

**A Mechanistic Study on Hooker Oxidation: Synthesis of Novel  
Indane Carboxylic acid Derivatives from Lapachol**

**Kenneth O. Eyong,<sup>a,b</sup> Manohar Puppala,<sup>a</sup> Ponminor Senthil Kumar,<sup>a</sup>  
Marc Lamshöft,<sup>c</sup> Gabriel N. Folefoc,<sup>\*b</sup> Michael Spiteller,<sup>\*c</sup> and Sundarababu  
Baskaran,<sup>\*a</sup>**

**General Considerations:** All the solvents were distilled prior to use. Dry solvents were prepared according to the standard procedures. Reactions requiring inert atmosphere were carried out under argon atmosphere. Infrared (IR) spectra were recorded on a Shimadzu IR 470 spectrometer (or) THERMO NICOLET 6700 FT-IR spectrometer.  $^1\text{H}$  NMR spectra were measured on Bruker ADVANCE 400 MHz spectrometers. Chemical shifts were reported in ppm using tetramethylsilane as an internal standard.  $^{13}\text{C}$  NMR spectra were recorded on Bruker 100 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. The high-resolution mass spectra (HRMS) were performed on Micromass Q-TOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were recorded using Bruker-AXS Kappa CCD-Diffractometer with graphite-monochromator  $\text{Cu}_{K\alpha}$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against  $F^2$  (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used. Acme (India) silica gel (100-200 mesh) was used for column chromatography.

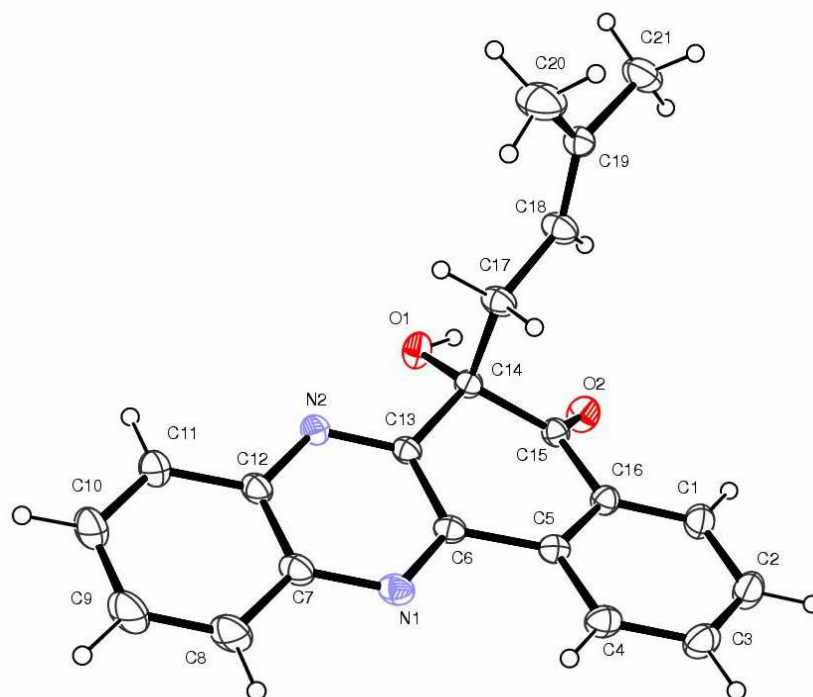
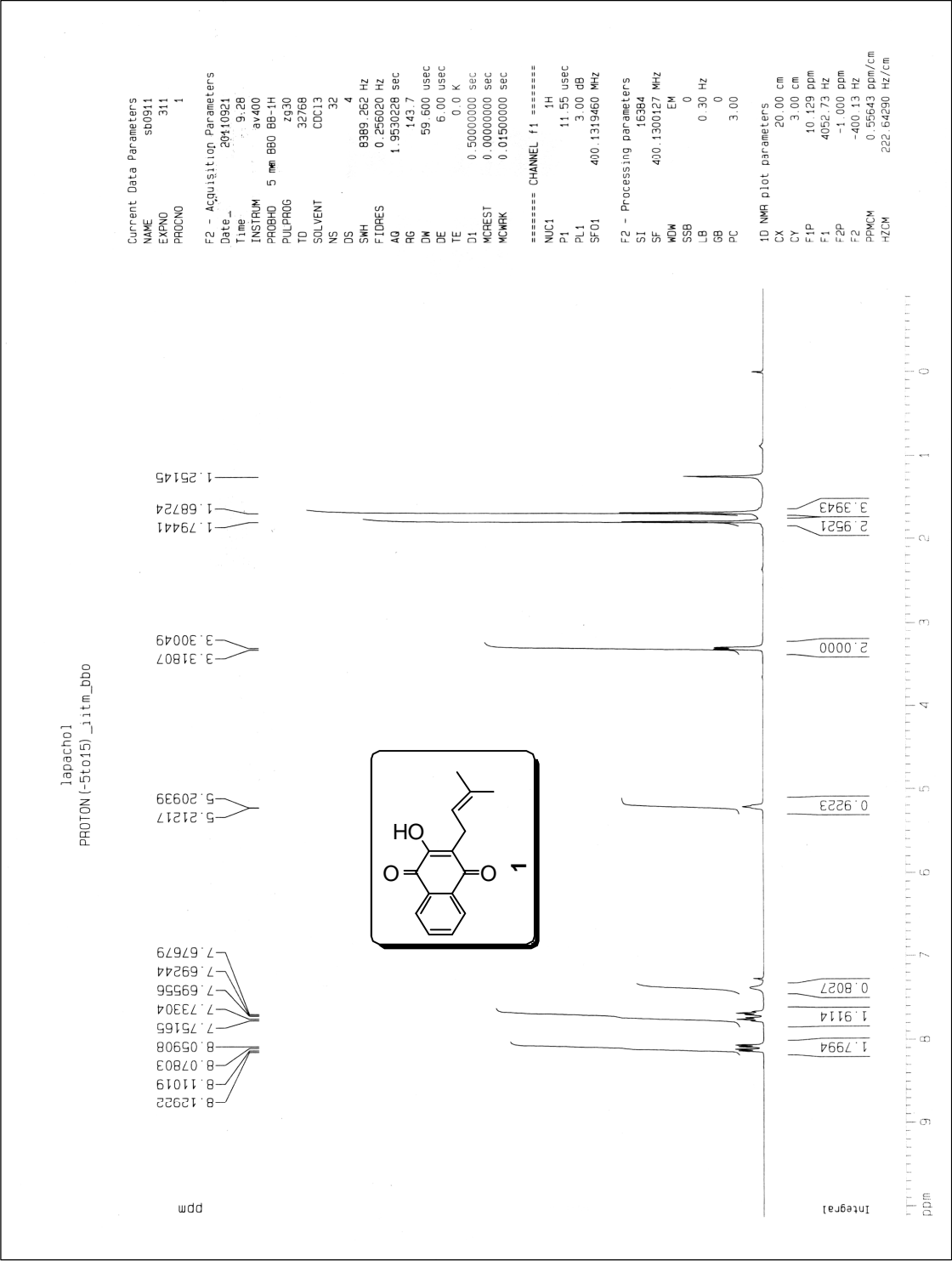


Table 1. Crystal data and structure refinement for new.

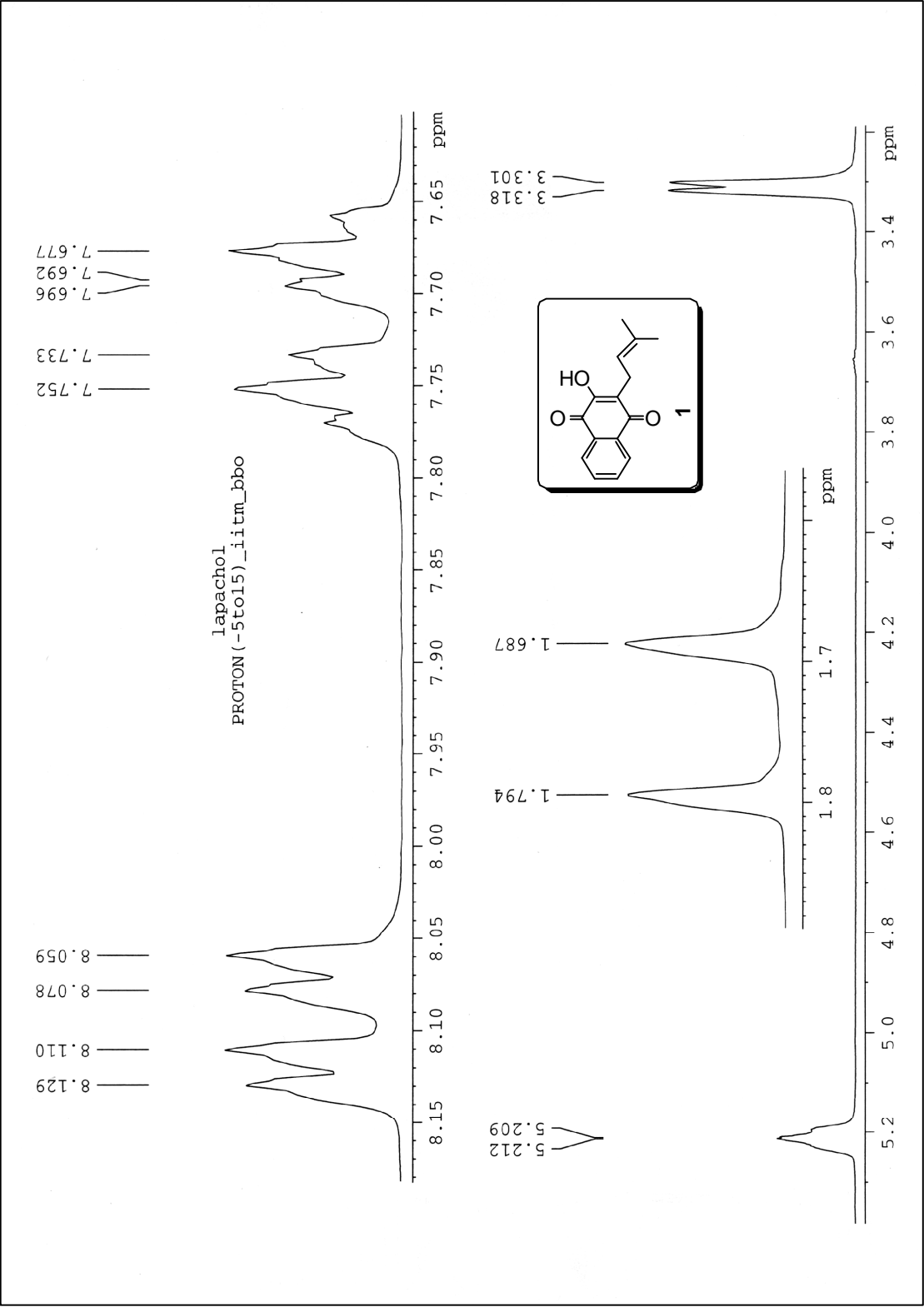
Identification code	new
Empirical formula	C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	330.37
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions deg.	a = 11.3037(4) Å    alpha = 90
105.439(2) deg.	b = 17.9419(6) Å    beta =
deg.	c = 8.3981(3) Å    gamma = 90
Volume	1641.76(10) Å <sup>3</sup>
Z, Calculated density	4, 1.337 Mg/m <sup>3</sup>
Absorption coefficient	0.087 mm <sup>-1</sup>

F(000)	696
Crystal size	0.48 x 0.35 x 0.28 mm
Theta range for data collection	1.87 to 34.28 deg.
Limiting indices 13<=l<=12	-13<=h<=17, -27<=k<=28, -
Reflections collected / unique	20040 / 6204 [R(int) = 0.0216]
Completeness to theta = 25.00	96.7 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9761 and 0.9594
Refinement method F <sup>2</sup>	Full-matrix least-squares on
Data / restraints / parameters	6204 / 0 / 232
Goodness-of-fit on F <sup>2</sup>	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1406
R indices (all data)	R1 = 0.0776, wR2 = 0.1633
Largest diff. peak and hole	0.377 and -0.192 e.A <sup>-3</sup>

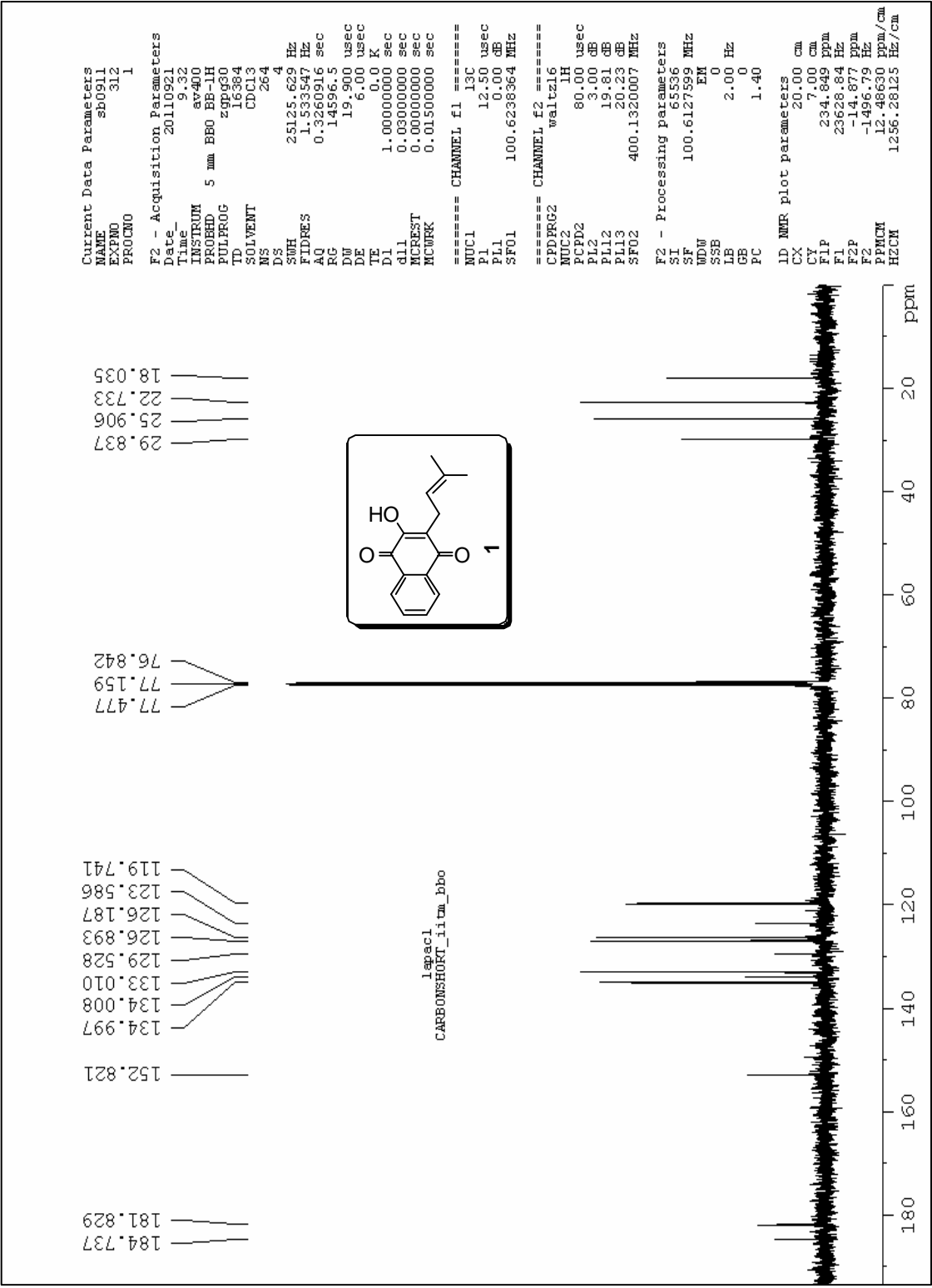


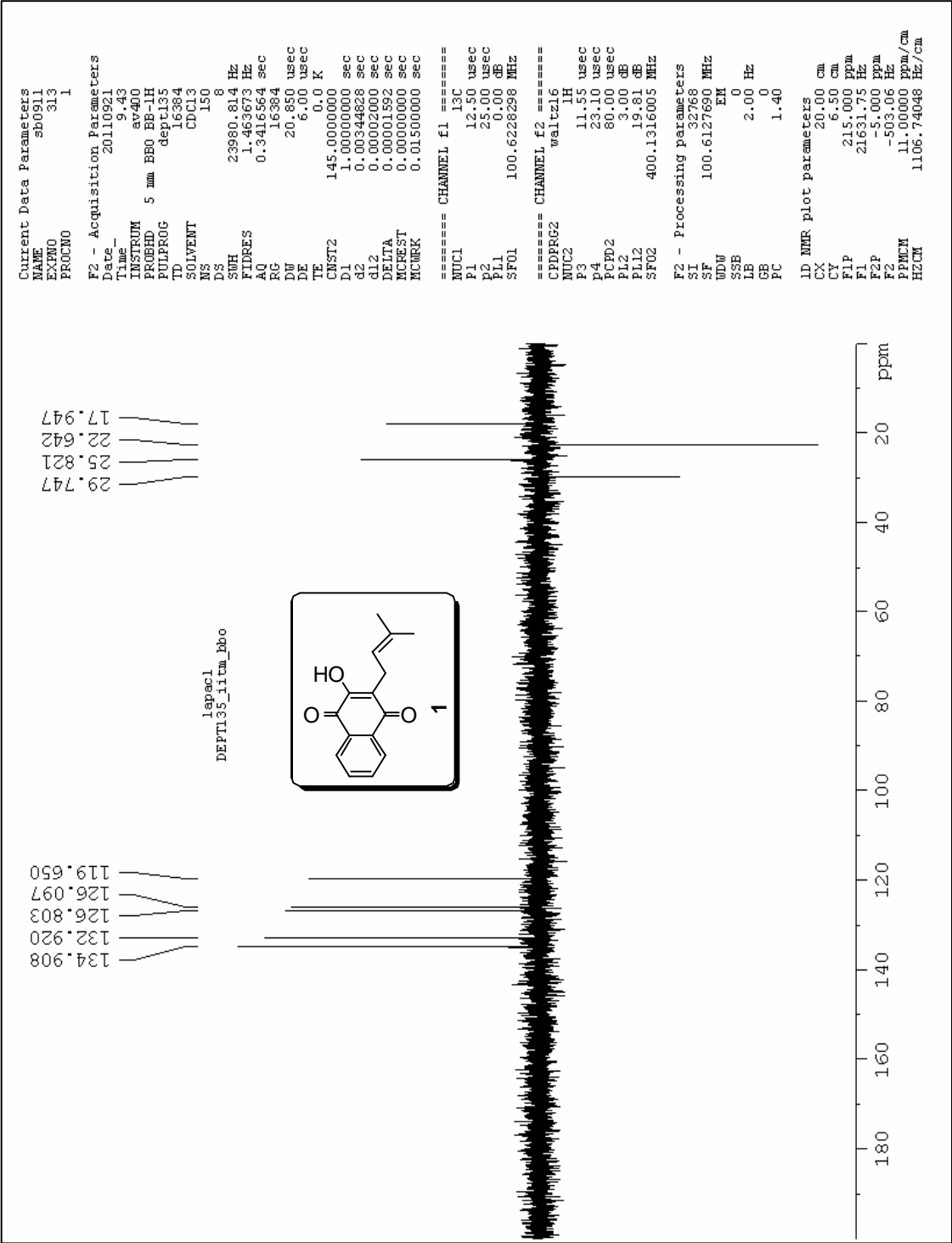


<sup>1</sup>H NMR spectrum of compound 1

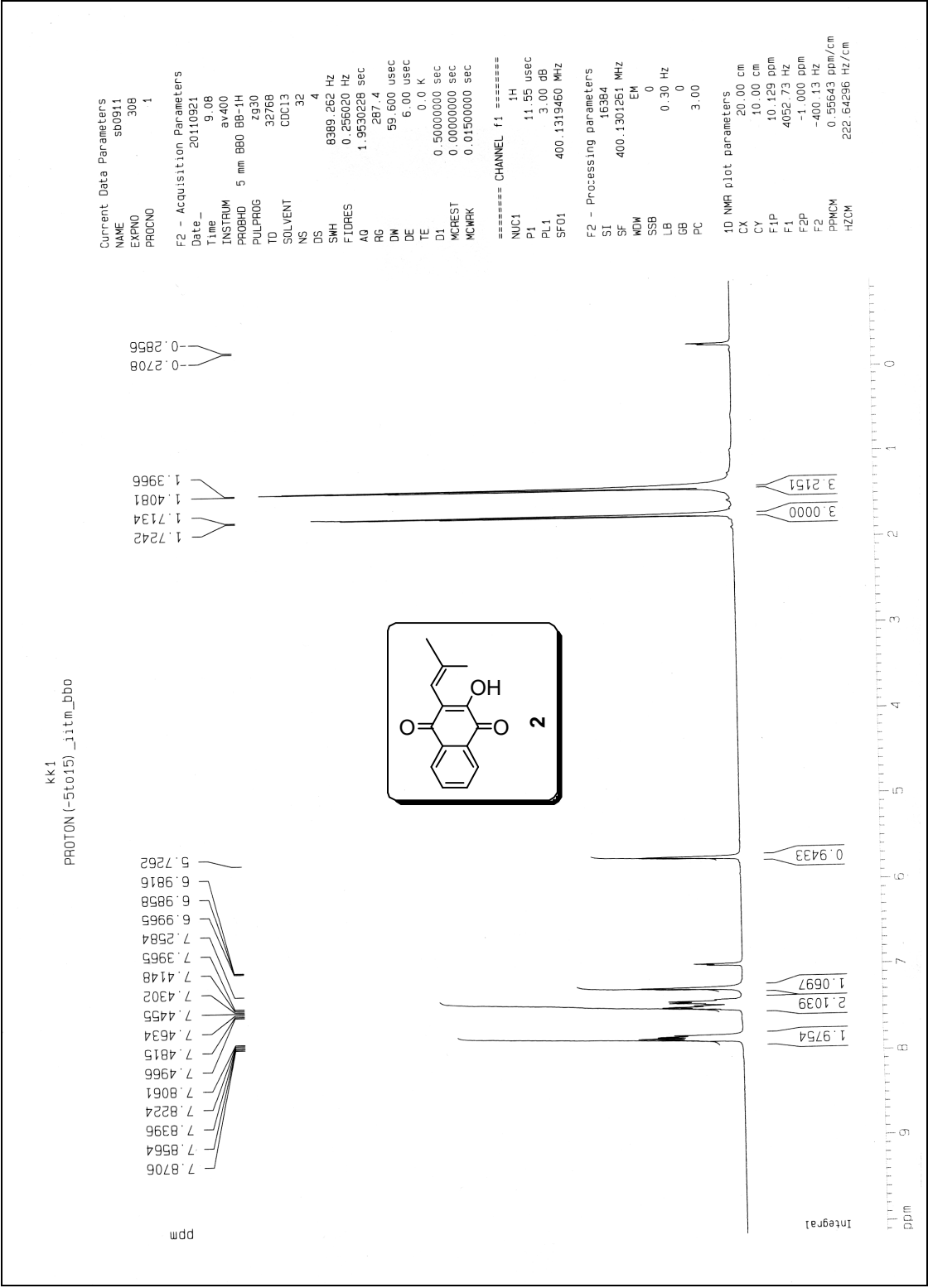


Expanded  $^1\text{H}$  NMR spectrum of compound **1**

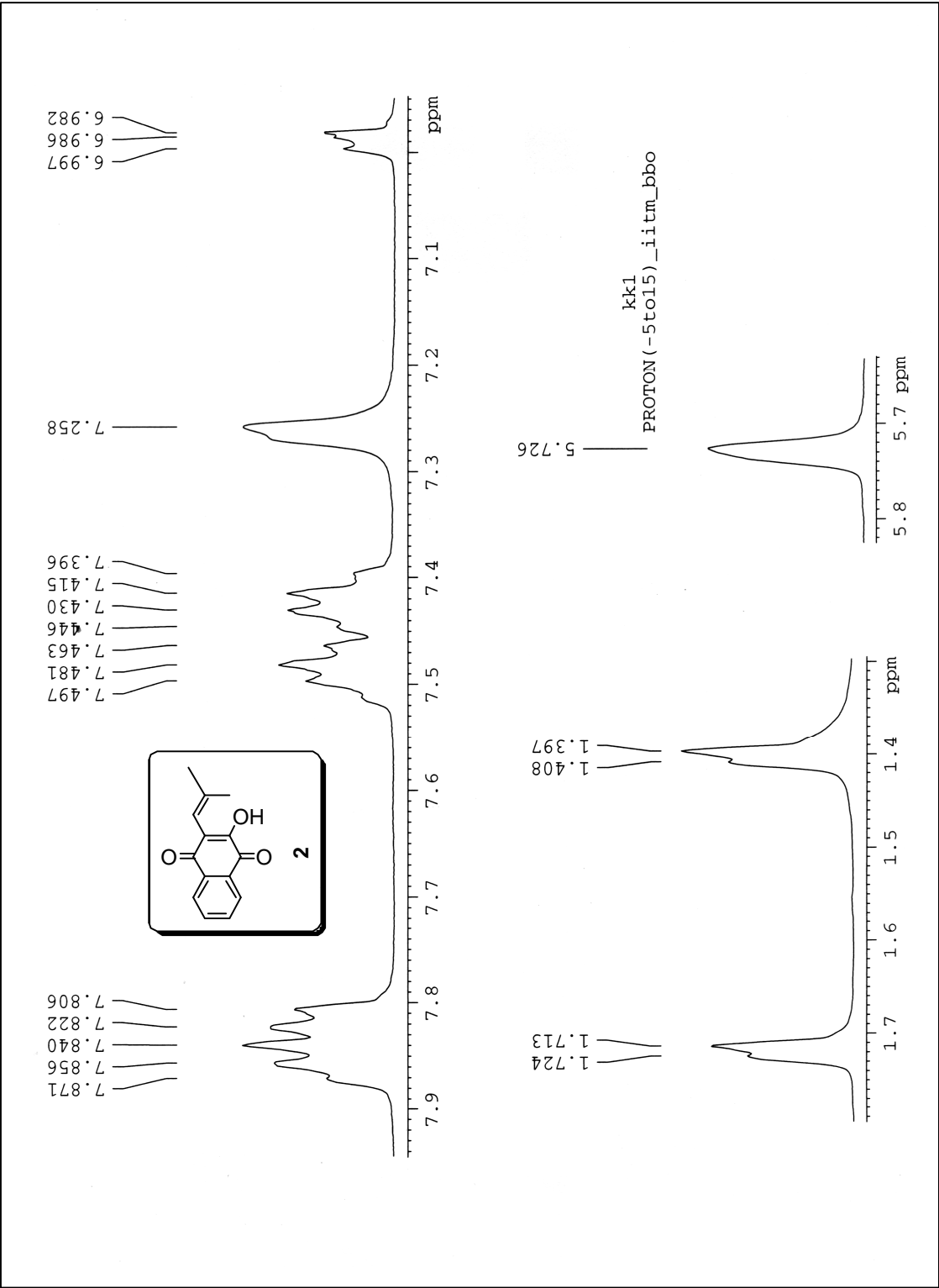




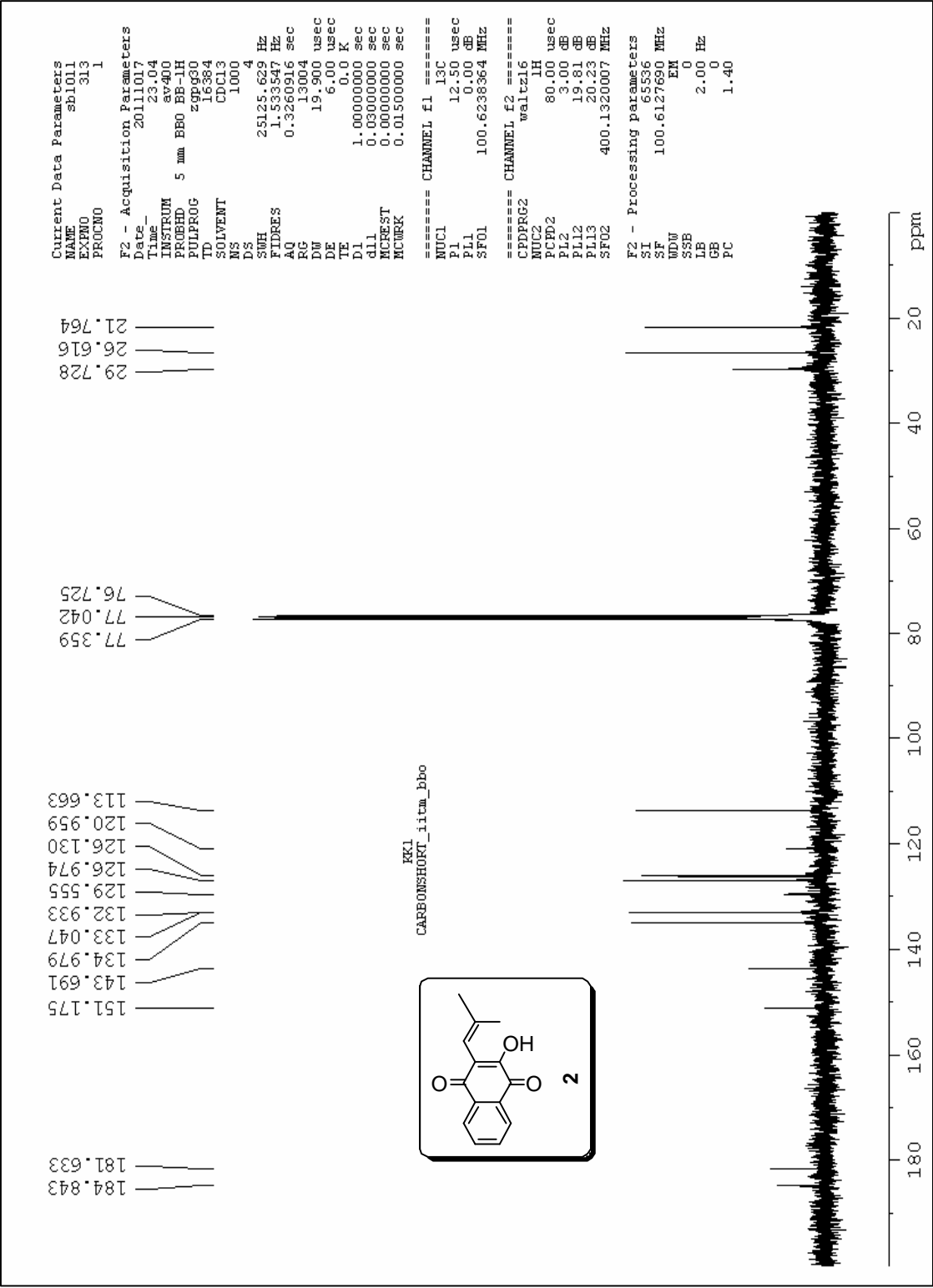
DEPT spectrum of compound 1



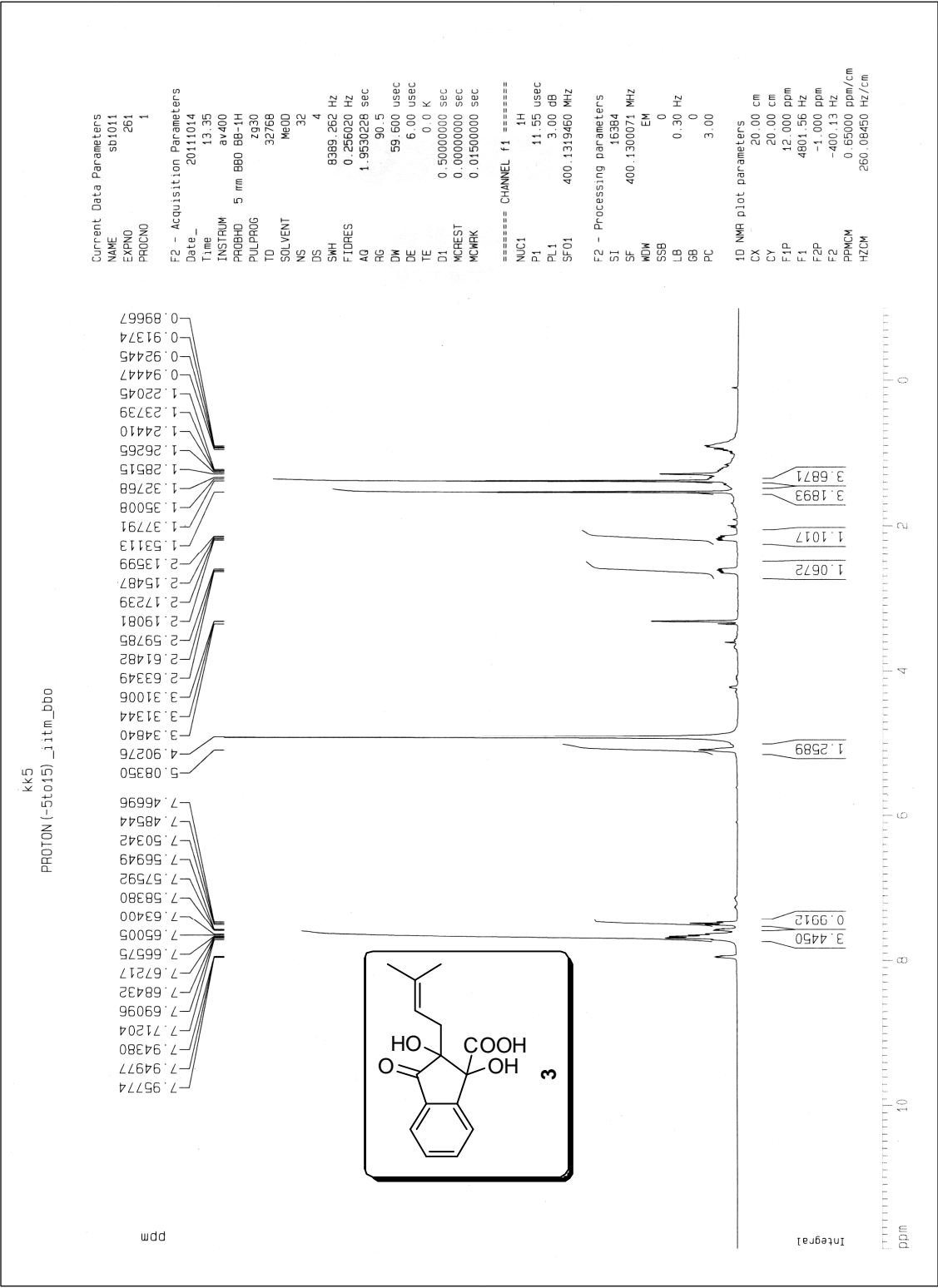
<sup>1</sup>H NMR spectrum of compound 2



