

Supporting Information for publication

Synthesis of Oxabicyclo [3.3.1]nonenes and Substituted Tetrahydropyrans via (3,5)-Oxonium-Ene Reaction

Pipas Saha, Paramartha Gogoi and Anil K. Saikia*

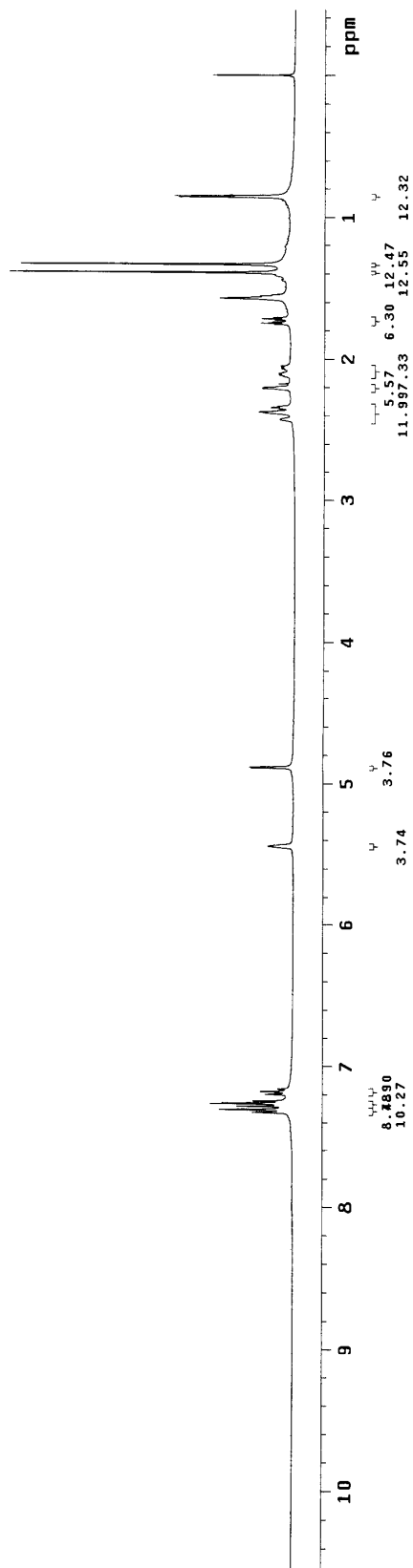
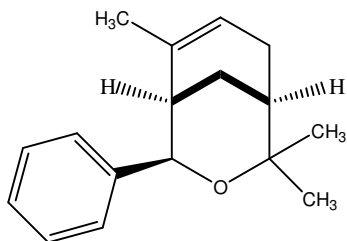
Supplementary Information: General experimental Procedure and ^1H and ^{13}C NMR spectra of all compounds & ^{19}F NMR of **3d**, NOE spectrum of **3a**, **4e** & **15**, COSY spectrum of **15**.

General Experimental Section: ^1H NMR spectra were recorded in CDCl_3 on 400 MHz NMR spectrometer using TMS as internal standard. The ^{13}C and ^{19}F NMR spectra were recorded at 100 MHz and 376 MHz, respectively. For ^{13}C and ^{19}F NMR CDCl_3 and C_6F_6 were used as internal standard. IR spectra were recorded on FT-IR spectrometer. Ratios of the compounds were determined from ^1H NMR signals of crude products. Only the well separated signals, irrespective of its chemical shift value, were used for these determinations. The spectra were expanded while calculating the ratios. Mass spectra were recorded using Waters LC-MS/MS system (Q-TOF–Premier). HRMS (ESCI-TOF) were calibrated with sodium formate solution and leucine enkephalin (SIGMA) was used as an external standard.

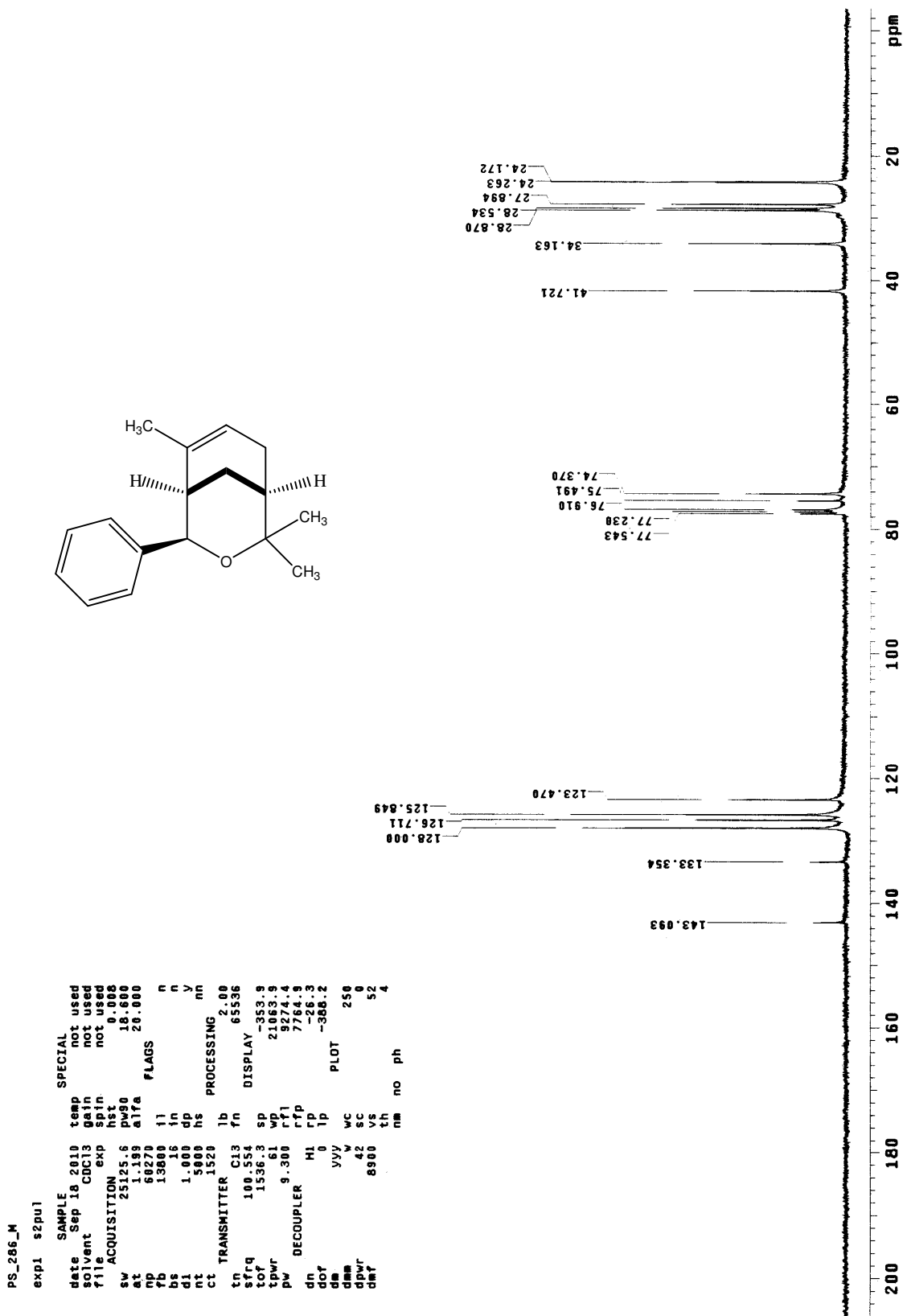
¹H NMR spectra of 3a

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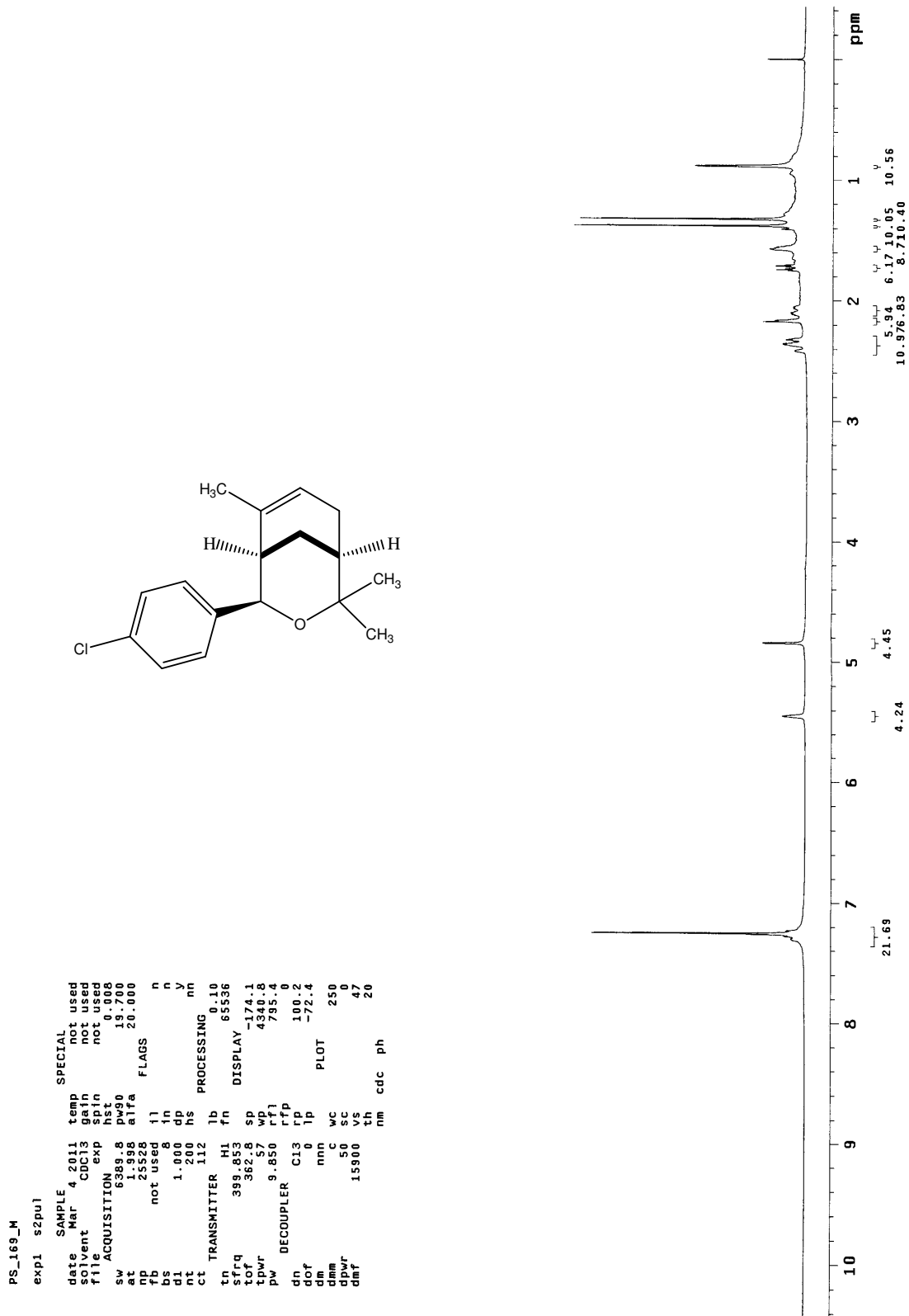
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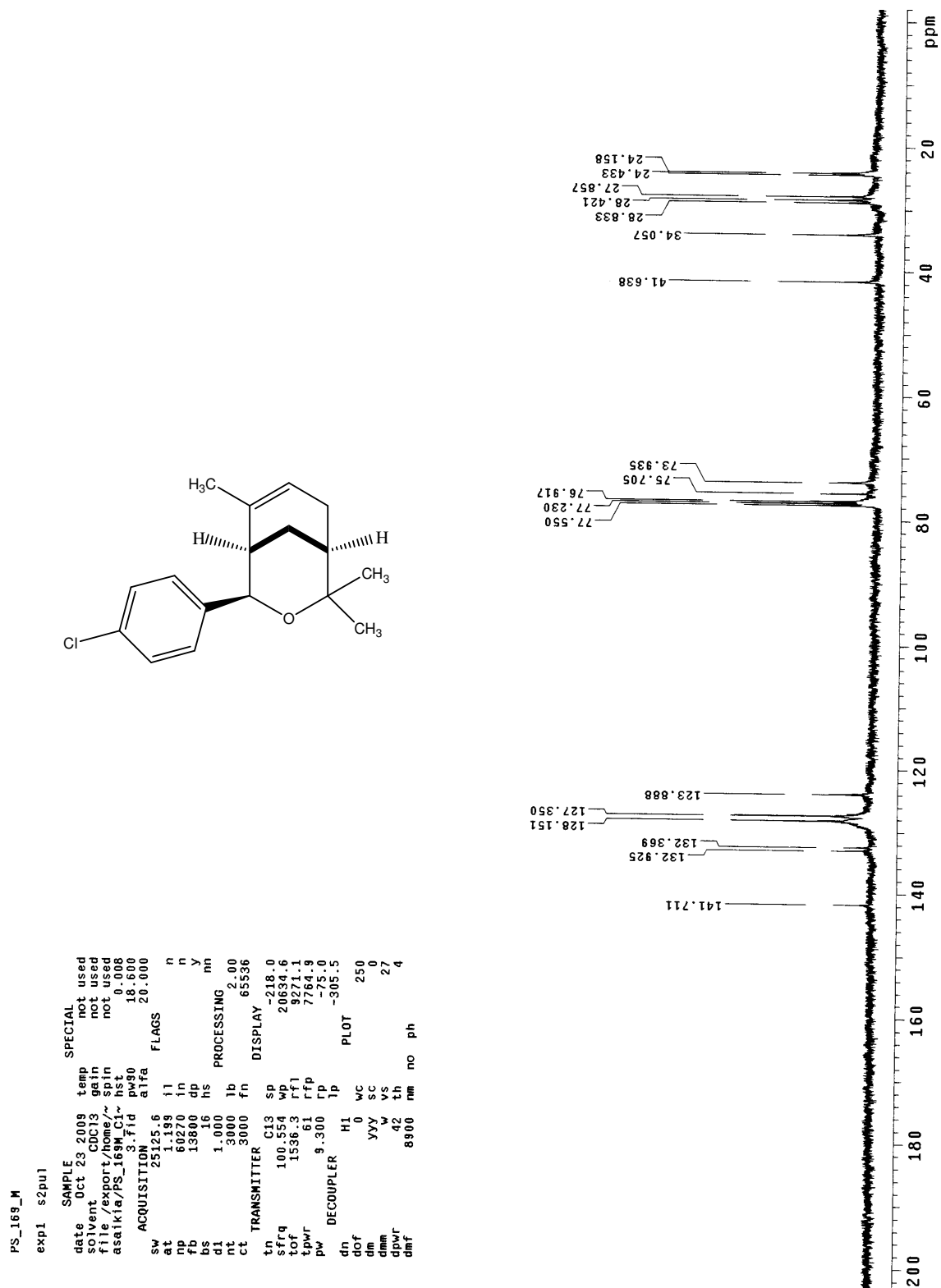
¹³C NMR spectra of 3a



