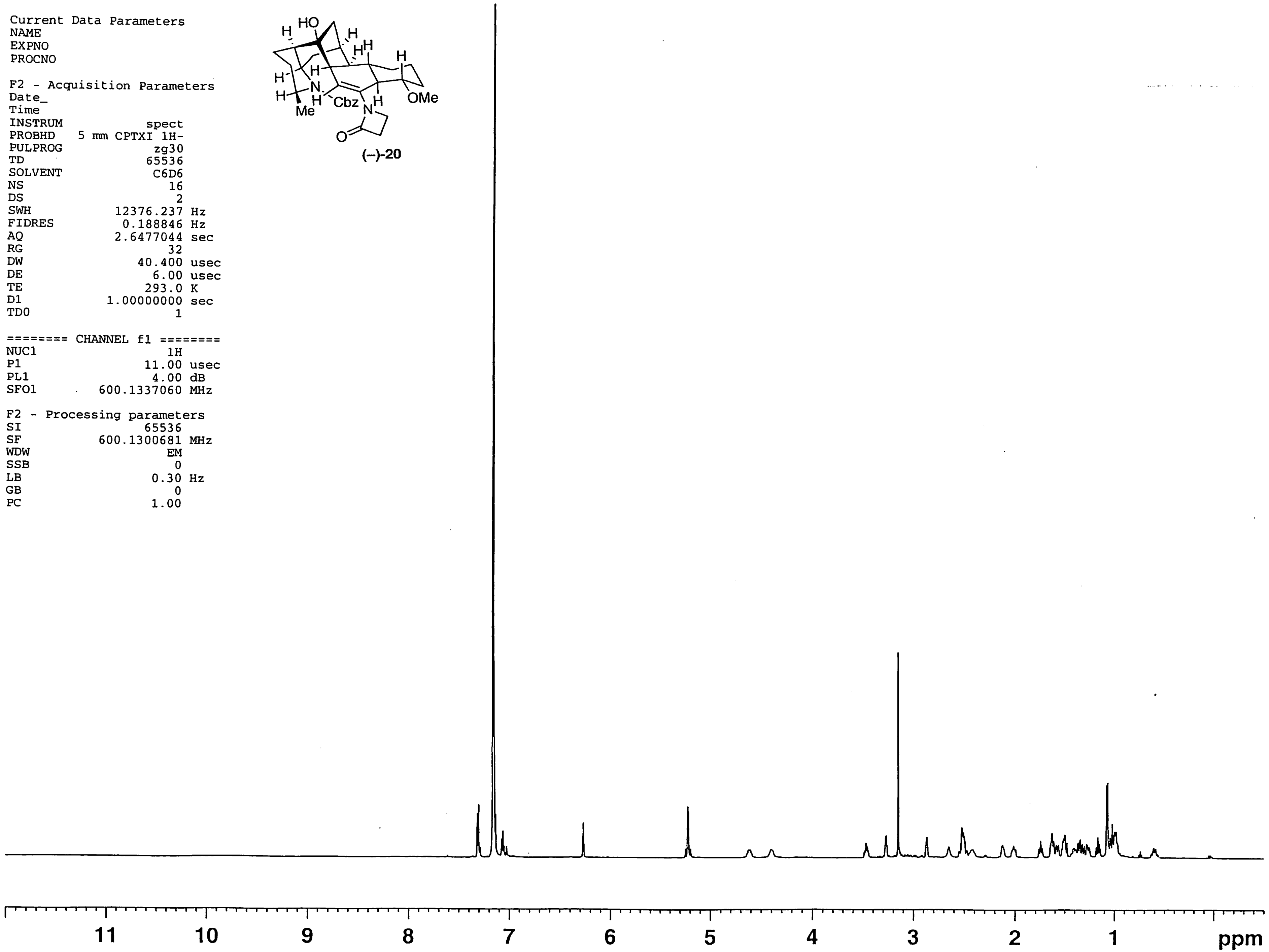
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD   5 mm CPTXI 1H-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110004 sec
RG                14596.5
DW                 13.900 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.00 usec
PL1                  1.60 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  4.00 dB
PL12                22.84 dB
PL13                22.84 dB
SFO2          600.1324005 MHz

F2 - Processing parameters
SI                  65536
SF            150.9027231 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```



(–)-15



```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD    5 mm CPTXI 1H-
PULPROG               zg30
TD                   65536
SOLVENT               C6D6
NS                      16
DS                       2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ               2.6477044 sec
RG                      32
DW                  40.400 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1           600.1337060 MHz

F2 - Processing parameters
SI                   65536
SF             600.1300681 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



(–)-20