Expanded  $^1\text{H}$  NMR spectrum of compound **2**

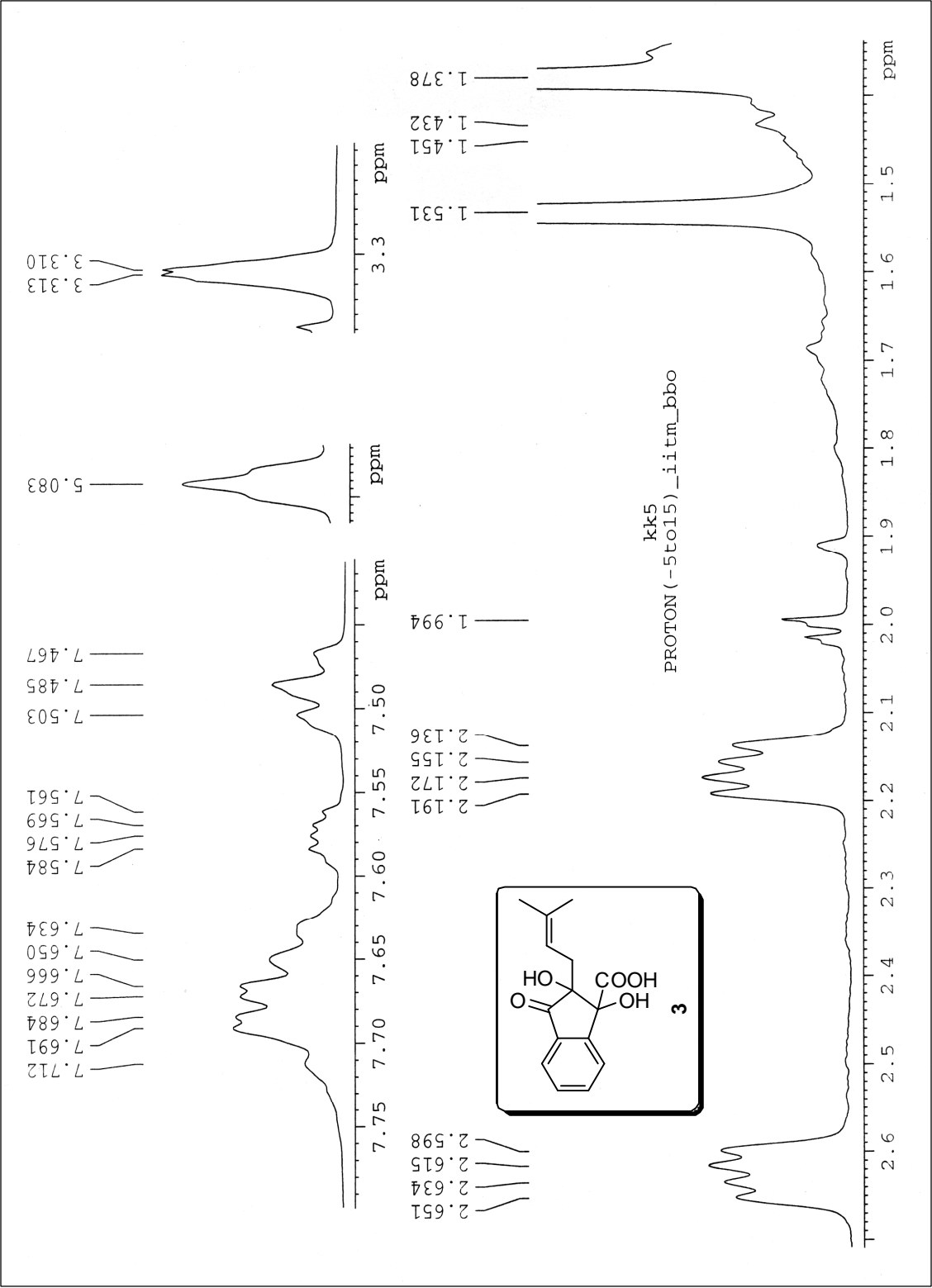


<sup>13</sup>C NMR spectrum of compound 2

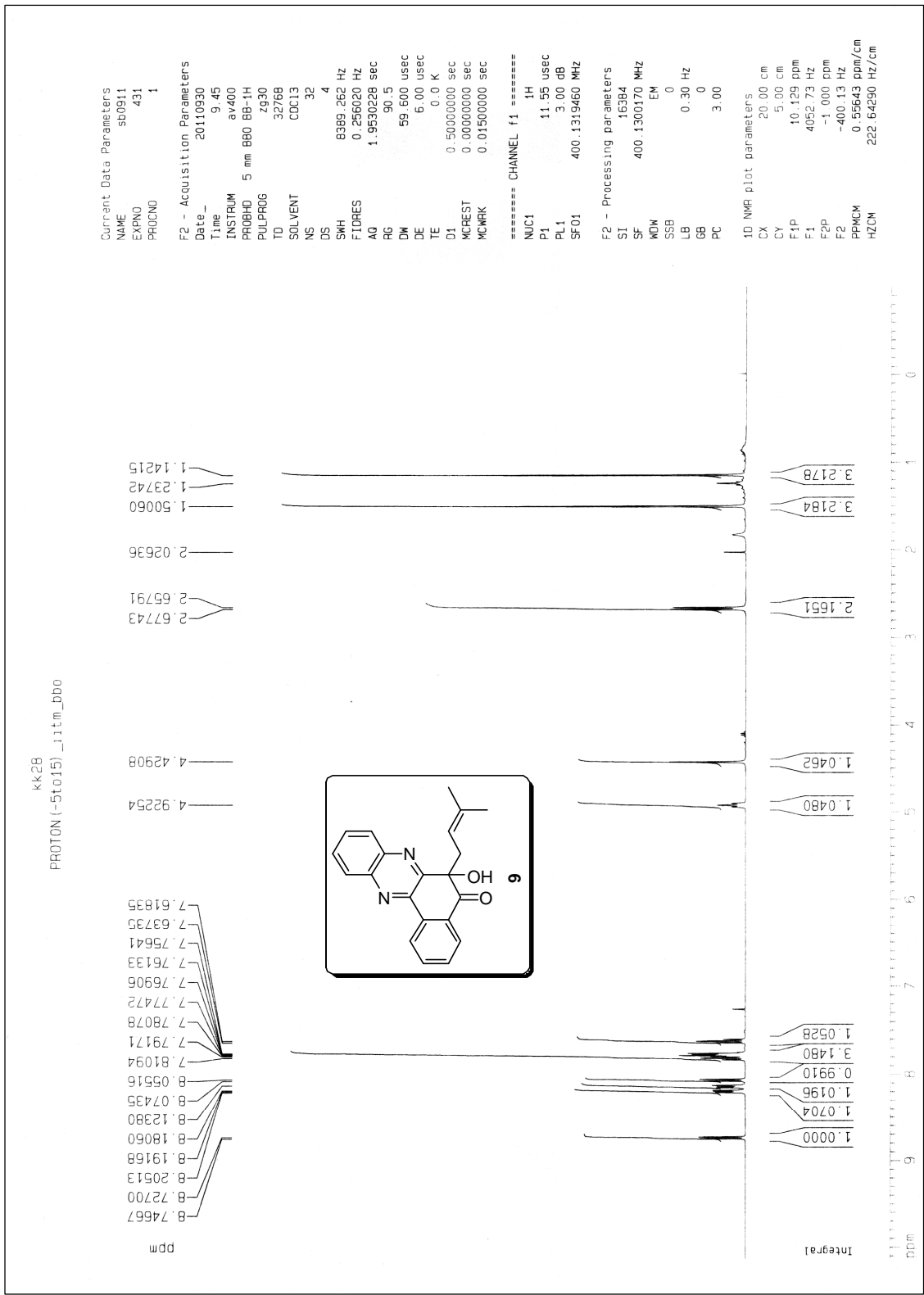


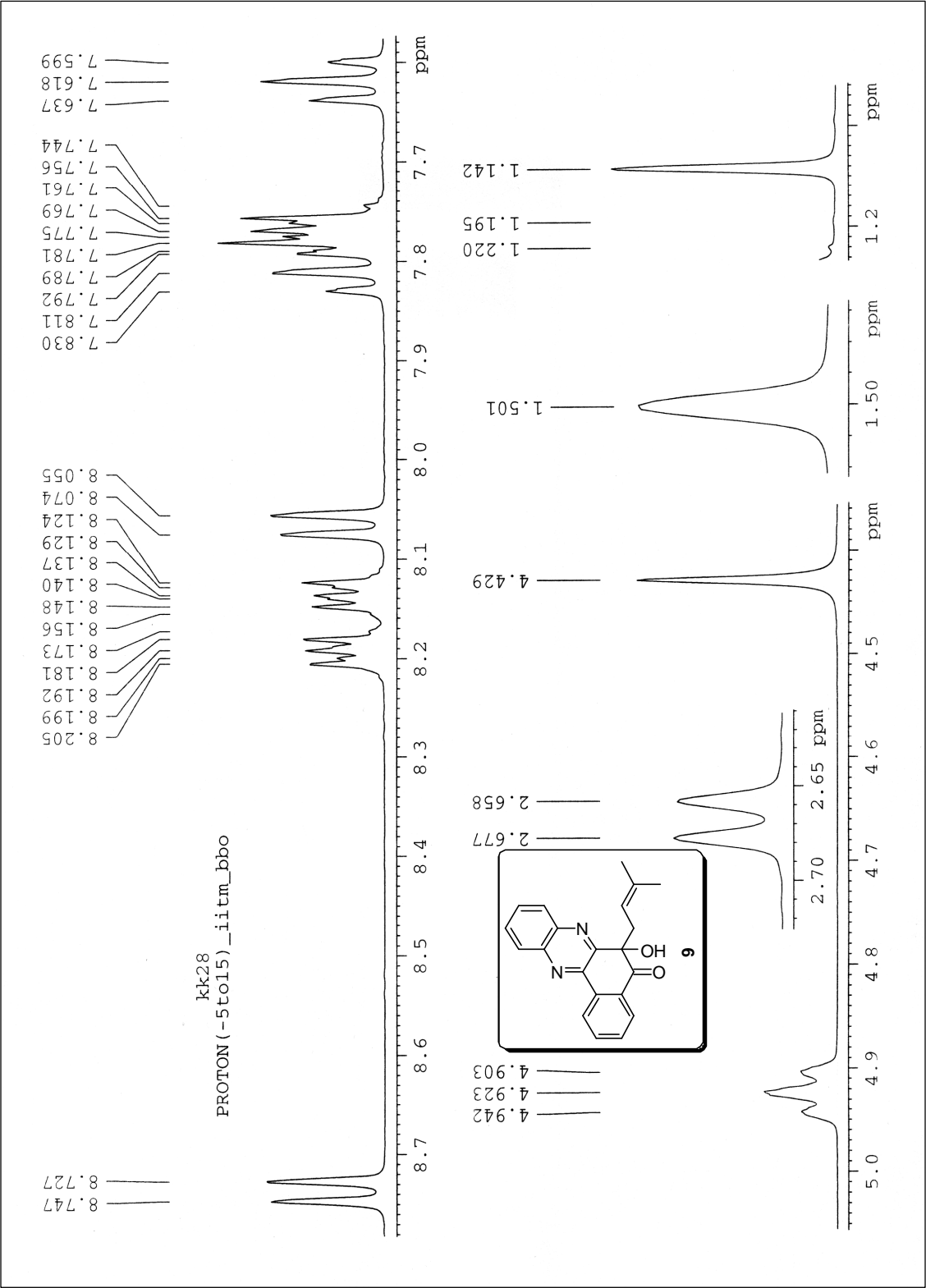
<sup>1</sup>H NMR spectrum of compound 3

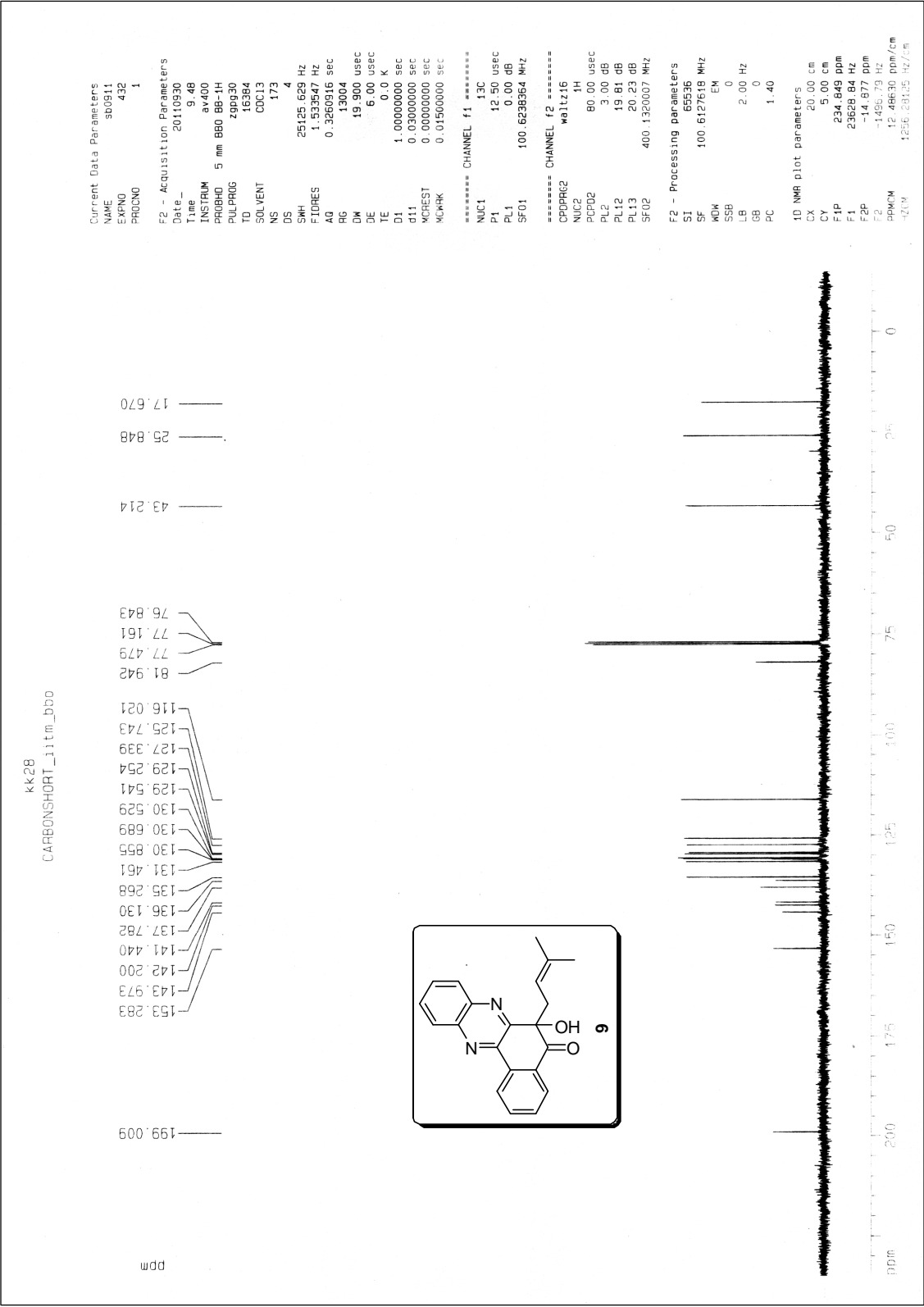


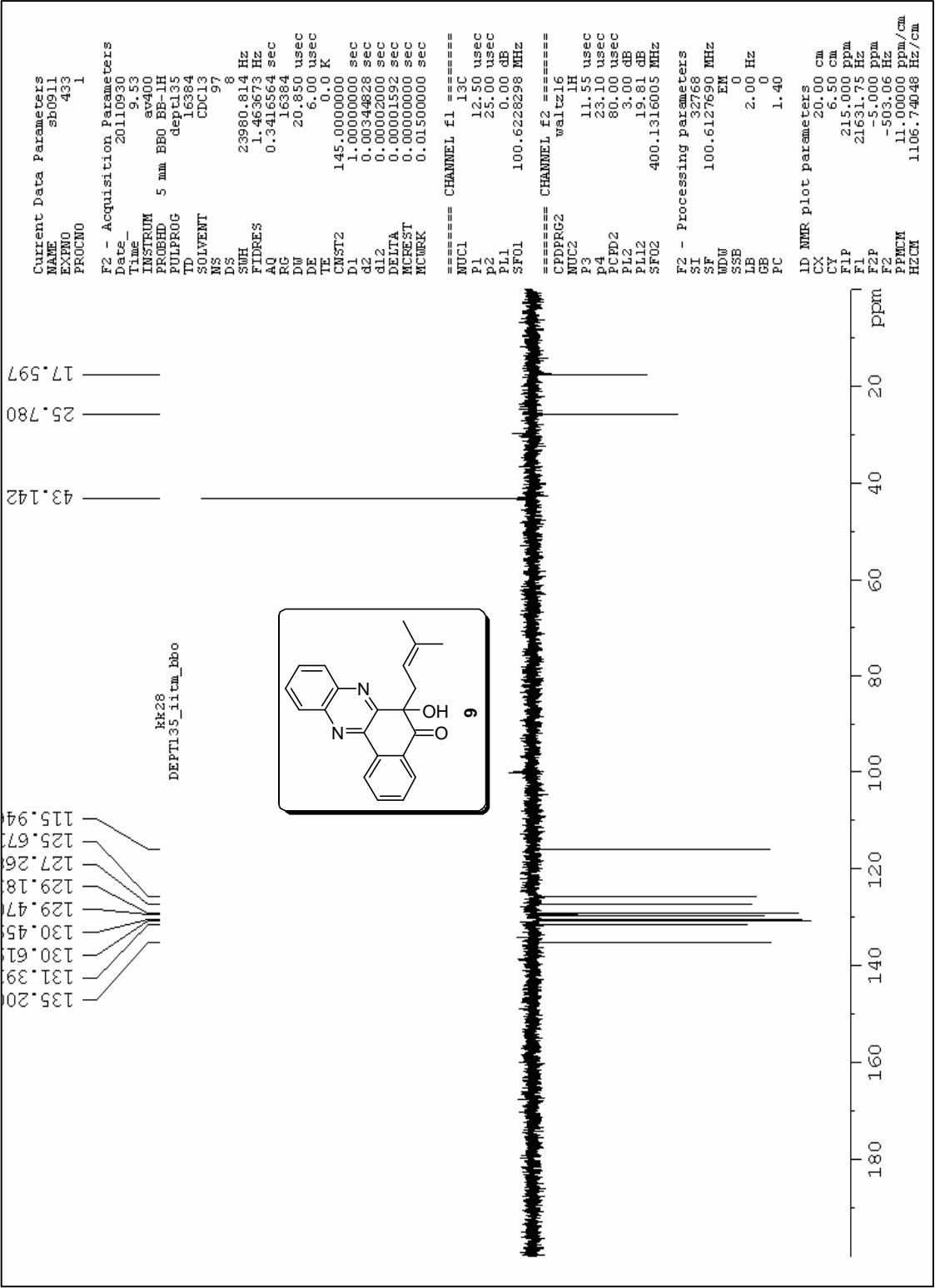






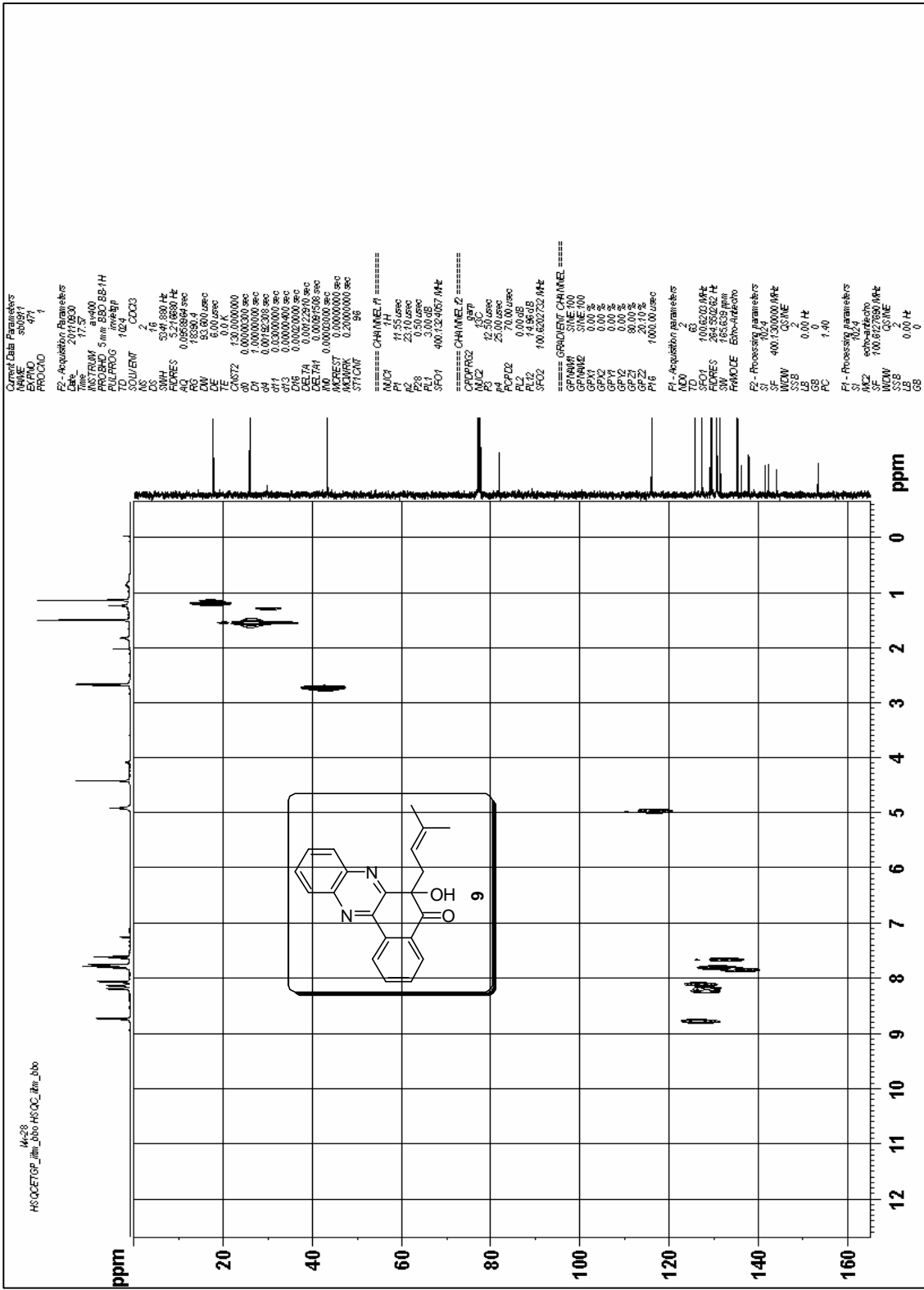




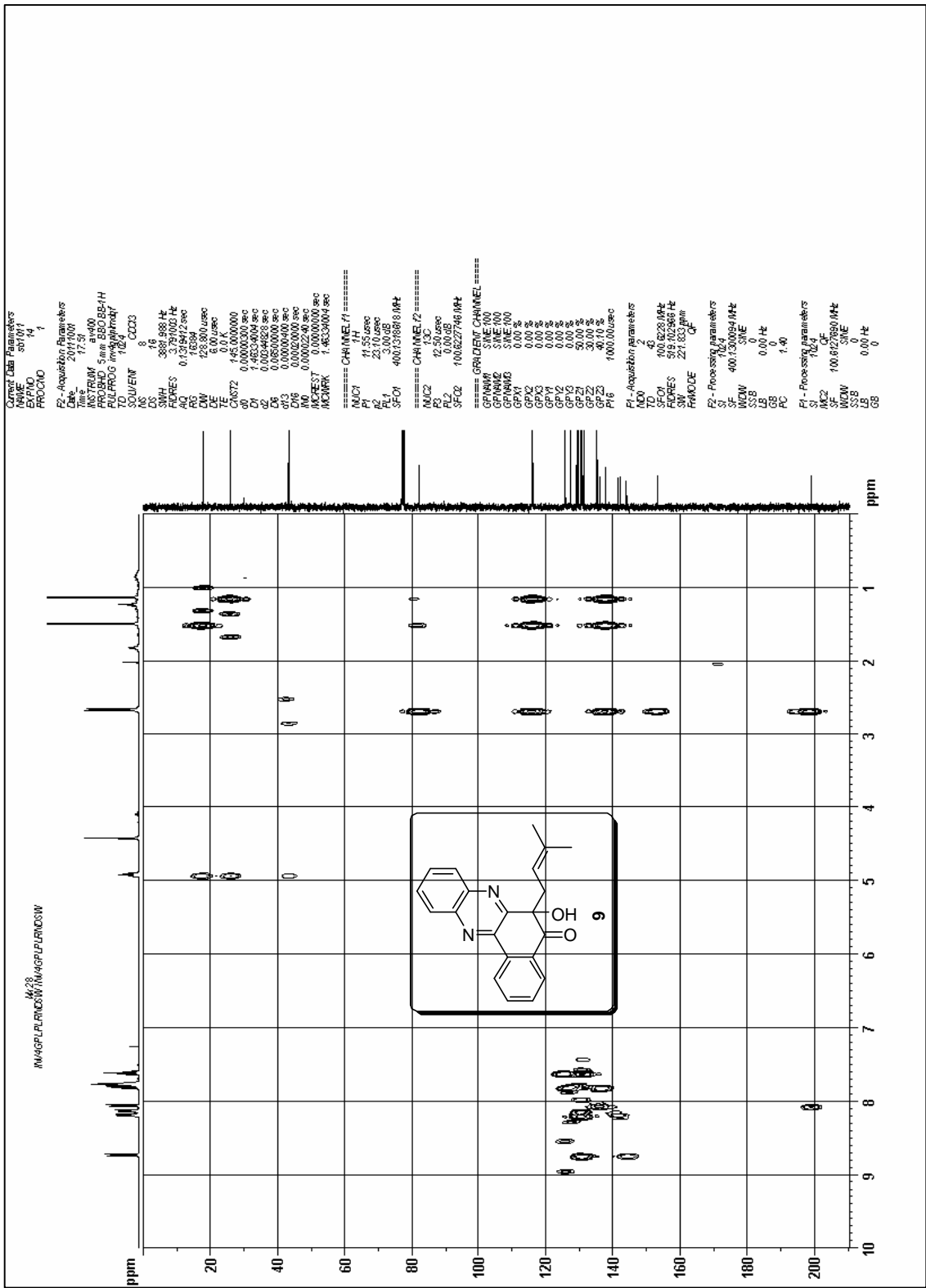


DEPT spectrum of compound **9**

$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **9**







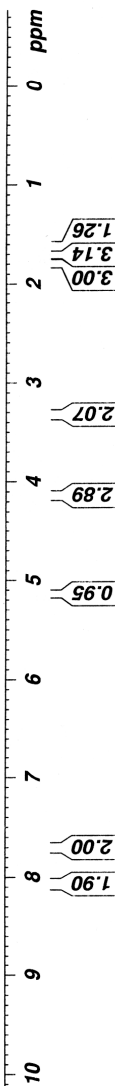
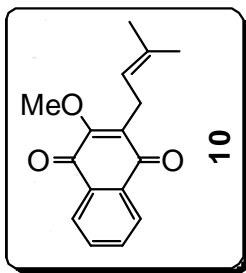
SB2/KK3.....Baskar, Chemistry

Current Data Parameters  
NAME Jul27-2009  
EXPNO 6  
PROCNO 1

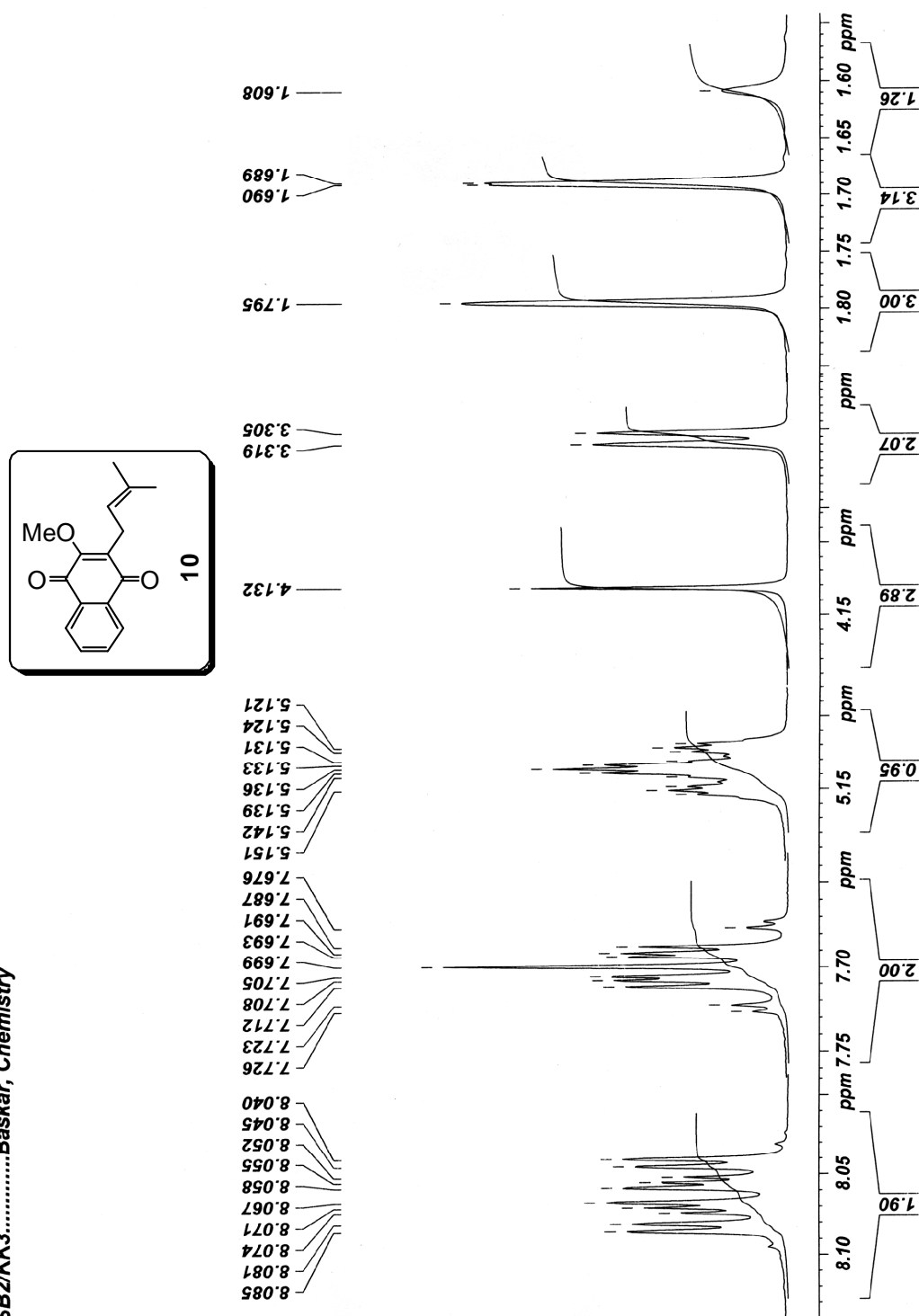
F2 - Acquisition Parameters  
Date\_ 20090727  
Time 10.47  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 32768  
SOLVENT CDC13  
NS 16  
DS 2  
SWH 10330.578 Hz  
FIDRES 0.315264 Hz  
AQ 1.5860212 sec  
RG 203  
DW 48.400 usec  
DE 6.00 usec  
TE 295.8 K  
D1 1.00000000 sec  
TD0 1

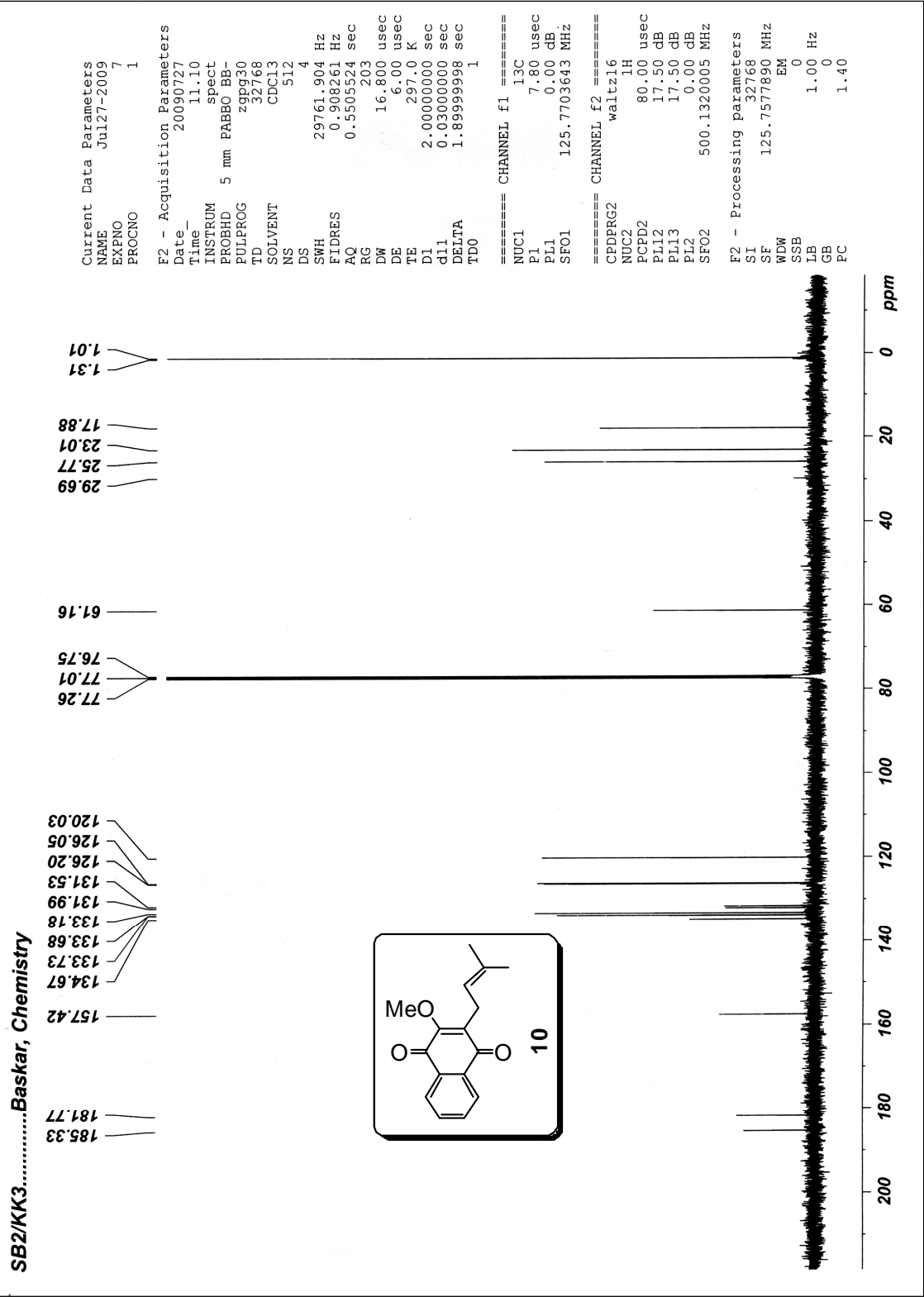
===== CHANNEL f1 =====  
NUC1 1H  
P1 10.65 usec  
PL1 0.00 dB  
SFO1 500.1330885 MHz

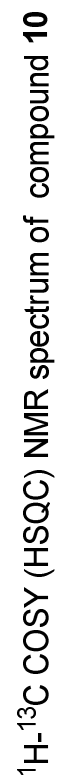
F2 - Processing parameters  
SI 32768  
SF 500.1300000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