¹H NMR spectra of 3b

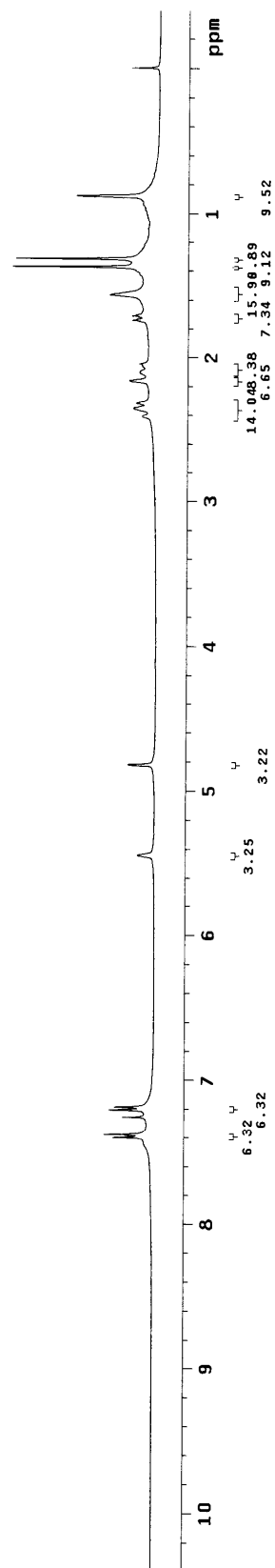
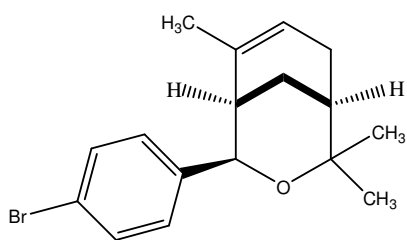


¹³C NMR spectra of 3b

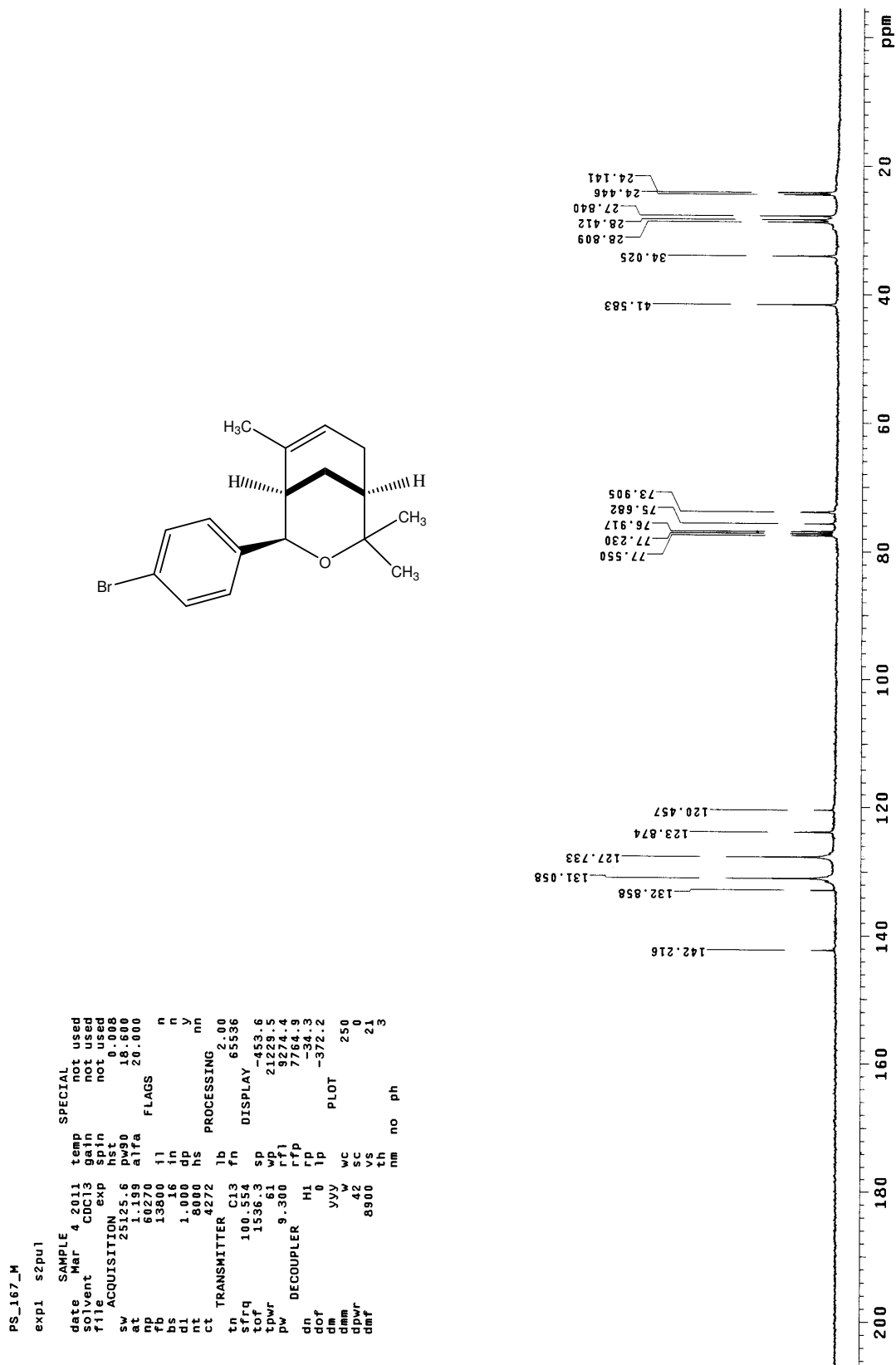


¹H NMR spectra of 3c

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dipw 50
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  20
  20
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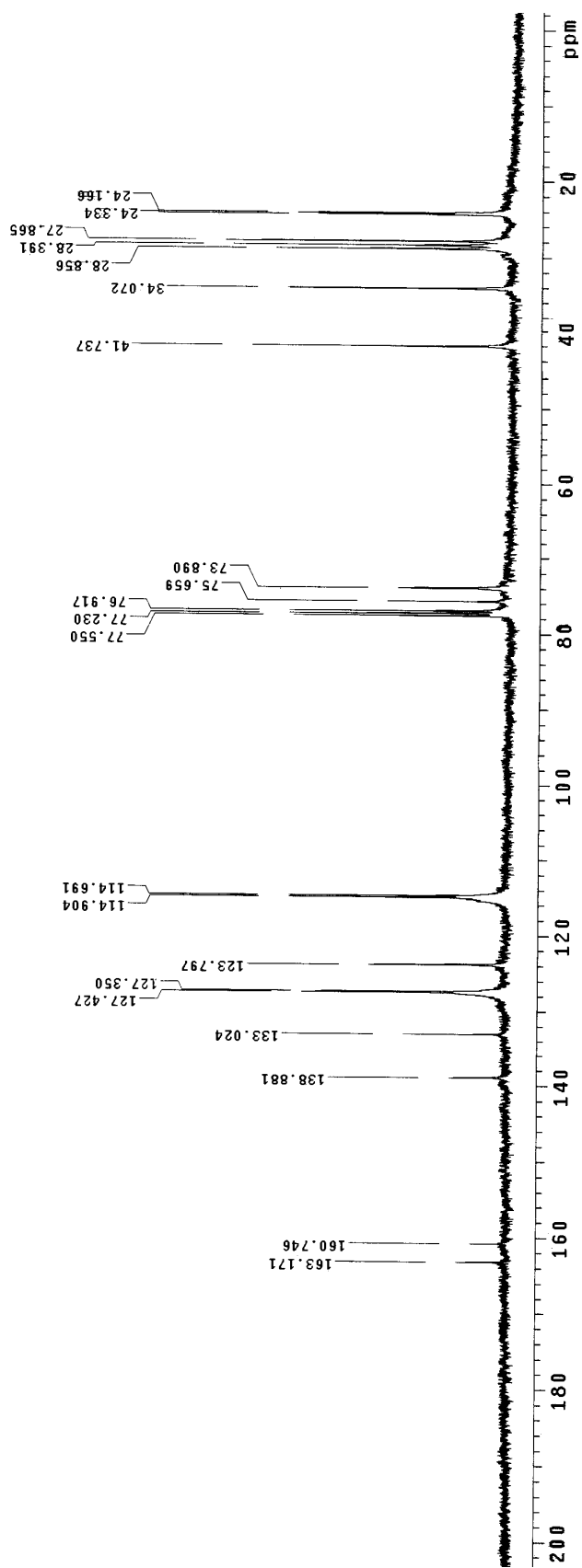
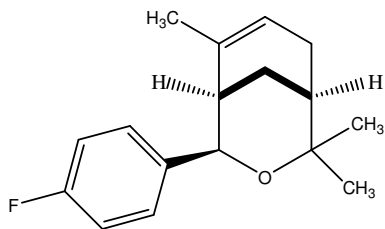
¹³C NMR spectra of 3c



