

Supporting Information for
Absolute Configuration of Scyphostatin

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^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-400 or Varian 400 spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet. Infrared spectra were recorded on a JASCO FT-IR-8900 spectrometer. Optical rotations were measured on a JASCO P-1030 polarimeter. Mass spectra were obtained on a JEOL HX-100, an SX-102A or a JMS-AX-505H mass spectrometer.

Compound 2

Colorless oil. $[\alpha]_{\text{D}}^{23}$ -2.5 (*c* 1.0, CHCl_3). ^1H NMR (400MHz, CDCl_3): 0.80 (3H, d, $J = 6.5\text{Hz}$), 0.84 (3H, t, $J = 7.4\text{Hz}$), 0.90 (3H, d, $J = 6.7\text{Hz}$), 0.98-1.05 (1H, m), 1.00 (3H, d, $J = 6.7\text{Hz}$), 1.14-1.24 (1H, m), 1.27-1.38 (1H, m), 1.51-1.61 (1H, m), 1.52 (3H, d, $J = 1.3\text{Hz}$), 1.76 (1H, dd, $J = 7.4$ and 13.1Hz), 1.88 (1H, dd, $J = 7.0$ and 13.1Hz), 2.20-2.27 (1H, m), 2.29-2.34 (1H, m), 3.74 (3H, s), 4.84 (1H, dd, $J = 1.3$ and 9.4Hz), 5.73 (1H, dd, $J = 8.5$ and 15.2Hz), 5.84 (1H, d, $J = 15.3\text{Hz}$), 6.10 (1H, dd, $J = 10.7$ and 15.2Hz), 6.22 (1H, dd, $J = 11.3$ and 14.9Hz), 6.52 (1H, dd, $J = 10.7$ and 14.9Hz), 7.31 (1H, dd, $J = 11.3$ and 15.3Hz). ^{13}C NMR (100MHz, CDCl_3): 12.1, 16.2, 19.5, 21.1, 21.4, 28.4, 30.6, 34.1, 35.0, 44.0, 48.4, 51.5, 119.5, 127.8, 128.3, 132.1, 133.1, 141.5, 145.1, 146.4, 167.7. IR (CHCl_3): 2959, 2919, 2871, 1703, 1616, 1457, 1436, 1267, 1134, 1007 cm^{-1} . HRMS: calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_2(\text{M}^+)$: 318.2559; found: 318.2541.

Compound 4

Colorless oil. $[\alpha]_{\text{D}}^{23}$ -7.0 (*c* 0.53, CHCl_3). ^1H NMR (400MHz, CDCl_3): 0.96 (3H, d, $J = 6.4\text{Hz}$), 1.04 (3H, d, $J = 6.7\text{Hz}$), 1.11-1.18 (1H, m), 1.39-1.45 (1H, m), 1.96-2.04 (1H, m), 2.12 (3H, s), 2.15-2.26 (2H, m), 2.43 (1H, dd, $J = 4.7$ and 15.5Hz), 4.10 (1H, dd, $J = 6.7$ and 10.8Hz), 4.24 (1H, dd, $J = 5.4$ and 10.8Hz), 7.43-7.48 (2H, m), 7.55-7.59 (1H, m), 8.04-8.06 (2H, m). ^{13}C NMR (100MHz, CDCl_3): 18.9, 21.7, 27.9, 31.5, 31.6, 42.2, 52.1, 70.6, 129.3, 130.5, 131.4, 133.8, 167.5, 209.4. IR (CHCl_3): 2963, 2931, 1713, 1603, 1278, 1114 cm^{-1} . HRMS: calcd. for $\text{C}_{16}\text{H}_{23}\text{O}_3(\text{M}+\text{H}^+)$: 263.1647; found: 263.1649.