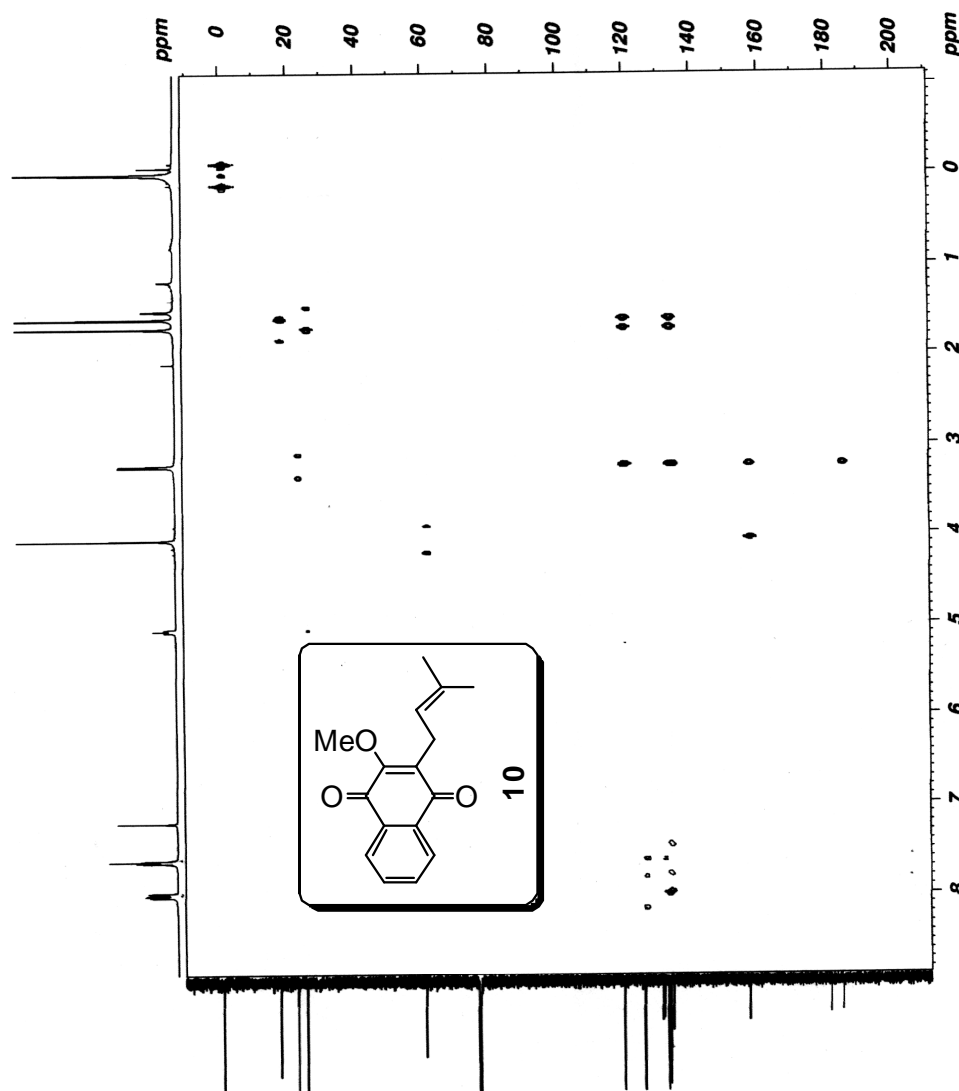
<sup>1</sup>H NMR spectrum of compound 10







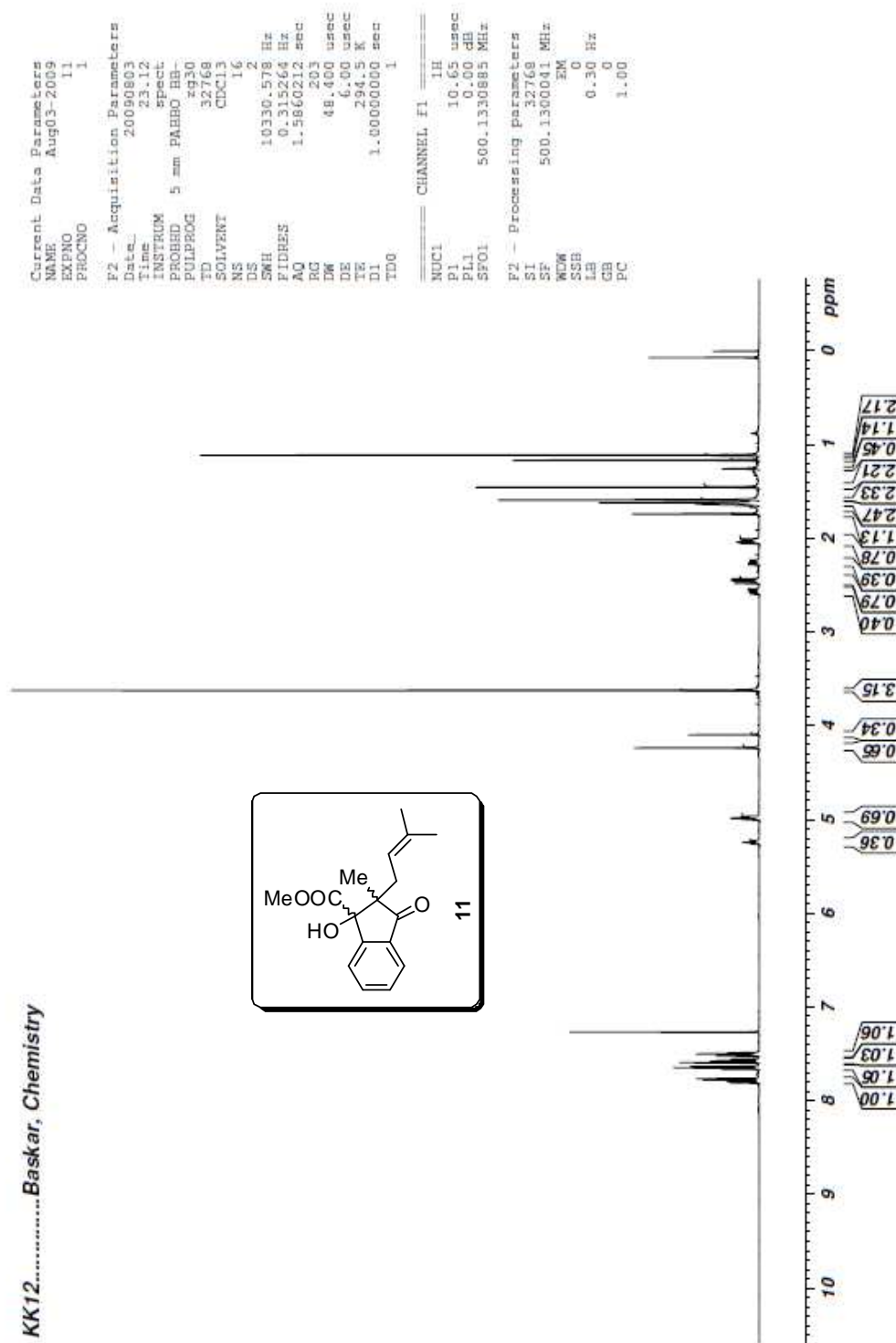
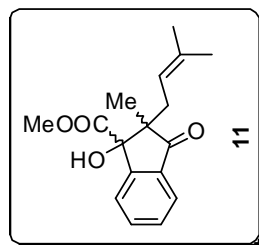
KK3.....Baskar, Chemistry



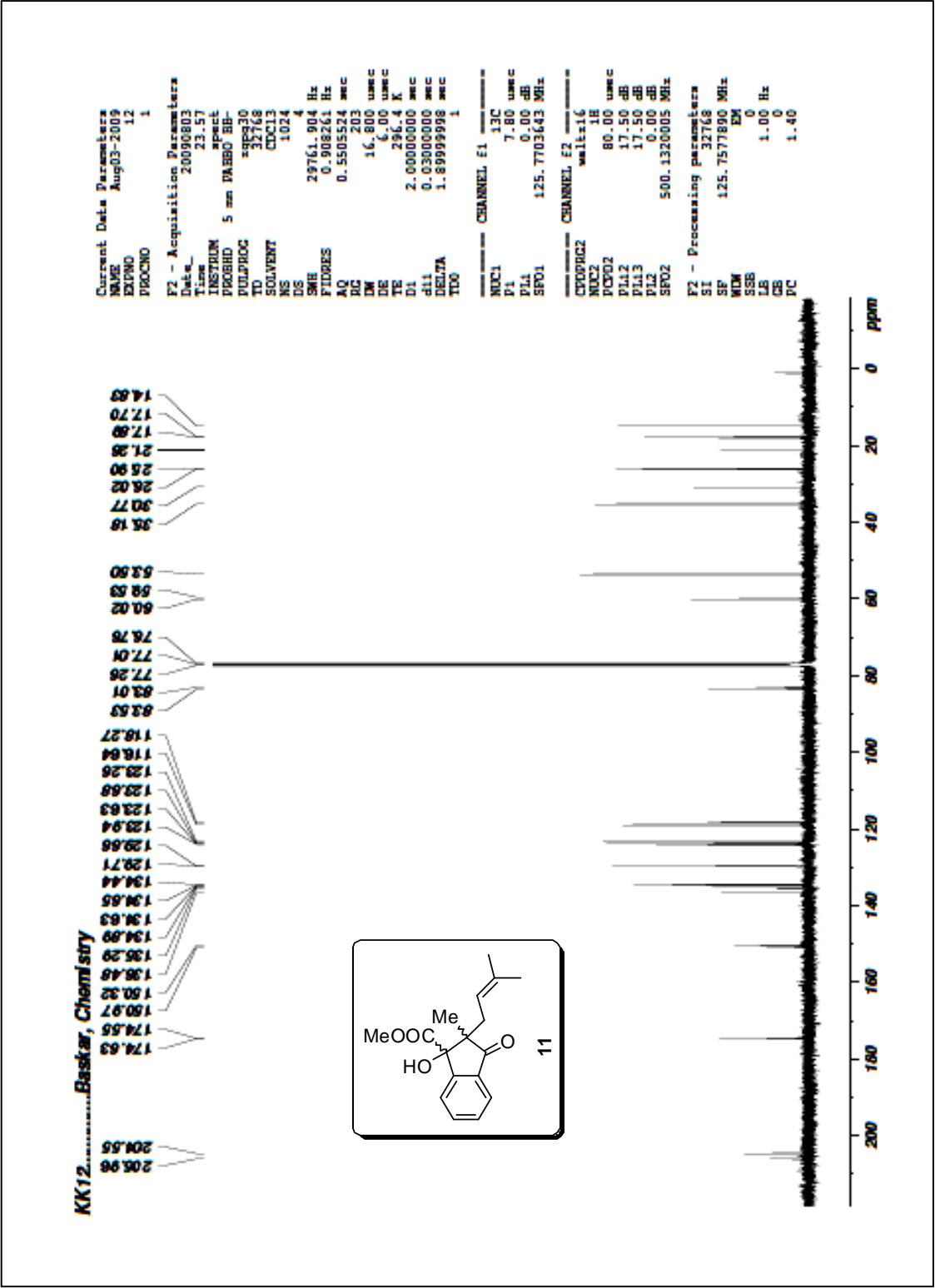
Current Data Parameters  
NAME C128-2009  
EXPNO 7  
PROCNO 1  
F2 - Acquisition Parameters  
Date\_ 20090729  
Time 12.00  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG hmcgpg36  
SOLVENT CDCl3  
NS 8  
DS 1  
SWH 5000.000 Hz  
FIDRES 1.420703 Hz  
AQ 0.4096500 sec  
RG 655  
DE 100.000 usec  
TE 300.2 K  
TEST13 8.000000  
G0 0.0000330 sec  
D1 1.3976005 sec  
D16 0.0500000 sec  
D17 0.0625000 sec  
INQ 0.0001790 sec  
===== CHANNEL f1 =====  
NUC1 1H  
P1 10.65 usec  
P2 21.30 usec  
P3 19.73 usec  
SFO1 500.1319800 MHz  
===== CHANNEL f2 =====  
NUC2 13C  
P1 7.80 usec  
P2 0.00 dB  
P3 125.7703495 MHz  
SFO2 125.7703495 MHz  
===== GRADIENT CHANNEL =====  
GENM1 SINE.100  
SFO1 222.035 DPM  
GENM2 SINE.100  
GENM3 SINE.100  
GR21 50.00 %  
GR22 50.00 %  
GR23 40.00 %  
P16 1000.00 usec  
F1 - Acquisition parameters  
ND0 2  
TD 128  
SFO1 125.7703495 MHz  
SFO2 222.035 DPM  
SFO3 222.035 DPM  
F2 - Processing parameters  
SI 1024  
SF 500.1300412 MHz  
WDW SINE  
SSB 0  
LB 0.00 Hz  
GB 0  
PC 1.40  
F1 - Processing parameters  
SI 1024  
SF 125.7703495 MHz  
WDW SINE  
SSB 0  
LB 0.00 Hz  
GB 0

$^1\text{H}$ - $^{13}\text{C}$  COSY (HMBC) NMR spectrum of compound 10

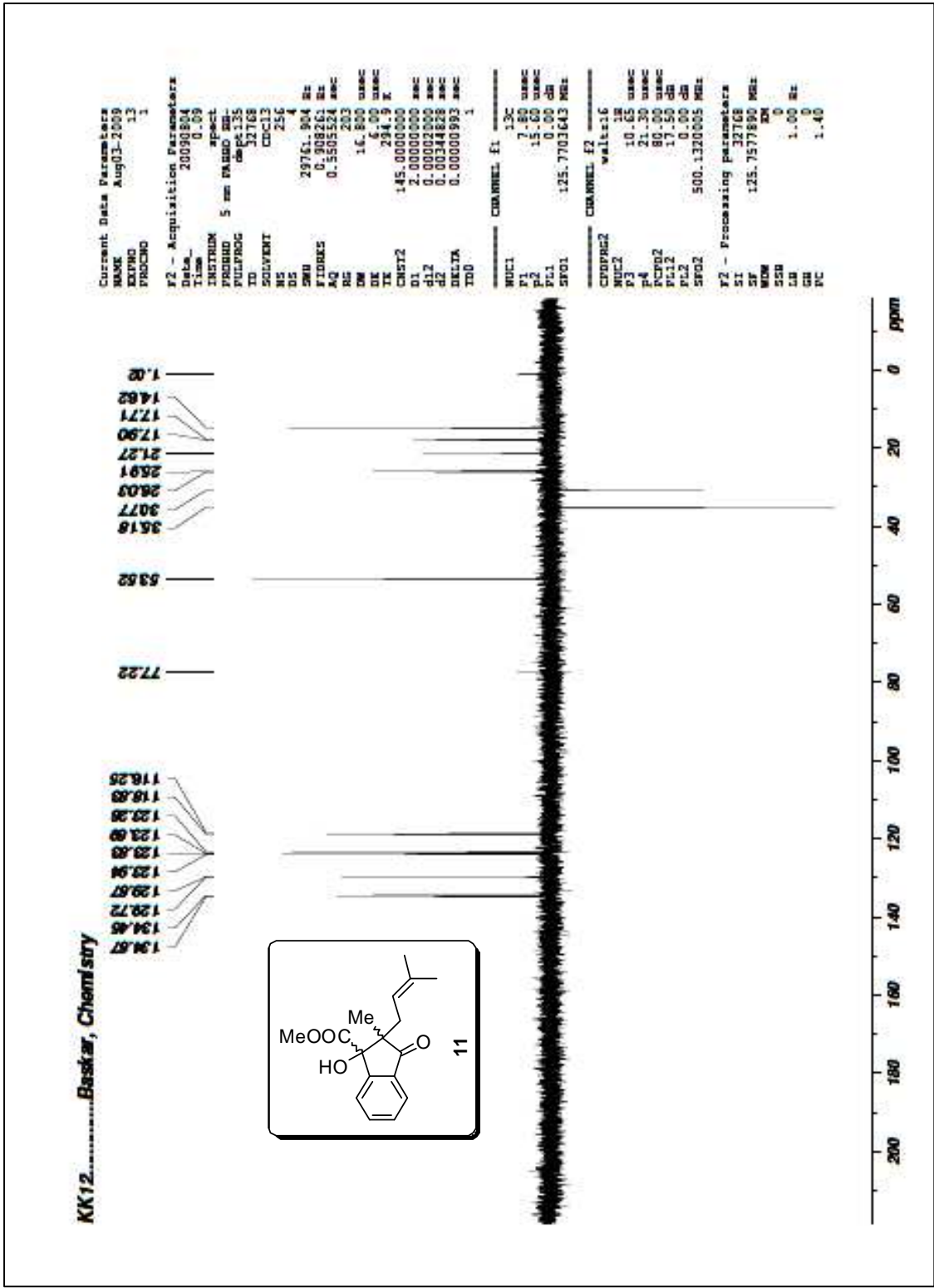
KK12.....Baskar, Chemistry



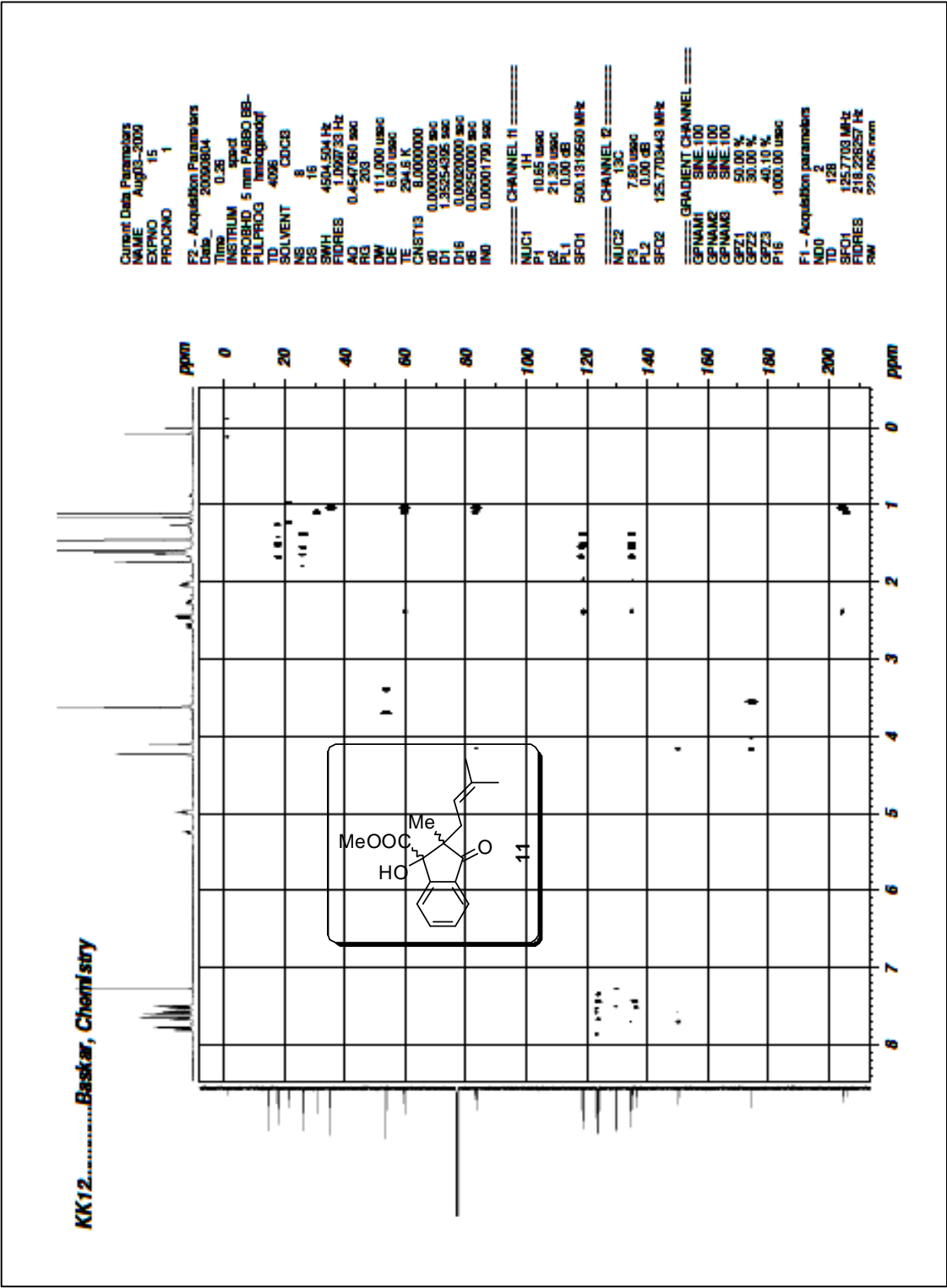
<sup>1</sup>H NMR spectrum of compound 11



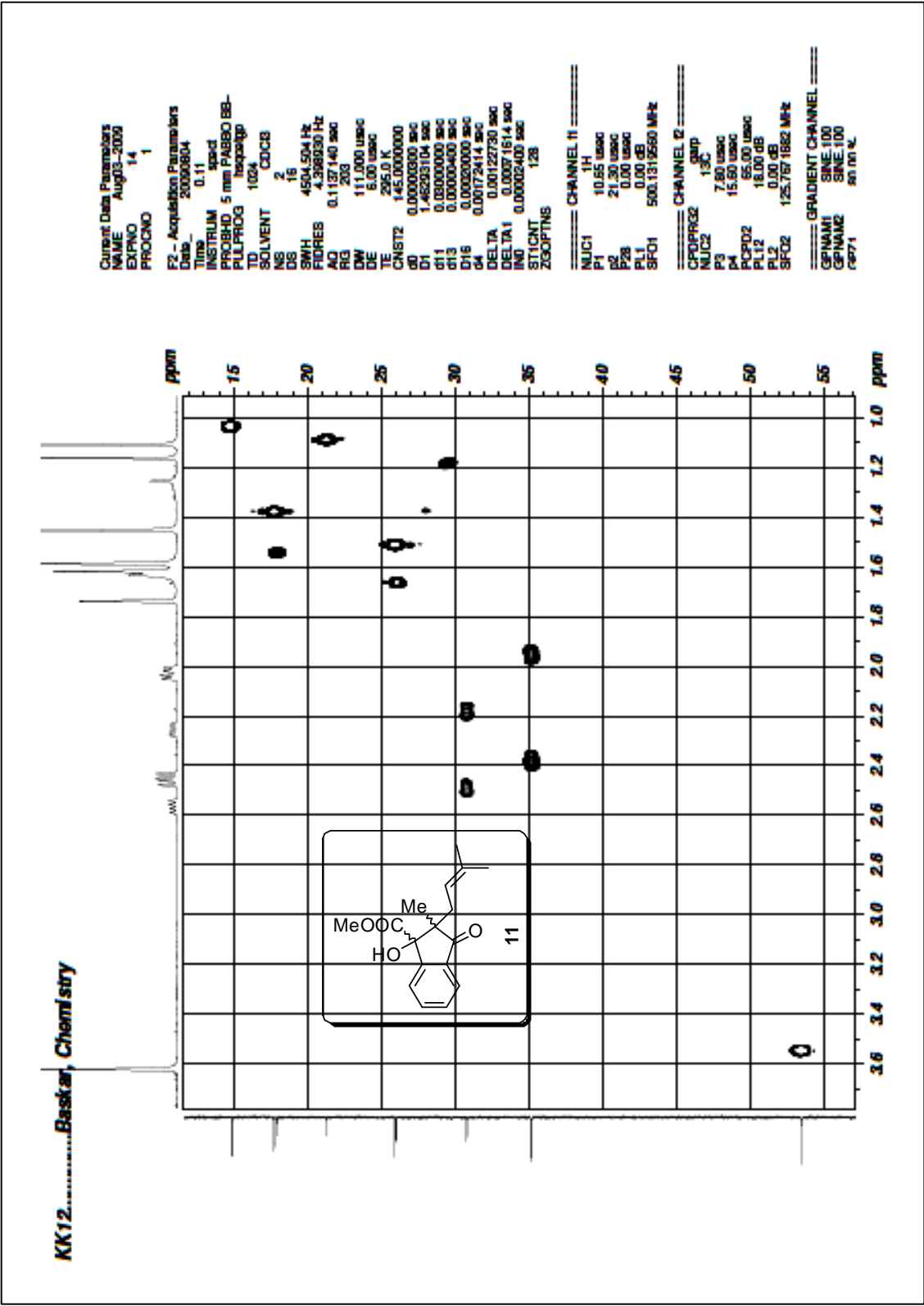




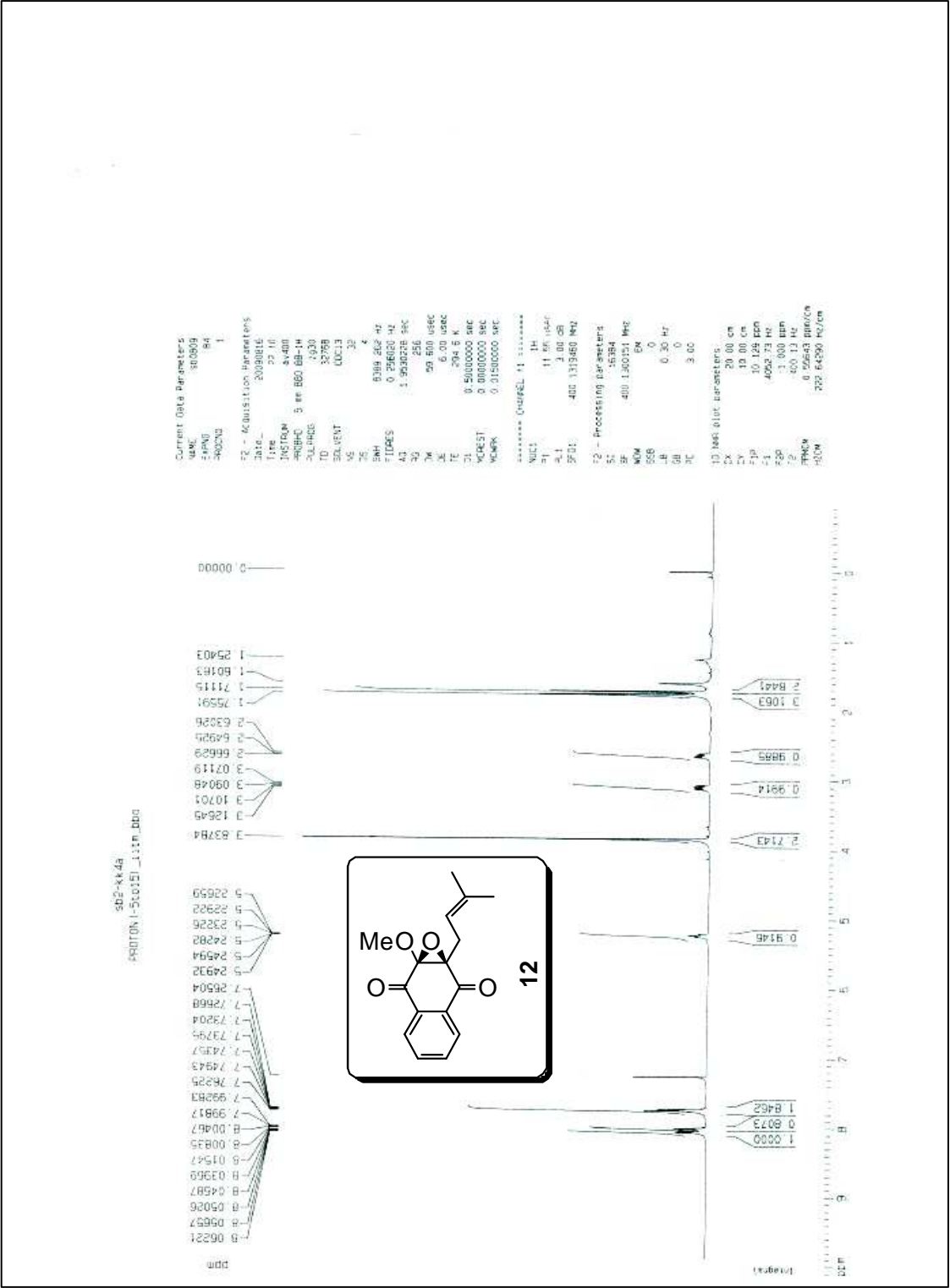
DEPT spectrum of compound 11



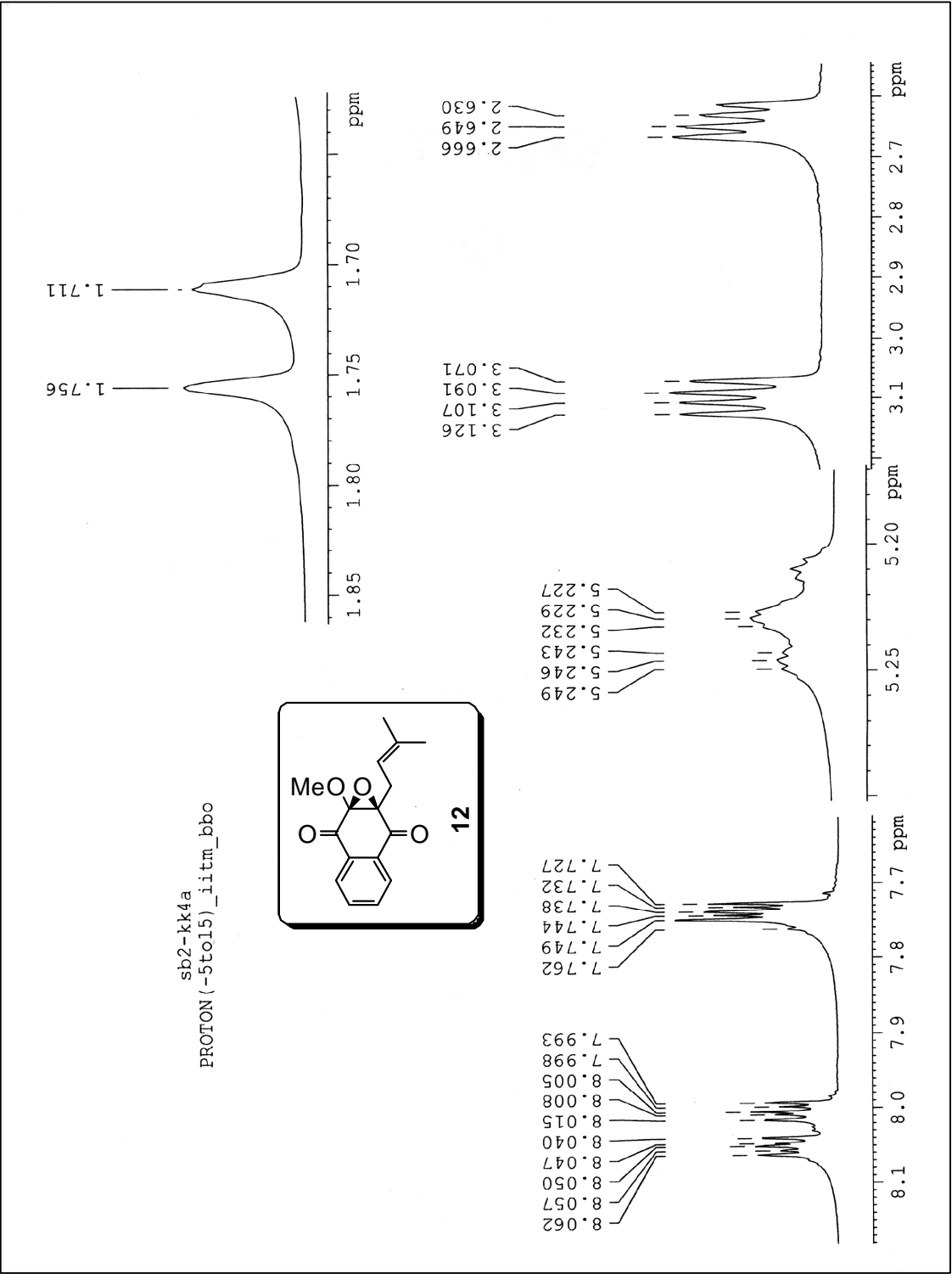
<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound 11



<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound 11

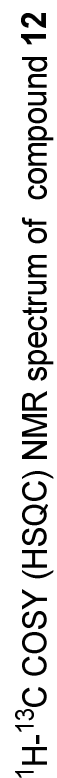


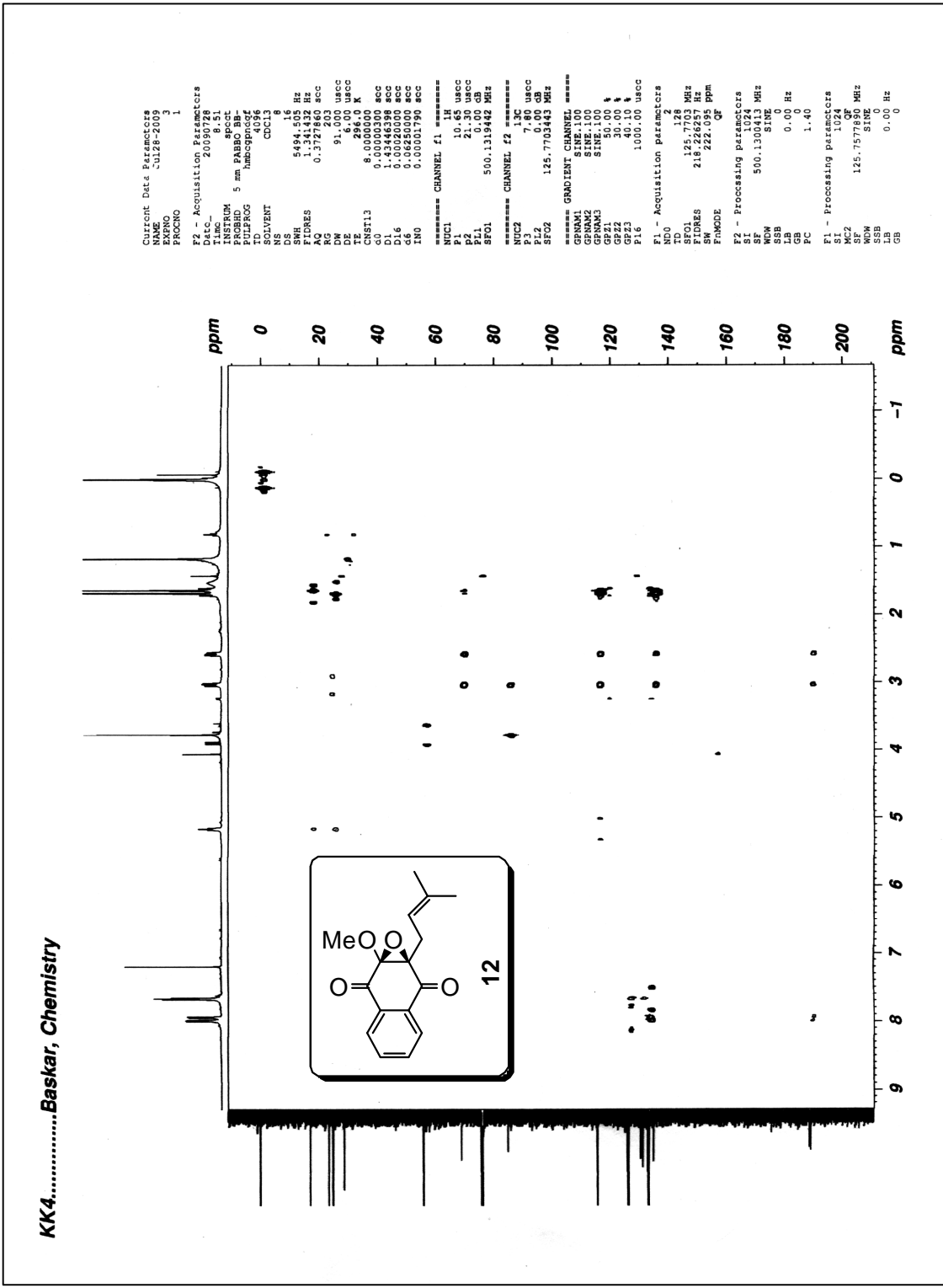
<sup>1</sup>H NMR spectrum of compound 12