```
                               DEC. & VT
date                          rq        500.229
solvent       Benzene       dn              H1
                            dpwr            37
                            dof         -500.0
                            dm               y
                            dmm              w
     ACQUISITION            dmf          10000
sfrq          125.795       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                  8       proc            ft
ss                  1       fn          131072
tpwr               53       math             f
pw                6.9
d1              0.763       werr
tof             631.4       wexp
nt             128000       wbs
ct               3064       wnt
alock               n
gain         not used
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp            -1960.7
wp            29007.8
vs               1238
sc                  0
wc                250
hzmm           116.03
is             500.00
rfl           18876.7
rfp           12651.0
th                 20
ins             1.000
ai     ph
```

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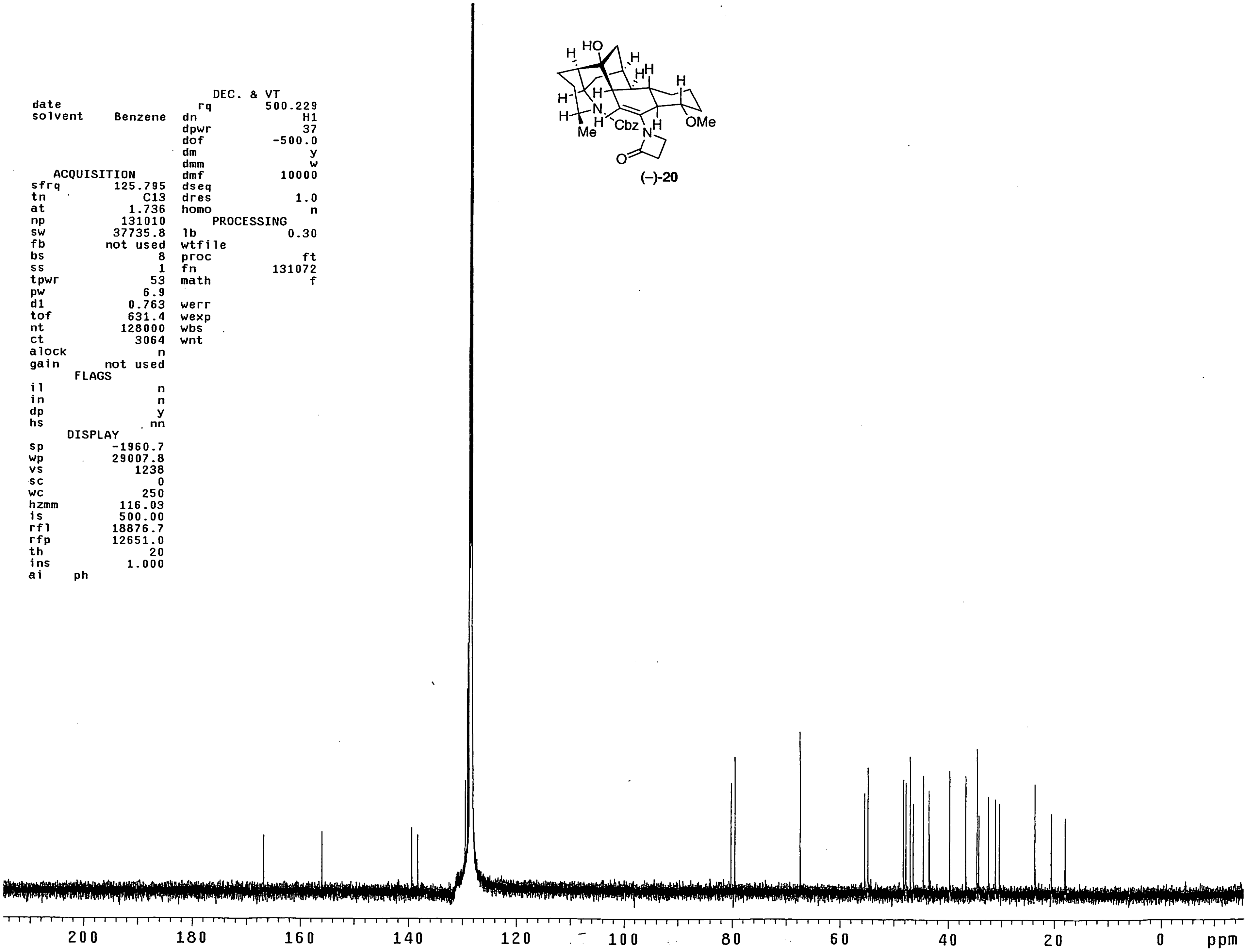

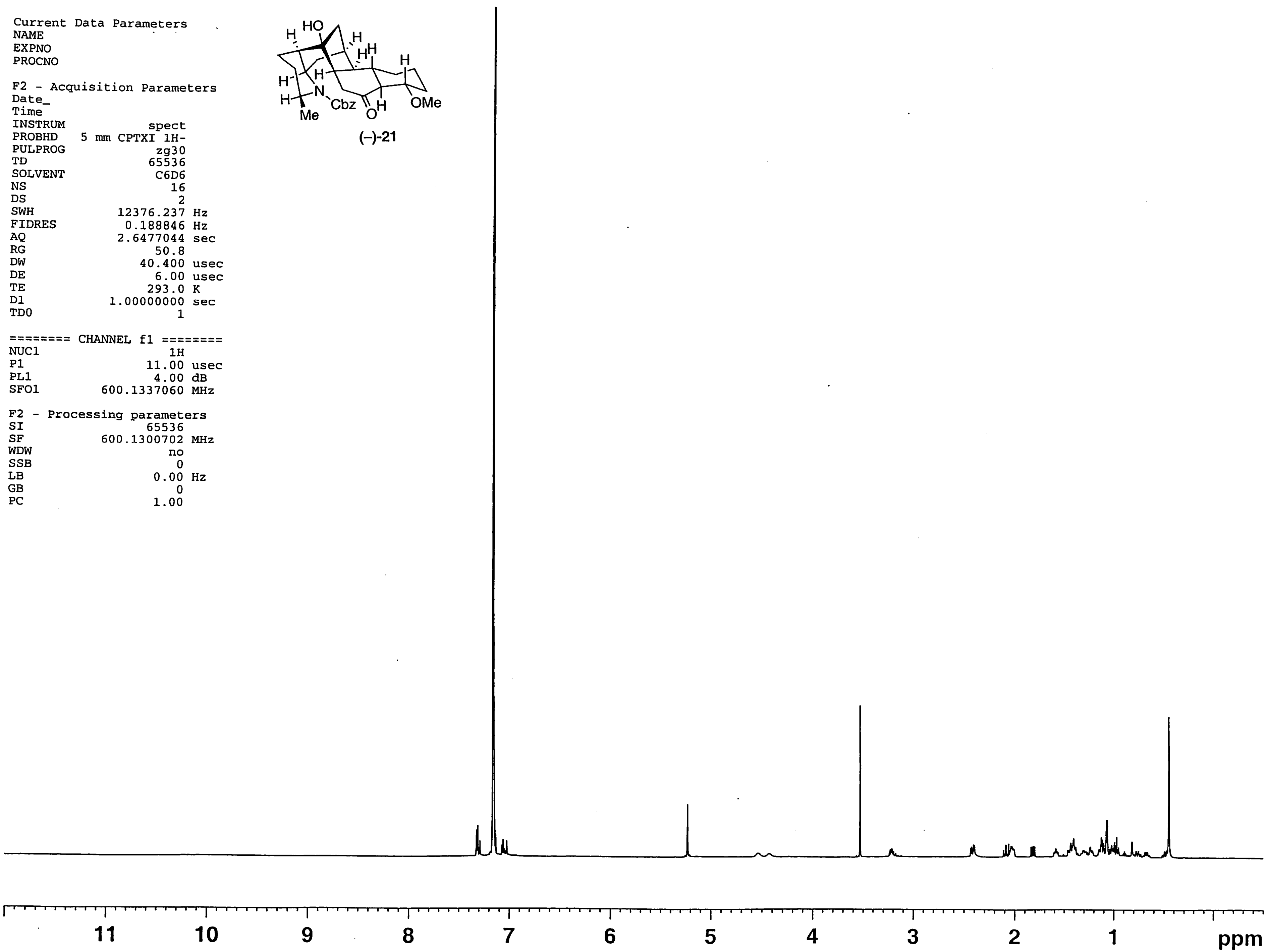

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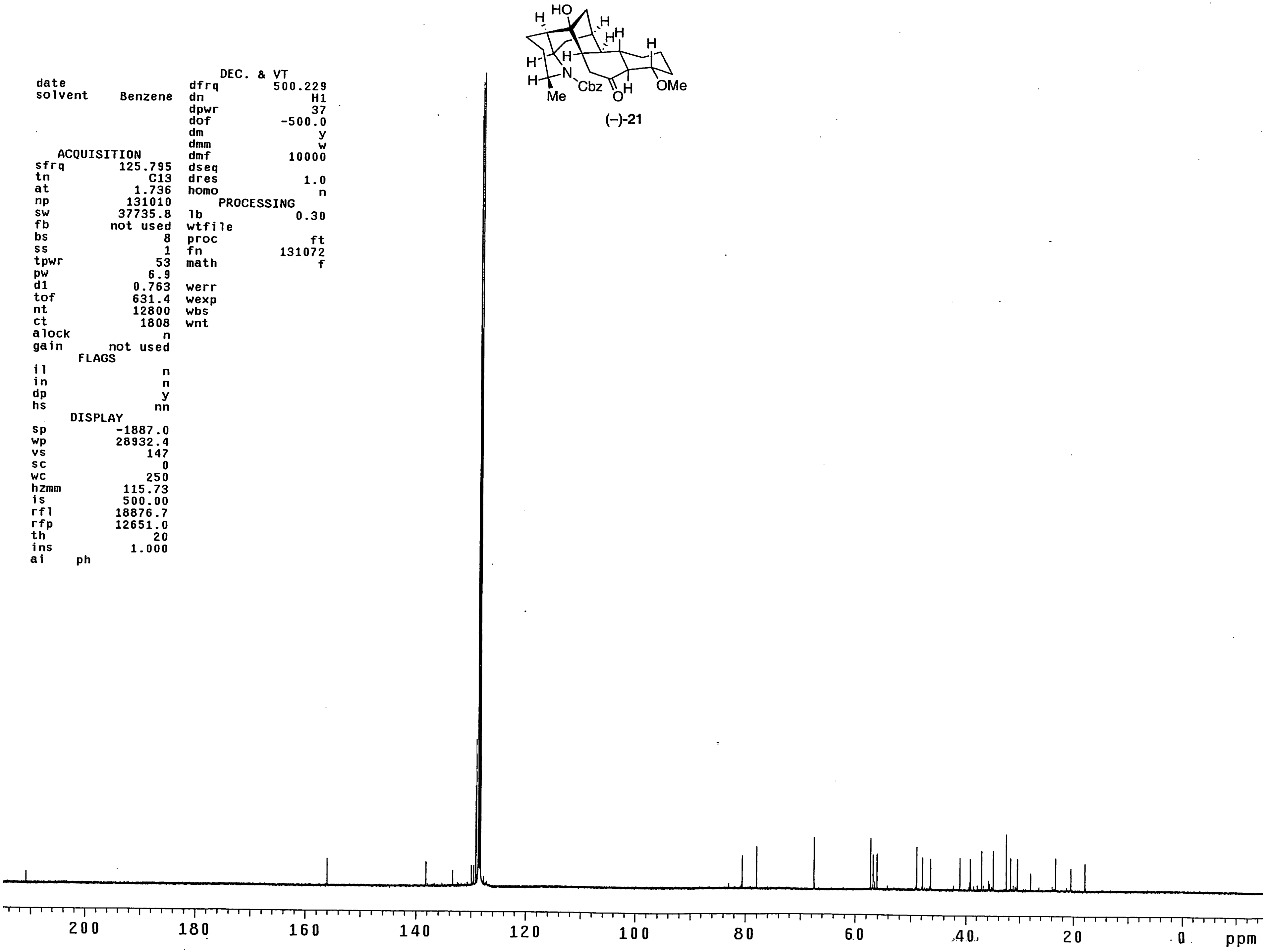
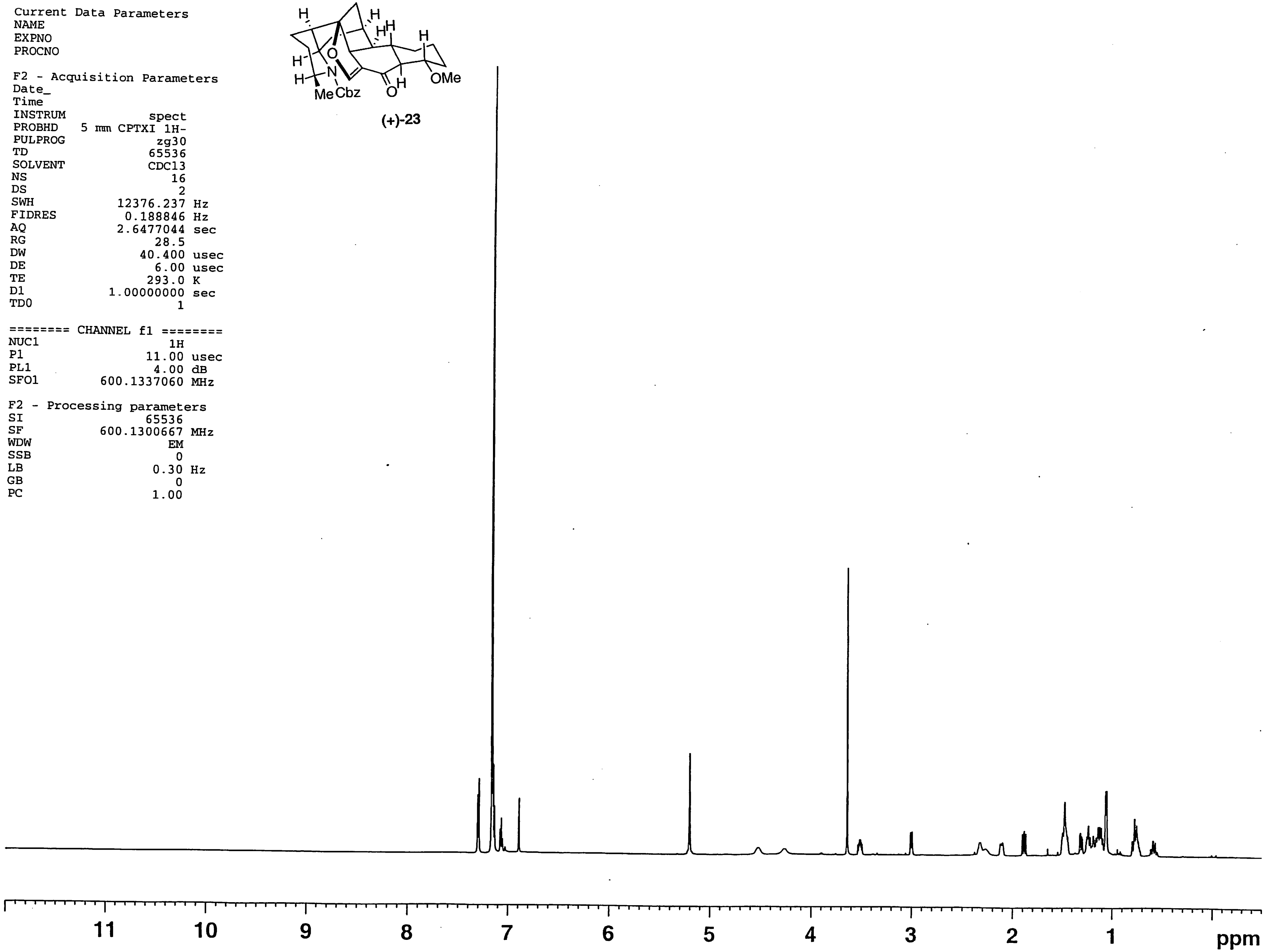
```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD     5 mm CPTXI 1H-
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                  50.8
DW                40.400 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300702 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