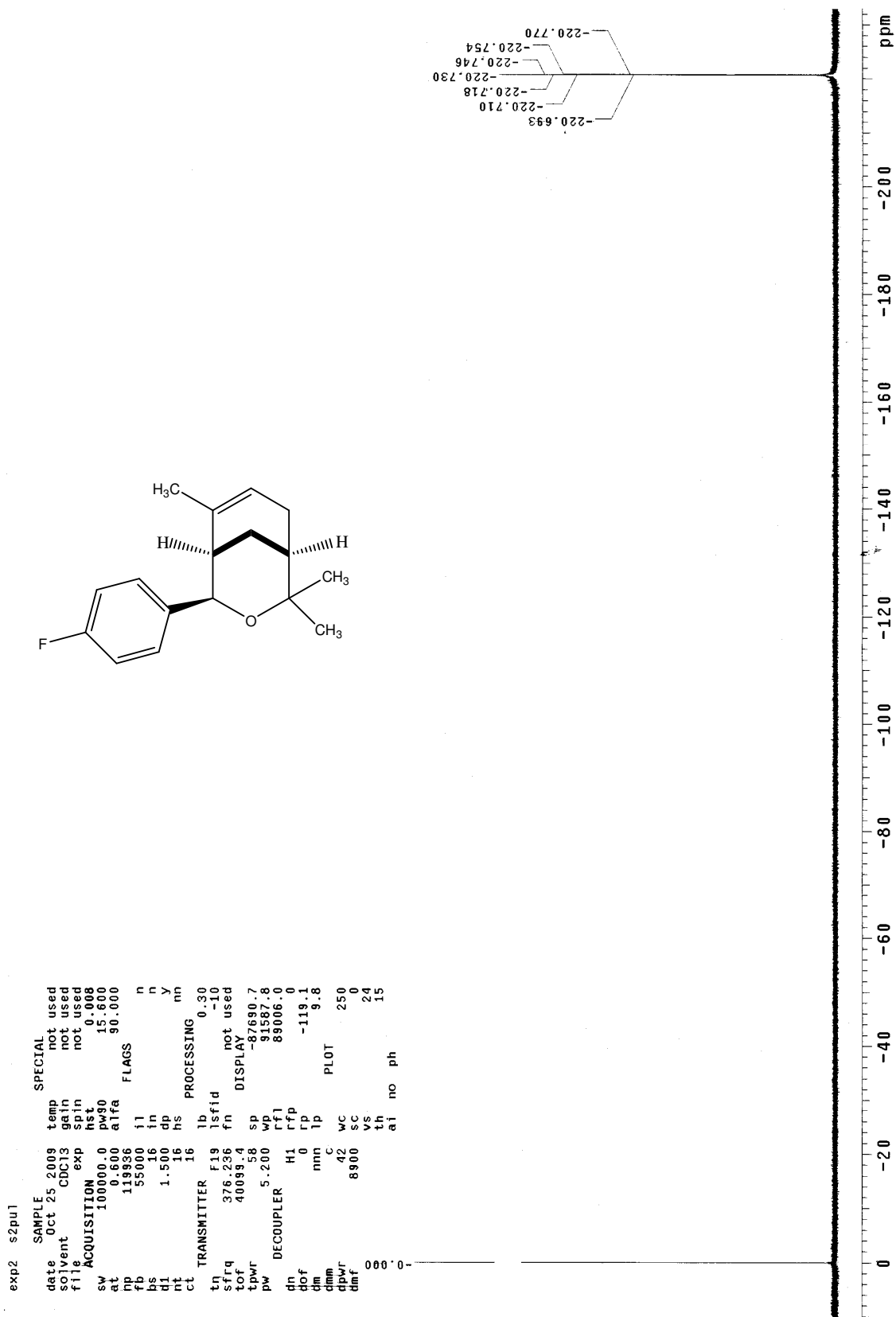
¹³C NMR spectra of 3d

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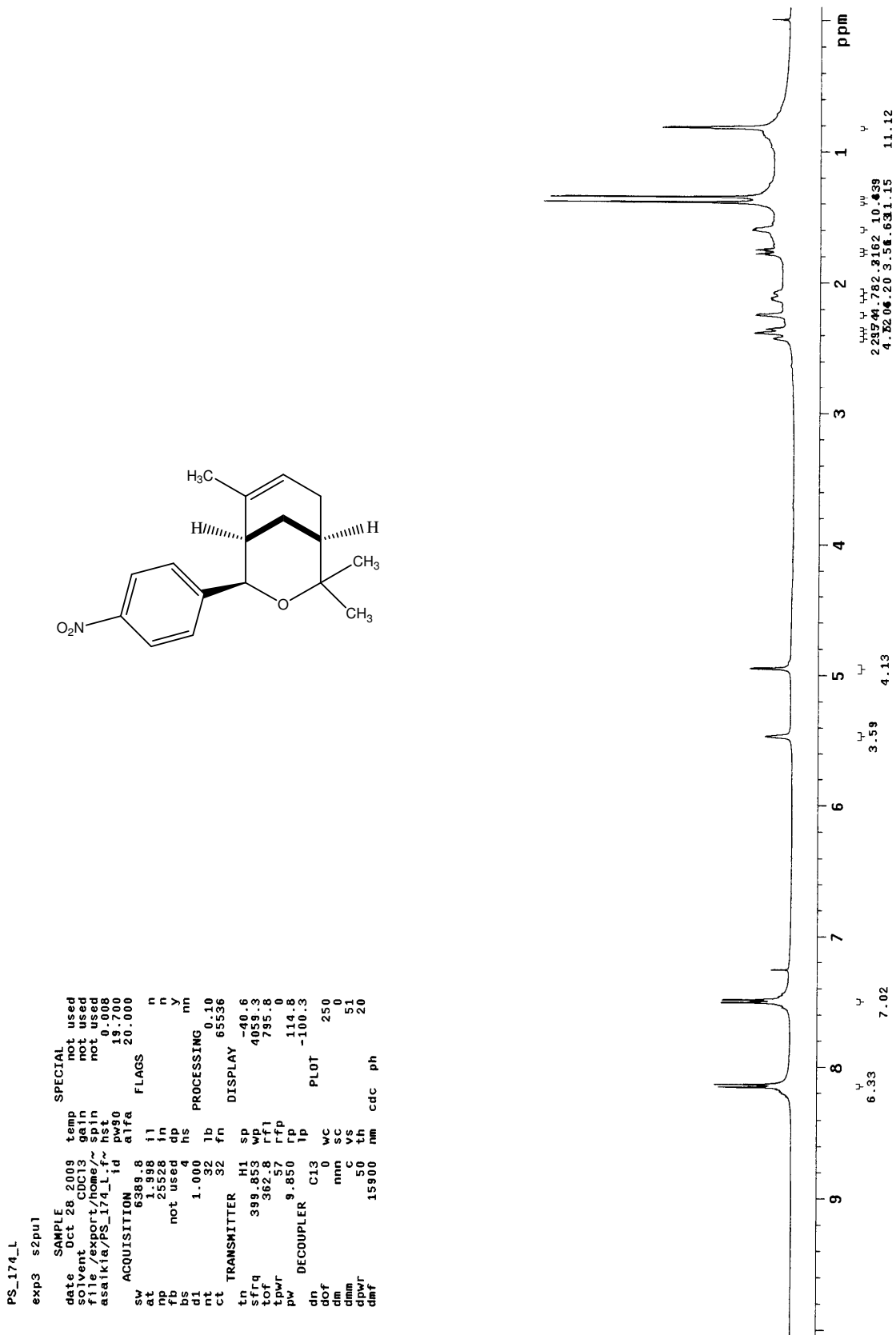
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gain not used
ht not used
ht 0.008
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FLAGS
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n
y
nn
PROCESSING
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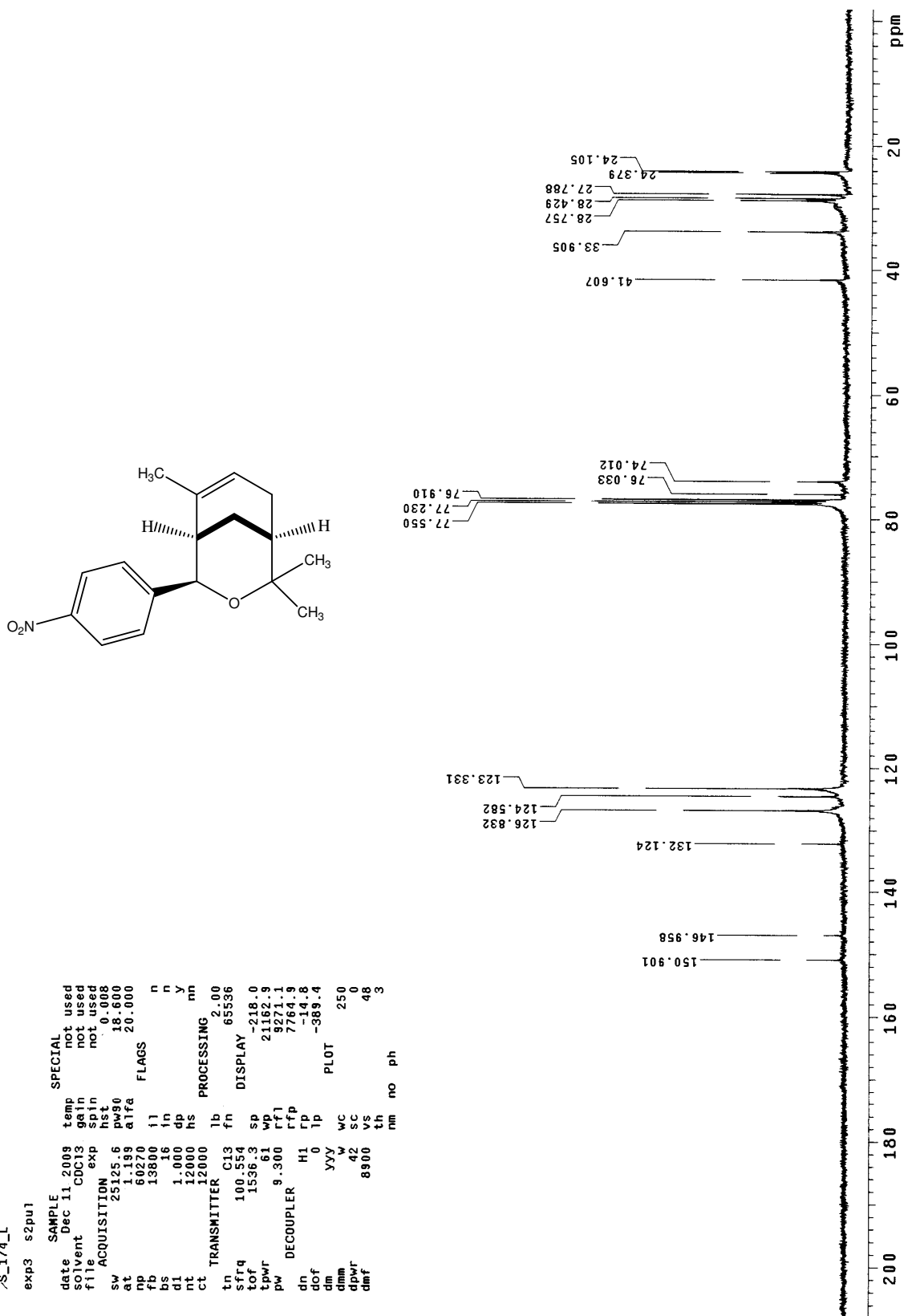
¹⁹F NMR spectra of 3d



¹H NMR spectra of 3e



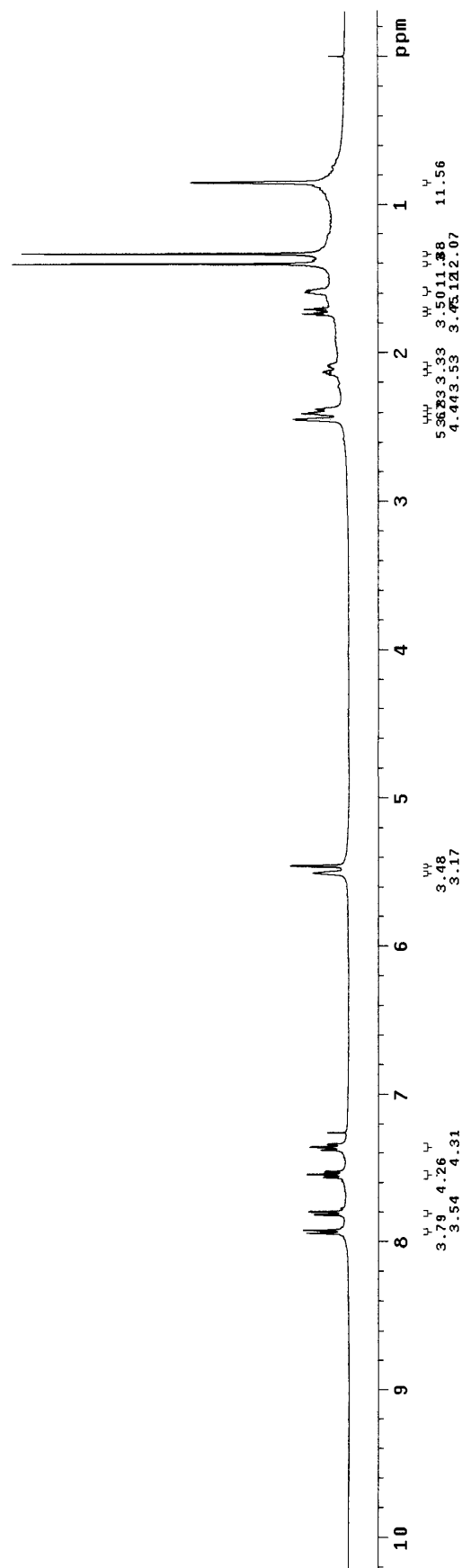
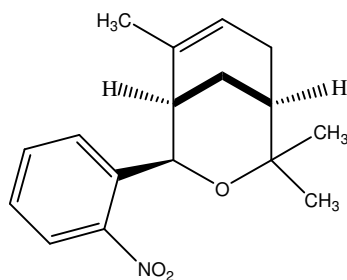
¹³C NMR spectra of 3e