Expanded <sup>1</sup>H NMR spectrum of compound **12**

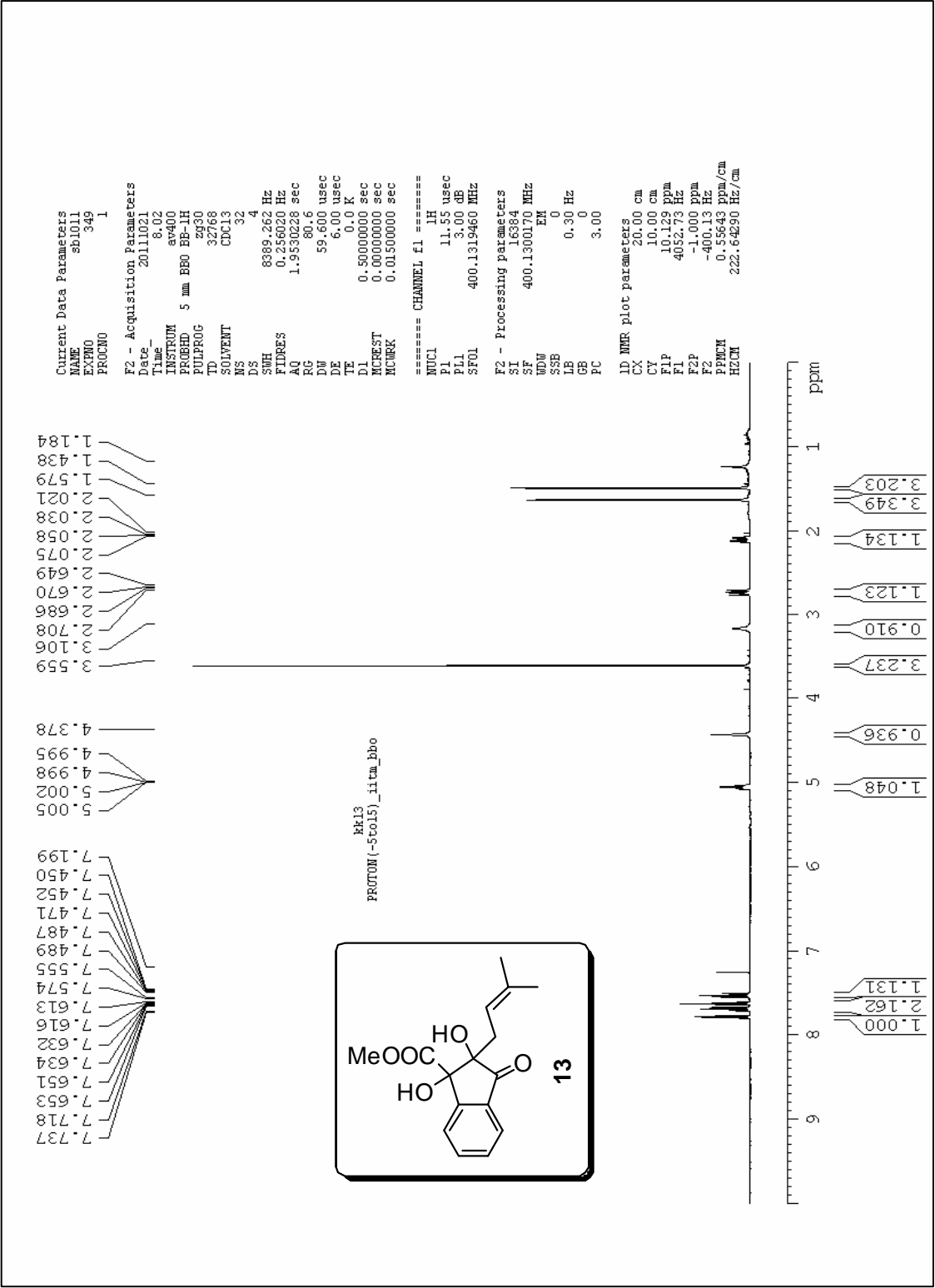
**<sup>13</sup>C NMR spectrum of compound 12**



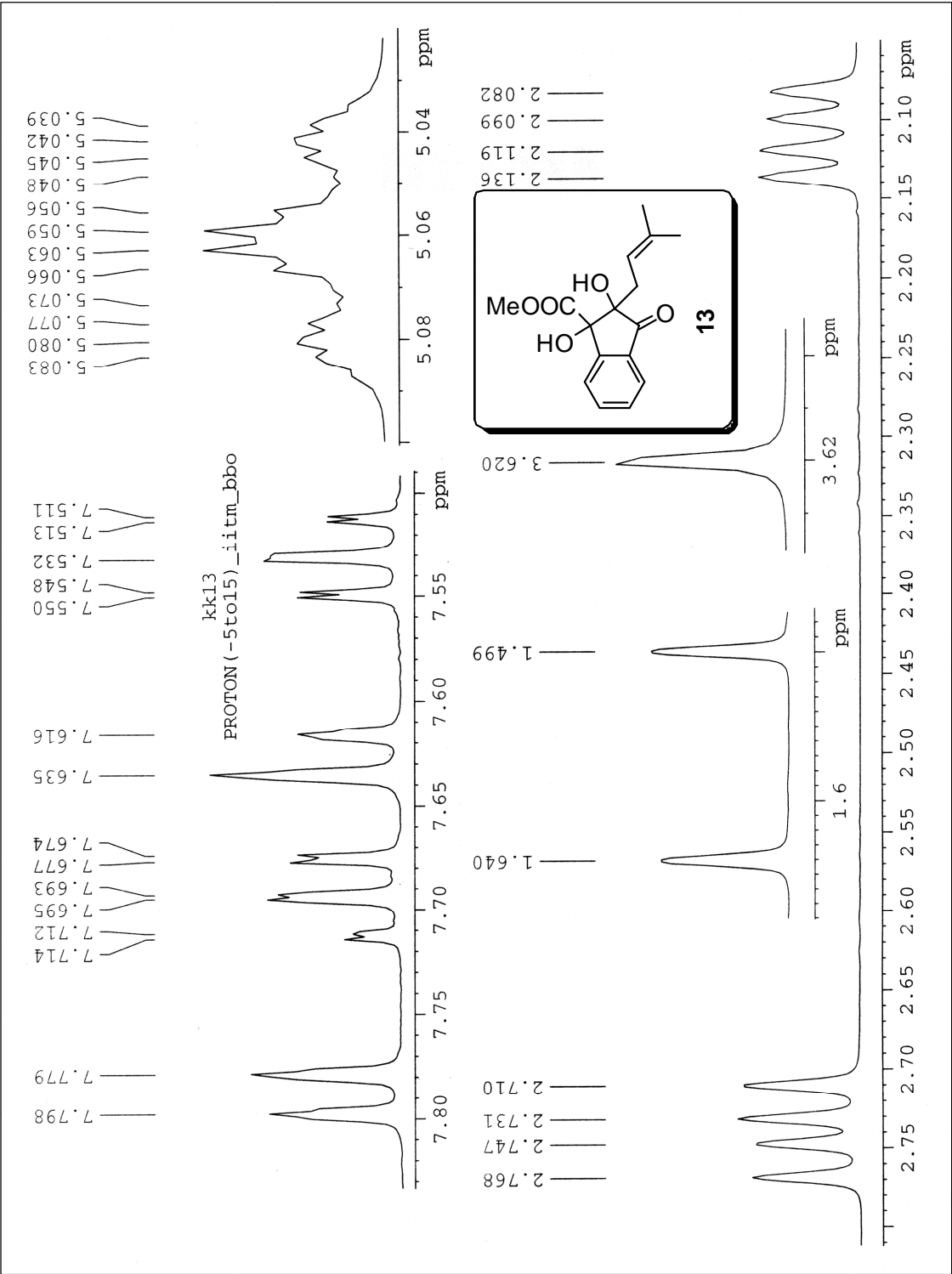


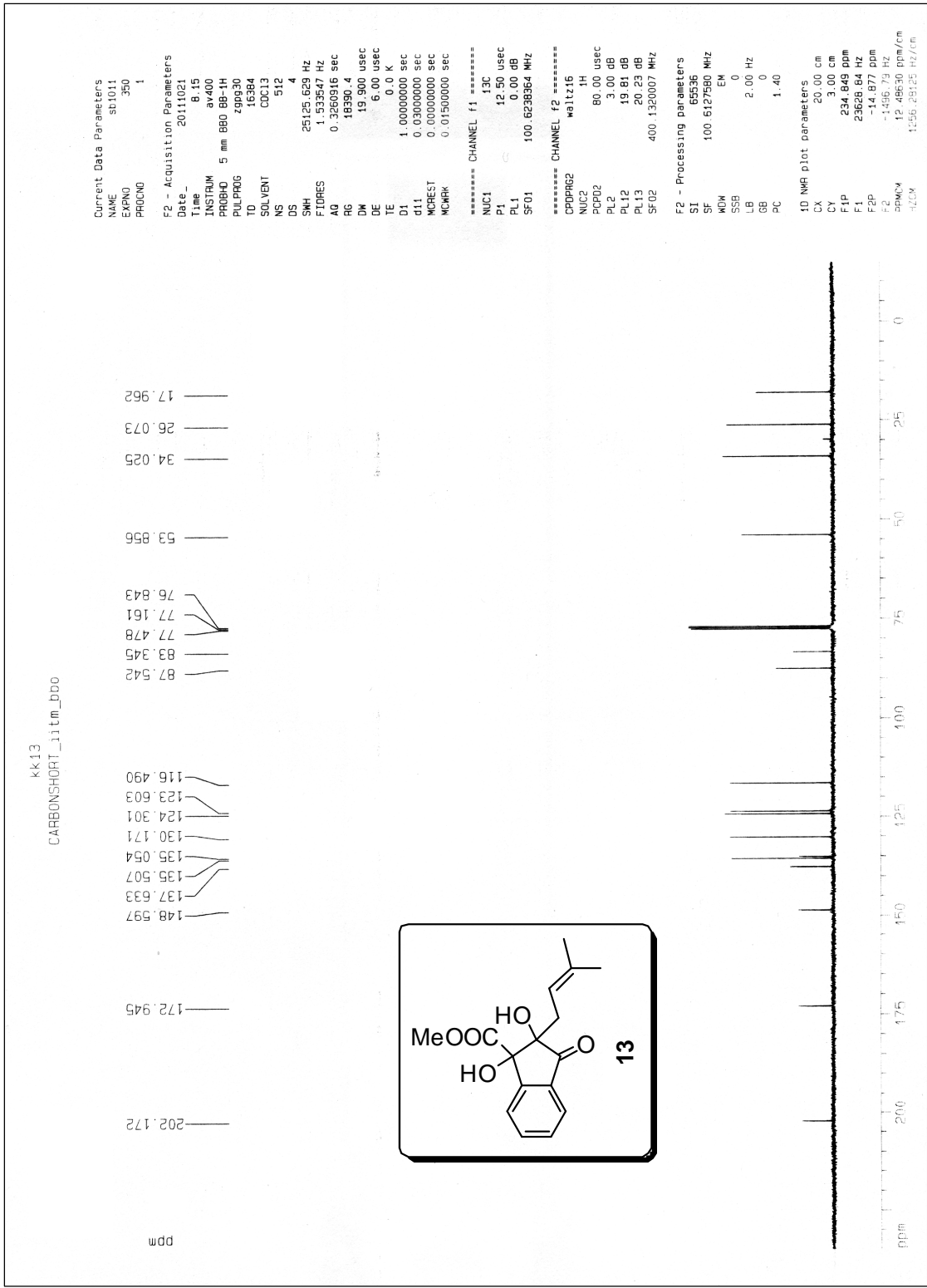
$^1\text{H}$ - $^{13}\text{C}$  COSY (HMBC) NMR spectrum of compound 12



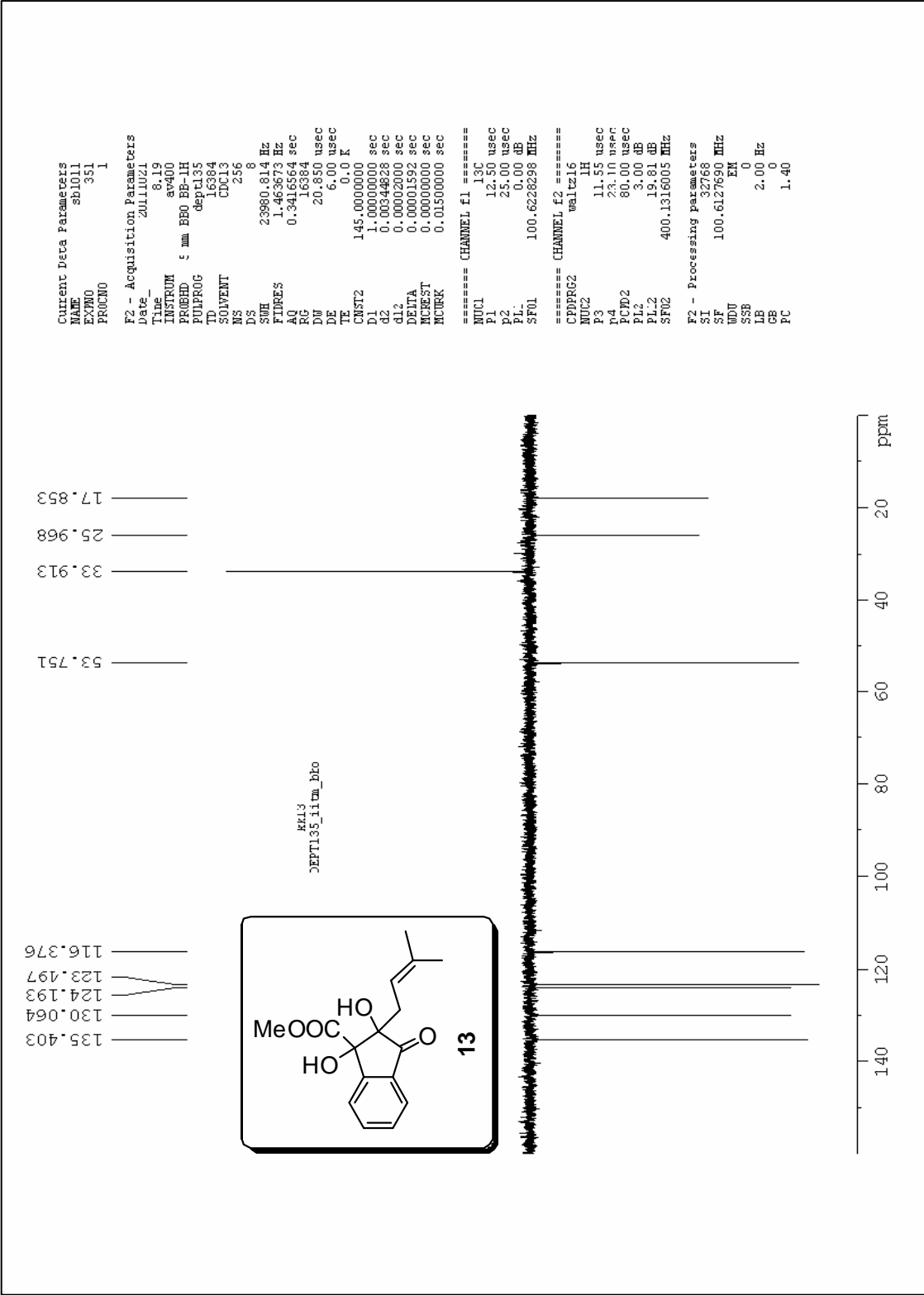


<sup>1</sup>H NMR spectrum of compound 13

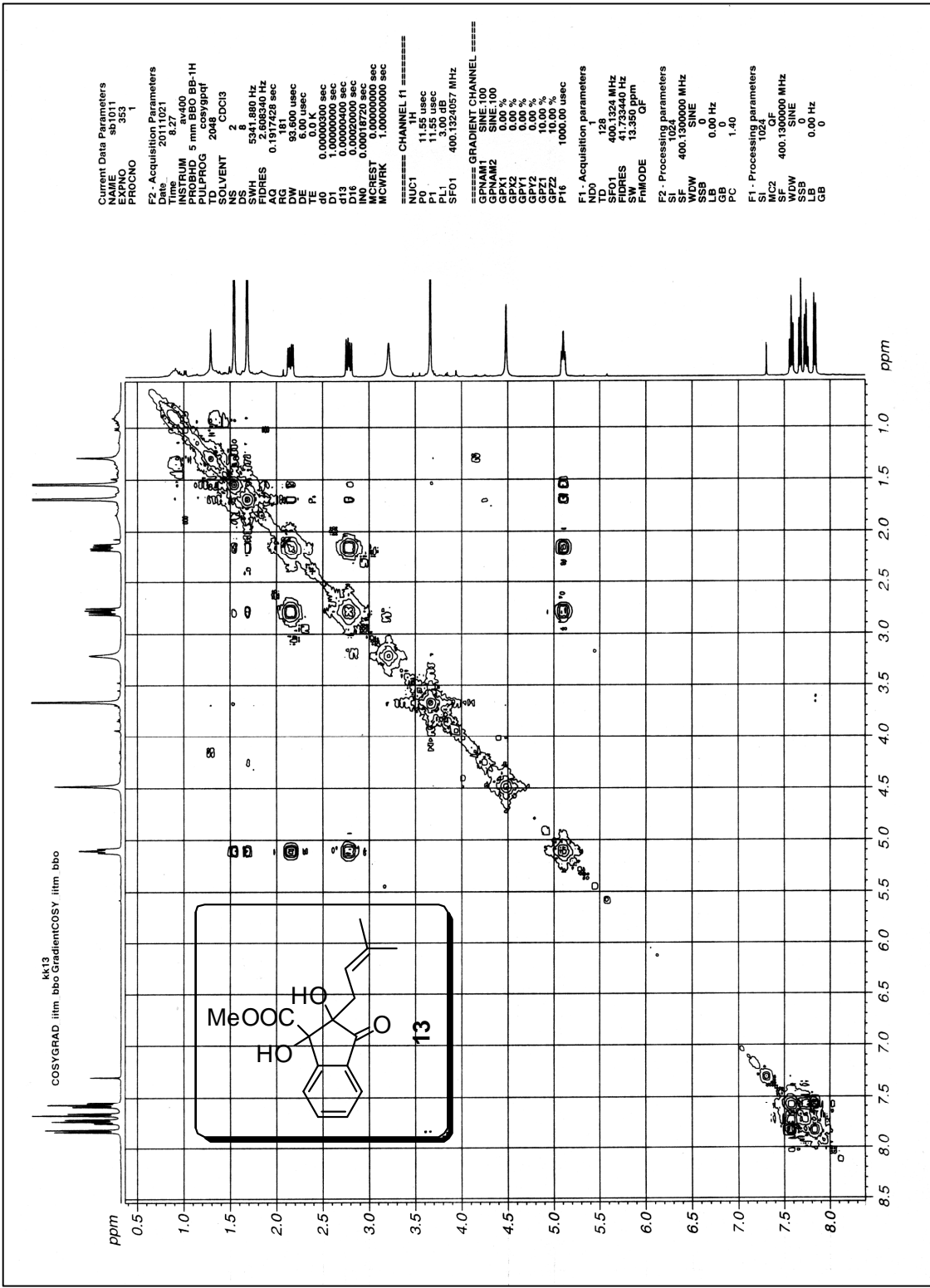




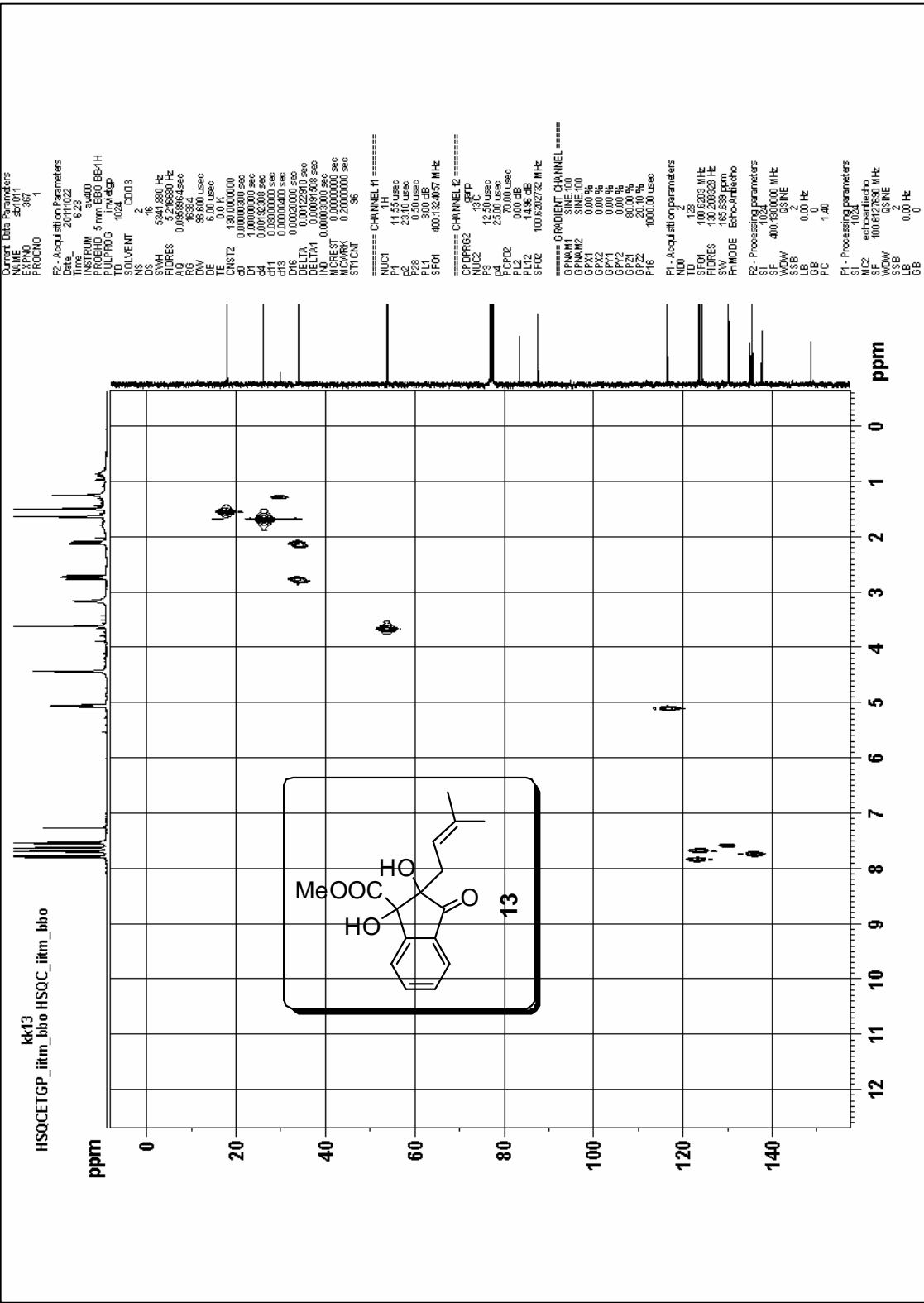
<sup>13</sup>C NMR spectrum of compound 13



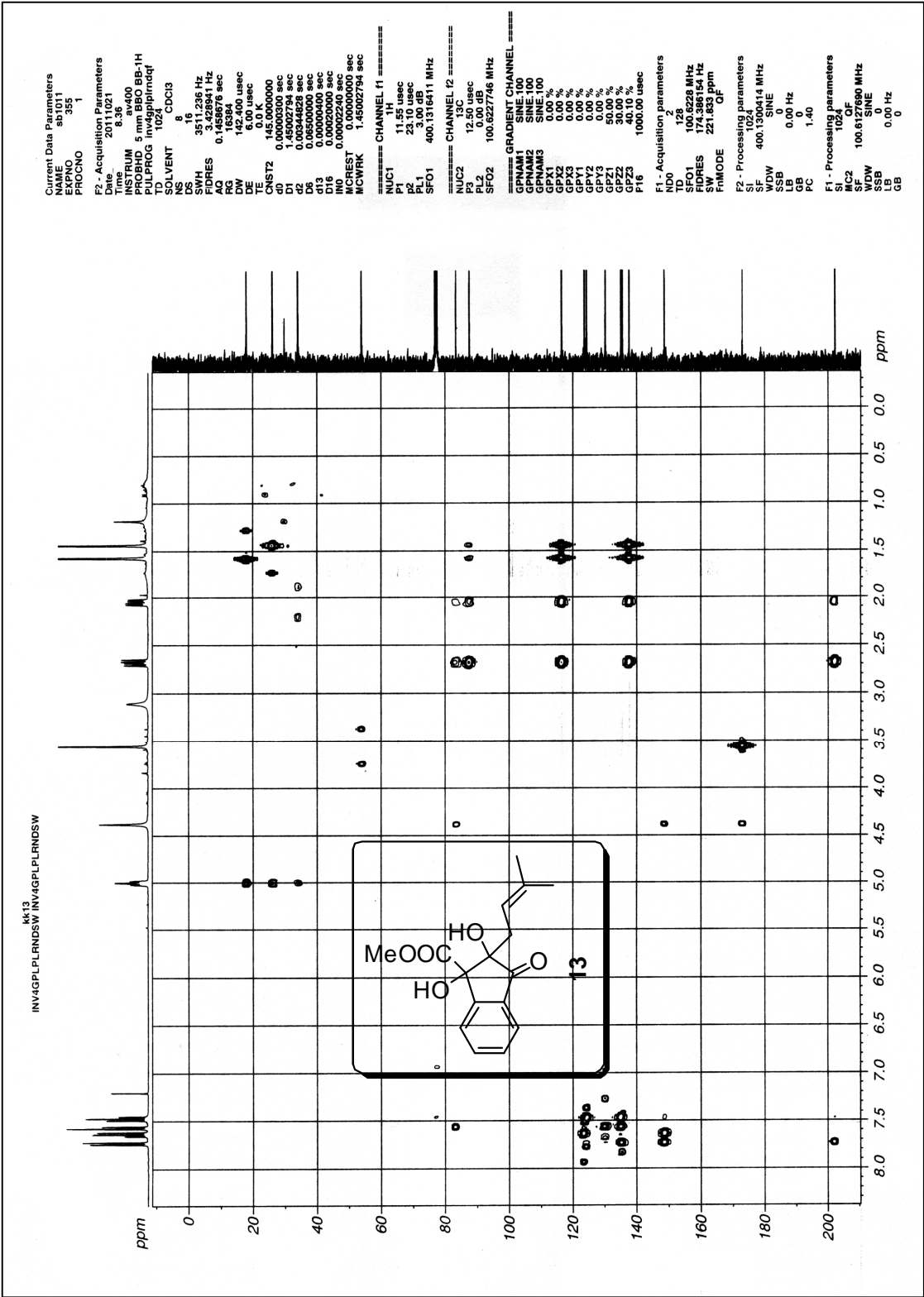
DEPT spectrum of compound 13



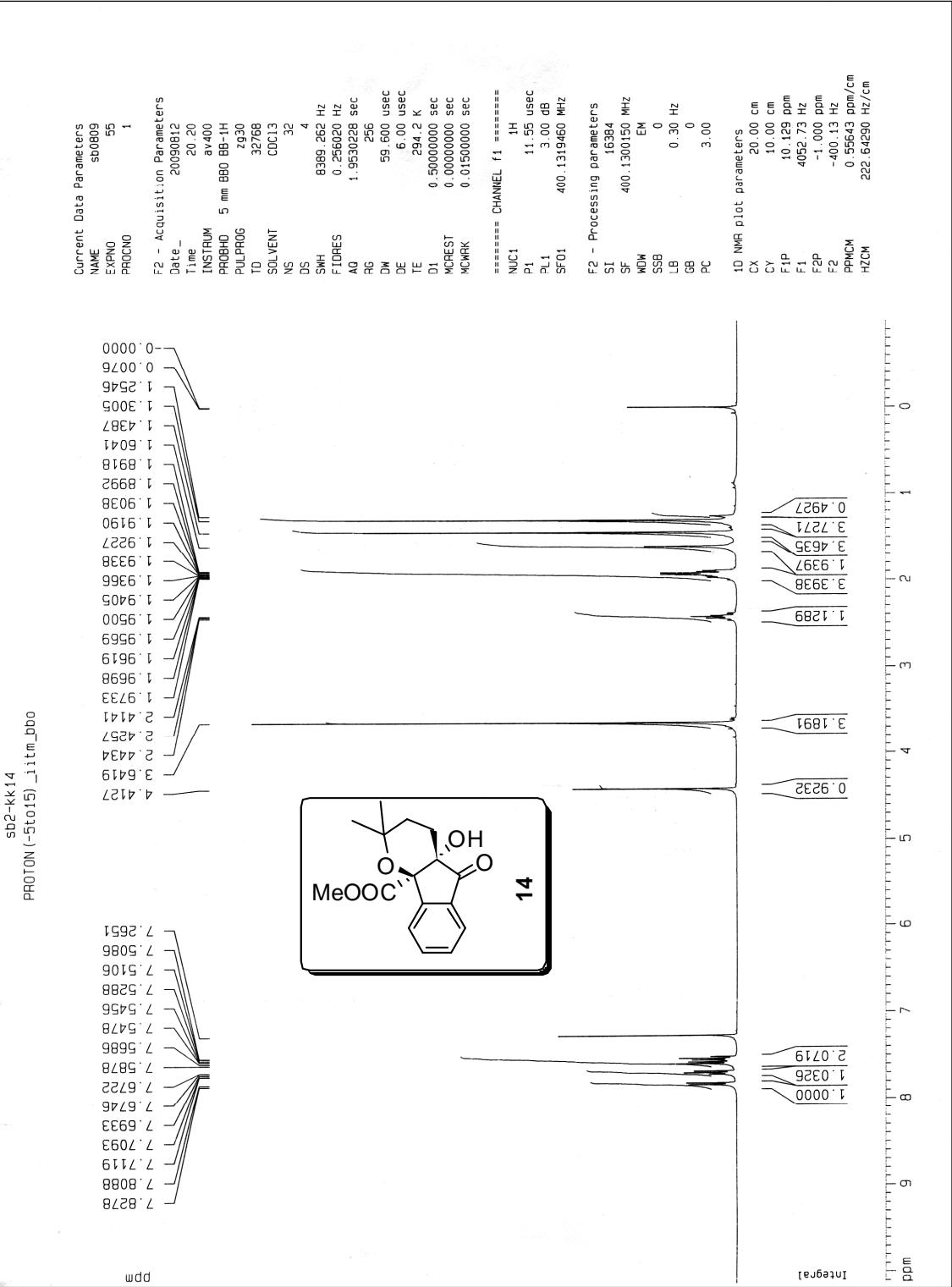
<sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound **13**



<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound 13

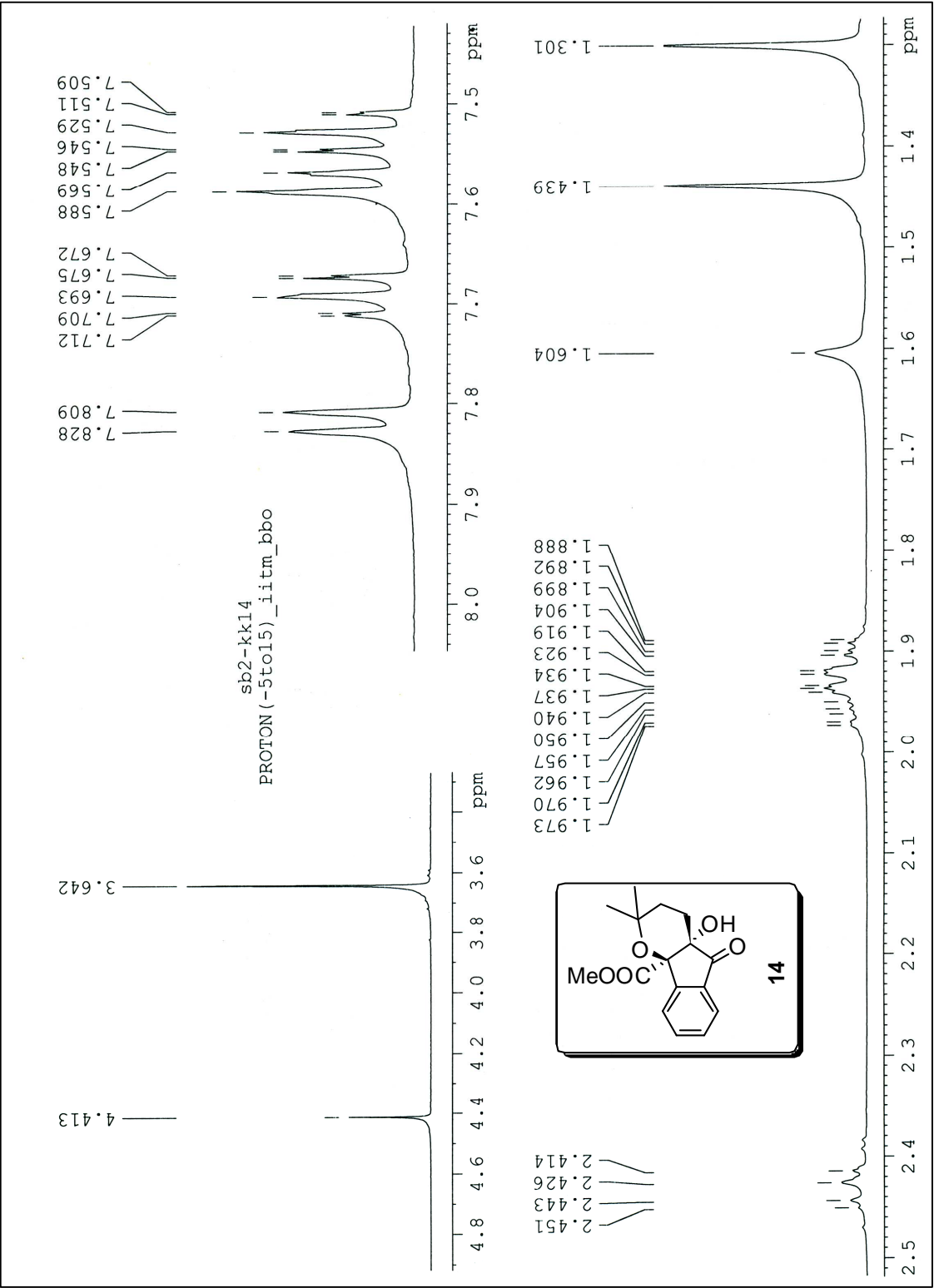


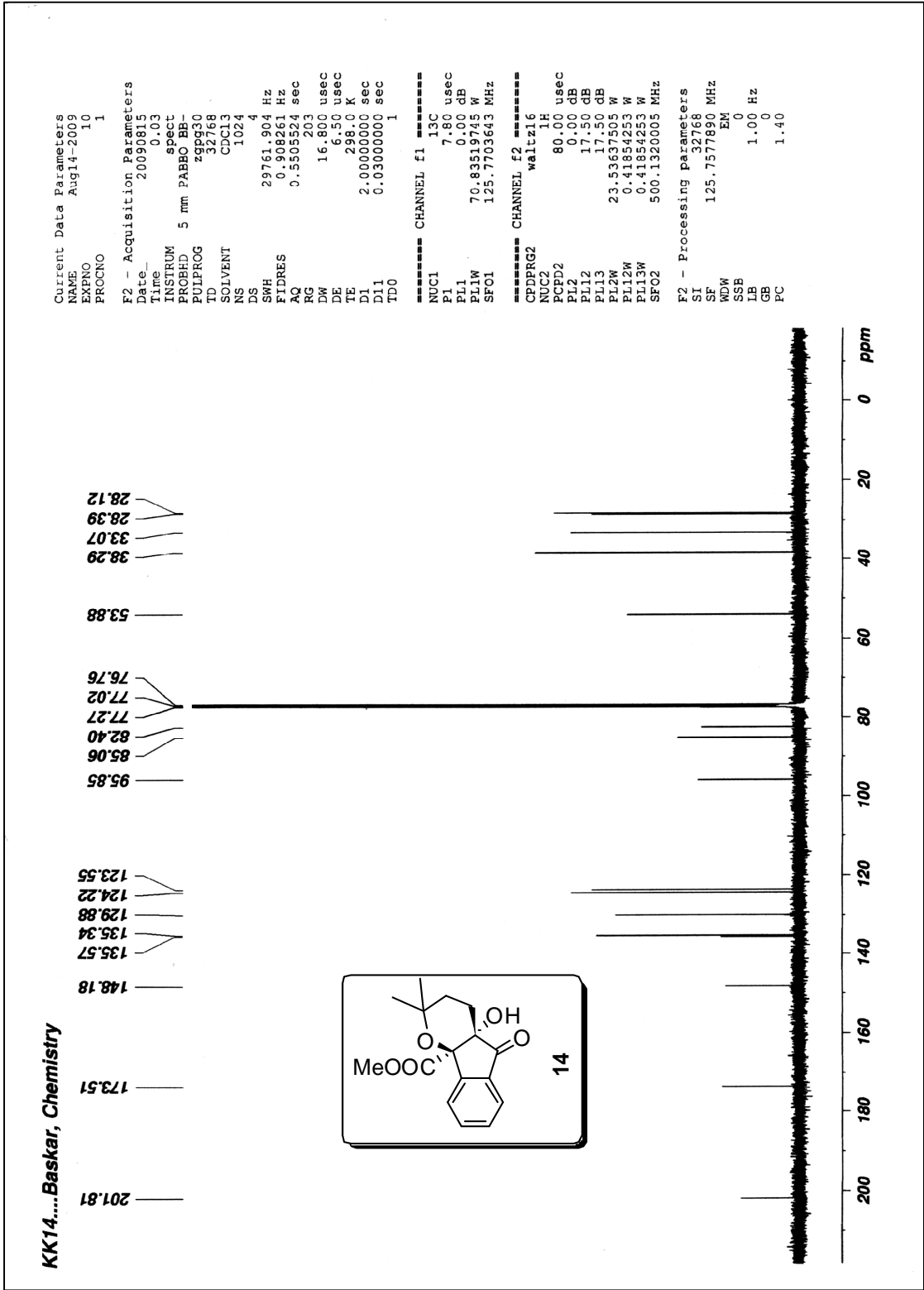
<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound 13