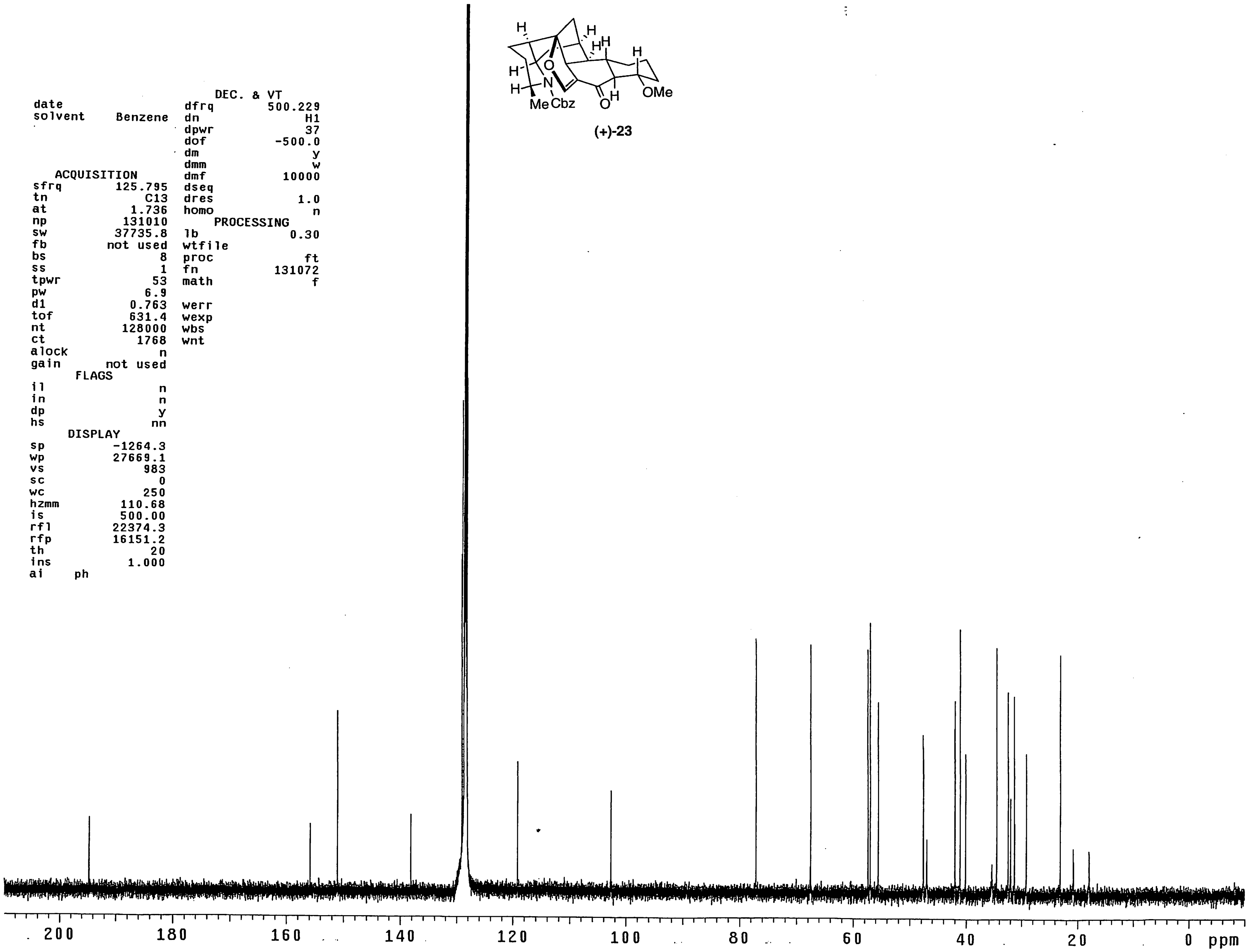
(−)-21

```
                                 DEC. & VT
date                    dfrq        500.229
solvent       Benzene   dn               H1
                        dpwr             37
                        dof          -500.0
                        dm                y
                        dmm               w
     ACQUISITION        dmf           10000
sfrq          125.795   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                  8   proc             ft
ss                  1   fn           131072
tpwr               53   math              f
pw                6.9
d1              0.763   werr
tof             631.4   wexp
nt              12800   wbs
ct               1808   wnt
alock               n
gain         not used
       FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp            -1887.0
wp            28932.4
vs                147
sc                  0
wc                250
hzmm           115.73
is             500.00
rfl           18876.7
rfp           12651.0
th                 20
ins             1.000
ai     ph
```



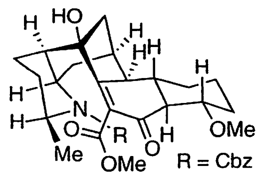
(+)-23

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD   5 mm CPTXI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                  28.5
DW                40.400 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300667 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



(+)-23

```
                            DEC. & VT
date                   dfrq        500.229
solvent     Benzene    dn               H1
                       dpwr             37
                       dof          -500.0
                       dm                y
                       dmm               w
   ACQUISITION         dmf           10000
sfrq        125.795    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                8    proc             ft
ss                1    fn           131072
tpwr             53    math              f
pw              6.9
d1            0.763    werr
tof           631.4    wexp
nt           128000    wbs
ct             1768    wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
      DISPLAY
sp          -1264.3
wp          27669.1
vs              983
sc                0
wc              250
hzmm         110.68
is           500.00
rfl         22374.3
rfp         16151.2
th               20
ins           1.000
ai    ph
```



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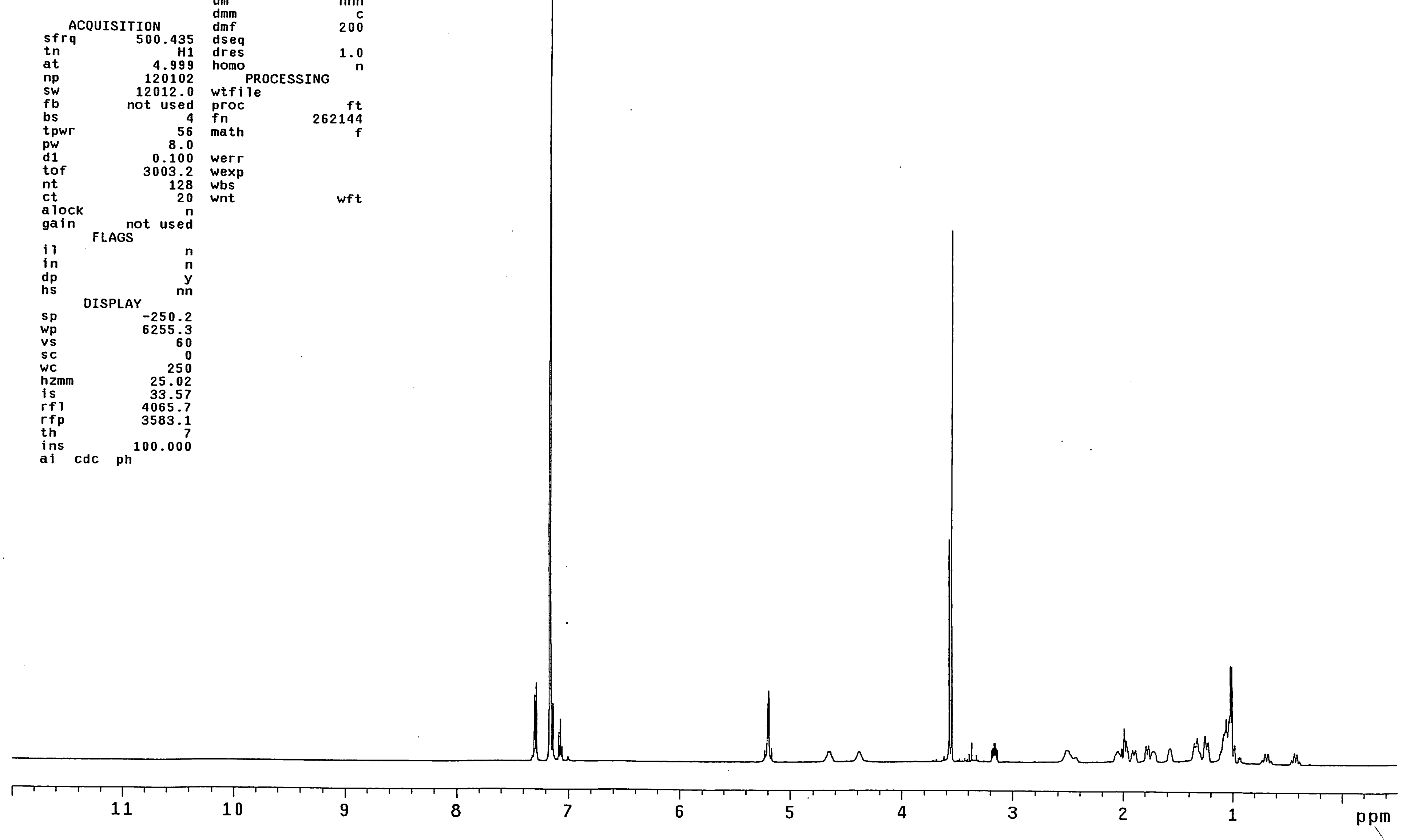
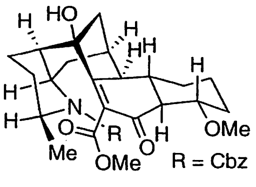


```
date                       DEC. & VT
solvent     Benzene  dfrq        125.845
                     dn              C13
                     dpwr             30
                     dof               0
                     dm              nnn
                     dmm               c
   ACQUISITION       dmf             200
sfrq        500.435  dseq
tn               H1  dres            1.0
at            4.999  homo              n
np           120102     PROCESSING
sw          12012.0  wtfile
fb         not used  proc             ft
bs                4  fn           262144
tpwr             56  math              f
pw              8.0
d1            0.100  werr
tof          3003.2  wexp
nt              128  wbs
ct               20  wnt             wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -250.2
wp           6255.3
vs               60
sc                0
wc              250
hzmm          25.02
is            33.57
rfl          4065.7
rfp          3583.1
th                7
ins         100.000
ai  cdc  ph
```