Compound 8

Colorless oil. $[\alpha]_{\text{D}}^{23}$ -7.0 (*c* 2.35, CHCl_3). ^1H NMR (400MHz, CDCl_3): 0.95 (3H, d, $J = 6.4\text{Hz}$), 1.03 (3H, d, $J = 6.7\text{Hz}$), 1.10-1.17 (1H, m), 1.38-1.45 (1H, m), 1.96-2.04 (1H, m), 2.12 (3H, s), 2.14-2.26 (2H, m), 2.42 (1H, dd, $J = 4.7$ and 15.5Hz), 4.10 (1H, dd, $J = 6.7$ and 10.8Hz), 4.24 (1H, dd, $J = 5.4$ and 10.8Hz), 7.43-7.47 (2H, m), 7.54-7.58 (1H, m), 8.03-8.05 (2H, m). ^{13}C NMR (100MHz, CDCl_3): 18.8, 21.6, 27.8, 31.4, 31.5, 42.1, 52.0, 70.6, 129.4, 130.5, 131.4, 133.9, 167.6, 209.6. IR (CHCl_3): 2963, 2932, 1713, 1603, 1278, 1115 cm^{-1} . HRMS: calcd. for $\text{C}_{16}\text{H}_{23}\text{O}_3(\text{M}+\text{H}^+)$: 263.1647; found: 263.1647.

Compound (-)-**9**