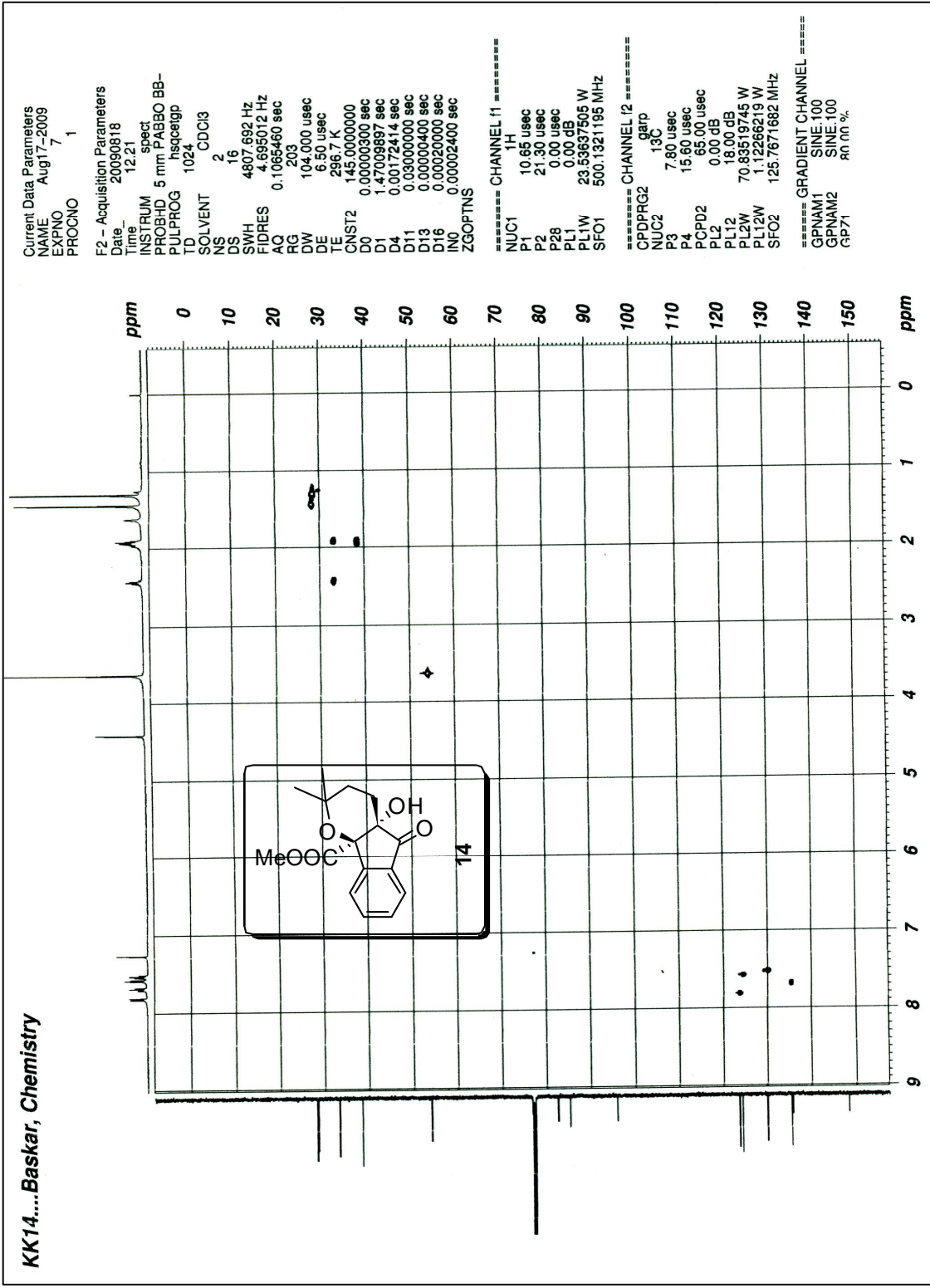
<sup>1</sup>H NMR spectrum of compound 14



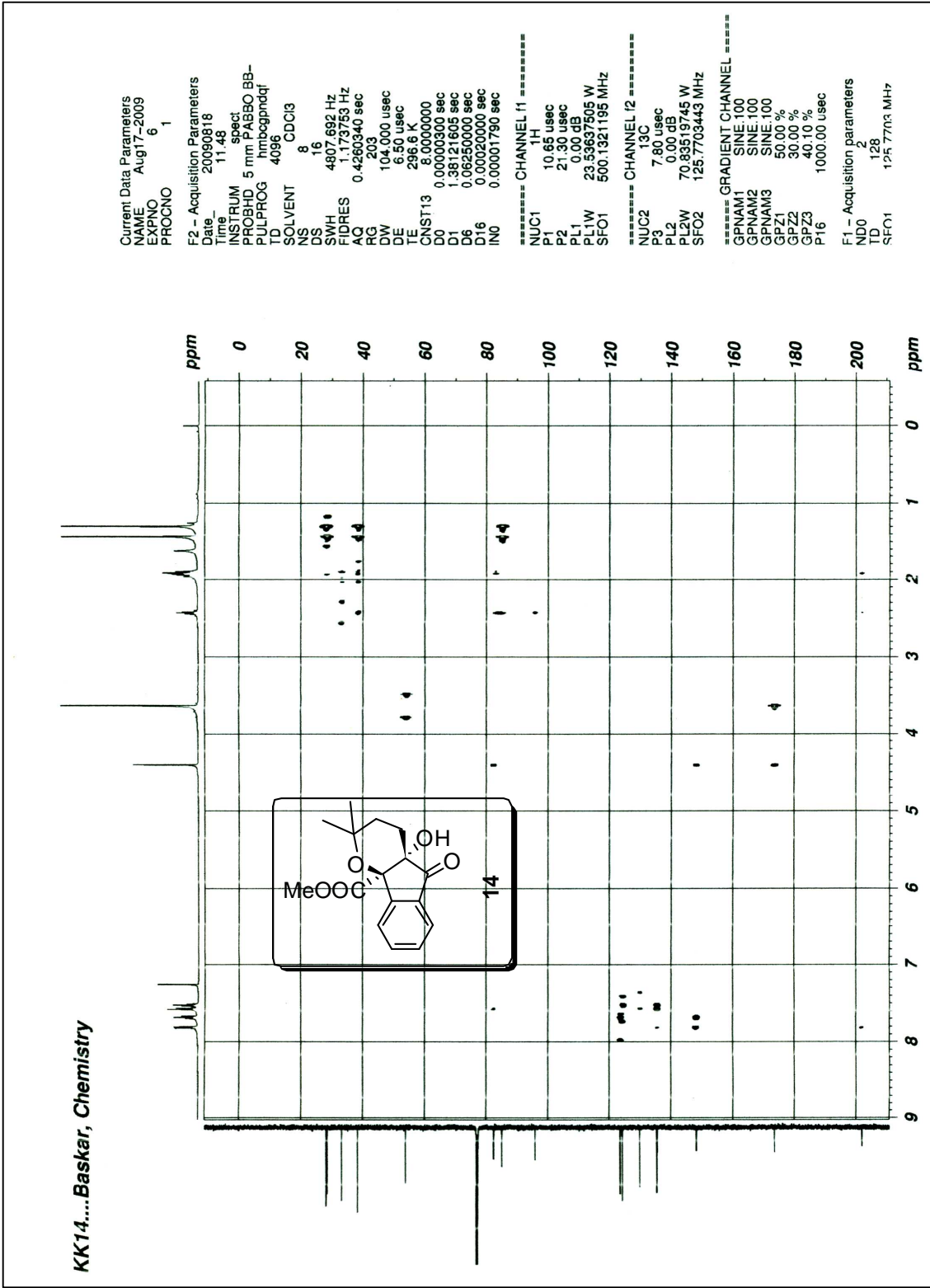




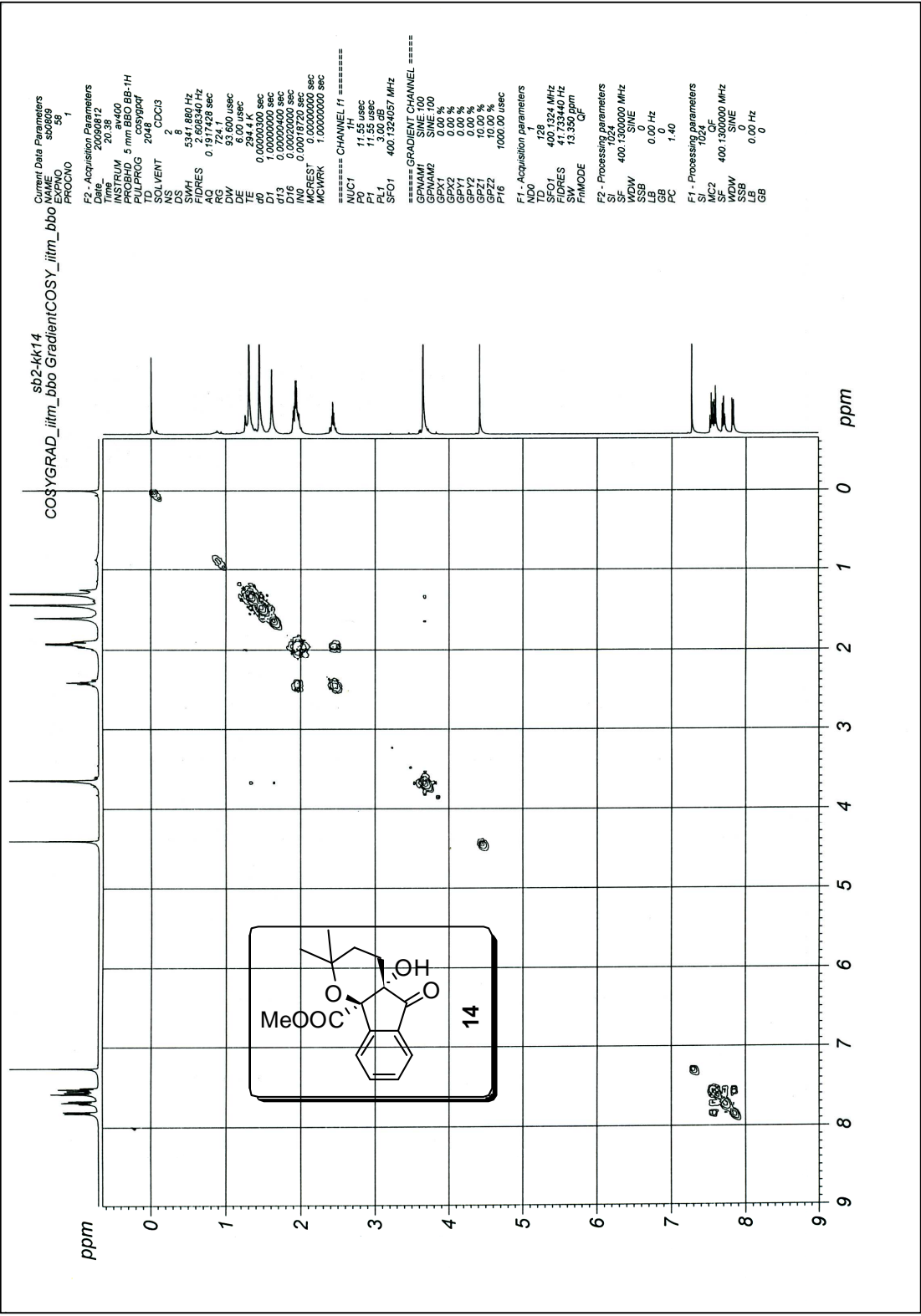
<sup>13</sup>C NMR spectrum of compound 14



<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound 14



<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound **14**



<sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 14

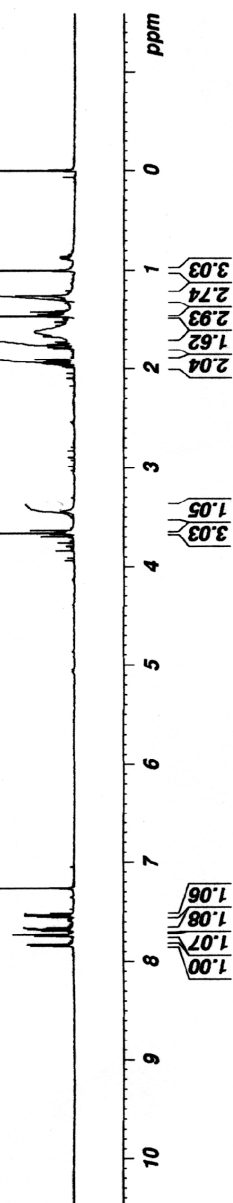
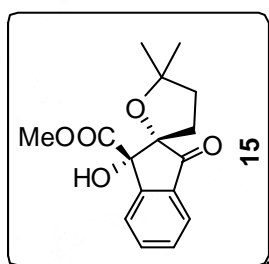
KK13a.....Baskar, Chemistry

Current Data Parameters  
NAME Aug14-2009  
EXPNO 18  
PROCNO 1

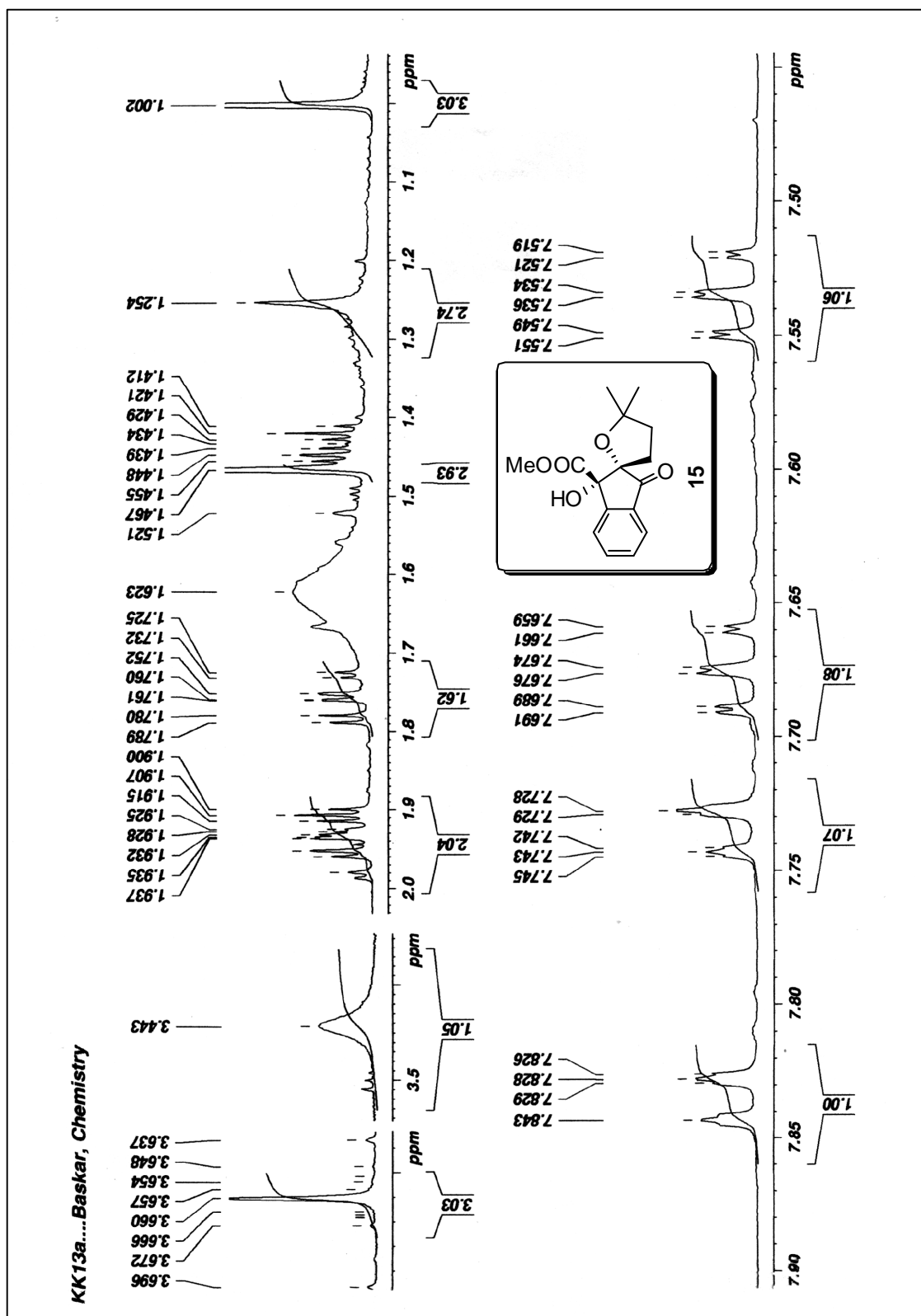
F2 - Acquisition Parameters  
Date\_ 20090815  
Time 1.04  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 32768  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 10330.578 Hz  
FIDRES 0.315264 Hz  
AQ 1.5860212 sec  
RG 203  
DE 48.400 usec  
TE 296.4 K  
D1 1.00000000 sec  
TD0 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 10.65 usec  
PL1 0.00 dB  
PL1W 23.53637505 W  
SF01 500.1330885 MHz

F2 - Processing parameters  
SI 32768  
SF 500.1300109 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

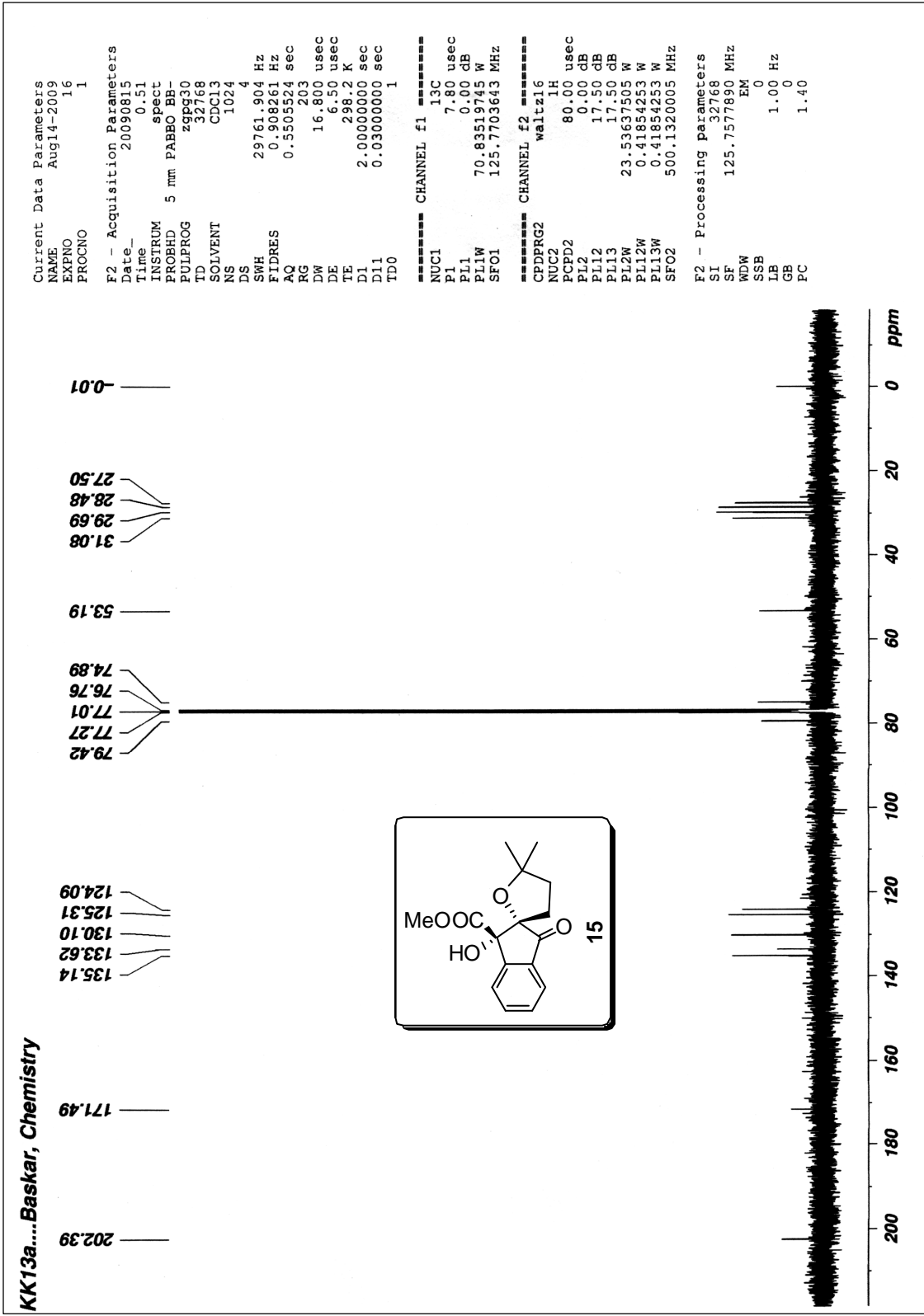


<sup>1</sup>H NMR spectrum of compound 15

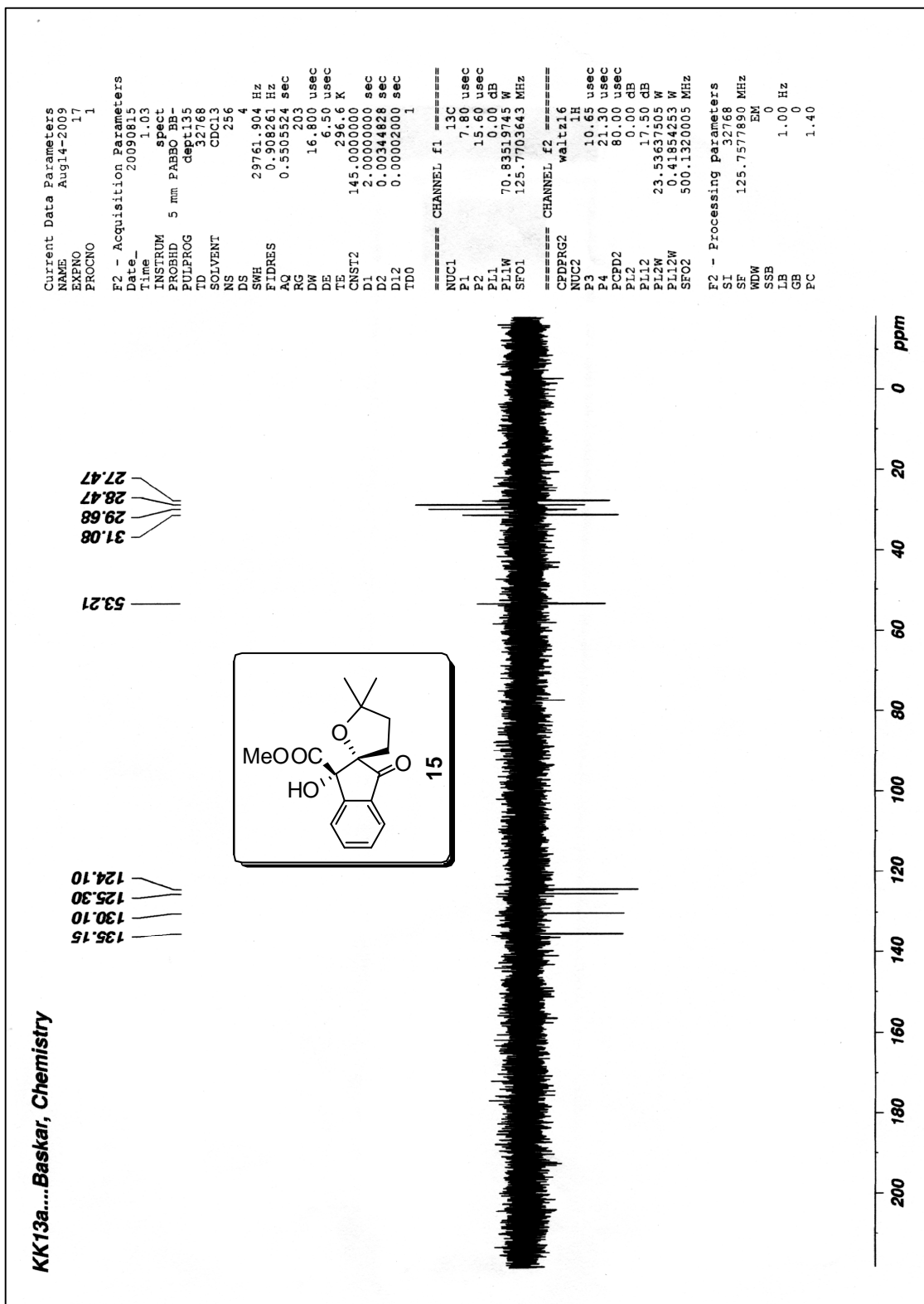


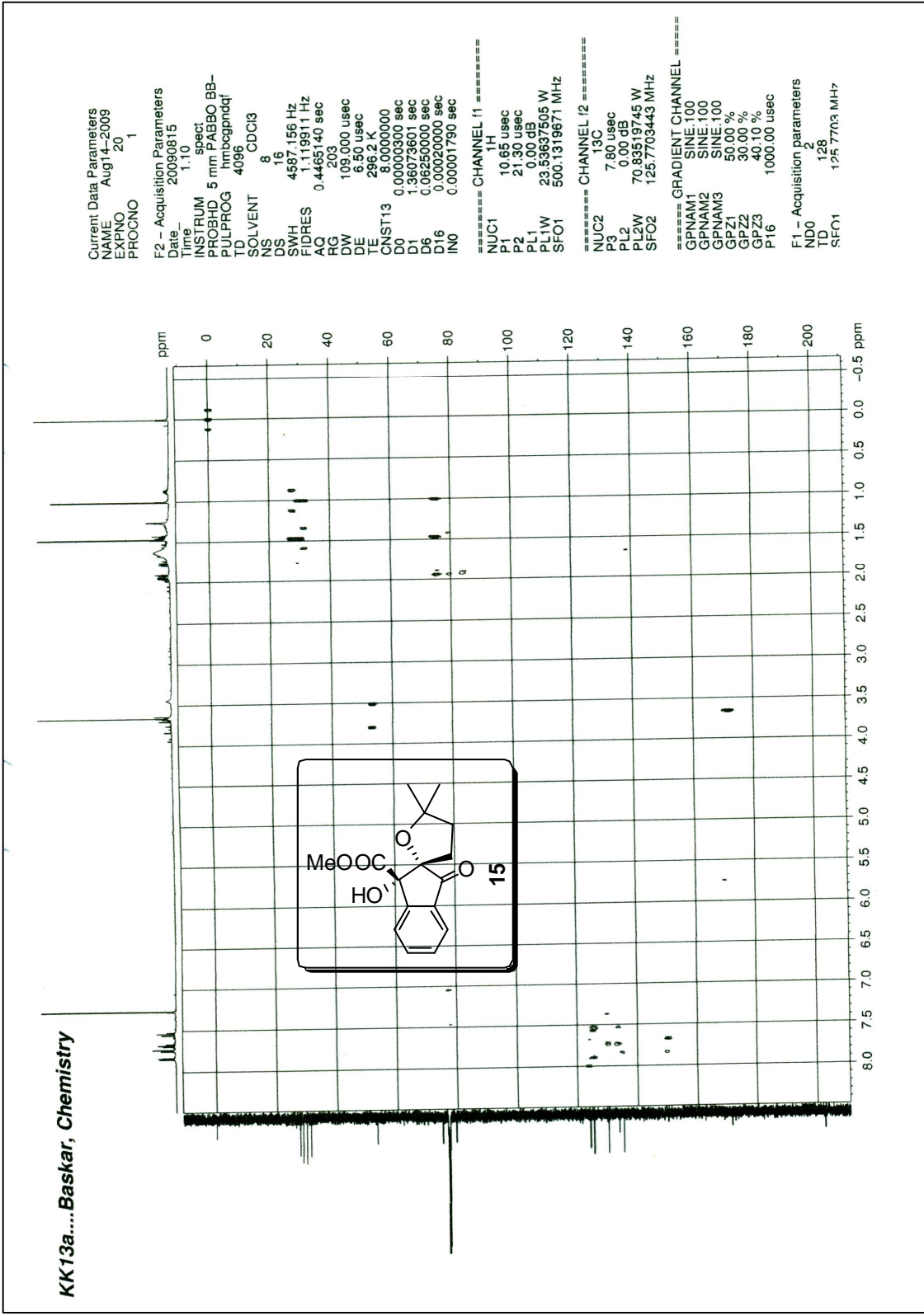
Expanded <sup>1</sup>H NMR spectrum of compound 15