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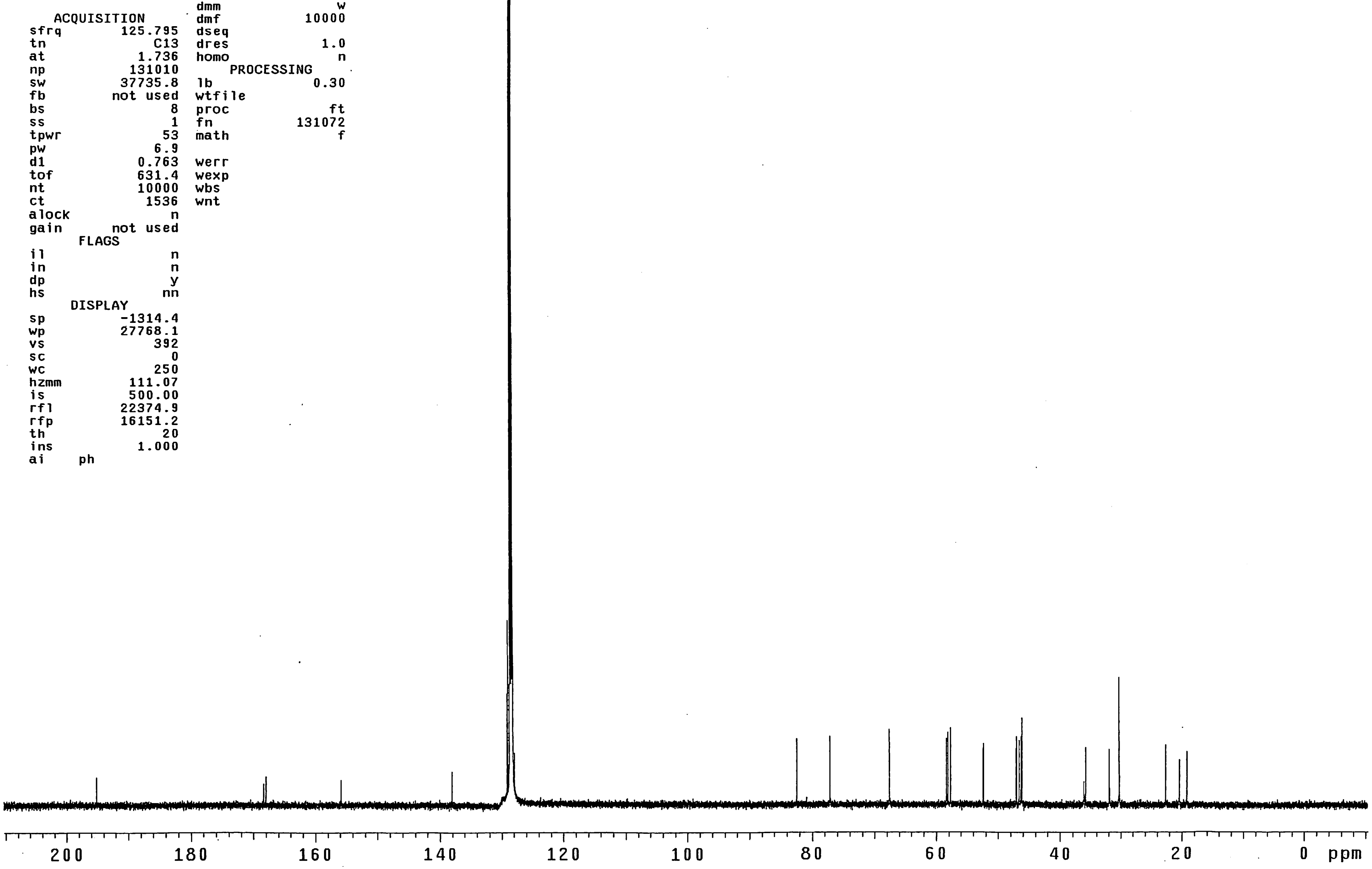
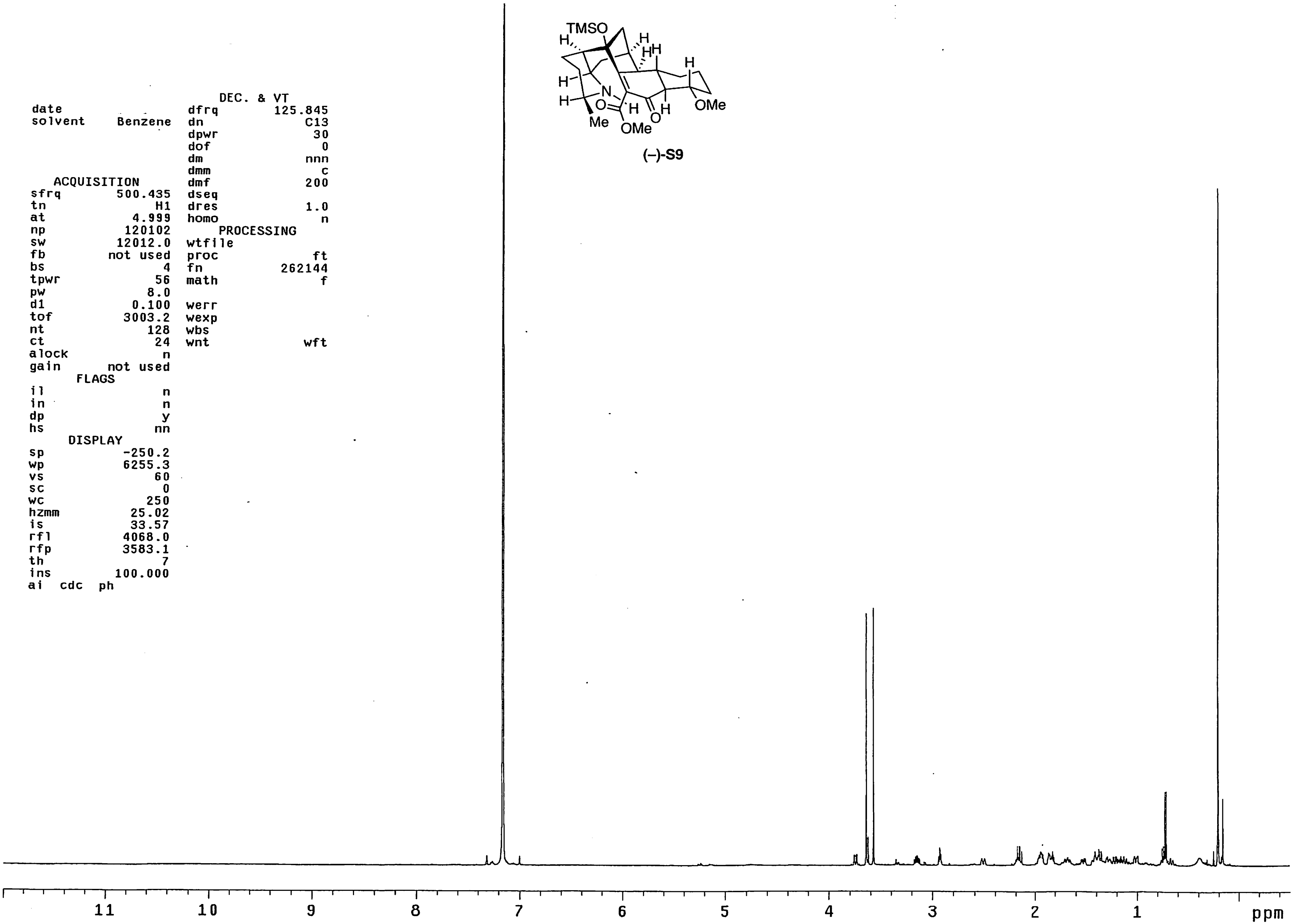
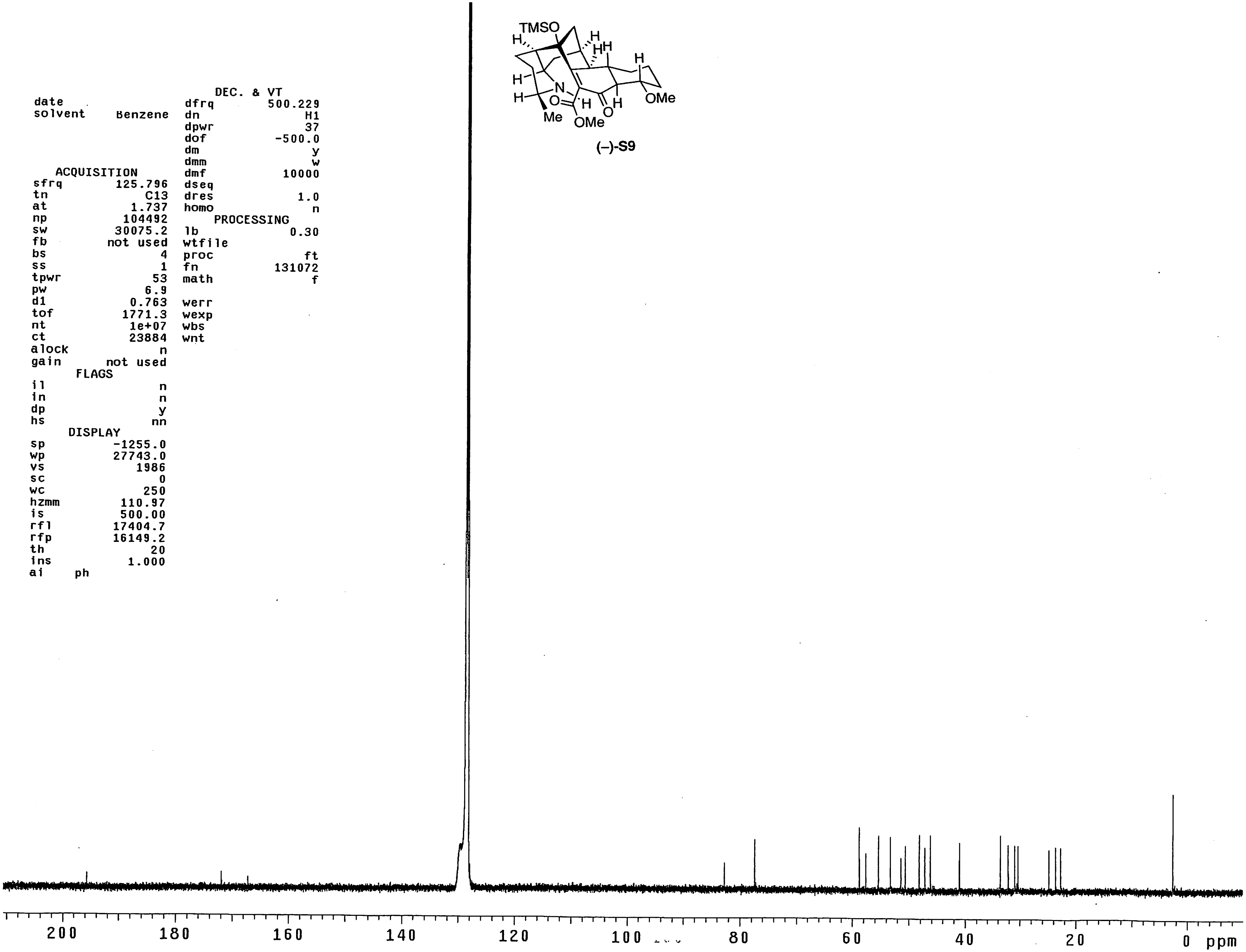
```
                                      DEC. & VT
date                         dfrq         500.229
solvent        Benzene       dn                H1
                             dpwr              37
                             dof           -500.0
                             dm                 y
                             dmm                w
   ACQUISITION               dmf            10000
sfrq           125.795       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                   8       proc              ft
ss                   1       fn            131072
tpwr                53       math               f
pw                 6.9
d1               0.763       werr
tof              631.4       wexp
nt               10000       wbs
ct                1536       wnt
alock                n
gain          not used
      FLAGS
il                   n
in                   n
dp                   y
hs                  nn
     DISPLAY
sp             -1314.4
wp             27768.1
vs                 392
sc                   0
wc                 250
hzmm            111.07
is              500.00
rfl            22374.9
rfp            16151.2
th                  20
ins              1.000
ai     ph
```