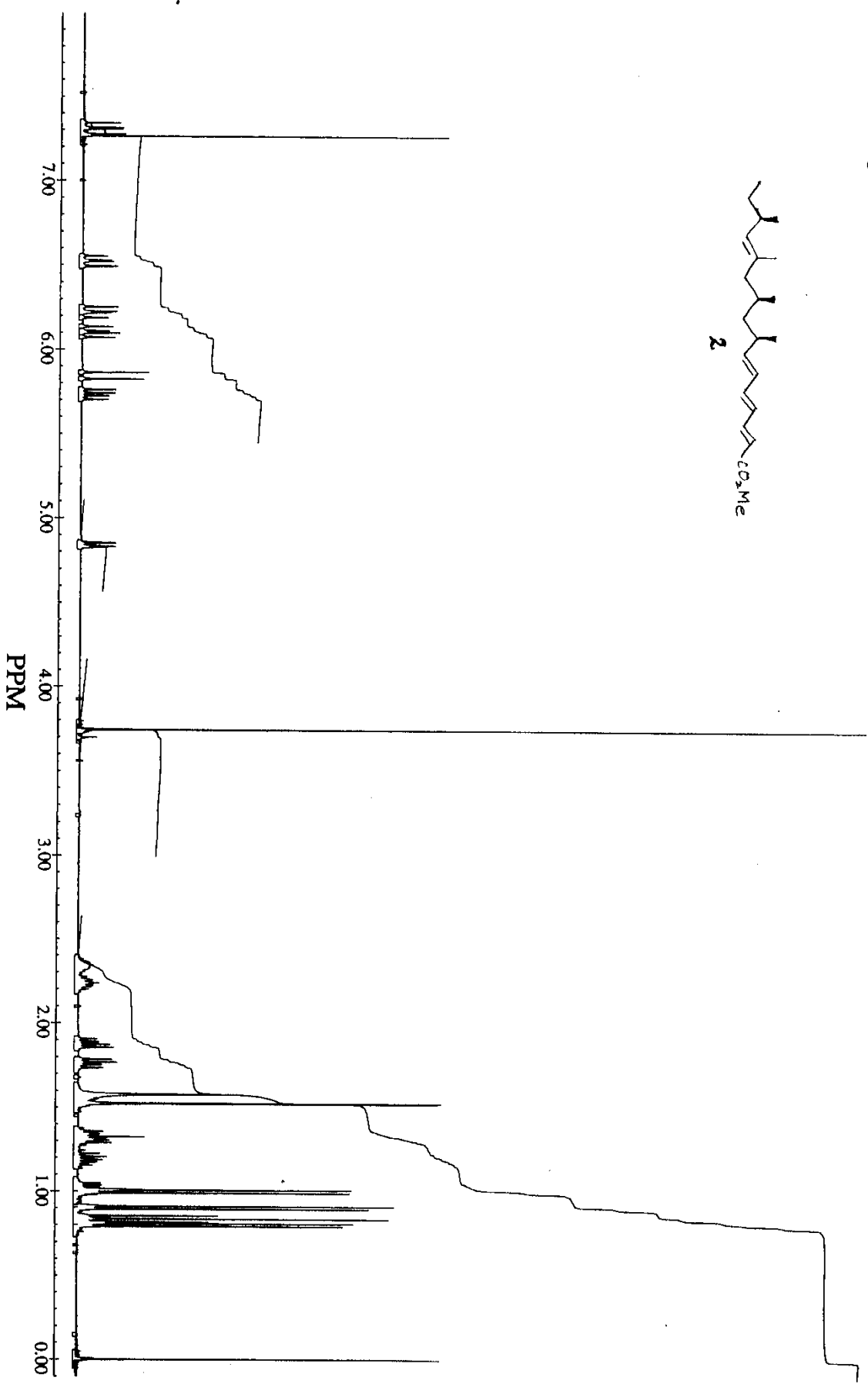
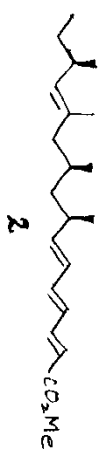
Colorless solid. mp 52.5-53.5 °C. $[\alpha]_D^{23} -12.6$ (*c* 0.64, CHCl₃). ¹H NMR (400MHz, CDCl₃): 0.98 (3H, t, *J* = 7.4Hz), 1.24 (3H, d, *J* = 7.3Hz), 1.50-1.61 (1H, m), 1.74-1.84 (1H, m), 2.52-2.60 (1H, m), 5.29 (2H, s), 7.64 (2H, d, *J* = 8.4Hz), 7.78 (2H, d, *J* = 8.4Hz). ¹³C NMR (100MHz, CDCl₃): 11.6, 16.6, 26.8, 40.8, 65.5, 129.0, 129.3, 132.2, 133.1, 176.1, 191.6. IR (CHCl₃): 2973, 2937, 2879, 1740, 1706, 1588, 1462, 1400, 1176, 1149, 1072, 1011, 971 cm⁻¹. HRMS: calcd, for C₁₃H₁₅BrO₃ (M⁺): 298.0205; found: 298.0194. Recrystallized from *n*-hexane. Colorless plates. mp 53-54 °C. Anal. Calcd for C₁₃H₁₅BrO₃: C, 52.19; H, 5.05, Br, 26.71. Found: C, 52.14; H, 5.11, Br, 26.77.