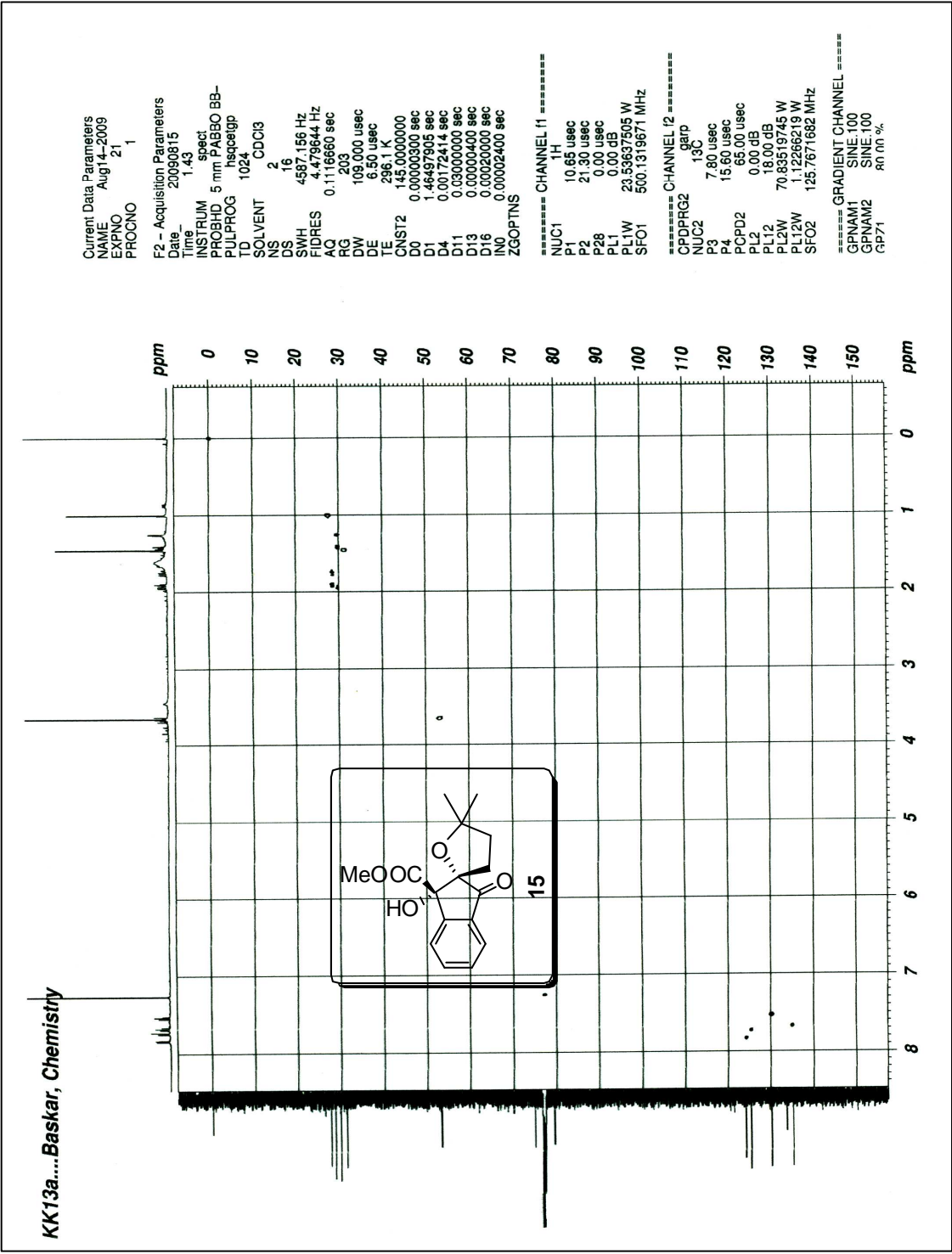




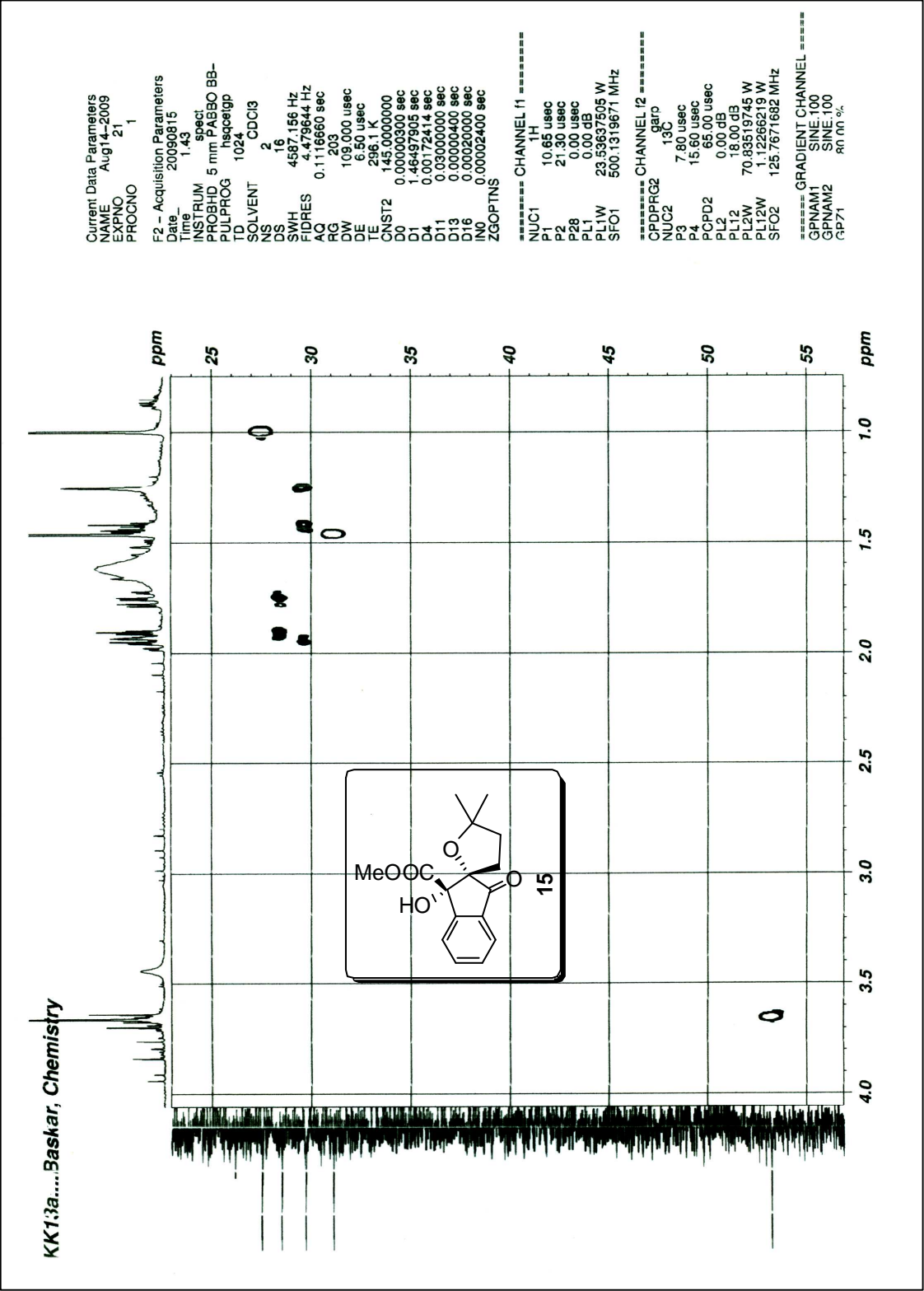


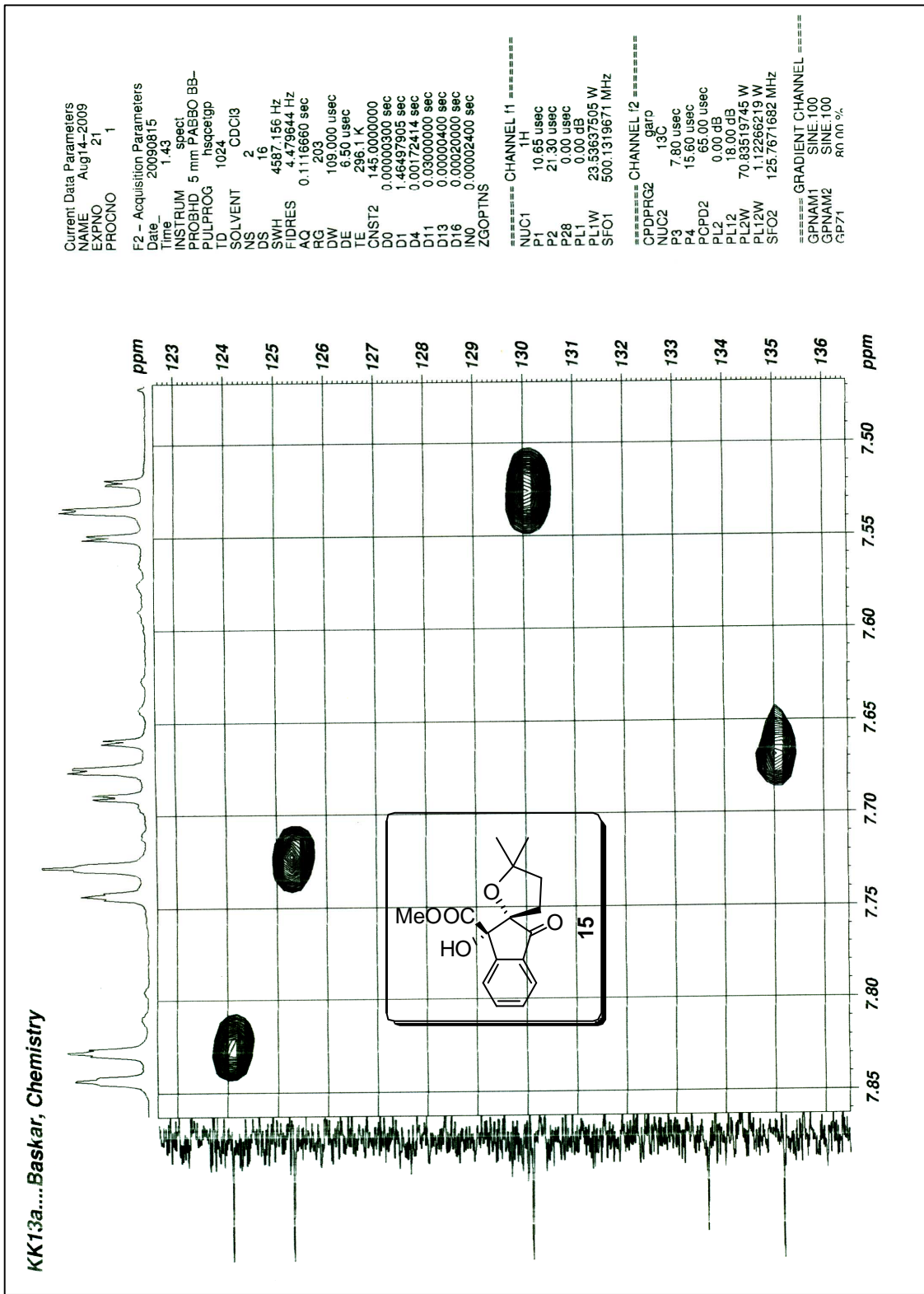


<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound **15**



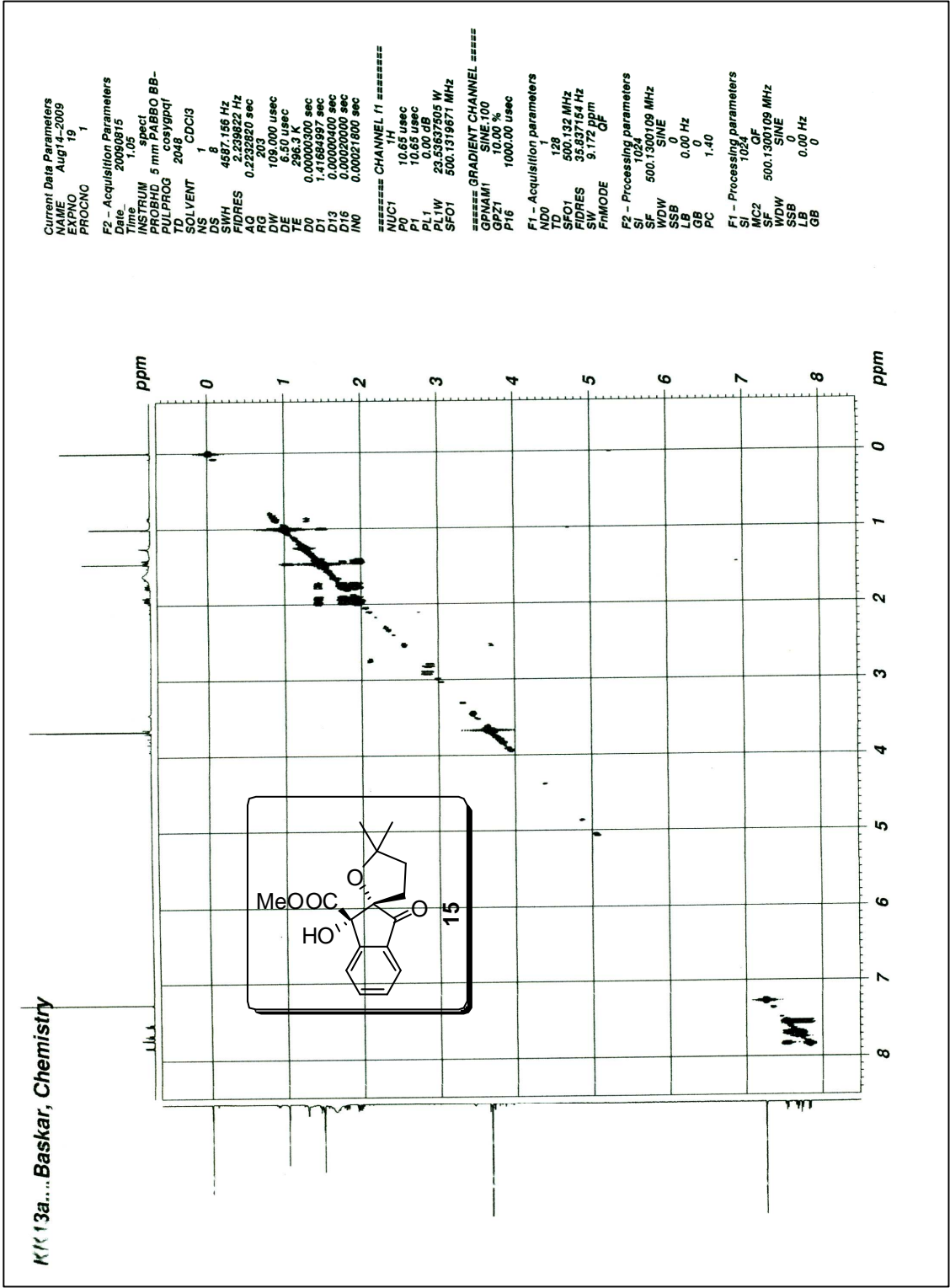
<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound 15



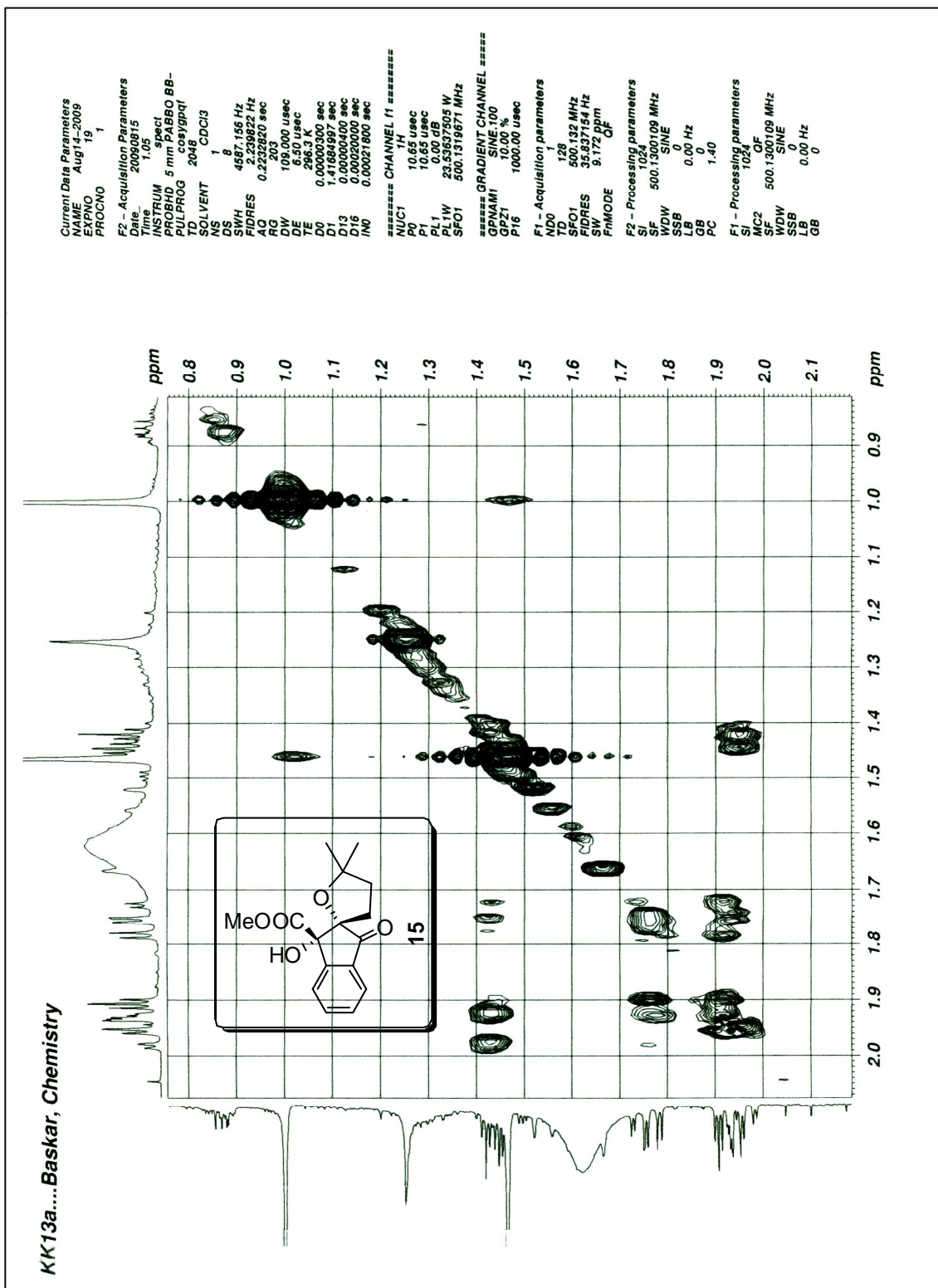


Expanded  $^1\text{H}$ - $^{13}\text{C}$  COSY (HSQC) NMR spectrum of compound **15**

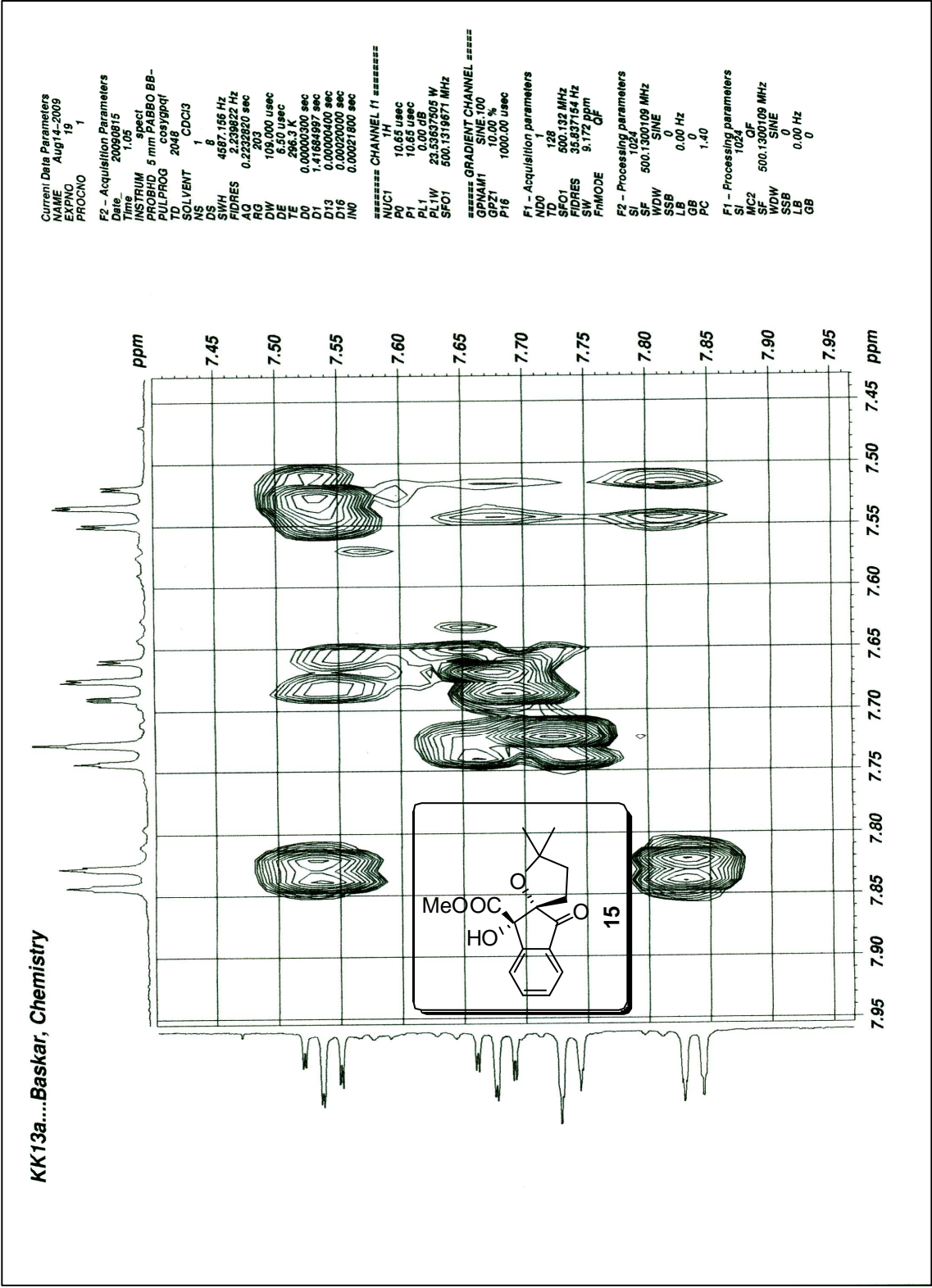




<sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound **15**

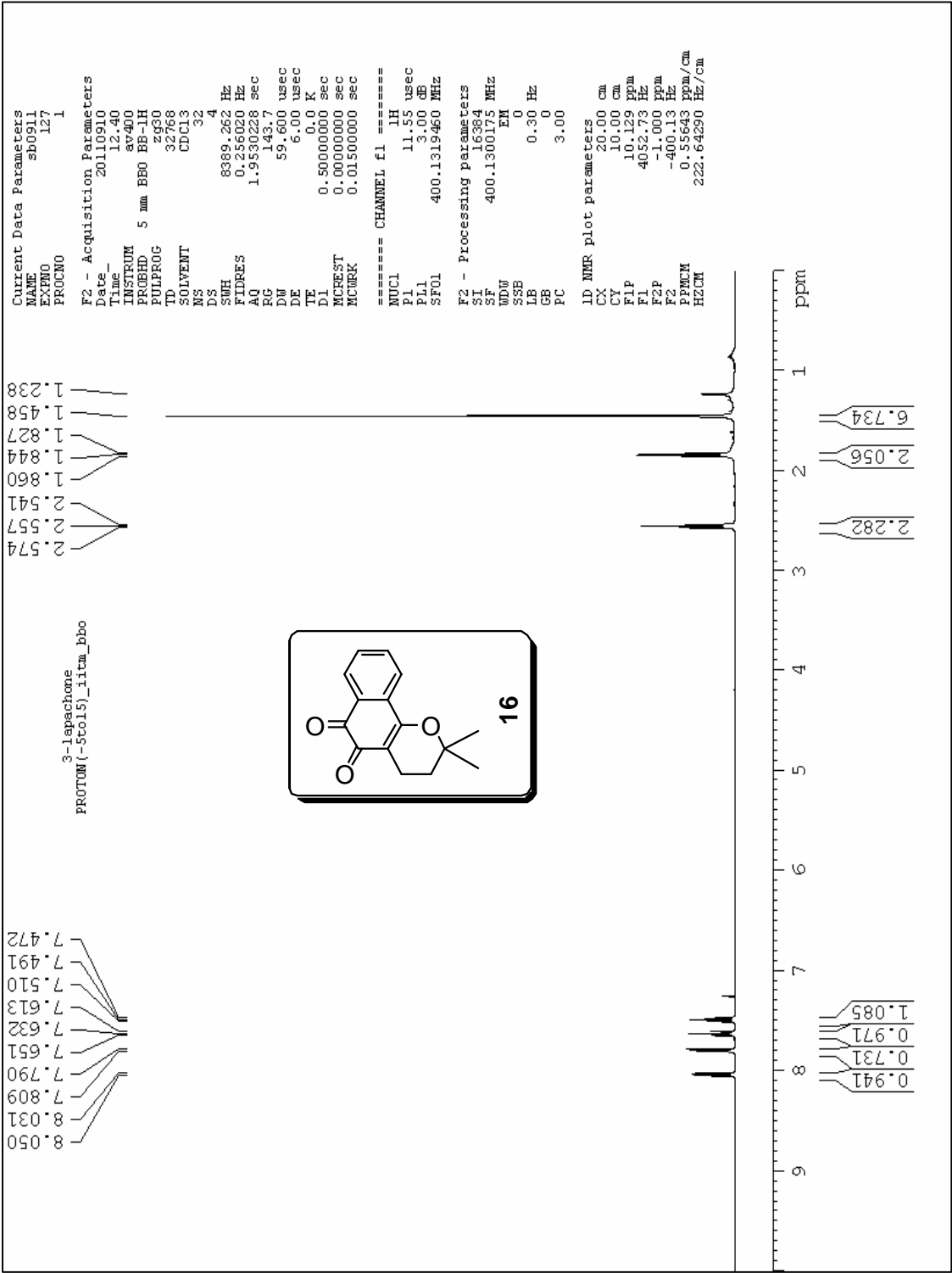


Expanded  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **15**

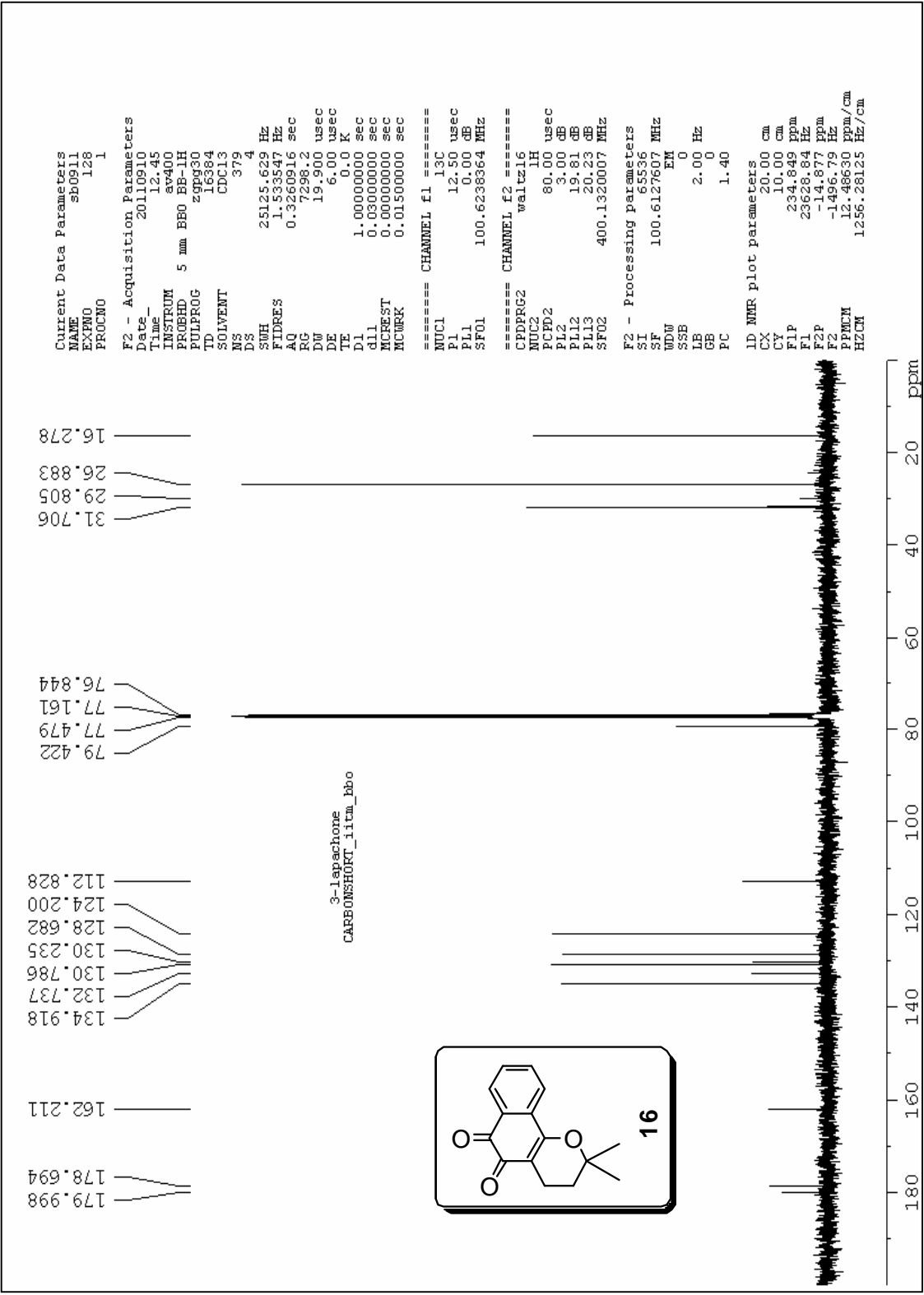


Expanded  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound 15



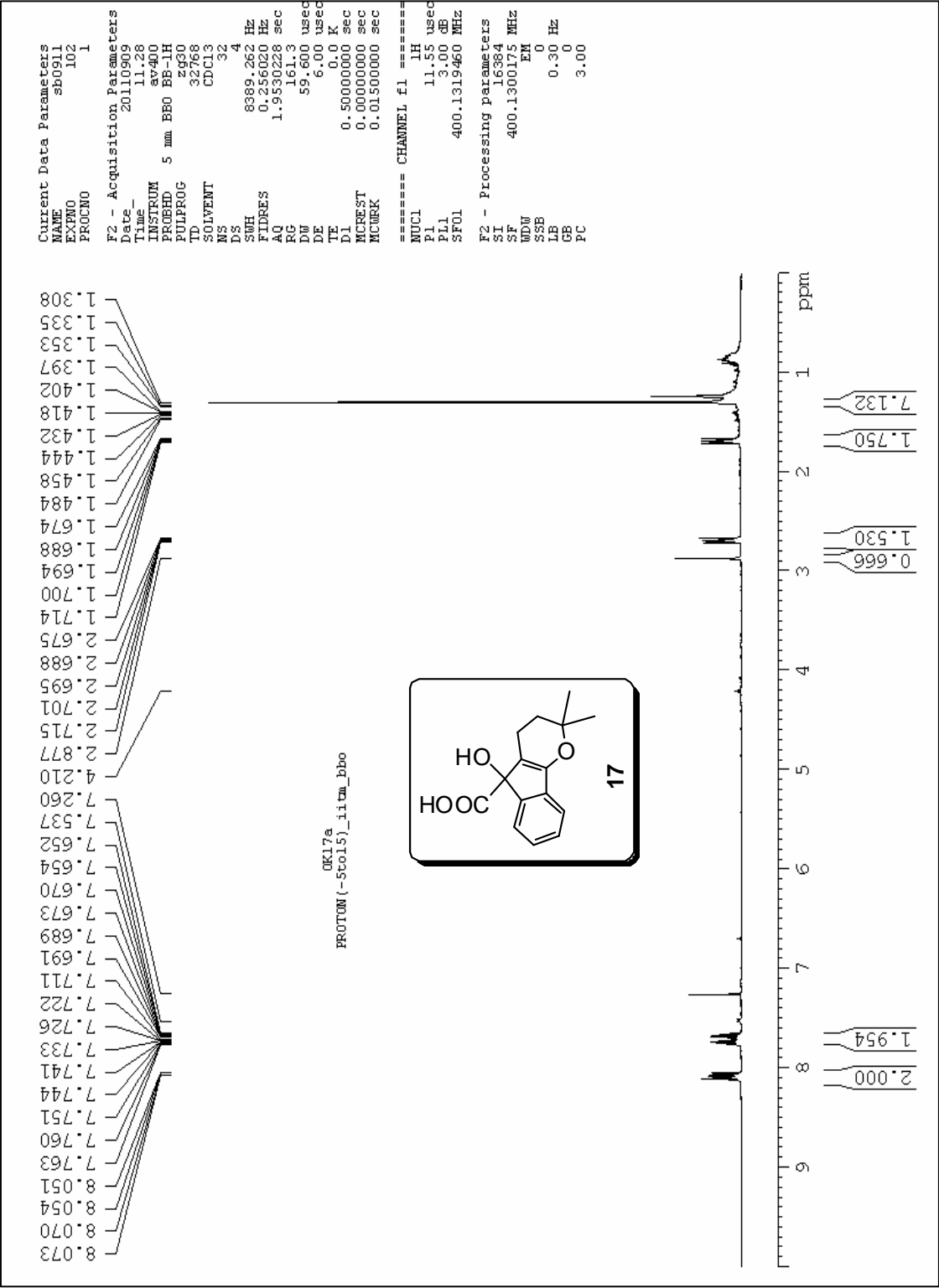


<sup>1</sup>H NMR spectrum of compound 16

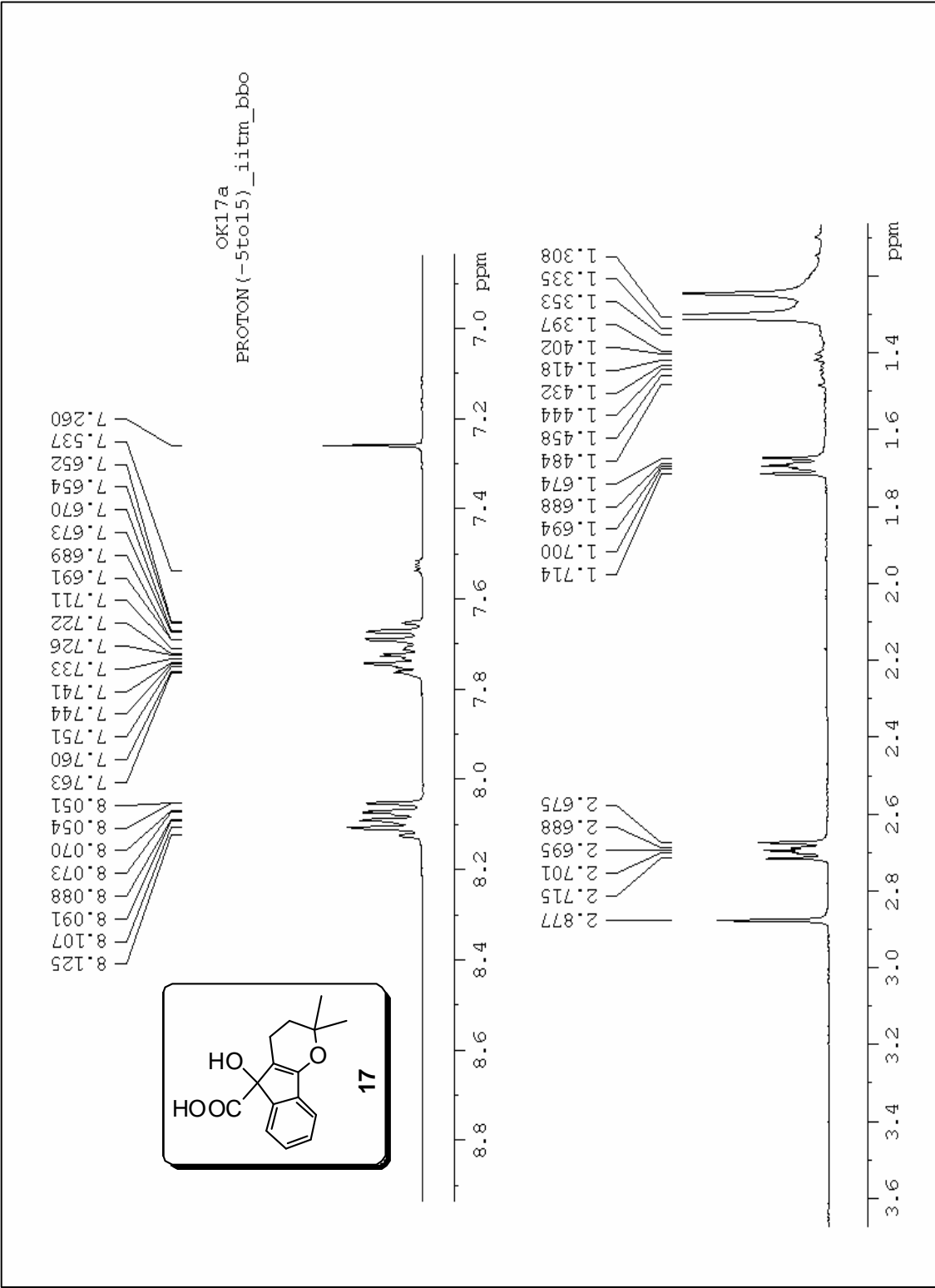


<sup>13</sup>C NMR spectrum of compound 16

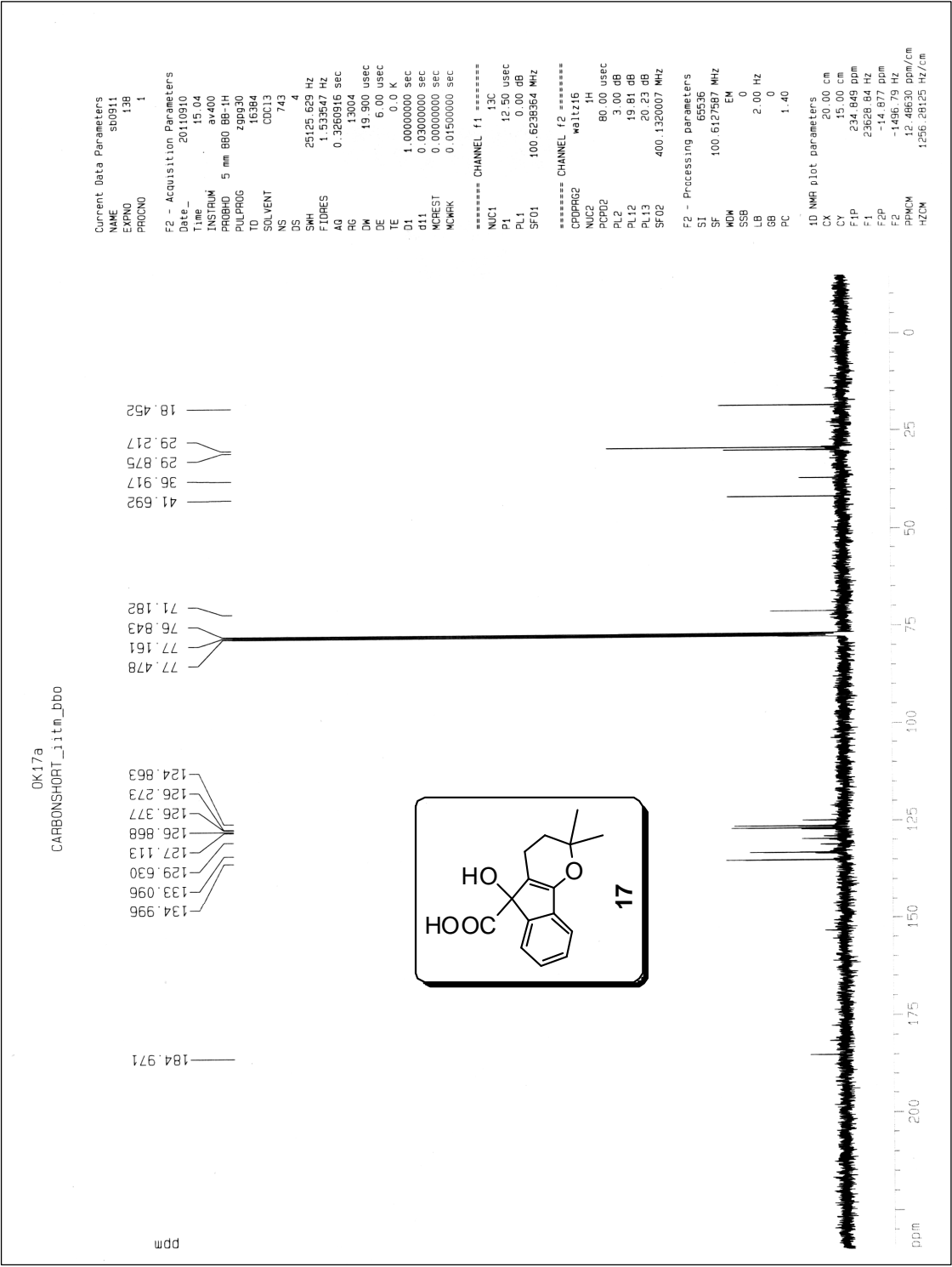




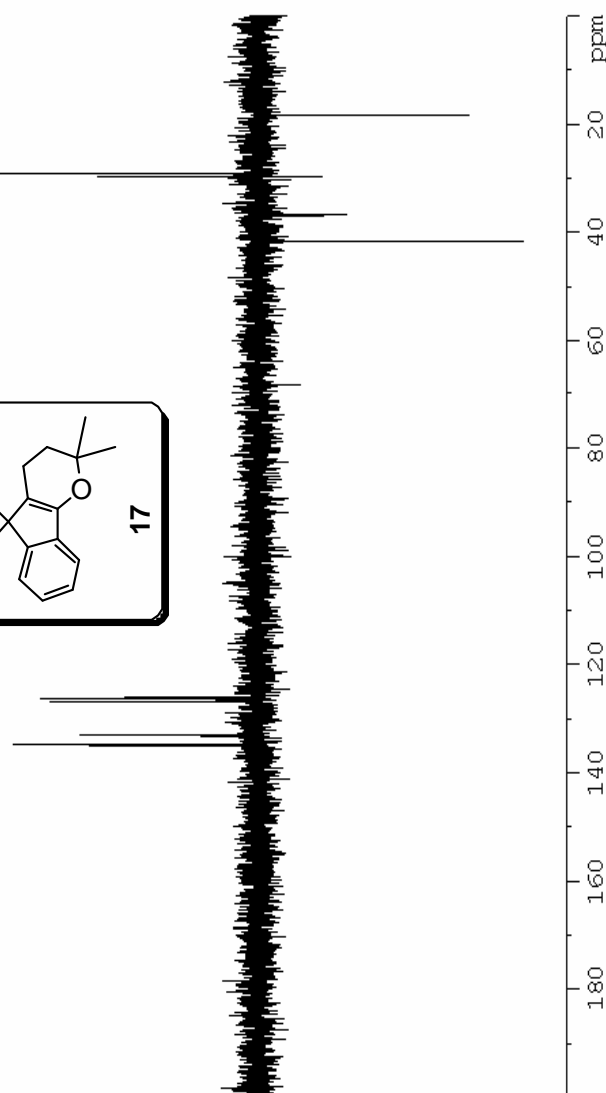
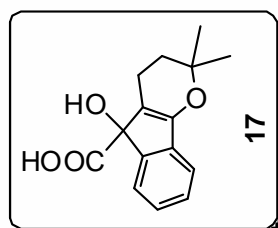
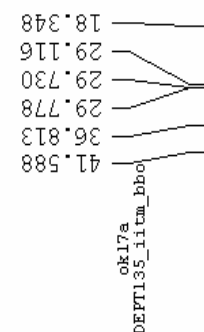
<sup>1</sup>H NMR spectrum of compound 17