(–)-S9

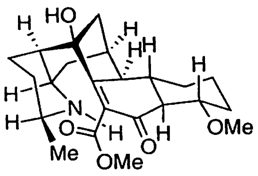
```
date                          DEC. & VT
solvent    Benzene      dfrq        125.845
                        dn              C13
                        dpwr             30
                        dof               0
                        dm              nnn
                        dmm               c
   ACQUISITION          dmf             200
sfrq        500.435     dseq
tn               H1     dres            1.0
at            4.999     homo              n
np           120102        PROCESSING
sw          12012.0     wtfile
fb         not used     proc             ft
bs                4     fn           262144
tpwr             56     math              f
pw              8.0
d1            0.100     werr
tof          3003.2     wexp
nt              128     wbs
ct               24     wnt             wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -250.2
wp           6255.3
vs               60
sc                0
wc              250
hzmm          25.02
is            33.57
rfl          4068.0
rfp          3583.1
th                7
ins         100.000
ai  cdc  ph
```



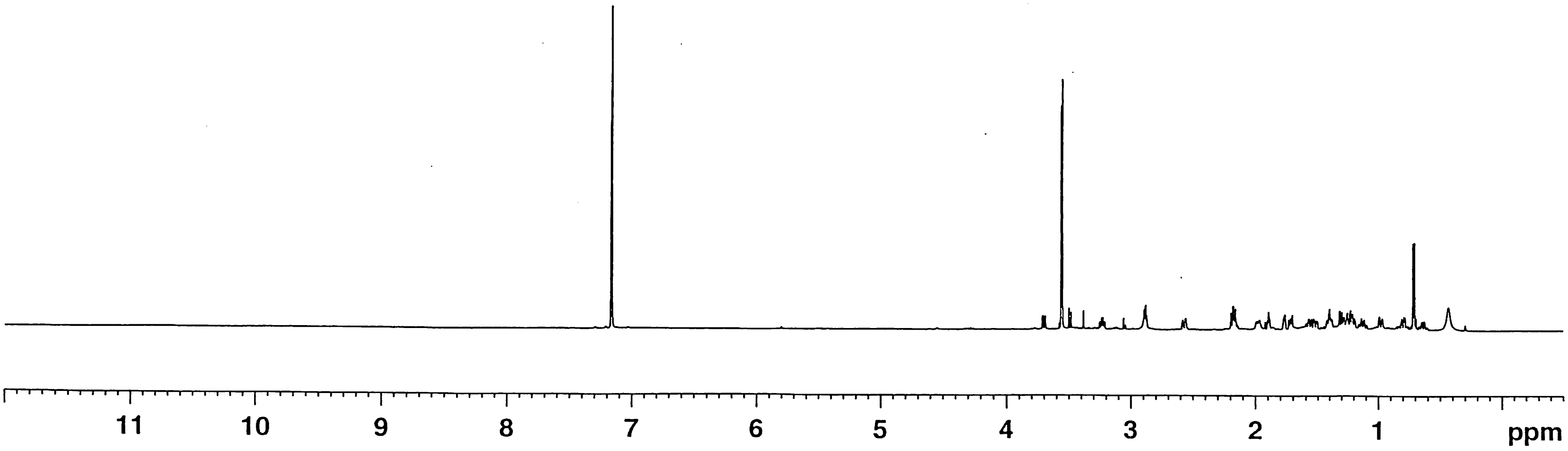
(–)-S9

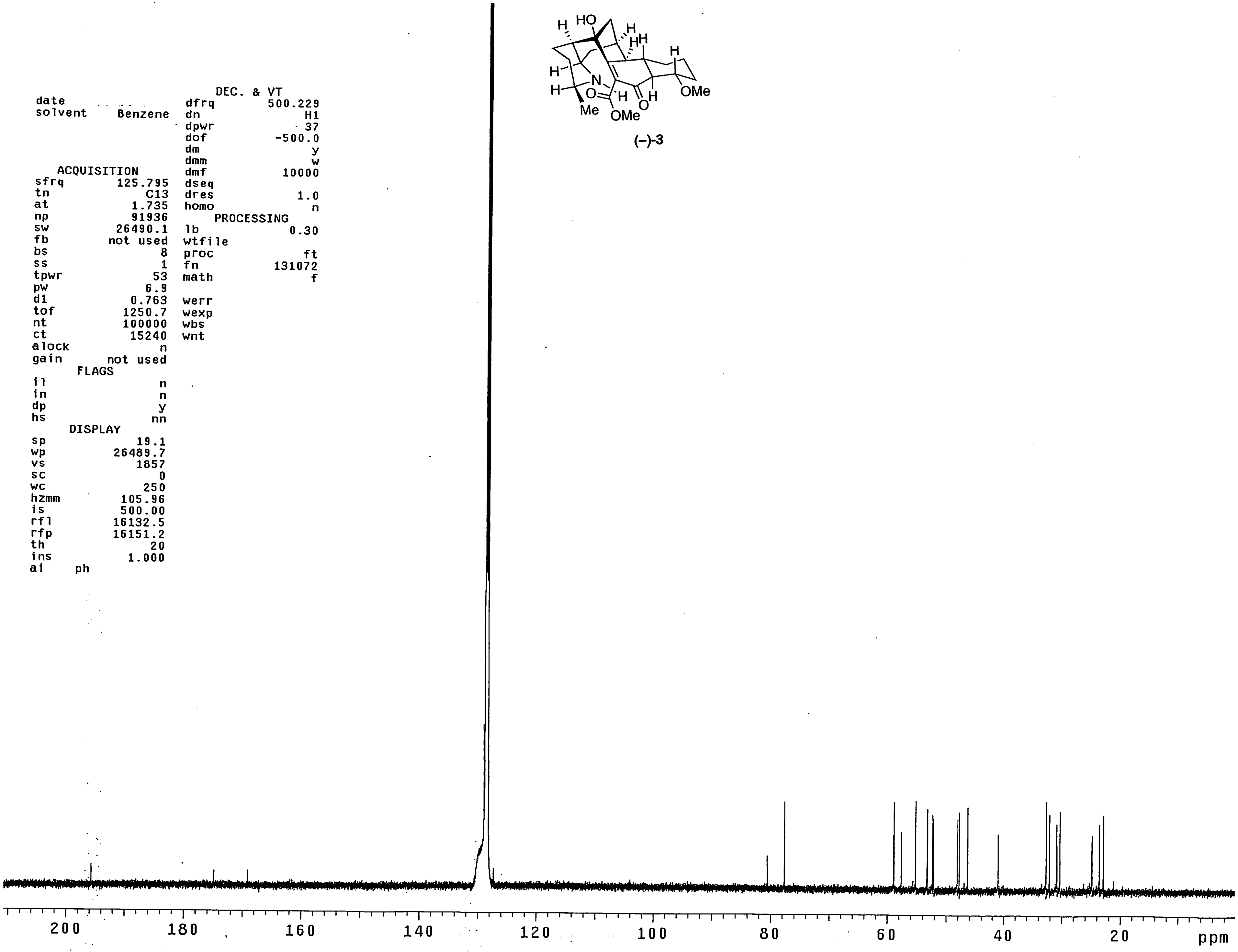
```
date                         DEC. & VT
solvent      Benzene   dfrq        500.229
                       dn               H1
                       dpwr             37
                       dof          -500.0
                       dm                y
                       dmm               w
   ACQUISITION         dmf           10000
sfrq         125.796   dseq
tn               C13   dres            1.0
at             1.737   homo              n
np            104492      PROCESSING
sw           30075.2   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           1771.3   wexp
nt             1e+07   wbs
ct             23884   wnt
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -1255.0
wp           27743.0
vs              1986
sc                 0
wc               250
hzmm          110.97
is            500.00
rfl          17404.7
rfp          16149.2
th                20
ins            1.000
ai    ph
```