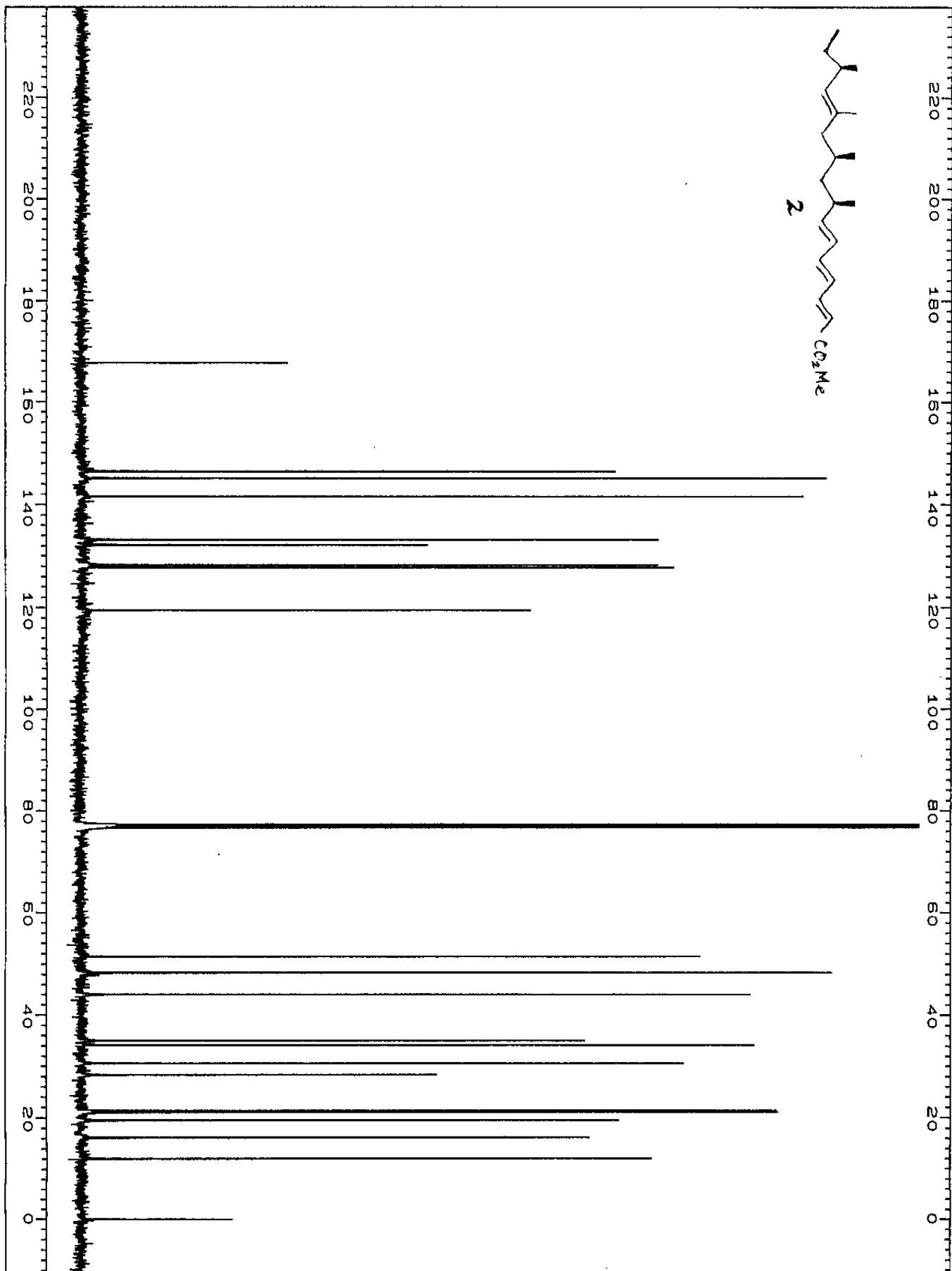
Compound (+)-**9**

Colorless plates (*n*-hexane). mp 53-54 °C. $[\alpha]_D^{23} -12.1$ (*c* 0.60, CHCl₃). ¹H NMR (400MHz, CDCl₃): 0.98 (3H, t, *J* = 7.4Hz), 1.24 (3H, d, *J* = 7.3Hz), 1.50-1.61 (1H, m), 1.74-1.84 (1H, m), 2.52-2.60 (1H, m), 5.29 (2H, s), 7.64 (2H, d, *J* = 8.4Hz), 7.78 (2H, d, *J* = 8.4Hz). ¹³C NMR (100MHz, CDCl₃): 11.6, 16.6, 26.8, 40.8, 65.5, 129.0, 129.3, 132.2, 133.1, 176.1, 191.6. IR (CHCl₃): 2973, 2937, 2879, 1740, 1706, 1588, 1462, 1400, 1176, 1149, 1072, 1011, 971 cm⁻¹. HRMS: calcd, for C₁₃H₁₅BrO₃ (M⁺): 298.0205; found: 298.0185. Anal. Calcd for C₁₃H₁₅BrO₃: C, 52.19; H, 5.05, Br, 26.71. Found: C, 51.98; H, 4.89, Br, 26.66.