¹H NMR spectra of 3f

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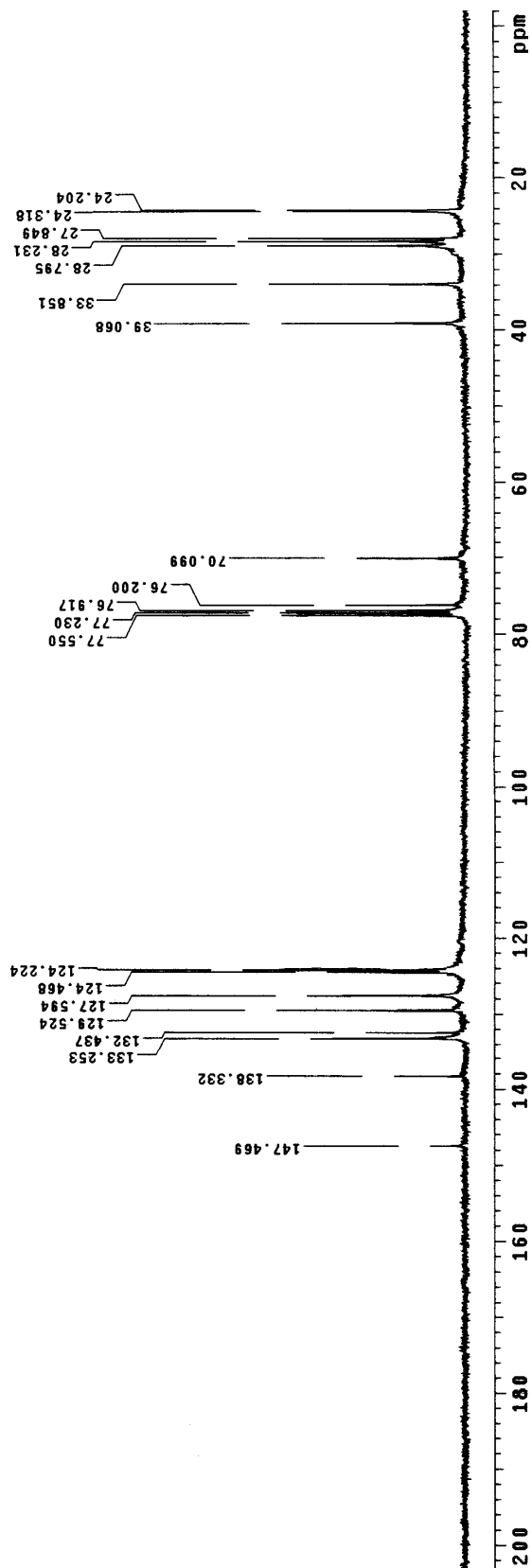
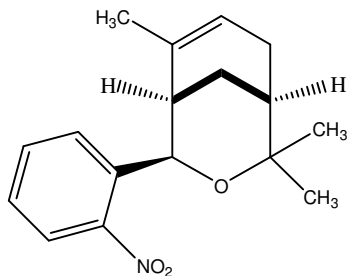
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alifa 20.000
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at 1.958 in n
rp 25528 dn y
bs not used dp n
d1 1.000 hs
nt 32 lb 0.10
ct 32 fn 65536
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tn 399.853 wp -122.3
tof 362.8 rfl 4206.4
tpwr 57 rfp 794.0
pw 9.850 rp 120.7
DECOUPLER C13 lp -93.7
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¹³C NMR spectra of 3f

```

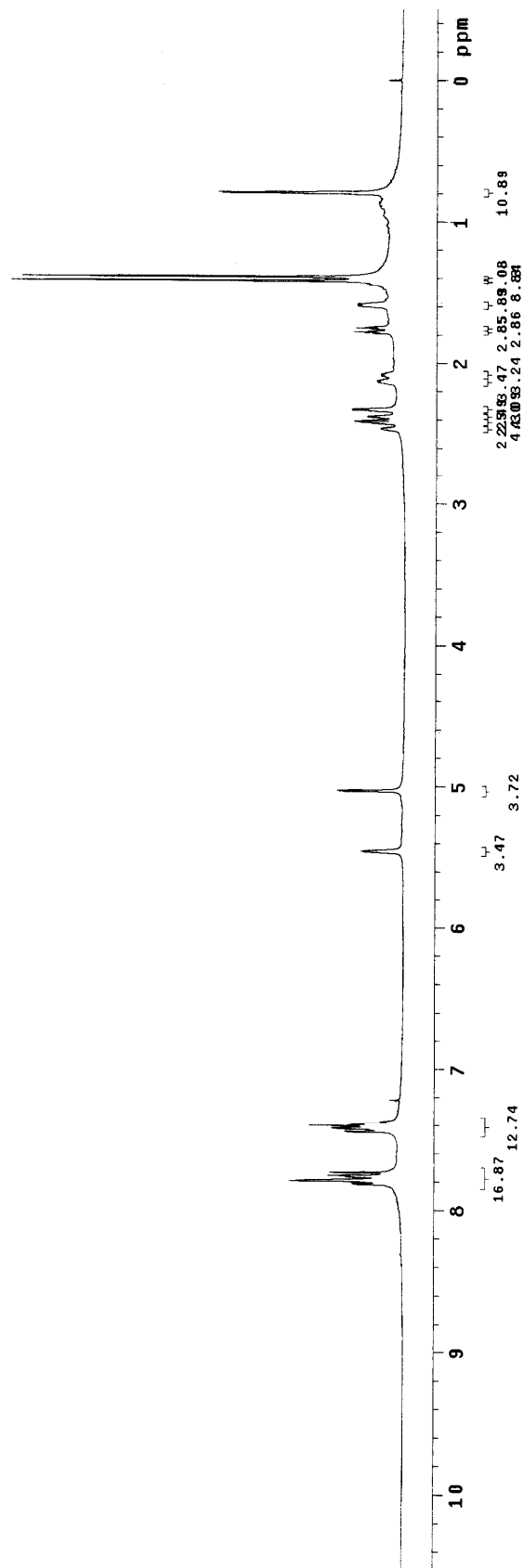
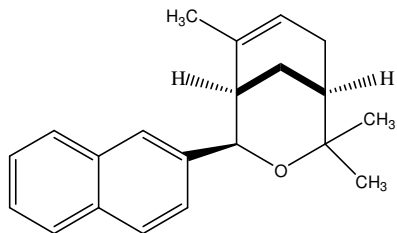
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fb 19800 dp y
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ct 3000 fn 65536
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tof 1536.3 rfl 9276.4
tpwr 61 rfp 7764.9
pw 9.300 rp -27.7
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¹H NMR spectra of 3g

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solvent exp
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l2 4
l3 1.002
l4 32
ct 32
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tn 0.10
sfrq 399.853
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dimf 15900