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM             spect
PROBHD   5 mm CPTXI 1H-
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                      8
DS                      2
SWH             12376.237 Hz
FIDRES           0.188846 Hz
AQ              2.6477044 sec
RG                   50.8
DW                 40.400 usec
DE                   6.00 usec
TE                  304.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                  65536
SF            600.1300659 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



(–)-3

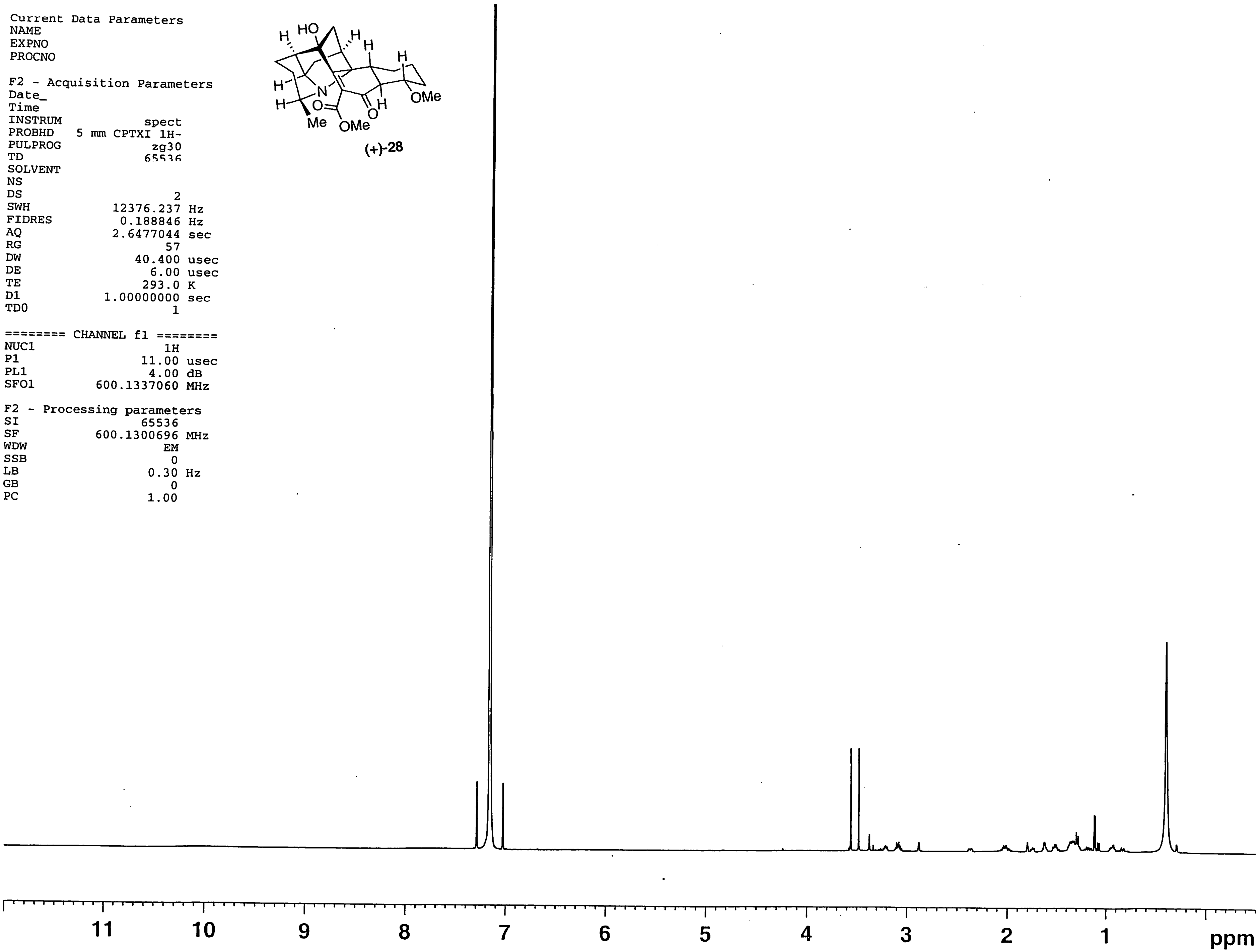




(–)-3

```
date                     DEC. & VT
solvent   Benzene   dfrq        500.229
                    dn               H1
                    dpwr             37
                    dof          -500.0
                    dm                y
                    dmm               w
    ACQUISITION     dmf           10000
sfrq       125.795  dseq
tn             C13  dres            1.0
at           1.735  homo              n
np           91936      PROCESSING
sw         26490.1  lb             0.30
fb        not used  wtfile
bs               8  proc             ft
ss               1  fn           131072
tpwr            53  math              f
pw             6.9
d1           0.763  werr
tof         1250.7  wexp
nt          100000  wbs
ct           15240  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp            19.1
wp         26489.7
vs            1857
sc               0
wc             250
hzmm        105.96
is          500.00
rfl        16132.5
rfp        16151.2
th              20
ins          1.000
ai    ph
```

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM             spect
PROBHD   5 mm CPTXI 1H-
PULPROG              zg30
TD                  65536
SOLVENT
NS
DS                      2
SWH             12376.237 Hz
FIDRES           0.188846 Hz
AQ              2.6477044 sec
RG                     57
DW                 40.400 usec
DE                   6.00 usec
TE                  293.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                  65536
SF            600.1300696 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



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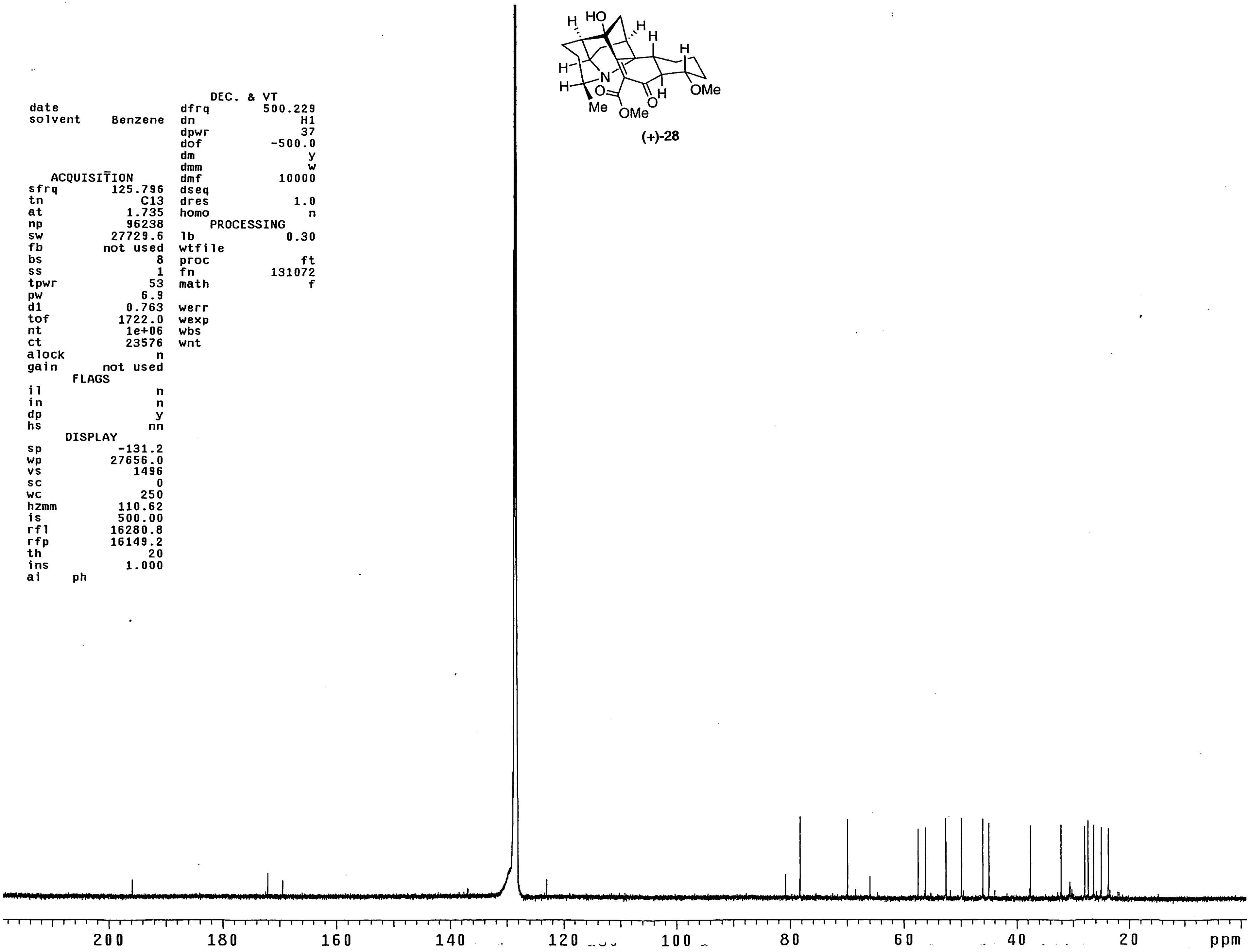
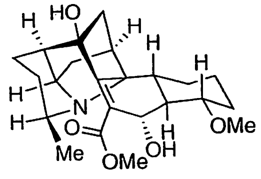
```
                          DEC. & VT
date                 dfrq       500.229
solvent     Benzene  dn              H1
                     dpwr            37
                     dof         -500.0
                     dm               y
                     dmm              w
   ACQUISITION       dmf          10000
sfrq        125.796  dseq
tn              C13  dres           1.0
at            1.735  homo             n
np            96238     PROCESSING
sw          27729.6  lb            0.30
fb         not used  wtfile
bs                8  proc            ft
ss                1  fn          131072
tpwr             53  math             f
pw              6.9
d1            0.763  werr
tof          1722.0  wexp
nt           1e+06   wbs
ct            23576  wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -131.2
wp          27656.0
vs             1496
sc                0
wc              250
hzmm         110.62
is           500.00
rfl         16280.8
rfp         16149.2
th               20
ins           1.000
ai    ph
```