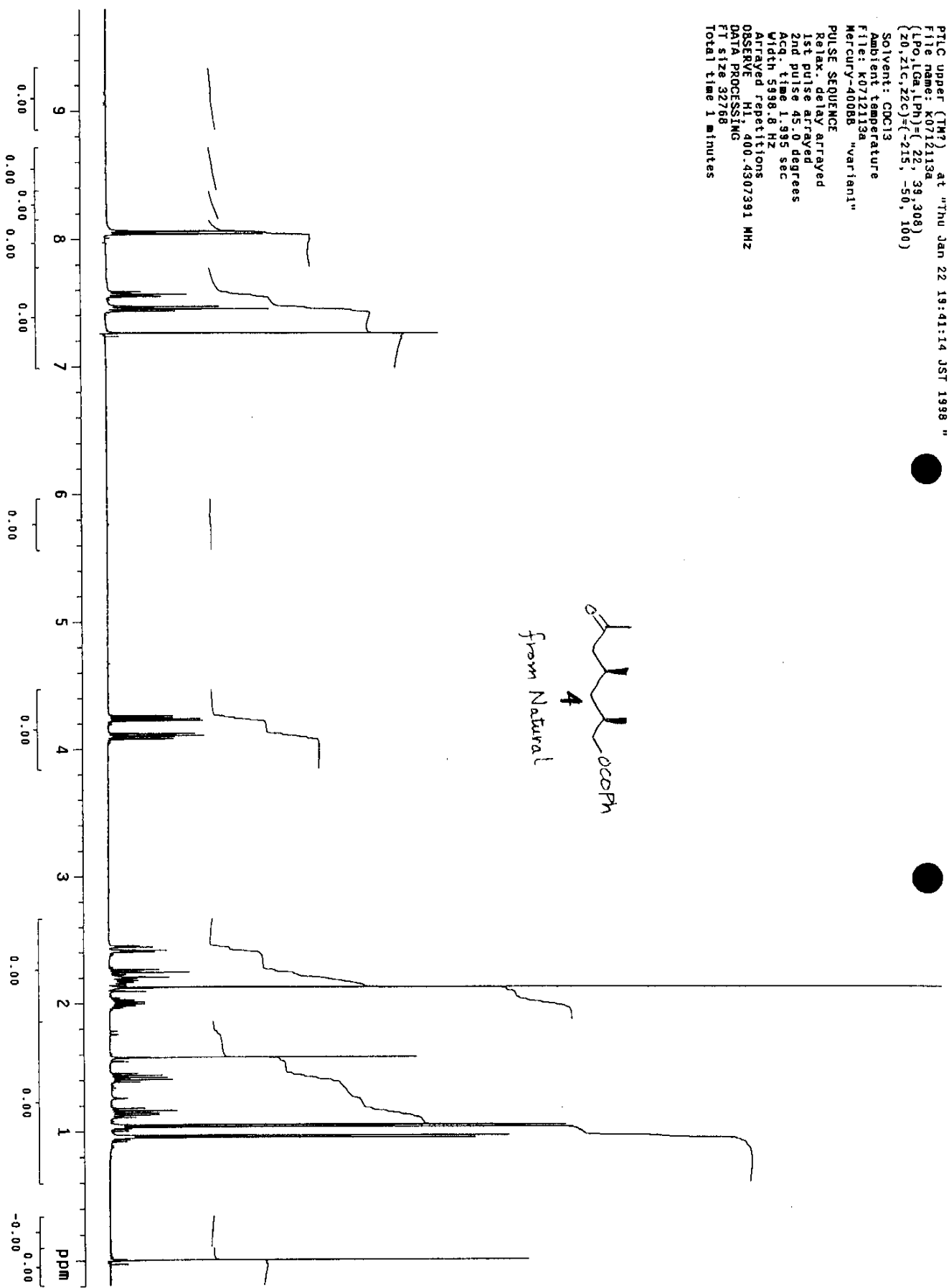
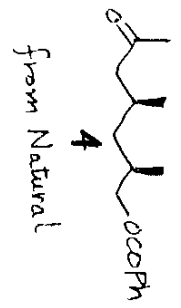
Compound **11**