nm cdc ph
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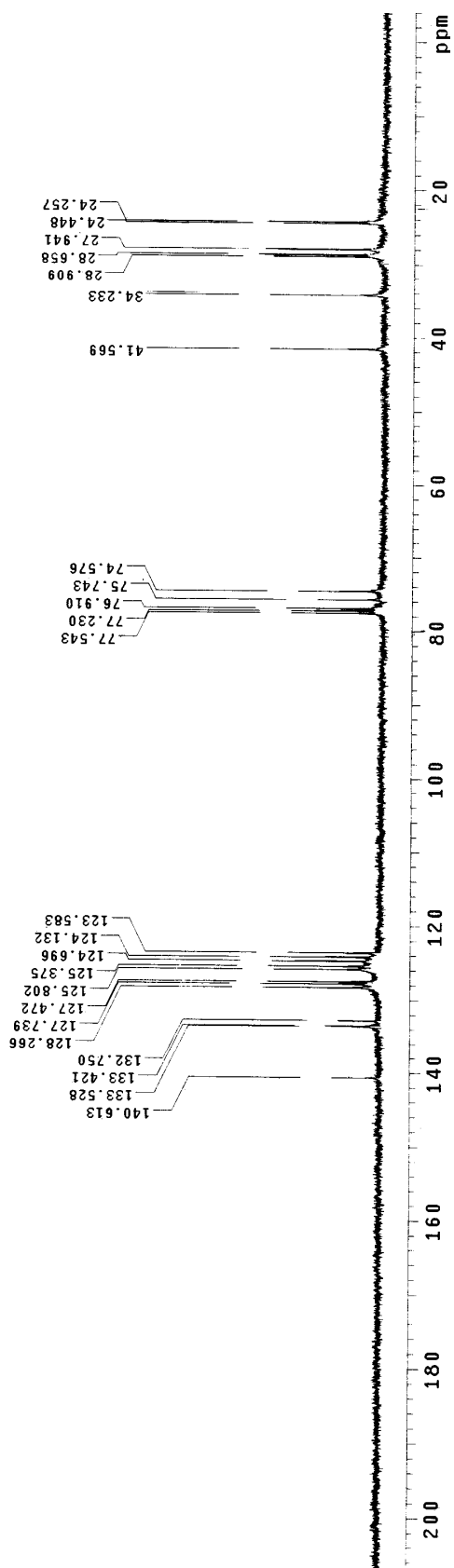
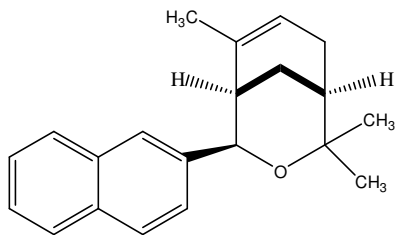
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wp 4424.8
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TH 18
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¹³C NMR spectra of 3g

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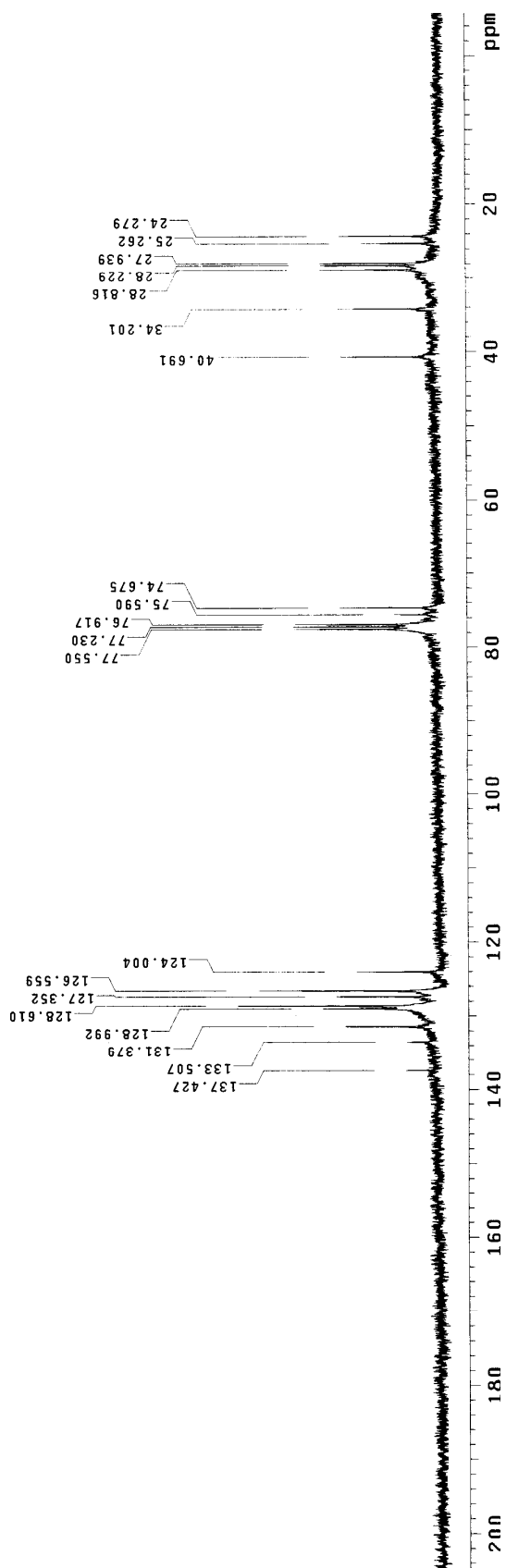
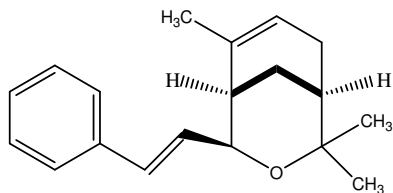
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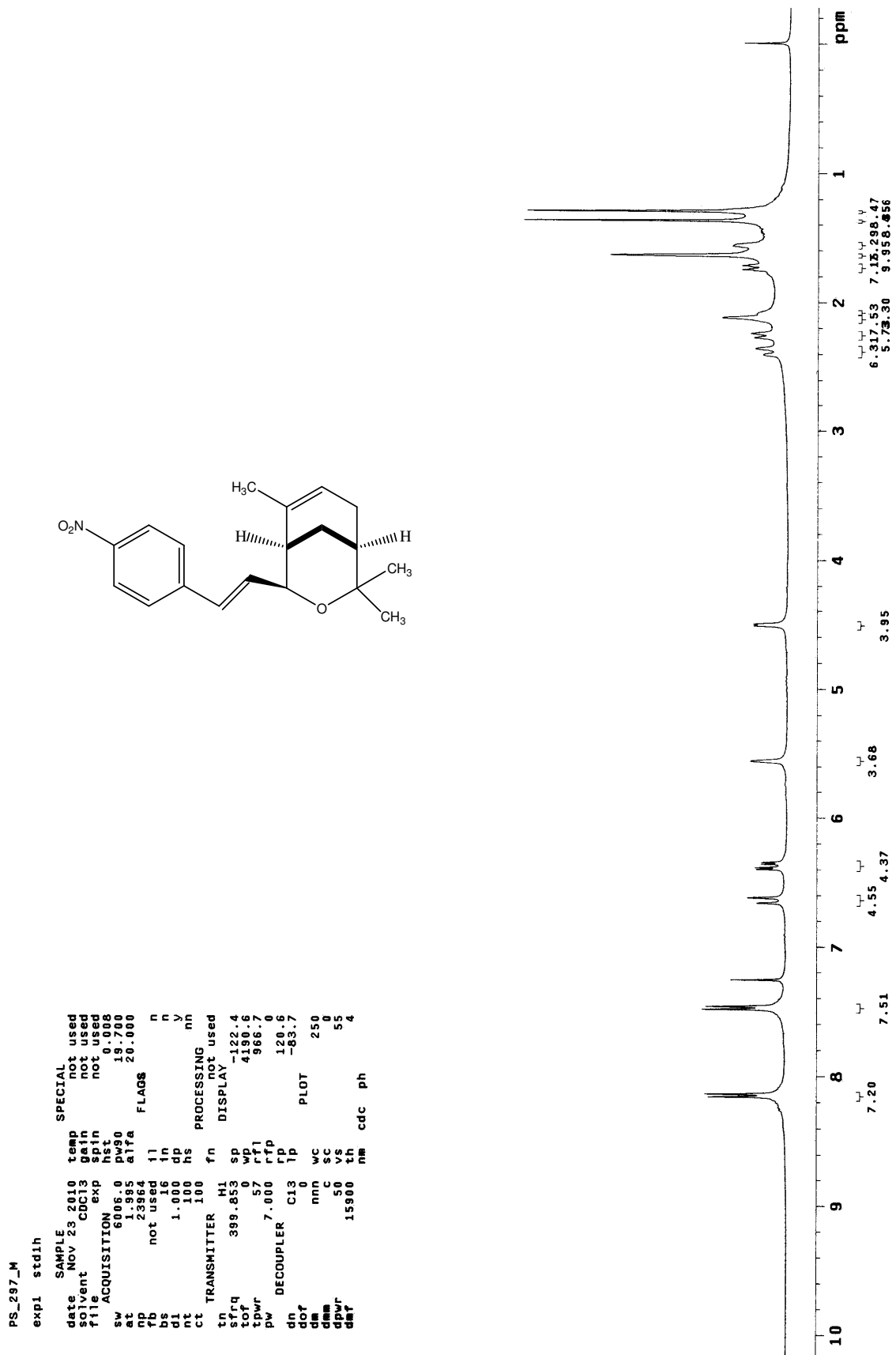
¹³C NMR spectra of 3h

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sfrq 100.554
tof 1536.3
tpwr 61
pw 9.300
DECOUPLER H1
dn 0
dof 0
dm VVY
dmm w
dpm 42
dmf 8900
nm no ph
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temp not used
gain not used
spin not used
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pws0 18.600
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y
nn
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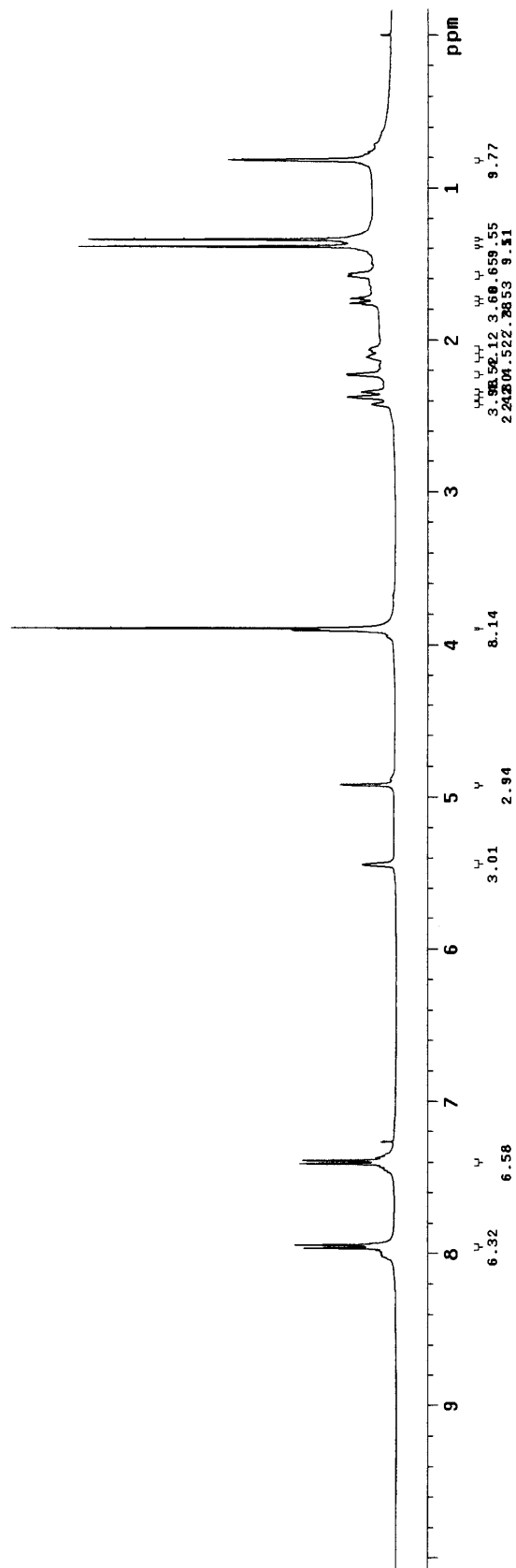
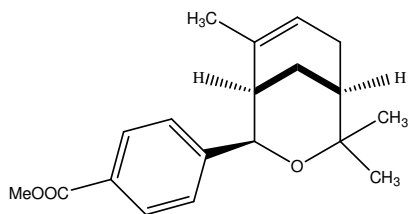
¹H NMR spectra of 3i



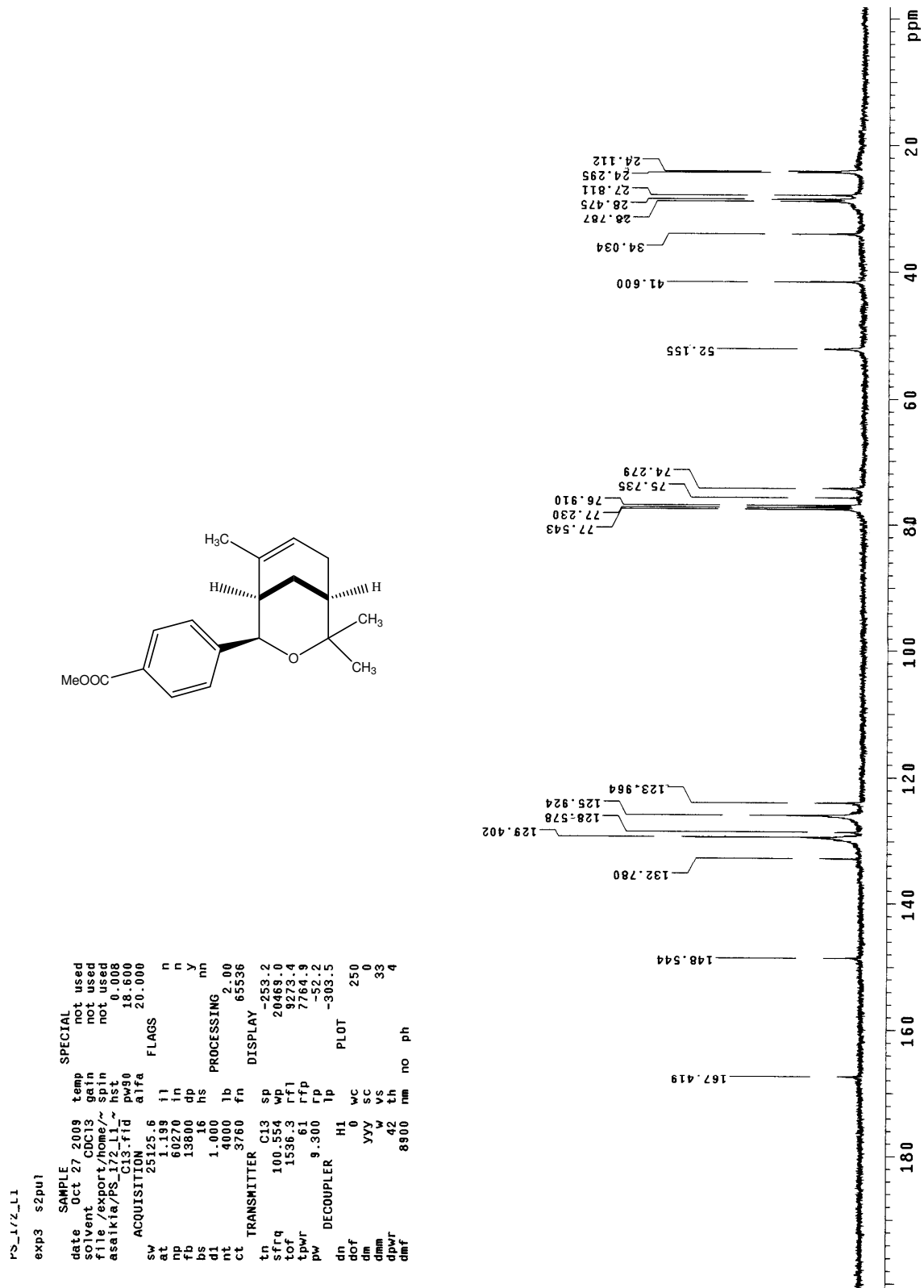
¹H NMR spectra of 3j

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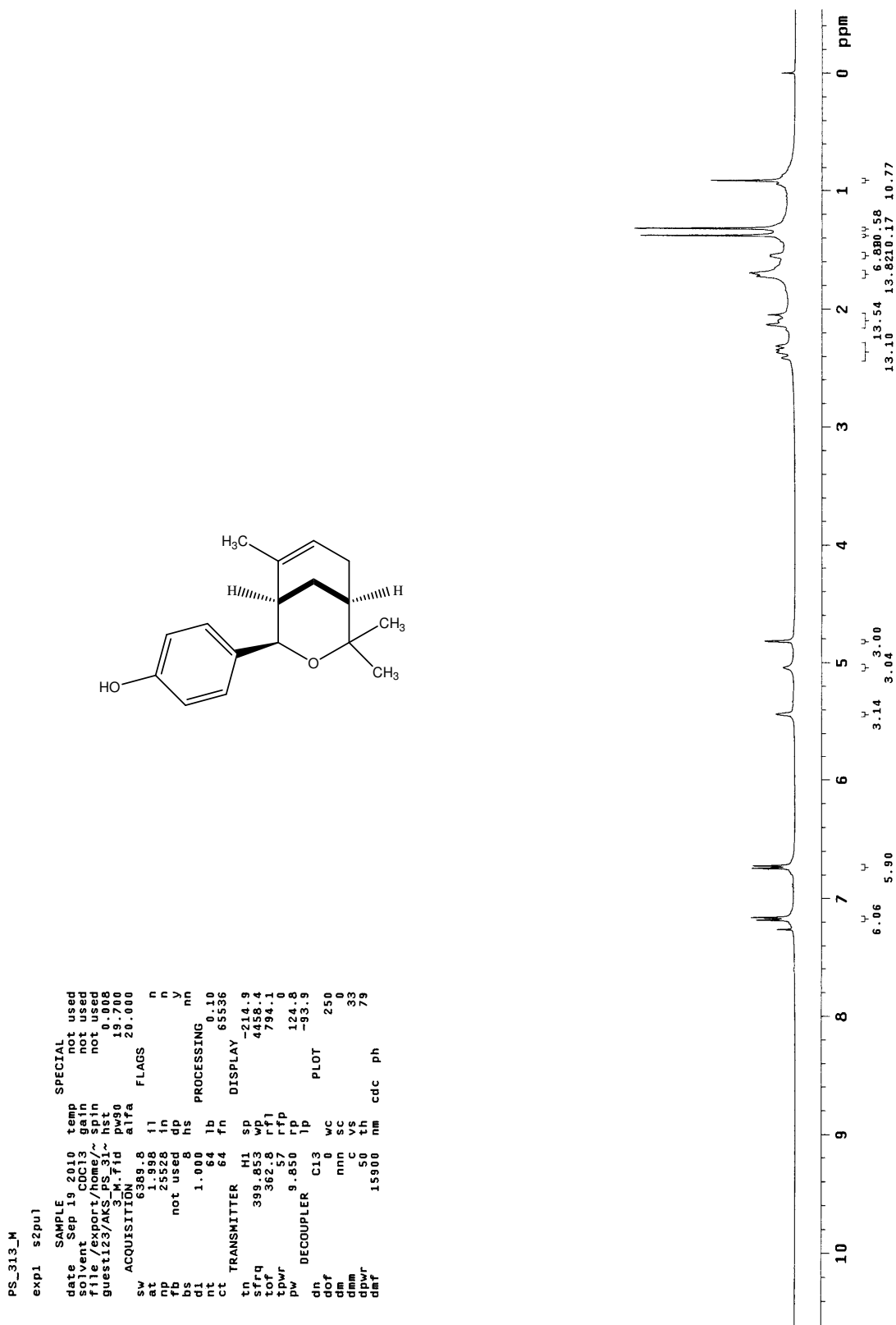