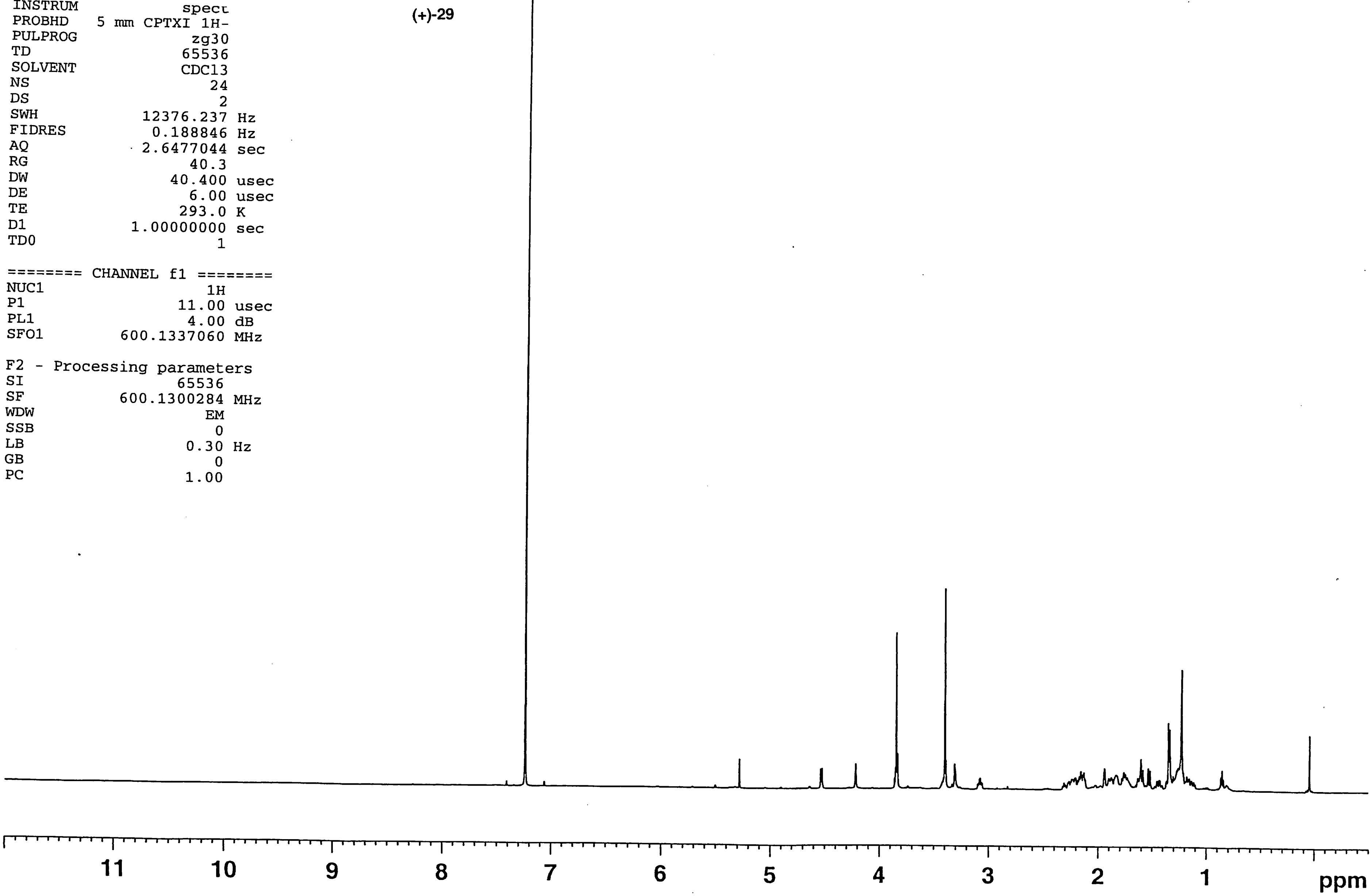


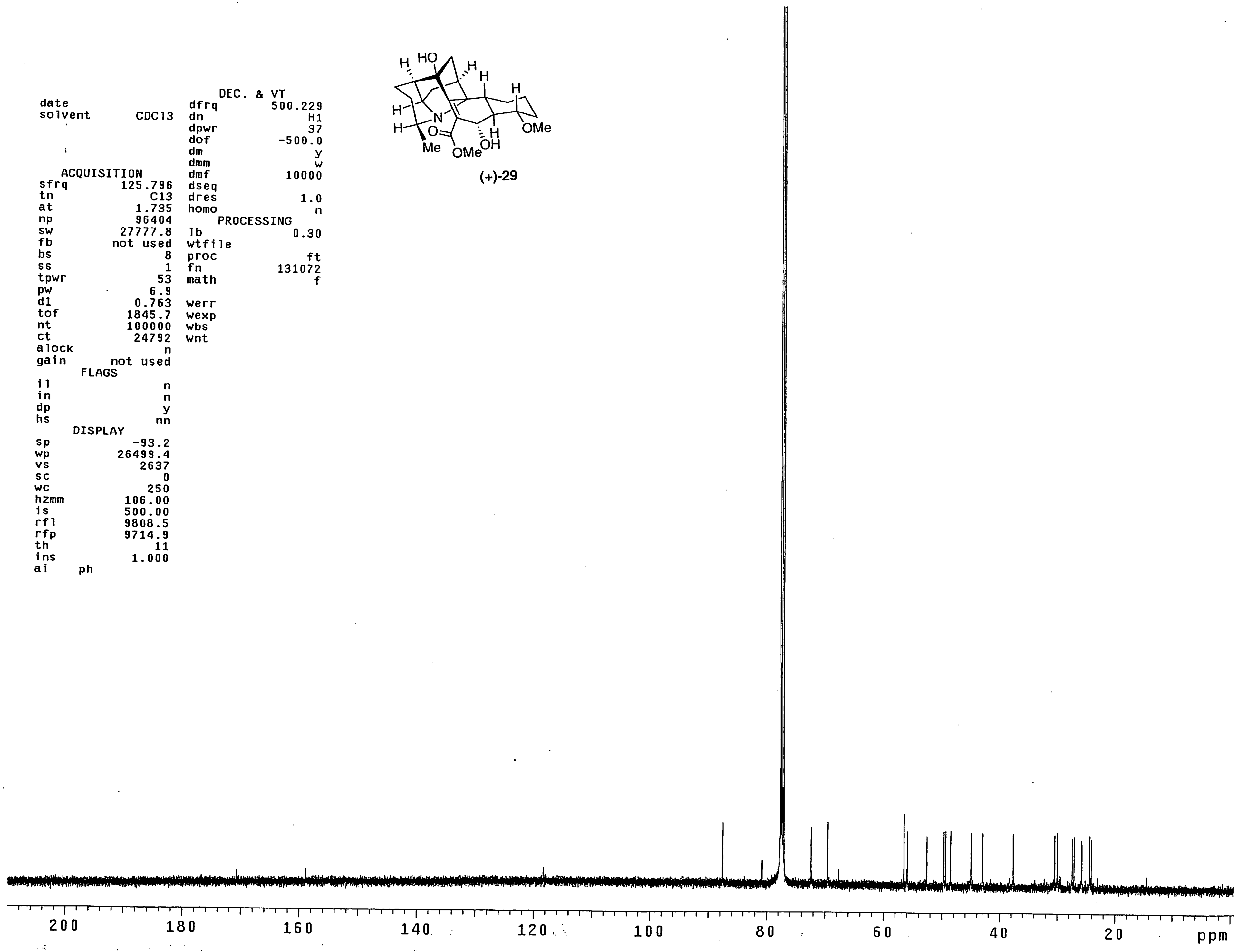
(+)-28

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM            spect
PROBHD   5 mm CPTXI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    24
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477044 sec
RG                  40.3
DW                40.400 usec
DE                  6.00 usec
TE                 293.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                 4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300284 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