Colorless solid. mp < 40 °C. $[\alpha]_D^{24} -18.1$ (*c* 1.07, CHCl₃). ¹H NMR (400MHz, CDCl₃): 0.97 (3H, d, *J* = 6.6Hz), 1.25-1.31 (1H, m), 1.26 (3H, d, *J* = 7.0Hz), 1.75-1.85 (1H, m), 2.11-2.21 (1H, m), 2.15 (3H, s), 2.28 (1H, dd, *J* = 8.1 and 15.7Hz), 2.42 (1H, dd, *J* = 5.6 and 15.7Hz), 2.66-2.75 (1H, m), 5.30 (2H, s), 7.65 (2H, d, *J* = 8.7Hz), 7.78 (2H, d, *J* = 7.0Hz). ¹³C NMR (100MHz, CDCl₃): 18.1, 19.8, 27.4, 30.2, 37.2, 41.1, 51.3, 65.6, 129.1, 129.2, 132.2, 133.0, 175.9, 191.4, 208.5. IR (CHCl₃): 2976, 2936, 2878, 1741, 1707, 1588, 1167, 1146, 1013, 1072, 1011, 970 cm⁻¹. HRMS: calcd, for C₁₇H₂₂BrO₄ (M+H⁺): 369.0704; found: 369.0677.





PTIC upper (TM2) at "Thu Jan 22 19:41:14 JST 1998 "
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{Z0,Z1C,Z2C}(-215, -50, 100)
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Ambient temperature
File: K0712113A
Mercury-400BB "variani"
PULSE SEQUENCE
Relax. delay arrayed
1st pulse arrayed
2nd pulse arrayed
Acq. time 45.0 degrees
Width 5998.8 Hz
ARRIVED repetitions
OBSERVE H1 400.4307391 MHz
DATA PROCESSING
F1 size 32768
Total time 1 minutes



13C OBSERVE

Solvent: CDCl3
Ambient temperature
Mercury-40088 "variani"

PULSE SEQUENCE

Relax. delay arrayed

1st pulse arrayed

2nd pulse 45.0 degrees

Acq. time 1.199 sec

Width 25000.0 Hz

Arrayed repetitions

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DECOUPLE H1, 400.4327594 MHz