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bs 1.000 hs
d1 1.000 lb 0.10
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tn 399.853 wp -67.7
sfrq 4094.8
tof 362.8 rf1 793.3
tpwr 57 rfp 117.3
pw 9.850 rp -83.0
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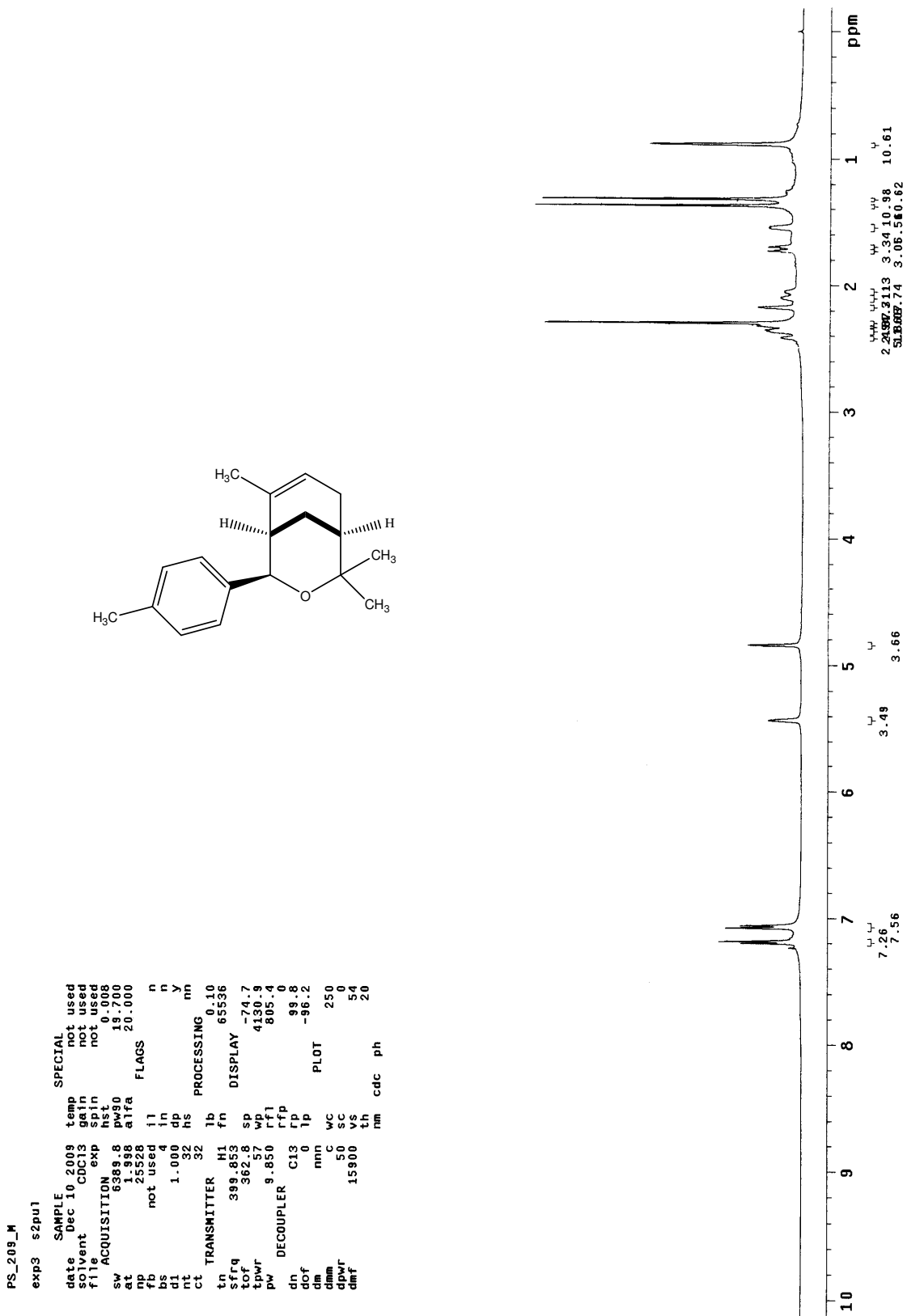
¹³C NMR spectra of 3j



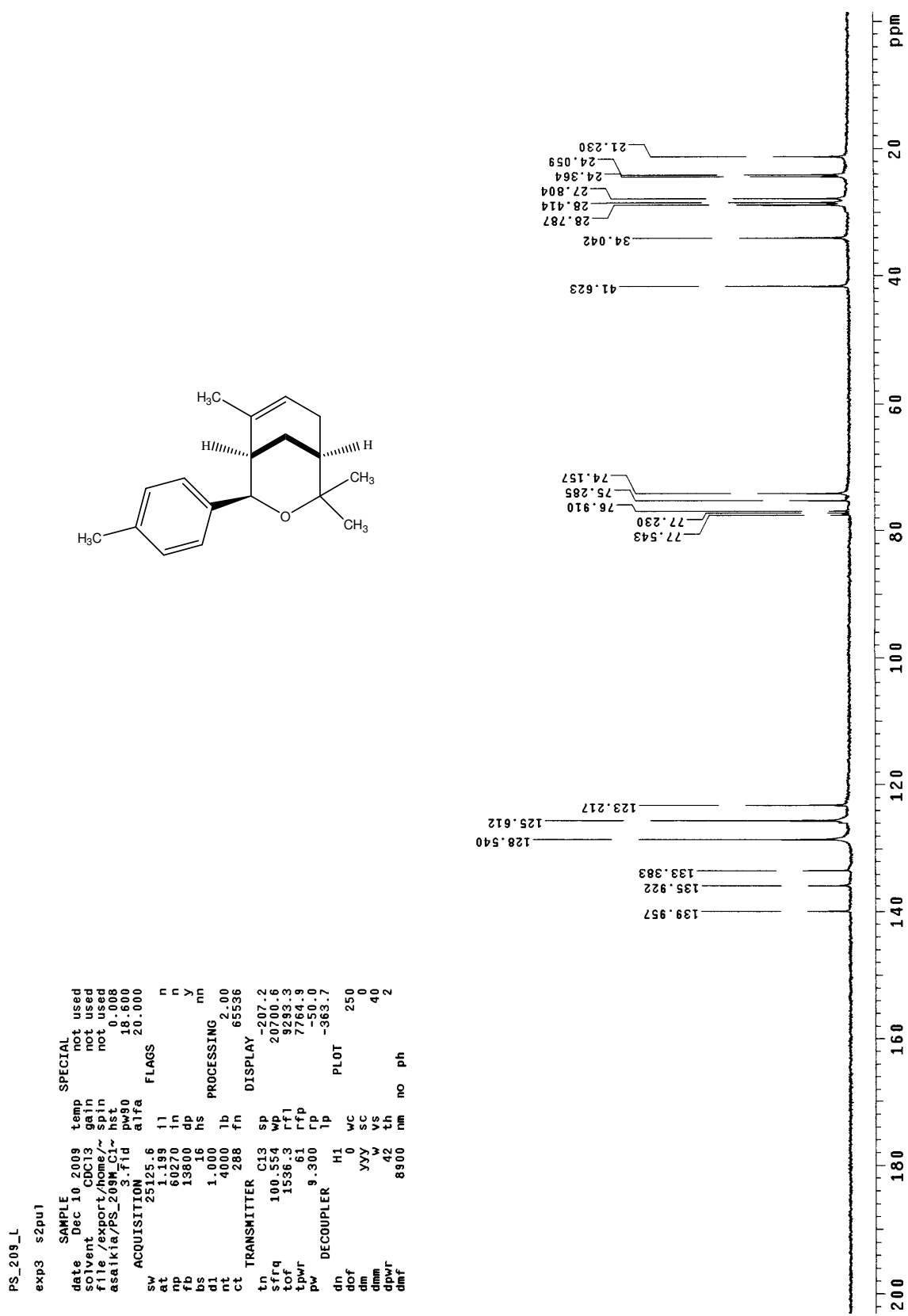
¹H NMR spectra of 3k



¹H NMR spectra of 3l



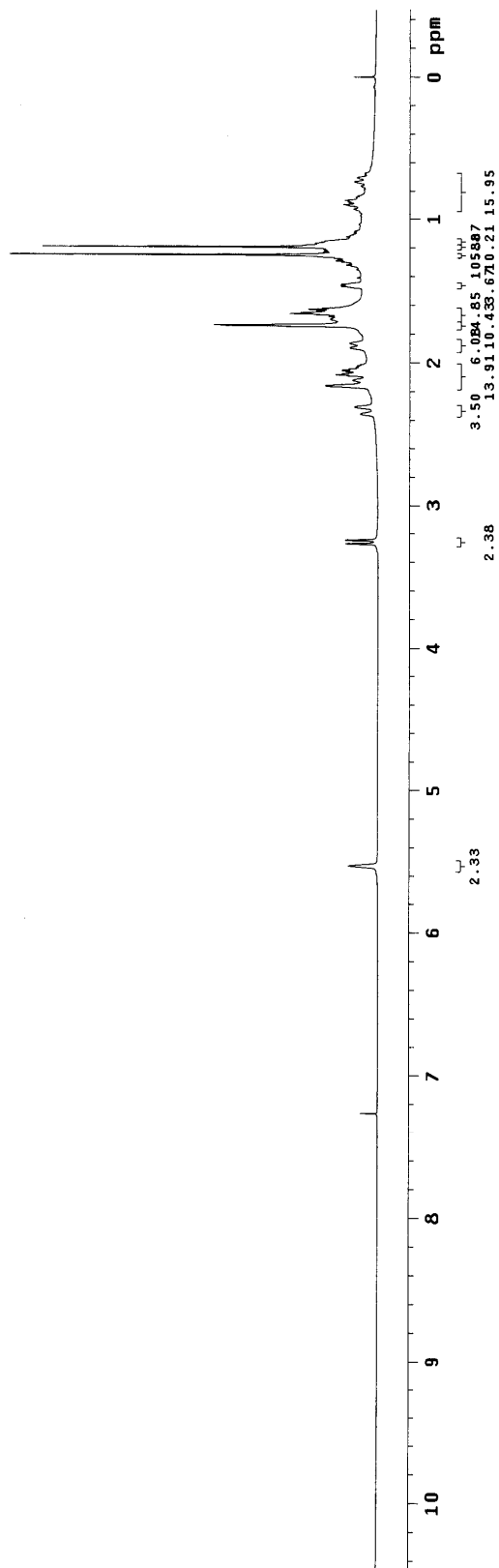
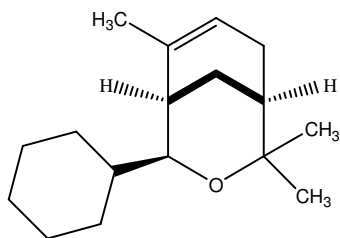
¹³C NMR spectra of 3l



¹H NMR spectra of 3m

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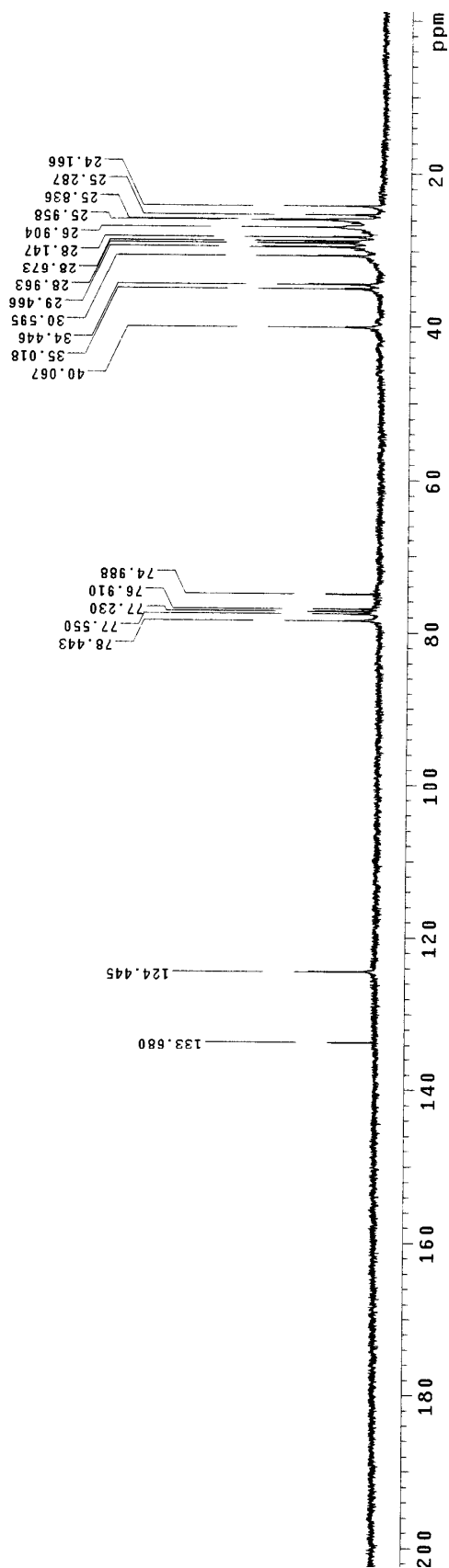
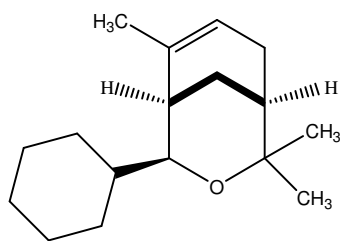
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pw 9.850 rp 106.1
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¹³C NMR spectra of 3m

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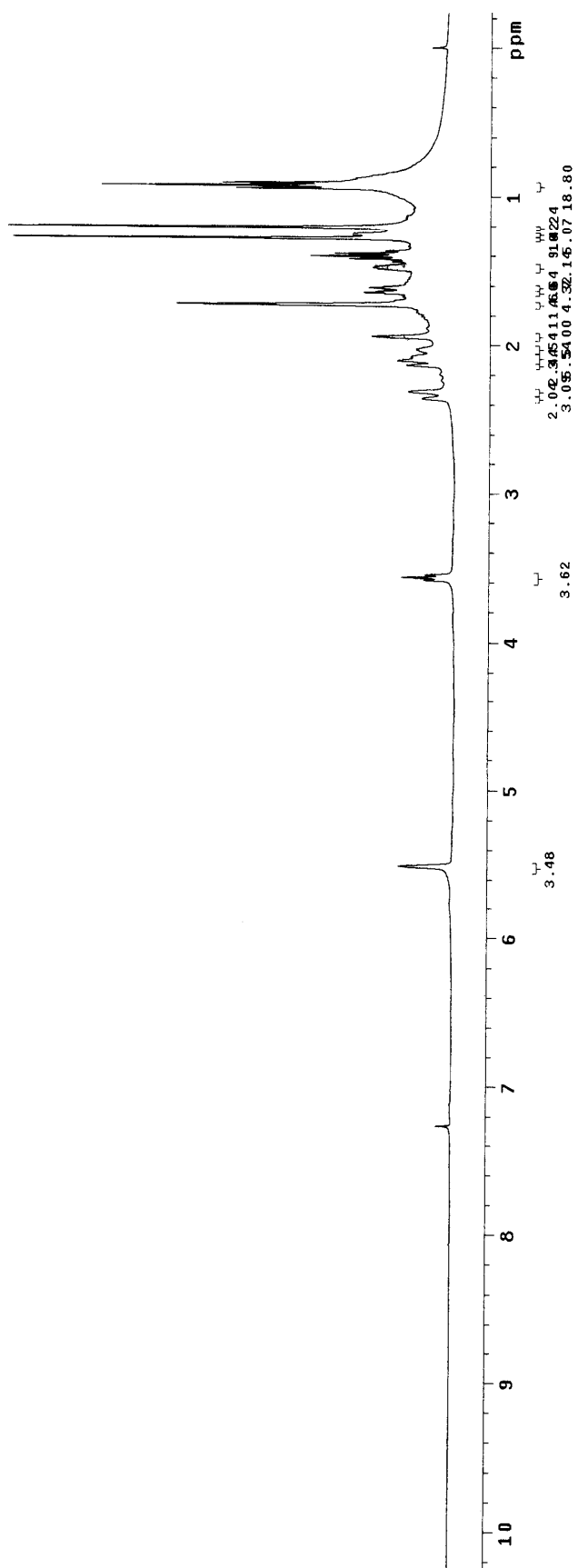
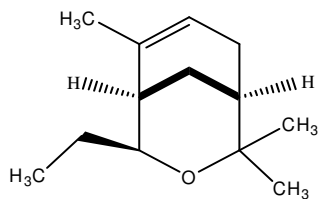
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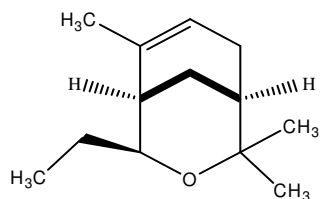
¹H NMR spectra of 3n

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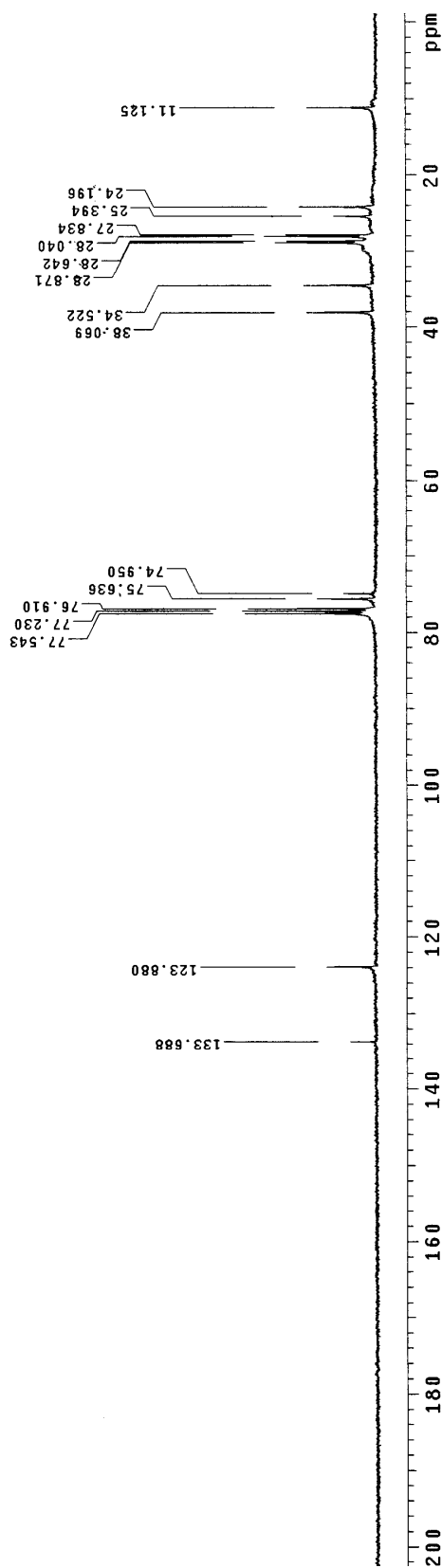


¹³C NMR spectra of 3n