(+)-29

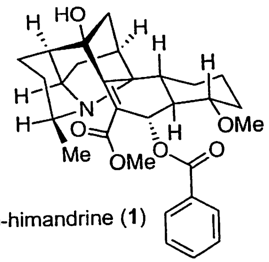




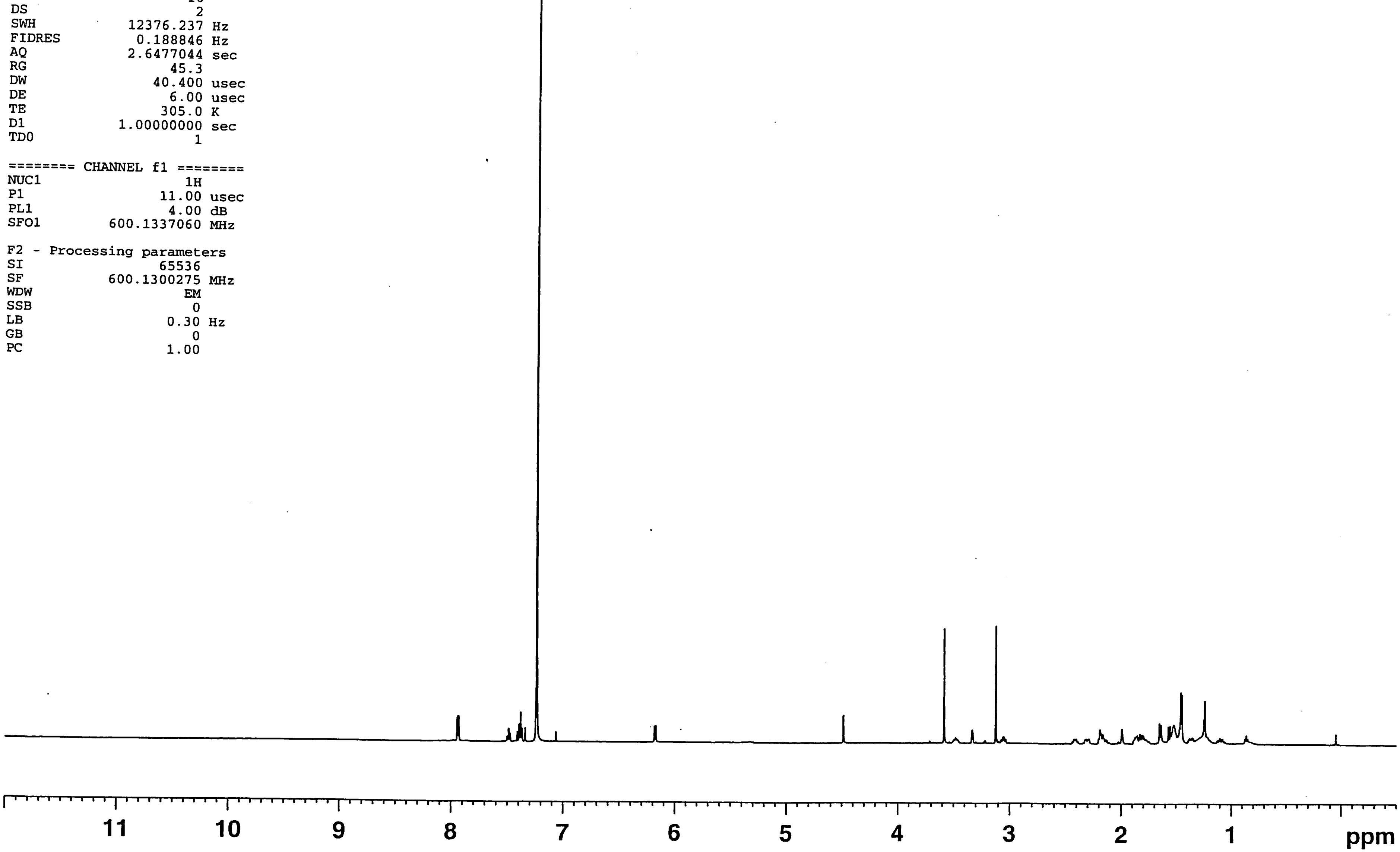
```
date                             DEC. & VT
solvent        CDC13     dfrq          500.229
                         dn                 H1
                         dpwr               37
                         dof            -500.0
                         dm                  y
                         dmm                 w
    ACQUISITION          dmf             10000
sfrq           125.796   dseq
tn                 C13   dres              1.0
at               1.735   homo                n
np               96404       PROCESSING
sw             27777.8   lb               0.30
fb            not used   wtfile
bs                   8   proc               ft
ss                   1   fn             131072
tpwr                53   math                f
pw                 6.9
d1               0.763   werr
tof             1845.7   wexp
nt              100000   wbs
ct               24792   wnt
alock                n
gain          not used
       FLAGS
il                   n
in                   n
dp                   y
hs                  nn
      DISPLAY
sp               -93.2
wp             26499.4
vs                2637
sc                   0
wc                 250
hzmm            106.00
is              500.00
rfl             9808.5
rfp             9714.9
th                  11
ins              1.000
ai    ph
```

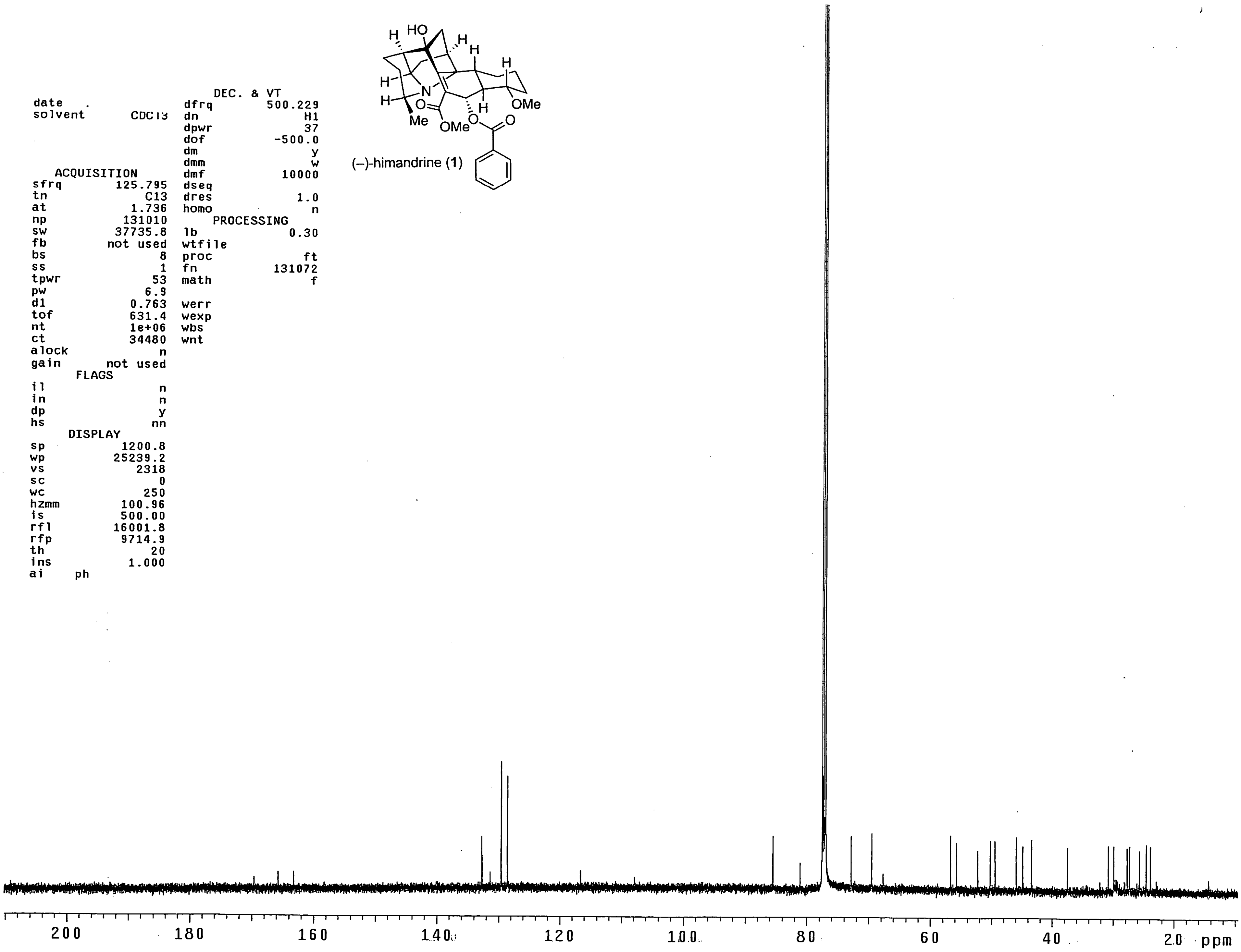
(+)-29

```
Current Data Parameters
NAME
EXPNO
PROCNO

F2 - Acquisition Parameters
Date_
Time
INSTRUM              spect
PROBHD    5 mm CPTXI 1H-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ               2.6477044 sec
RG                    45.3
DW                  40.400 usec
DE                    6.00 usec
TE                   305.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1           600.1337060 MHz

F2 - Processing parameters
SI                   65536
SF             600.1300275 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



(–)-himandrine (1)





(–)-himandrine (**1**)

```
date    .                    DEC. & VT
solvent       CDCl3   dfrq         500.229
                      dn                H1
                      dpwr              37
                      dof           -500.0
                      dm                 y
                      dmm                w
   ACQUISITION        dmf            10000
sfrq         125.795  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                 8  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             34480  wnt
alock              n
gain        not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp            1200.8
wp           25239.2
vs              2318
sc                 0
wc               250
hzmm          100.96
is            500.00
rfl          16001.8
rfp           9714.9
th                20
ins            1.000
ai     ph
```