Power 43 dB

continuously on

GARP-1 modulated

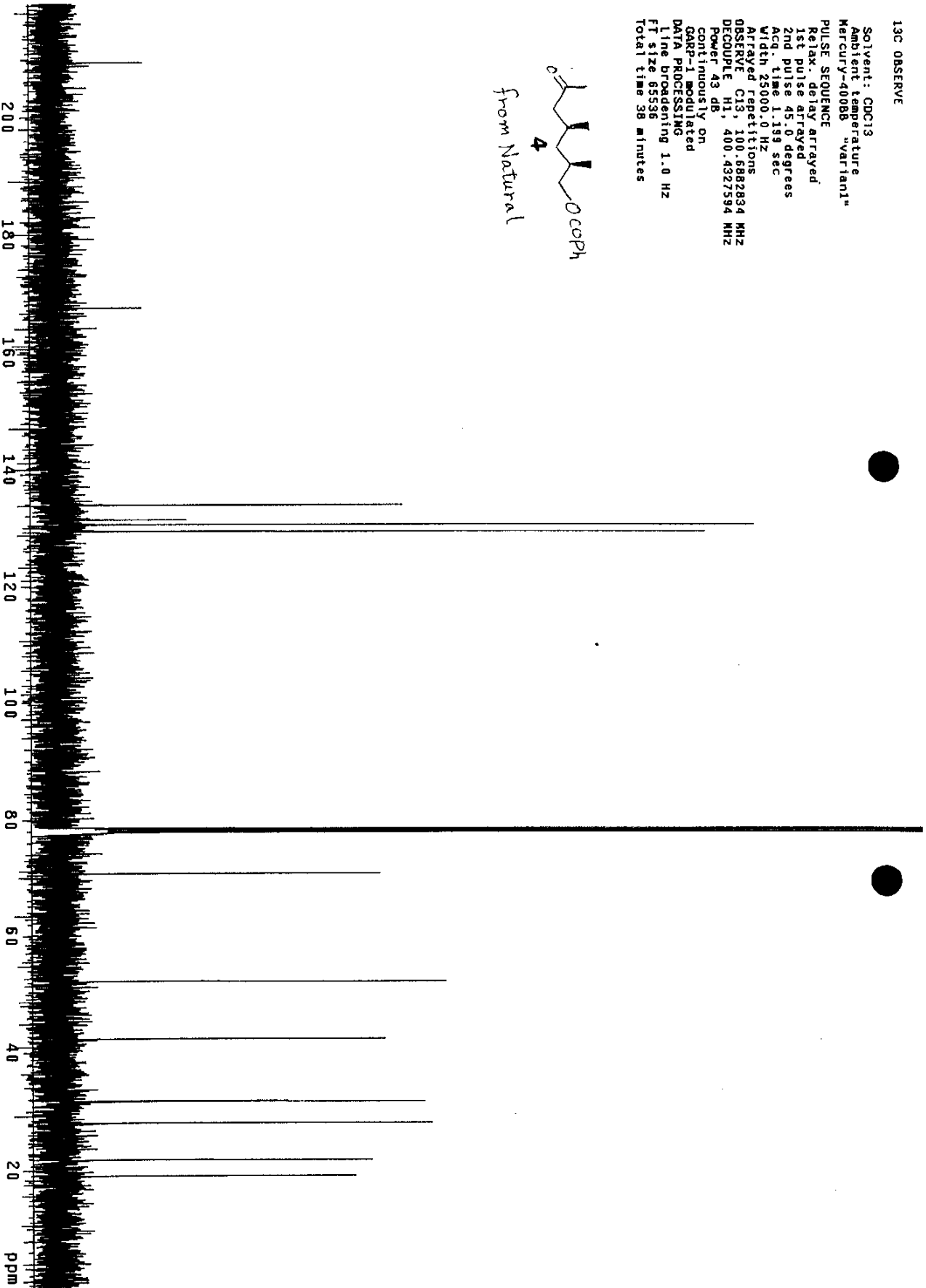
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Line broadening 1.0 Hz