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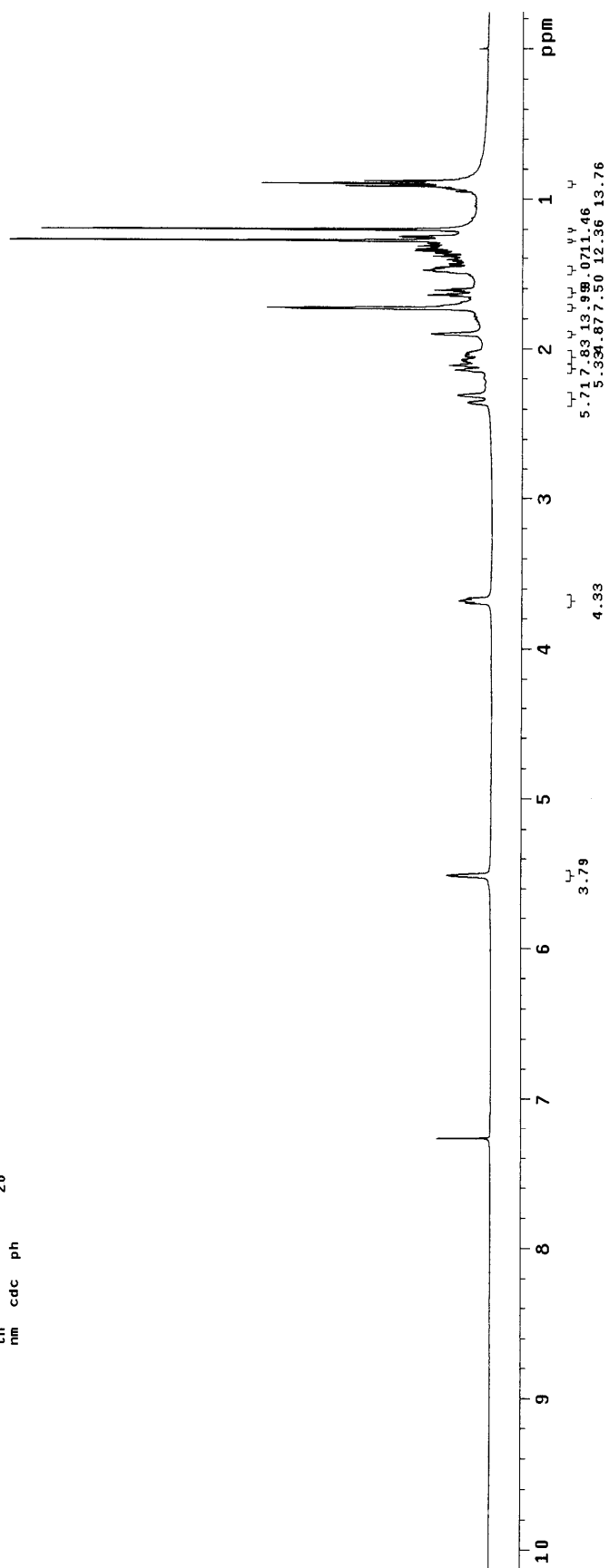
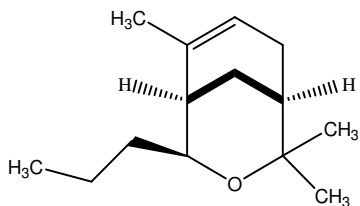
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¹H NMR spectra of 3o

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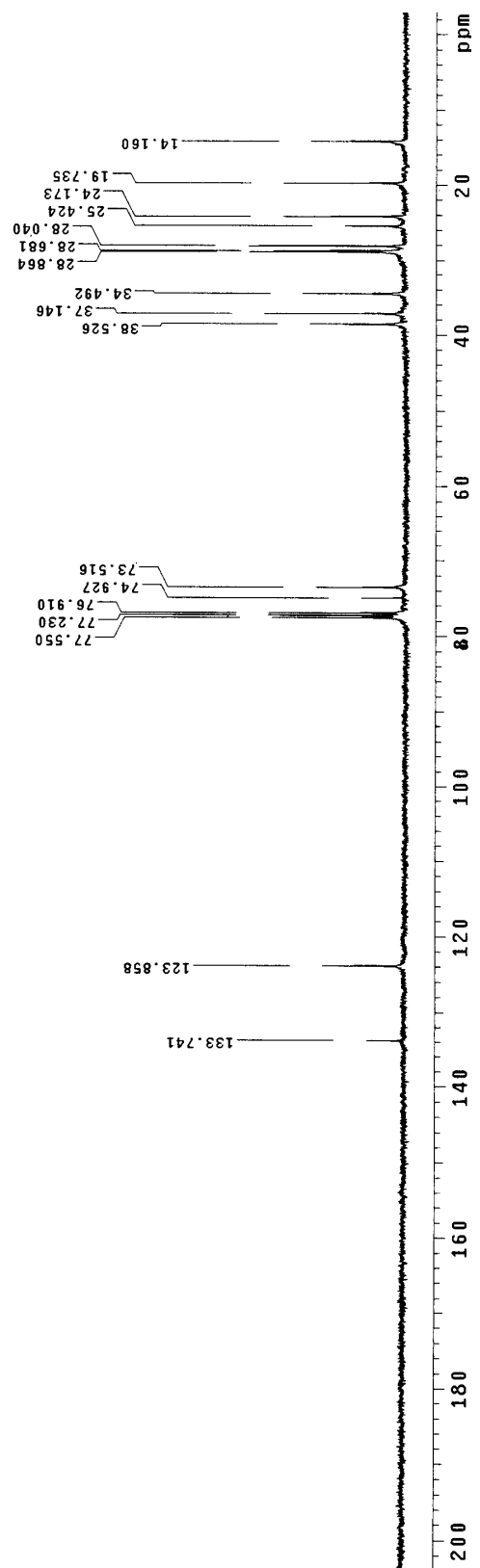
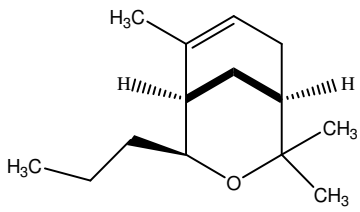
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pw 9.850 rfp
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dm mnn wc
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dpr 86
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nm cdc ph
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gain not used
spin not used
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a1fa 20.000
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20
    
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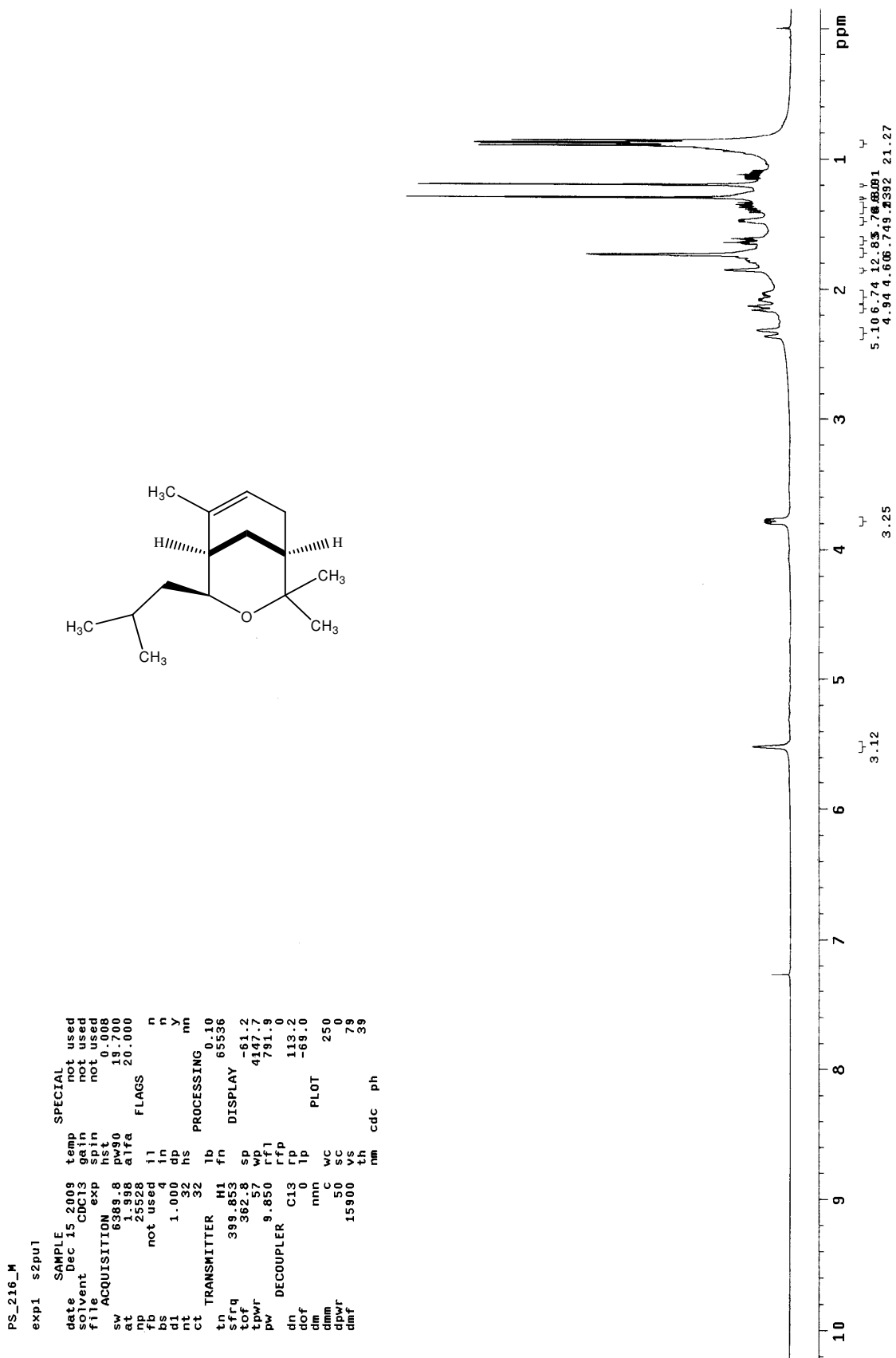
¹³C NMR spectra of 3o

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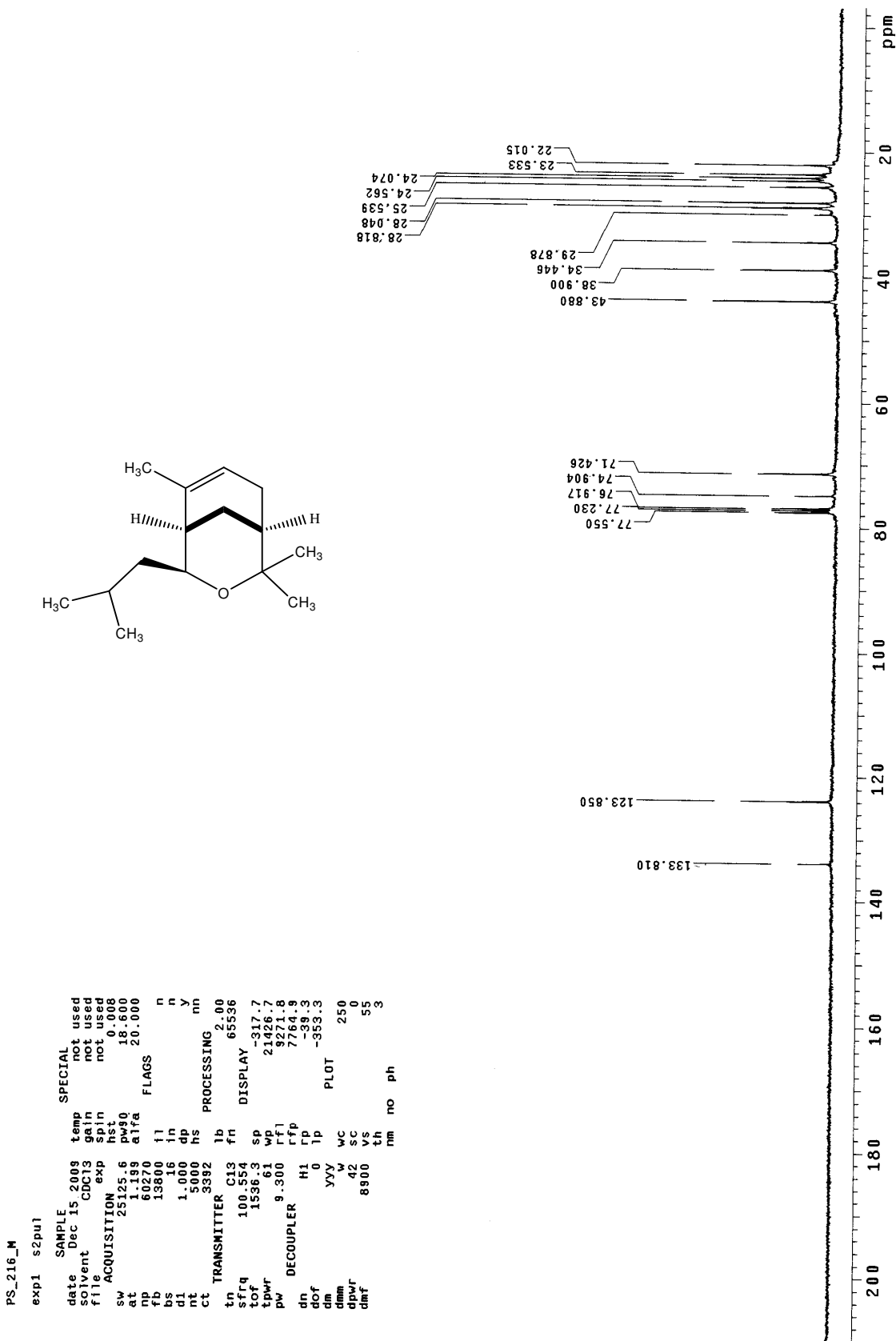
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spin not used
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nn
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wp 20888.4
rf1 9271.1
rfp 7764.9
rp -35.7
lp -354.5
PLOT
wc 250
sc 0
vs 24
th 5
nm no ph
    
```