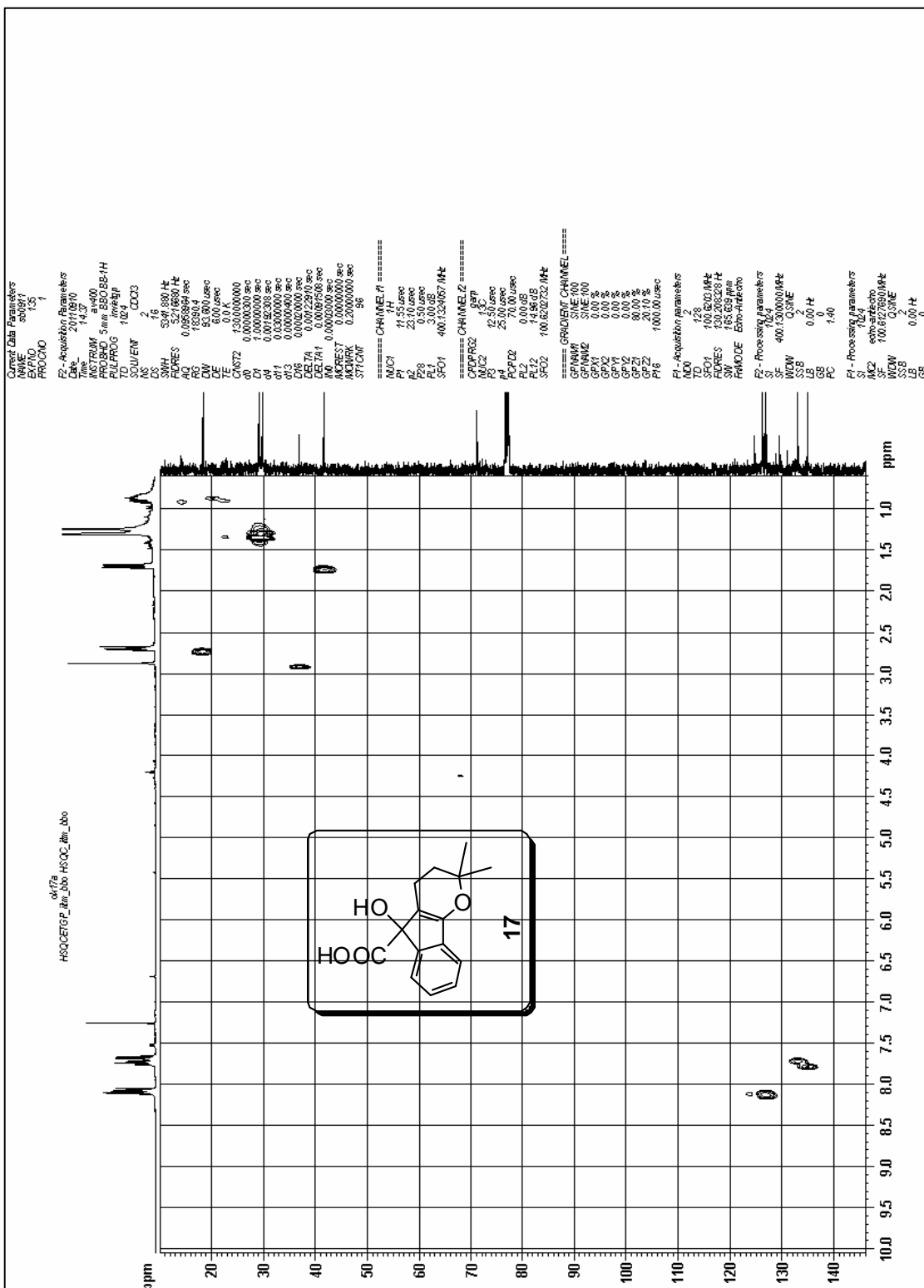
Expanded <sup>1</sup>H NMR spectrum of compound 17



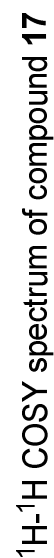
<sup>13</sup>C NMR spectrum of compound 17

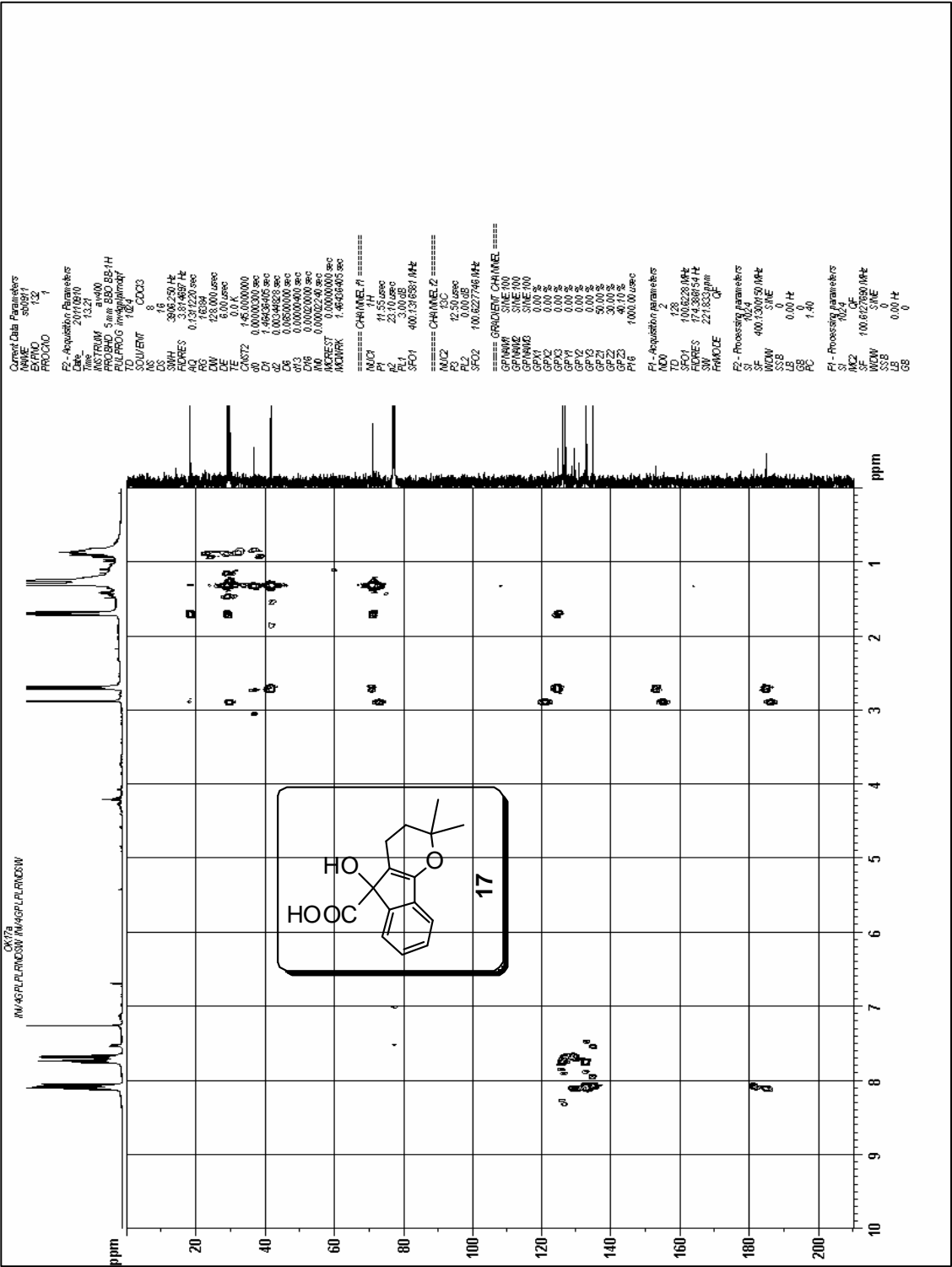
[illegible]

DEPT spectrum of compound 17

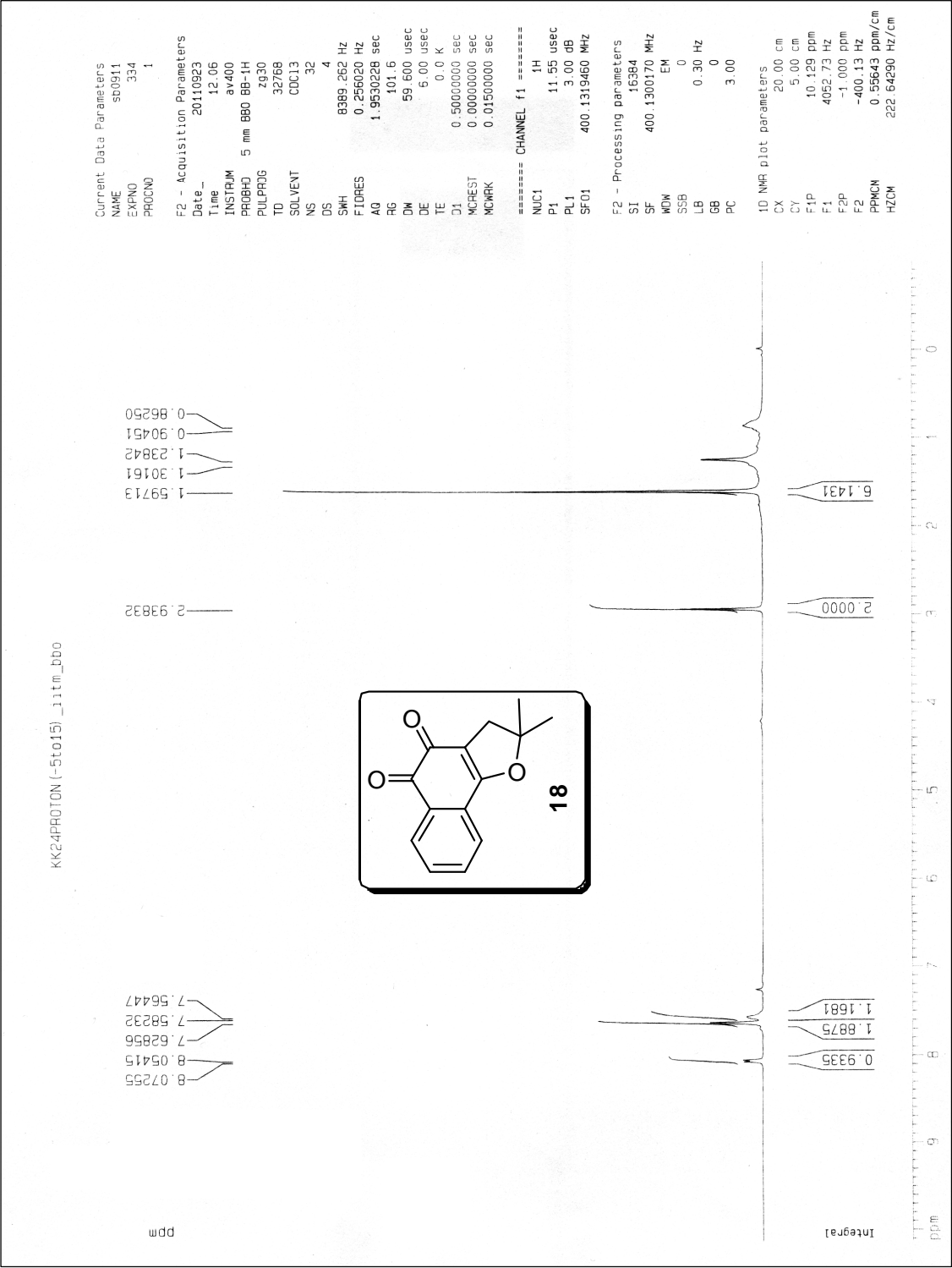




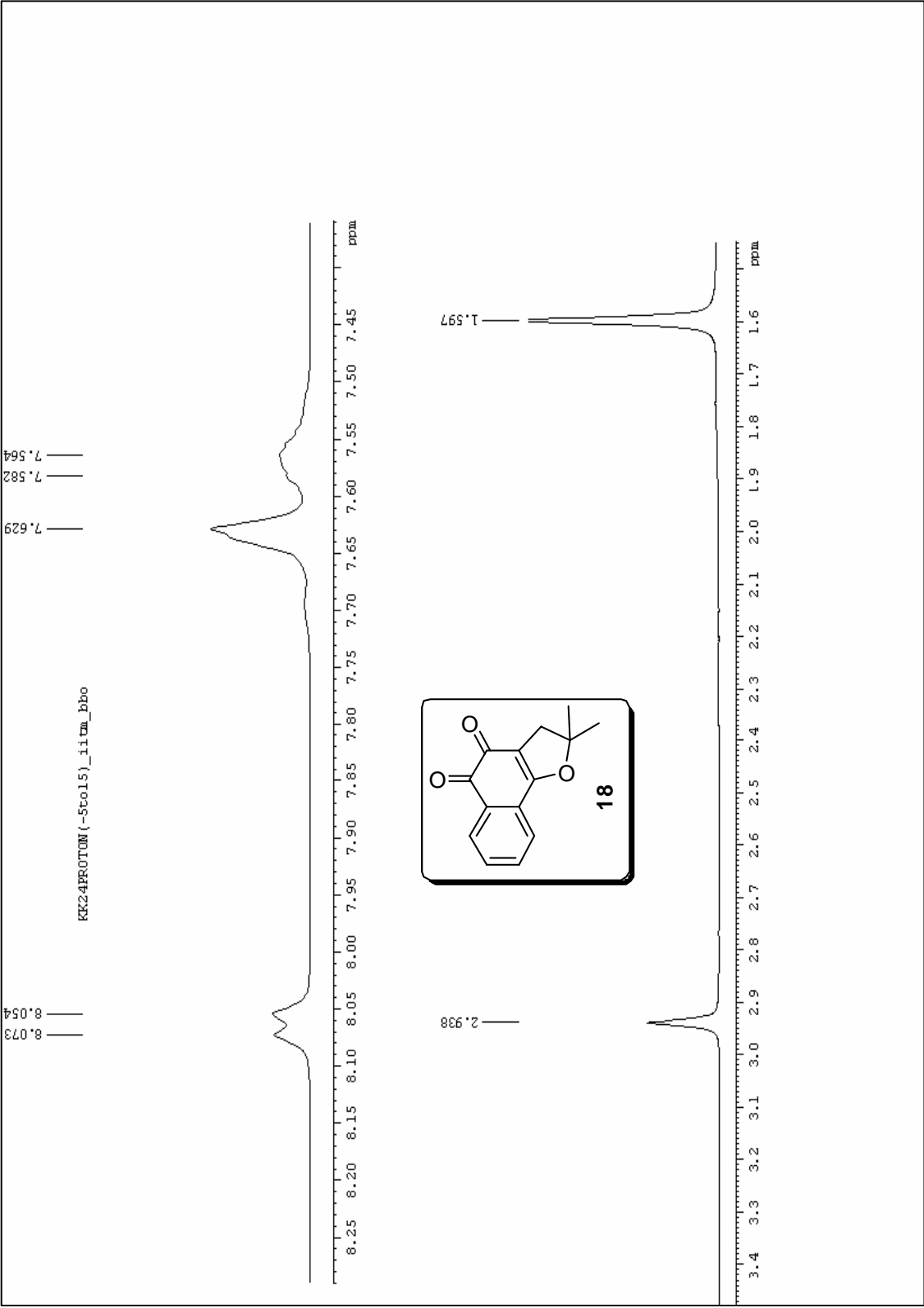




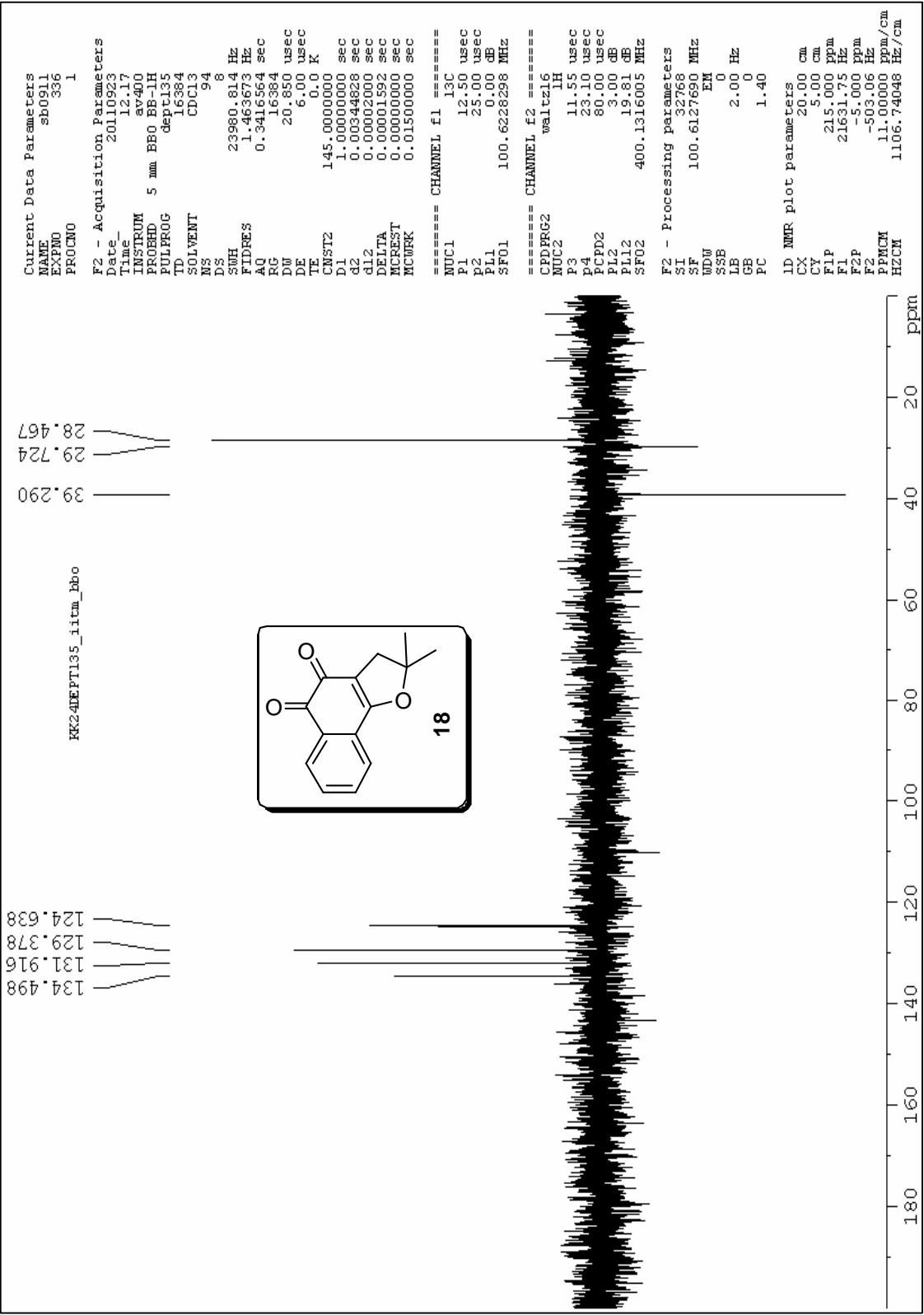
<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound 17

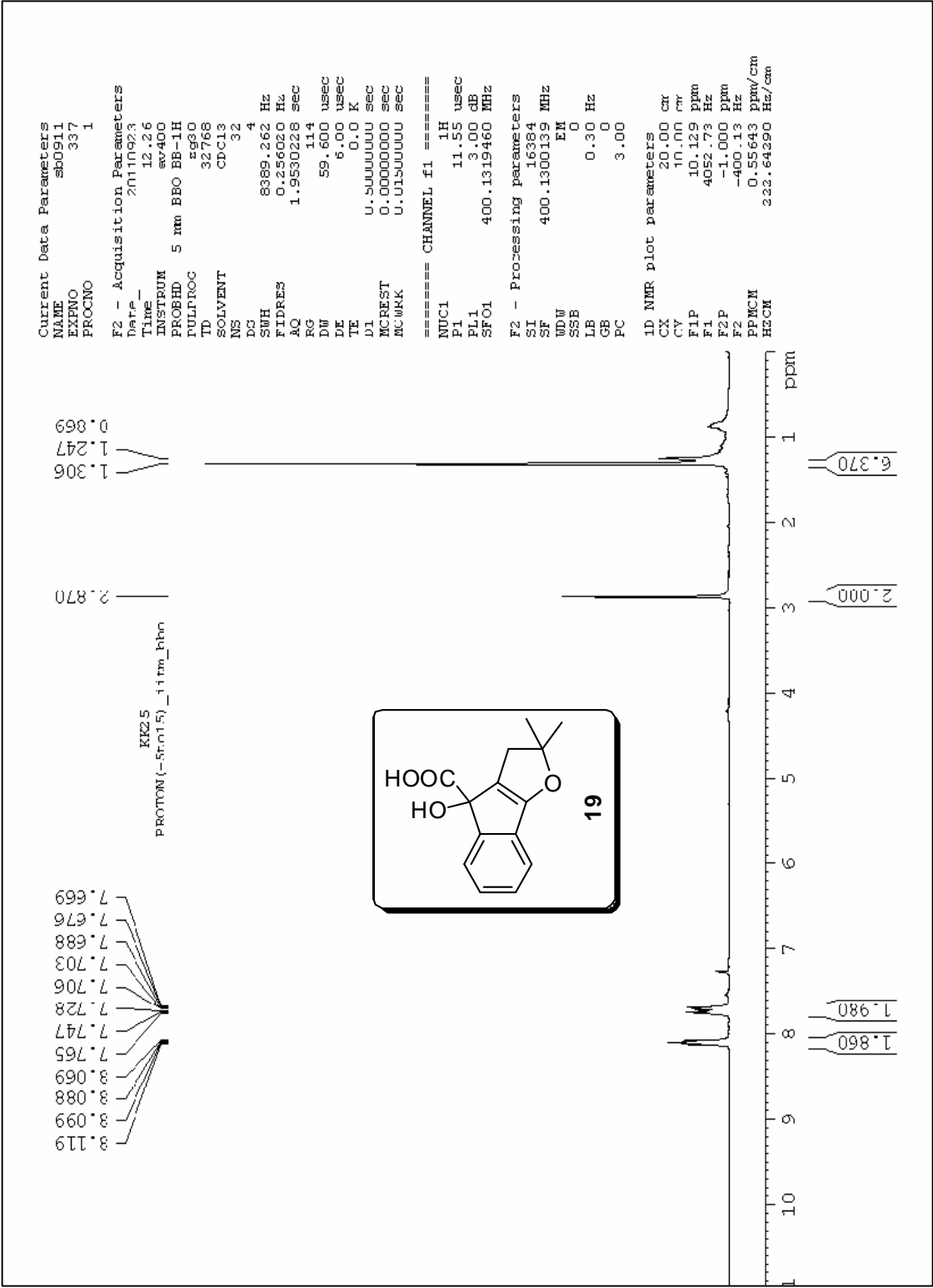


<sup>1</sup>H NMR spectrum of compound 18

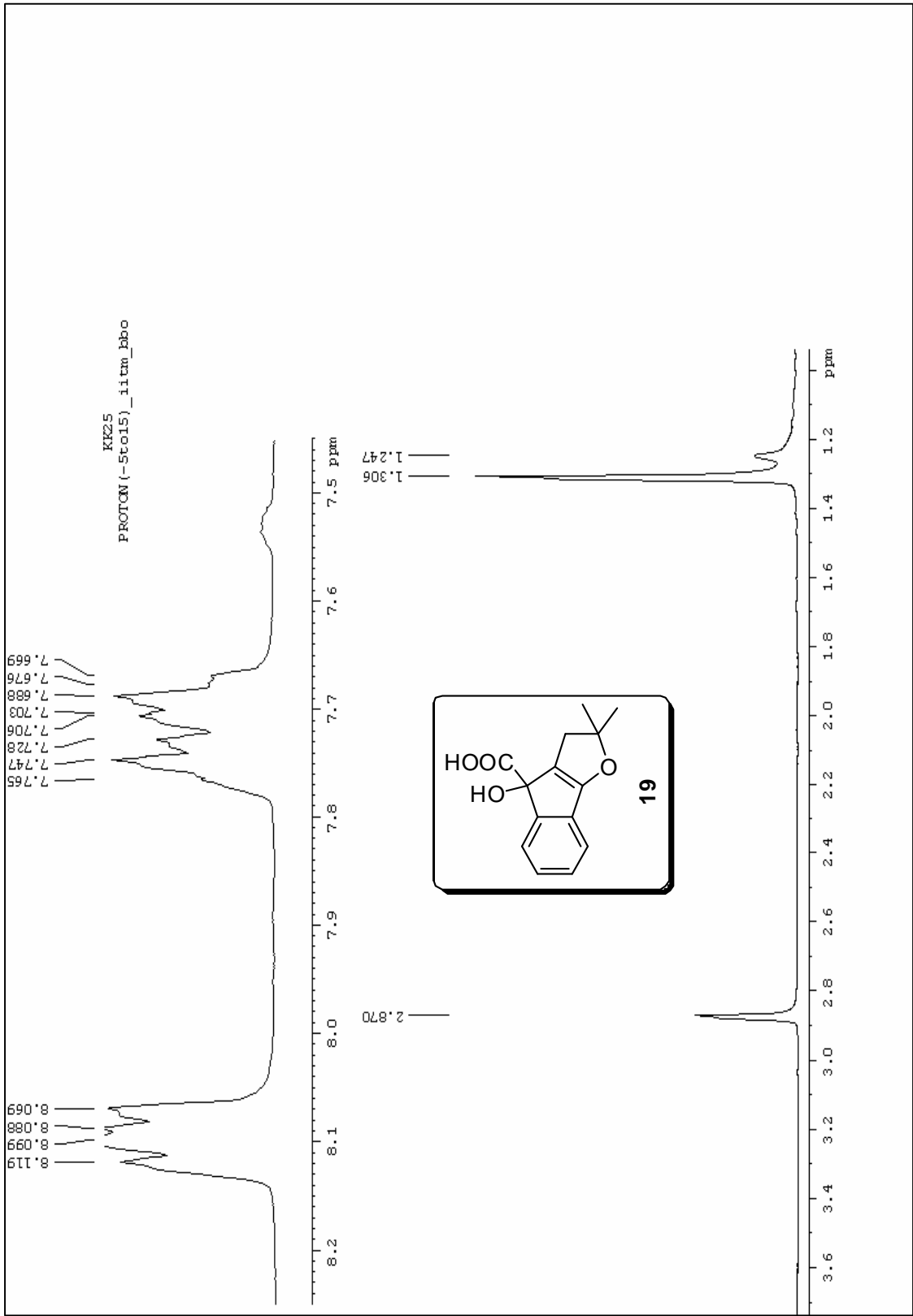






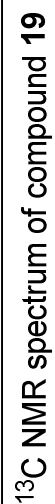


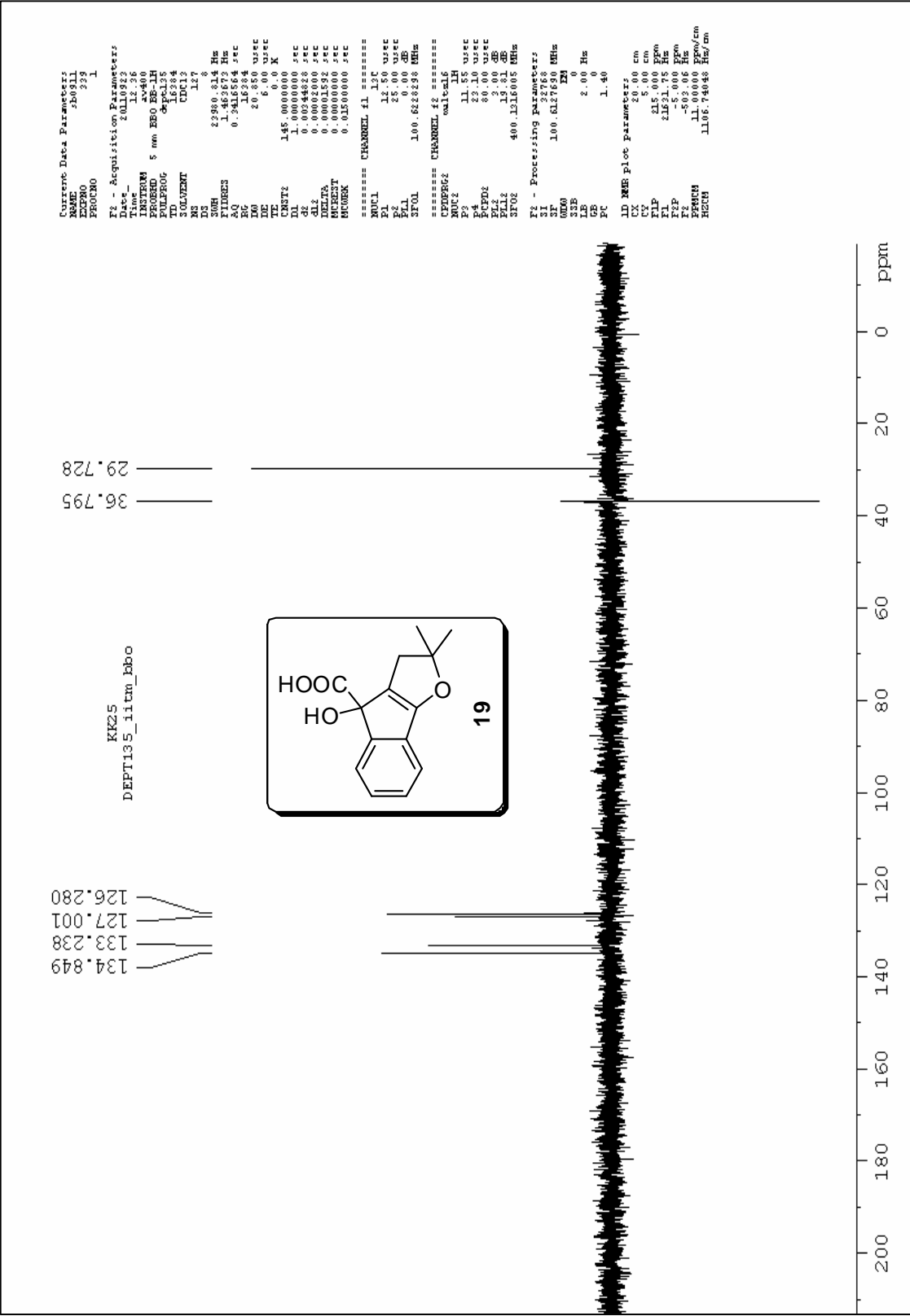
<sup>1</sup>H NMR spectrum of compound 19