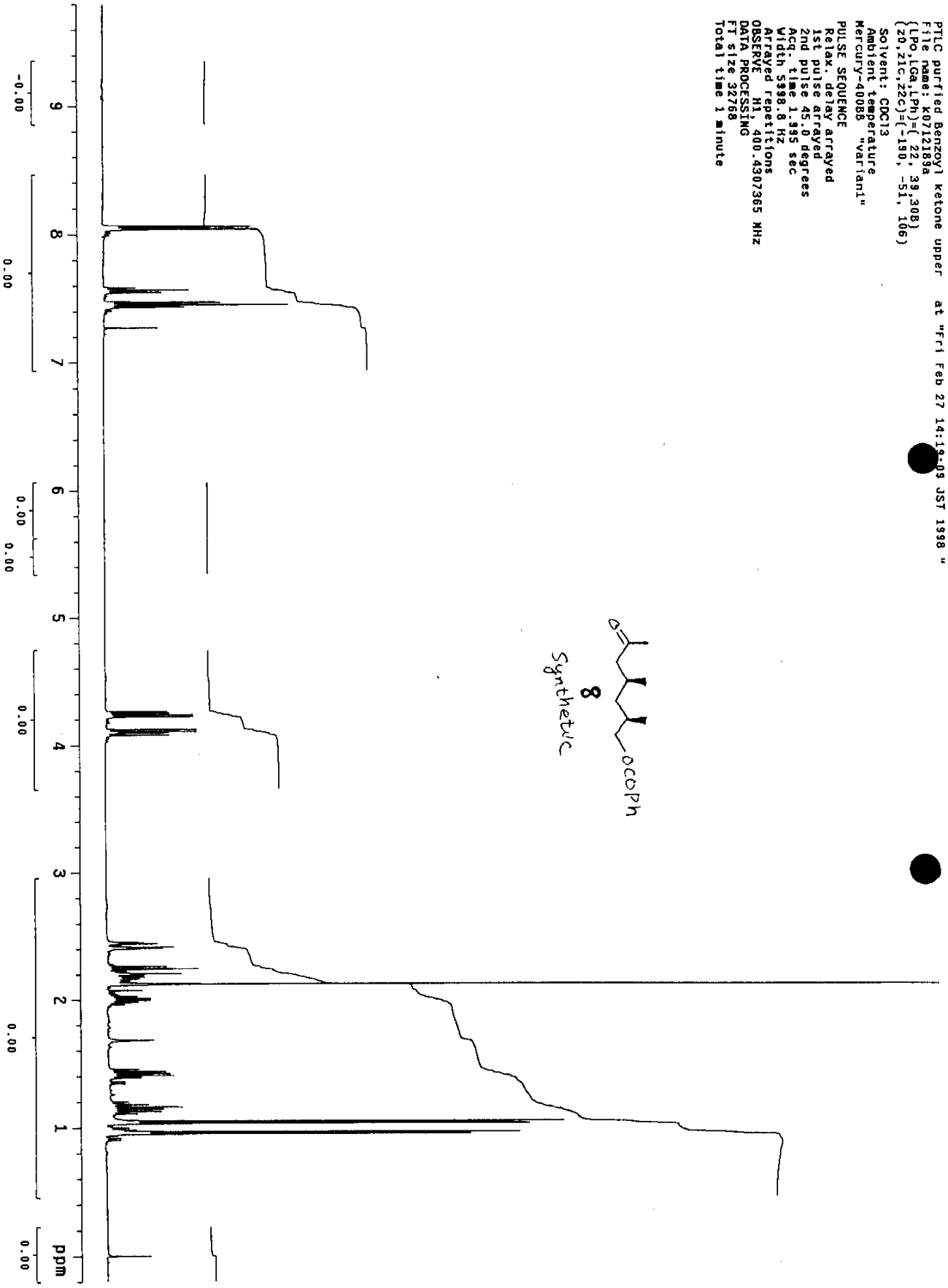
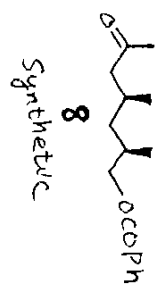
FT size 65536

Total time 38 minutes

from Natural



PLIC purified Benzoyl ketone upper at "Fri Feb 27 14:19:09 JST 1998 "
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 (20, z1c, z2c)=[-190, -51, 106]
 Solvent: CDCl3
 Ambient temperature
 Mercury-40088 "var1an1"
 PULSE SEQUENCE
 Relax delay arrayed
 1st pulse arrayed
 2nd pulse arrayed
 Acq: 1.495 sec
 Width: 5398.0 Hz
 Arrayed repetitions
 OBSERVE: H1, 400.4307365 MHz
 DATA PROCESSING
 FT size 32768
 Total time 1 minute



Synthetic sample at "Fri Mar 6 15:50:56 JST 1998 "
File name: K0712189b
(LPO,GA,LPN)=(22, 39,308)
(Z0,Z1C,Z2C)=(-144, -56, 113)

Solvent: CDCl3
Ambient temperature
Mercury-400DB "var-tan1"

PULSE SEQUENCE

Relax. delay arrayed
1st pulse arrayed
2nd pulse 45.0 degrees
Acq. time 1.199 sec
Width 30000.0 Hz
Arrayed repetitions
OBSERVE C13, 100.6882834 MHz
DECOUPLE H1, 400.4327594 MHz
Power 43 db
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
F1 size 131072
Total time 9 minutes