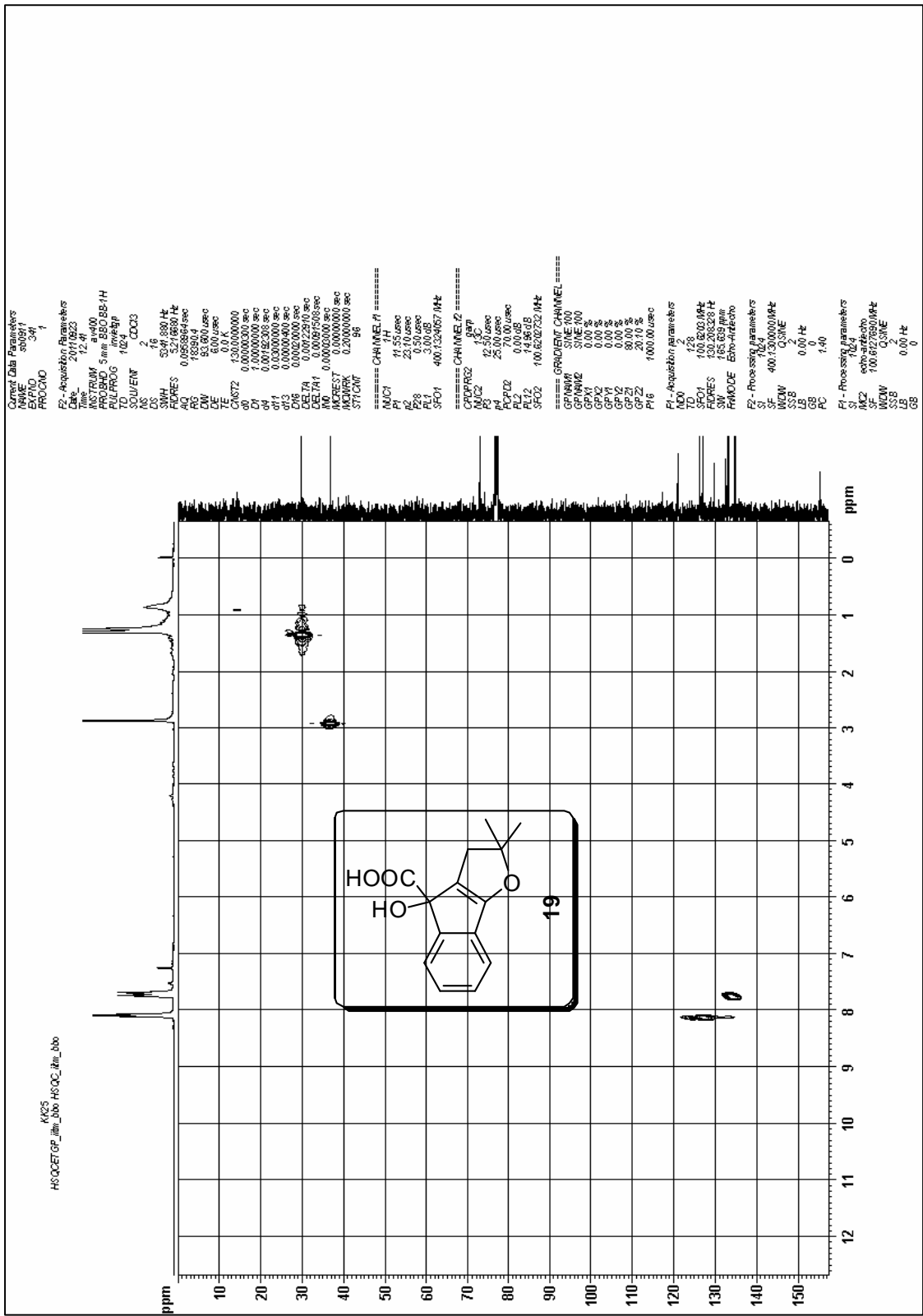


Expanded <sup>1</sup>H NMR spectrum of compound **19**

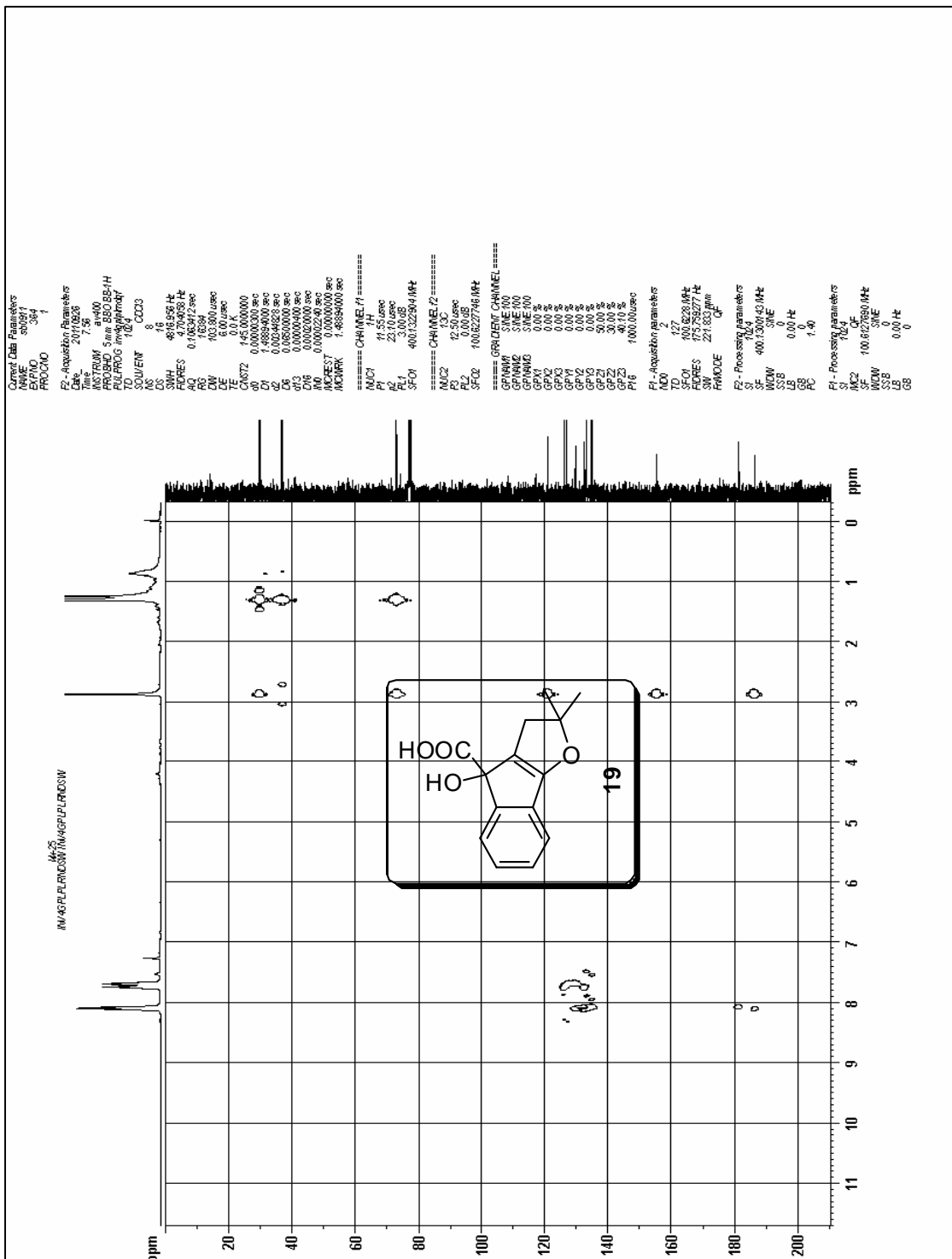


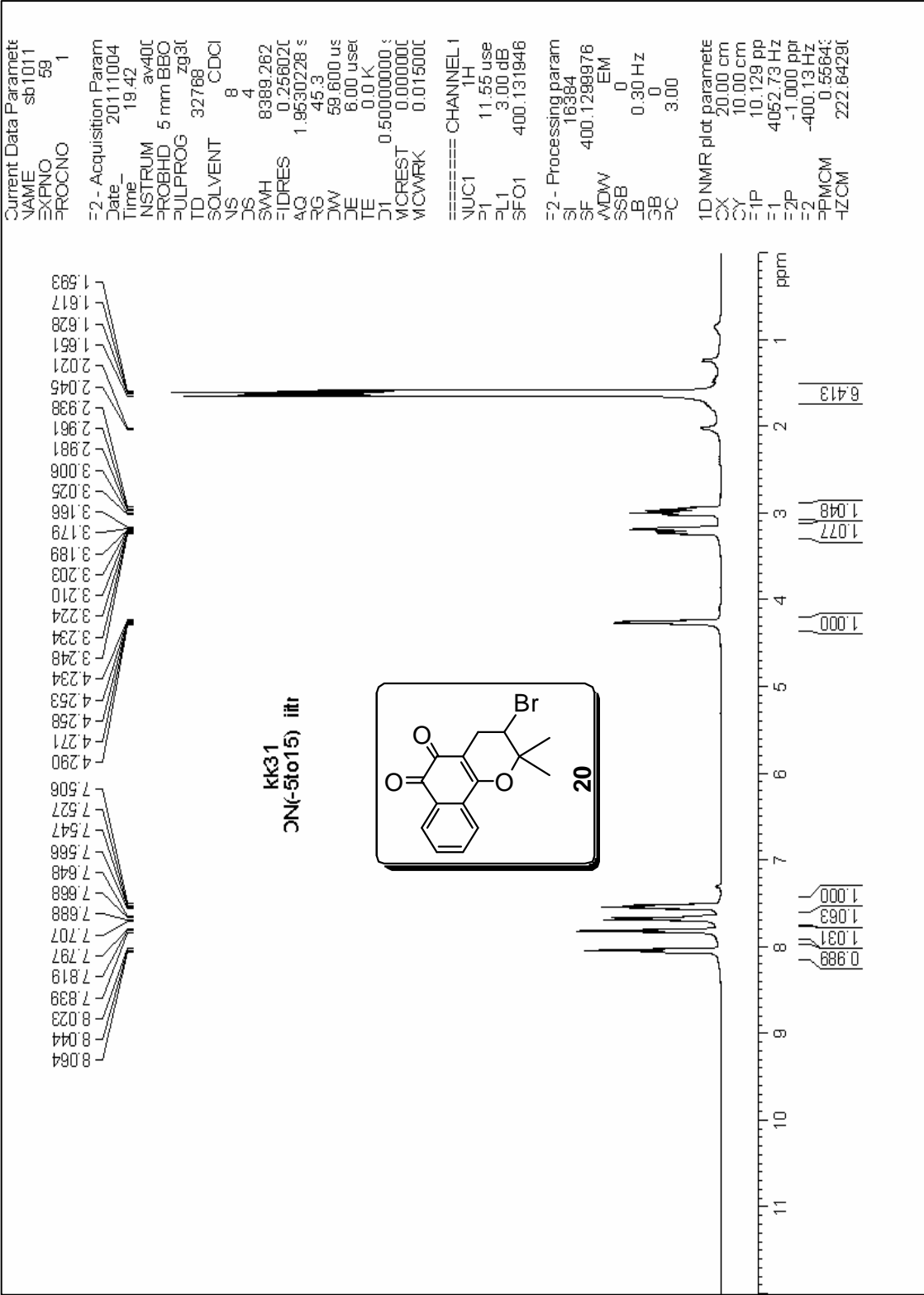




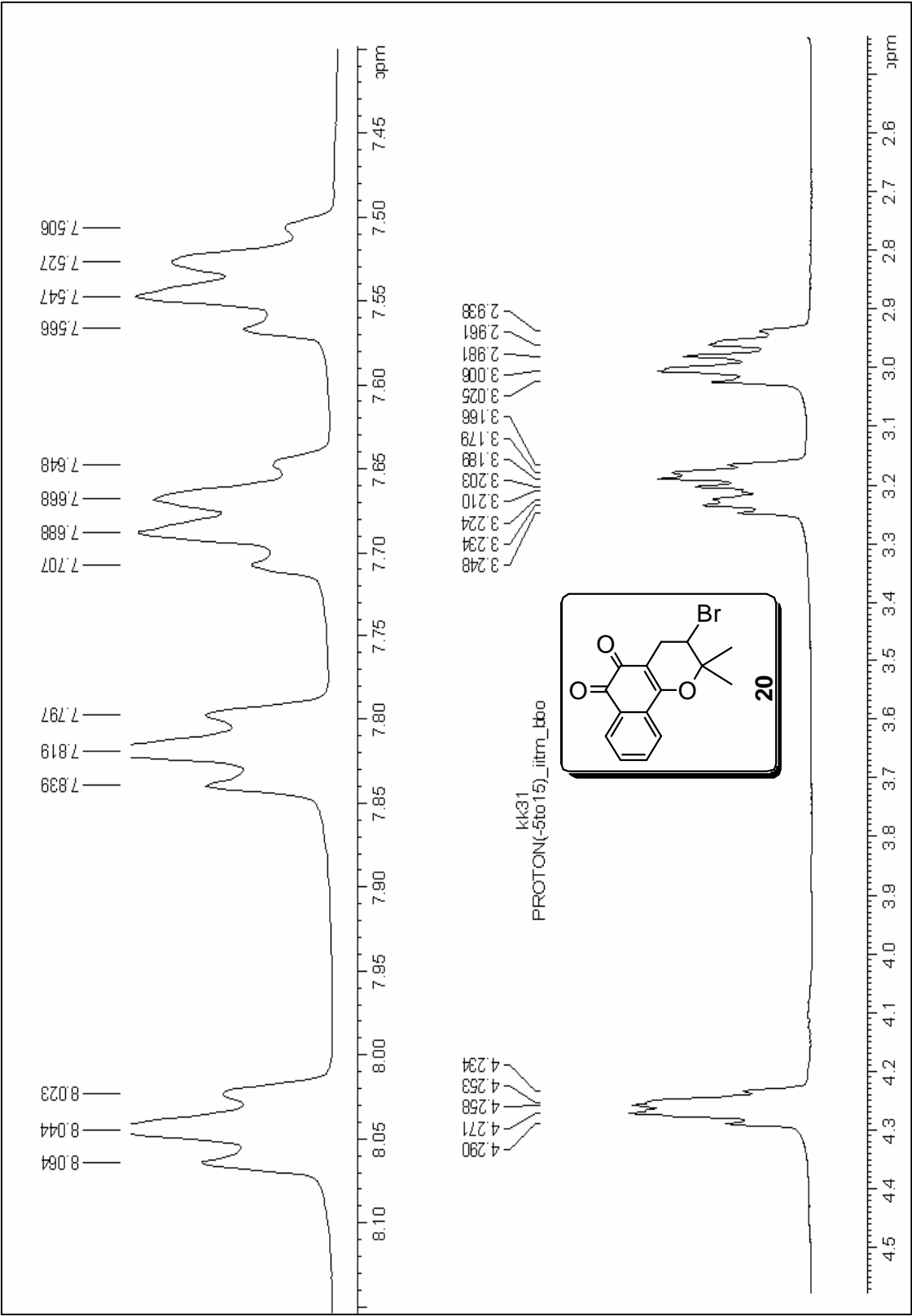


<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound 19

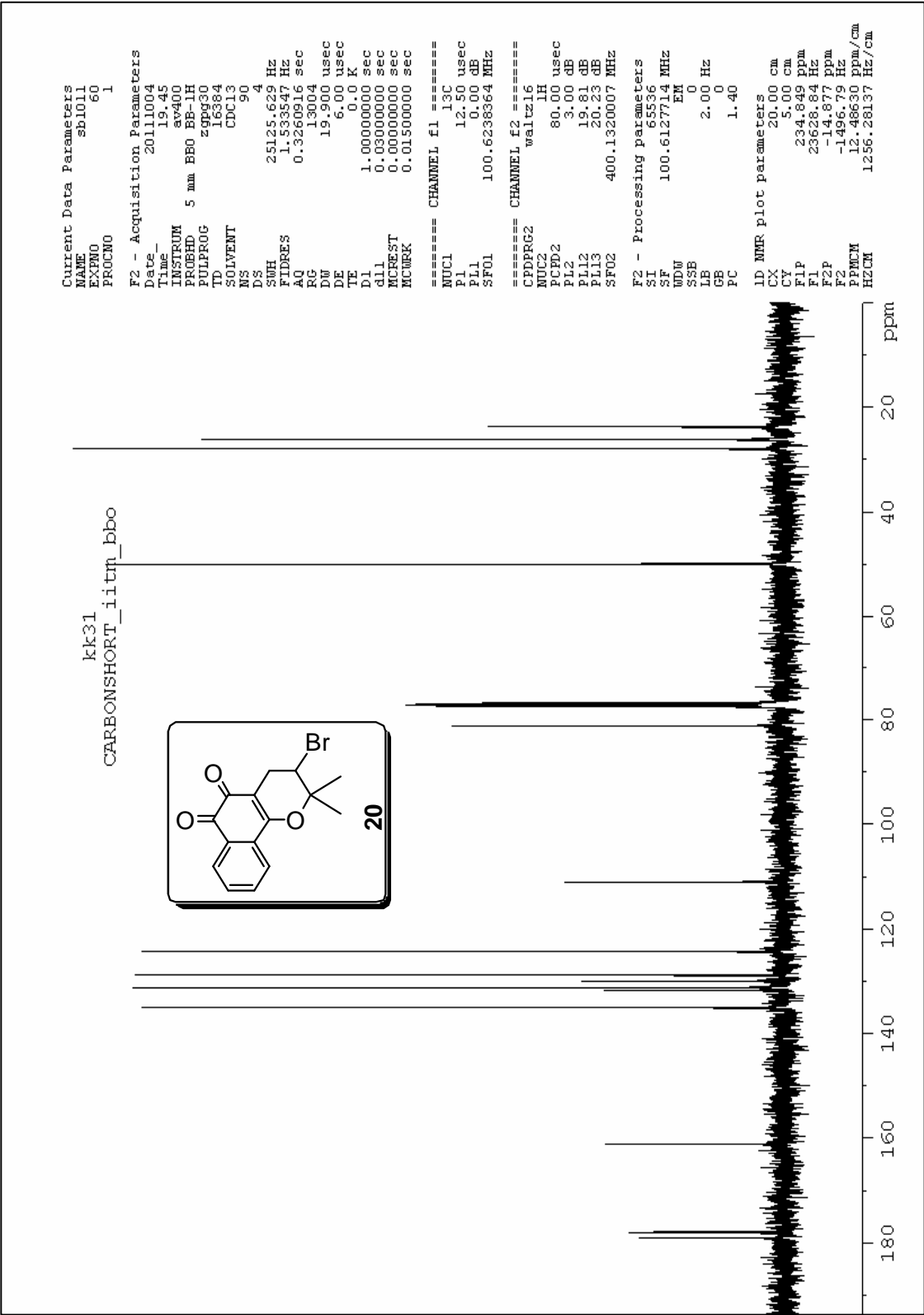


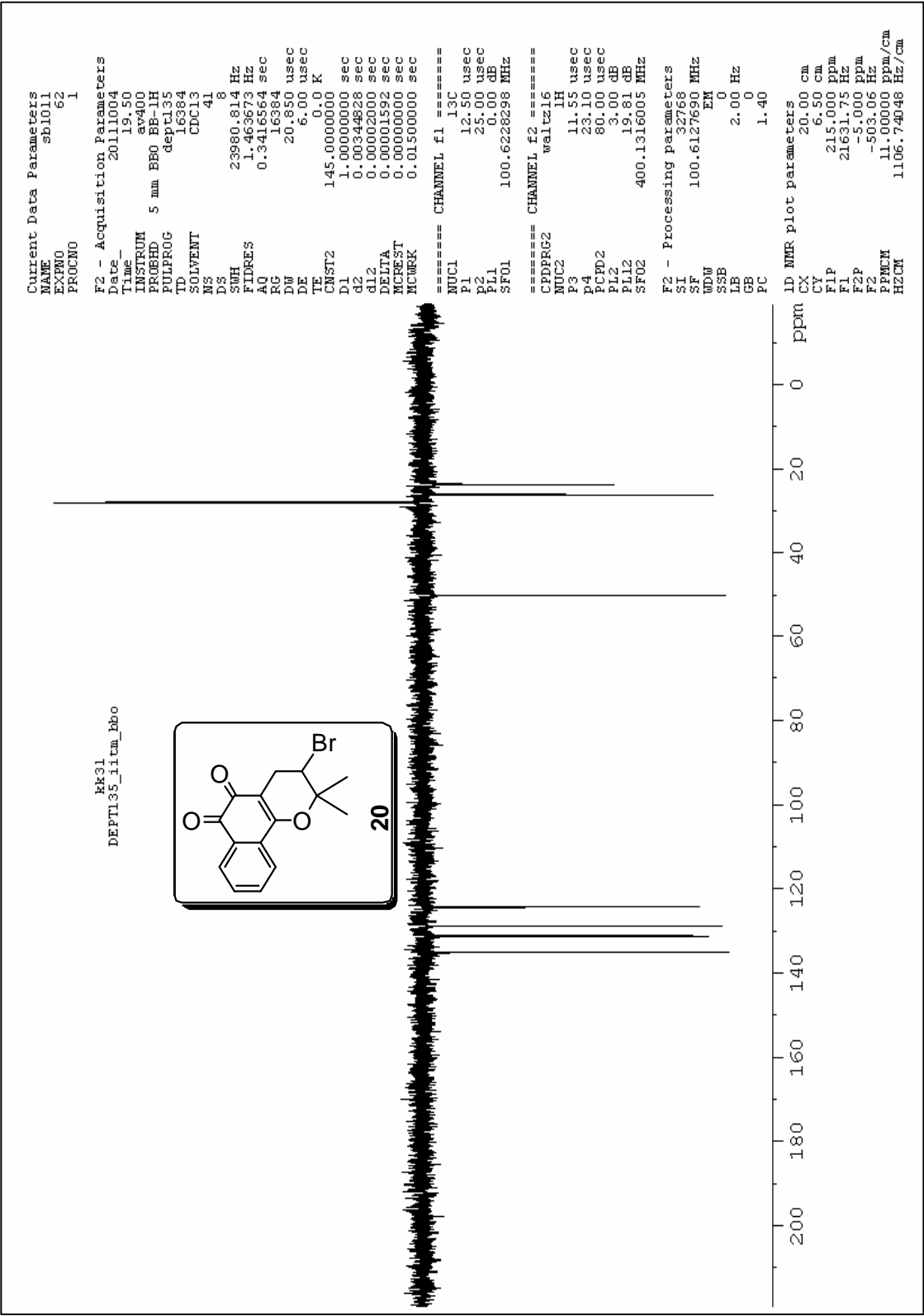


<sup>1</sup>H NMR spectrum of compound 20



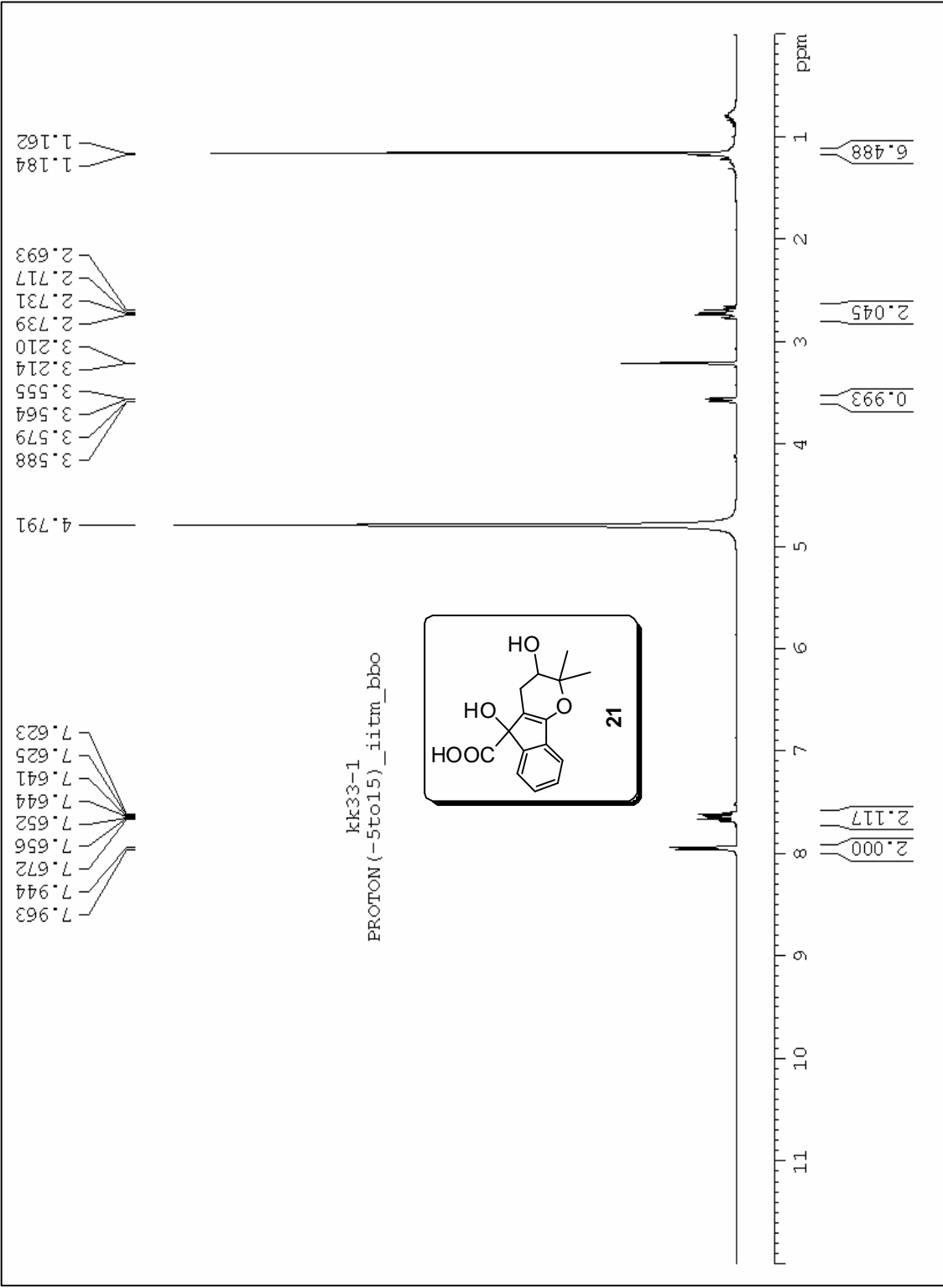
Expanded  $^1\text{H}$  NMR spectrum of compound **20**

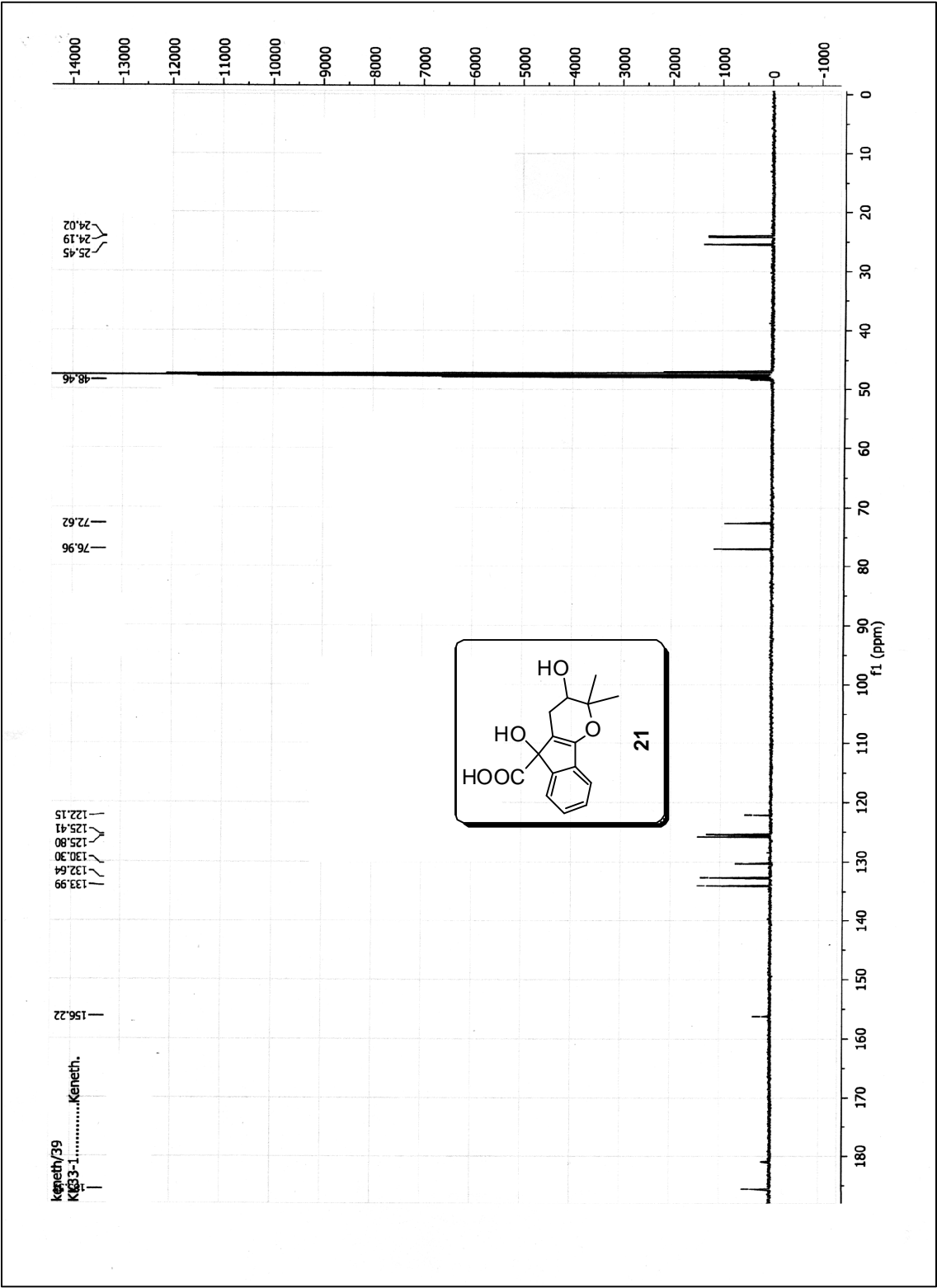


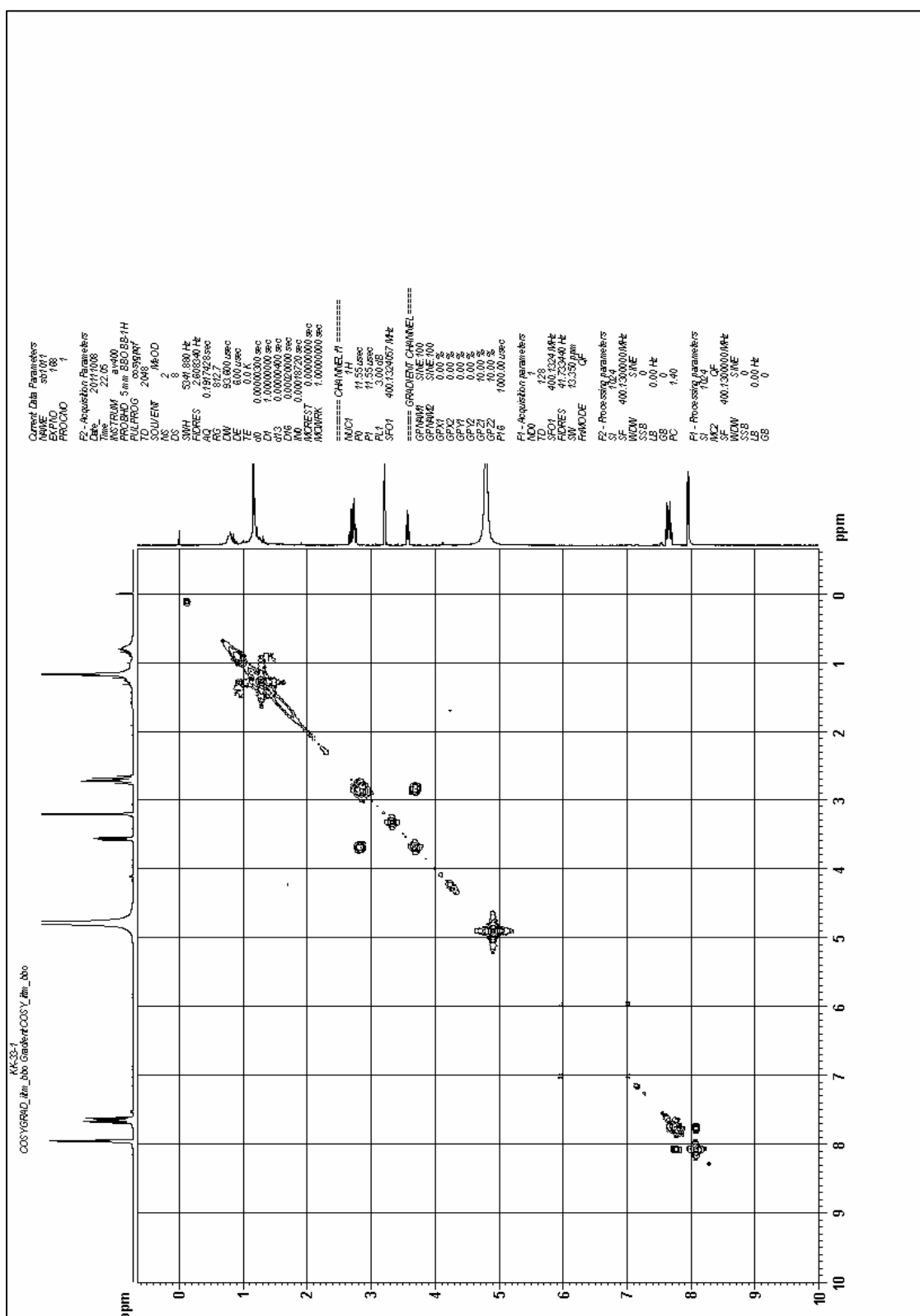


DEPT spectrum of compound 20

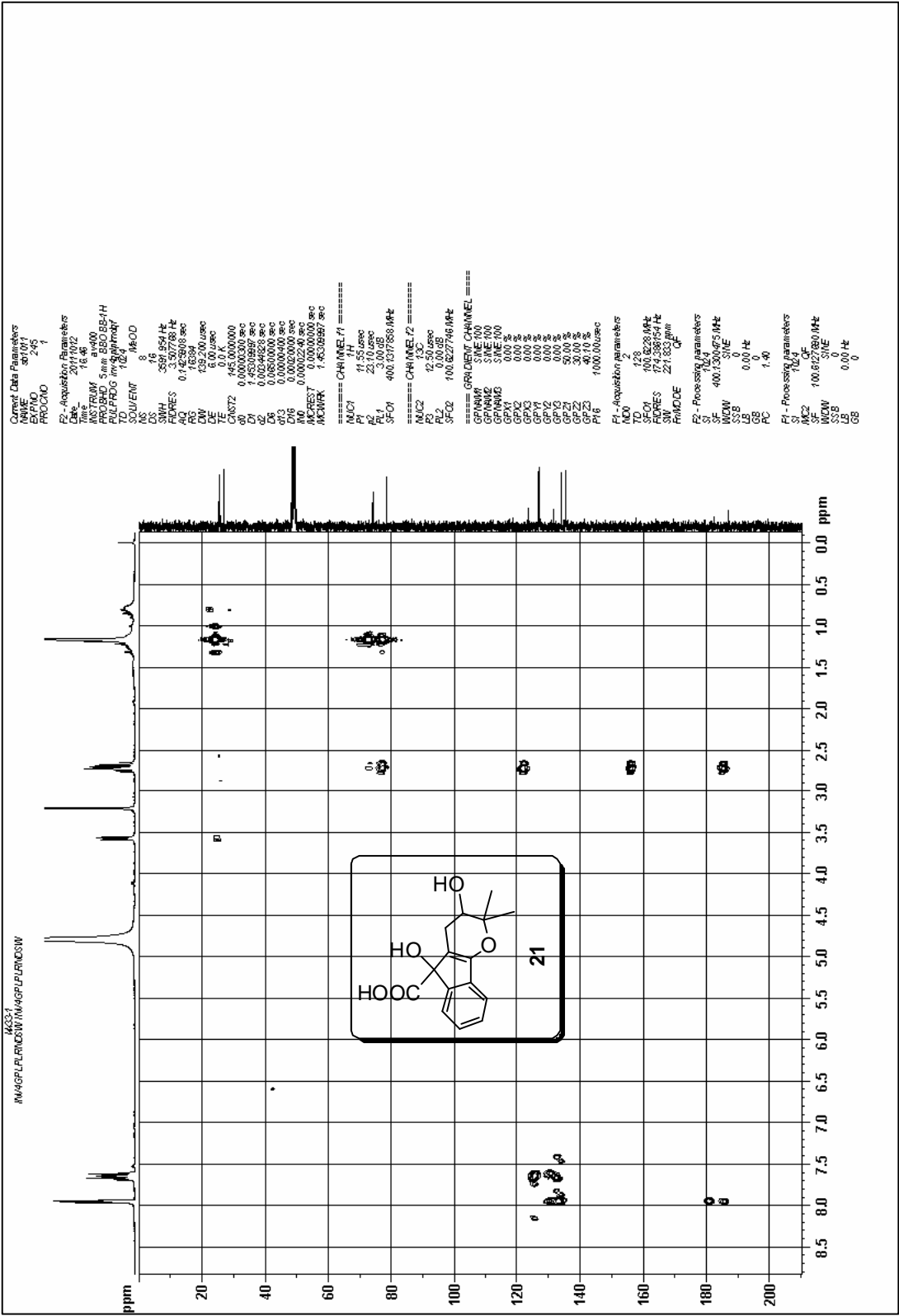






 $^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound **21**

<sup>1</sup>H-<sup>13</sup>C COSY (HSQC) NMR spectrum of compound **21**



<sup>1</sup>H-<sup>13</sup>C COSY (HMBC) NMR spectrum of compound 21