¹H NMR spectra of 3p



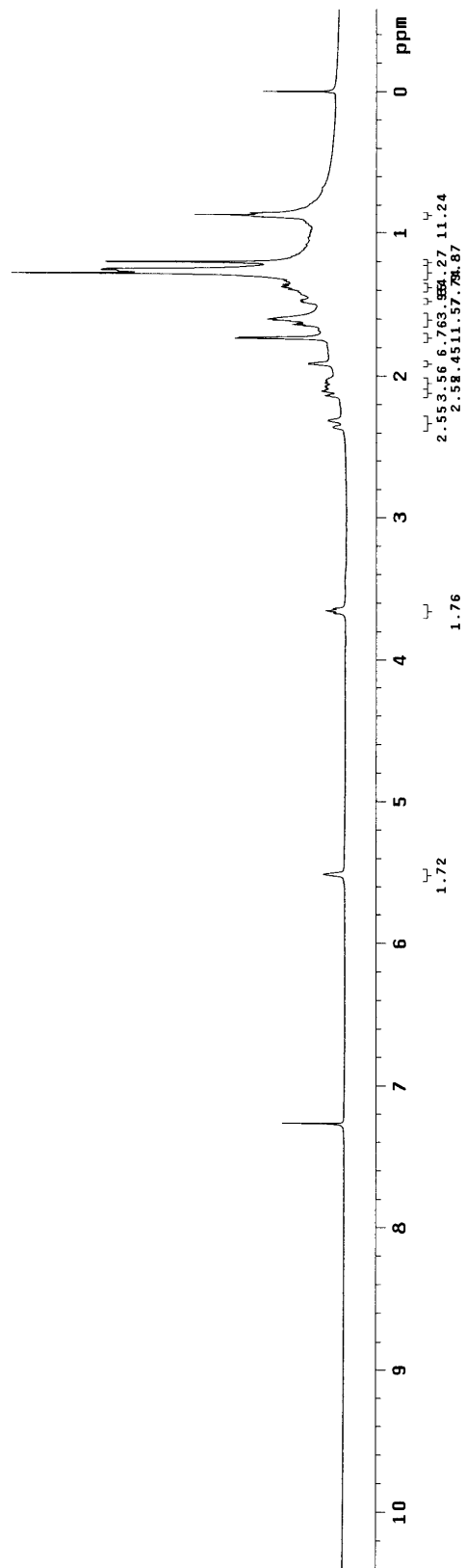
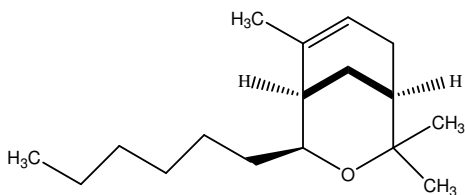
¹³C NMR spectra of 3p



¹H NMR spectra of 3q

```

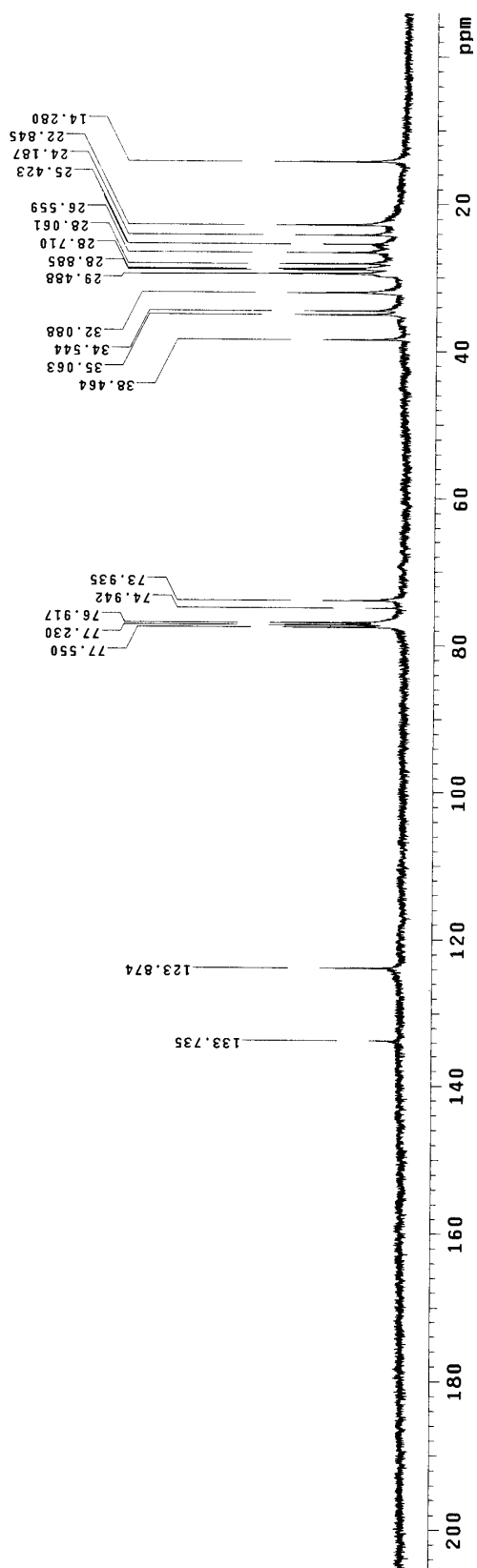
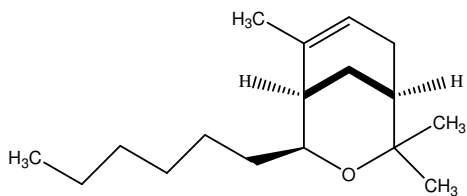
PS_302_M
exp1 s2pu1
SAMPLE
date Mar 3 2011 temp not used
solvent Mar CDCl3 gain not used
file /export/home/~ spin not used
c1temp/AKS_M_21d 19.700
ns90 20.000
atfa 20.000
ACQUISITION
sw 6389.8 n
at 1.998 f1 n
np 25528 in n
fb not used dp y
bs 8 hs
di 1.000 lb PROCESSING nn
ct 100 fh 65536
TRANSMITTER H1 SP DISPLAY
tn 230.5
sfrq 399.853 wdr 4391.4
tof 362.8 rfl 792.9
tpwr 57
pw 9.850 rp 92.6
DECOUPLER C13 PLOT
dn 0
dor nn 250
dpc vs 57
dmm 50 th 20
dpr 15900 nm cdc ph
    
```



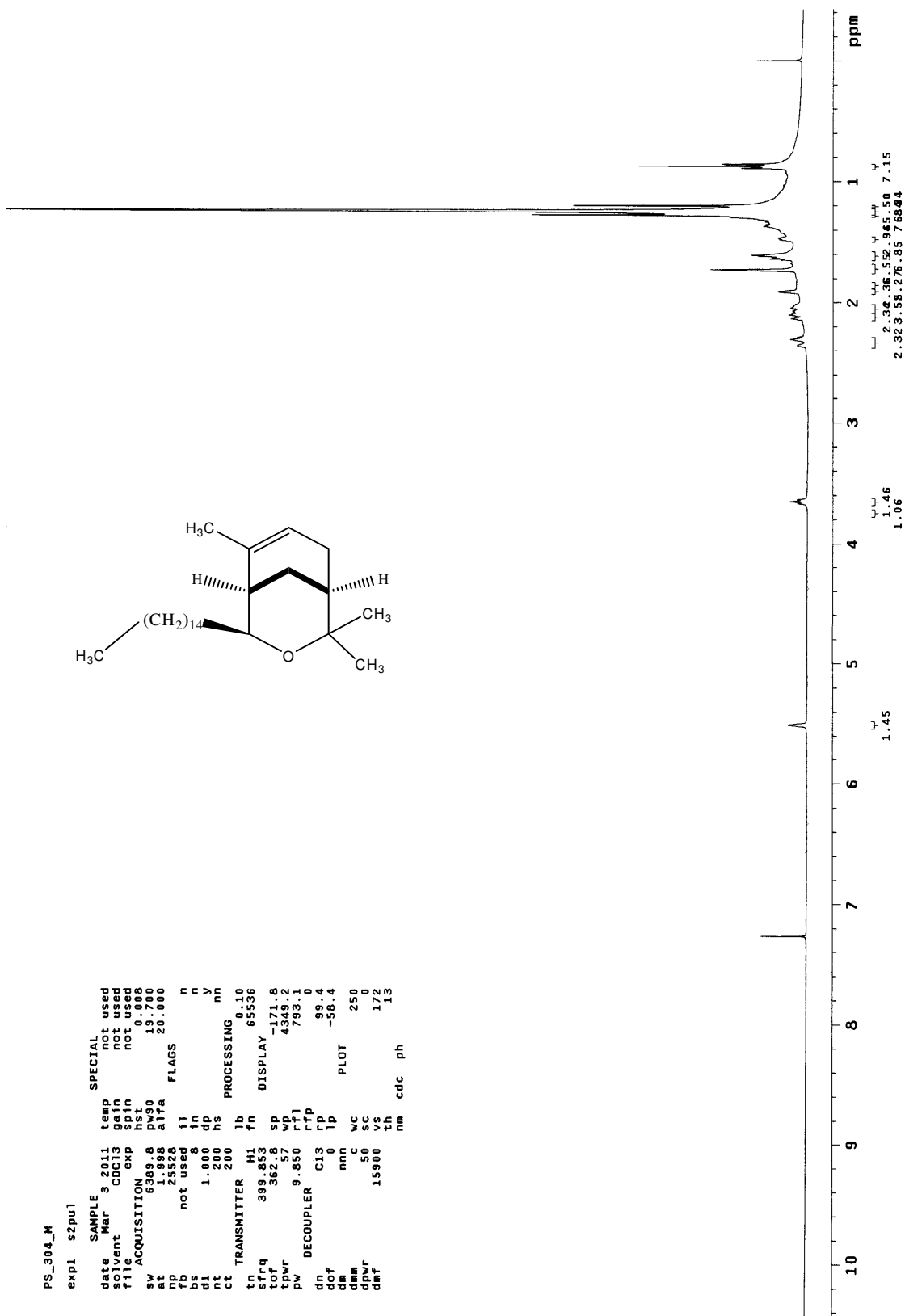
¹³C NMR spectra of 3q

```

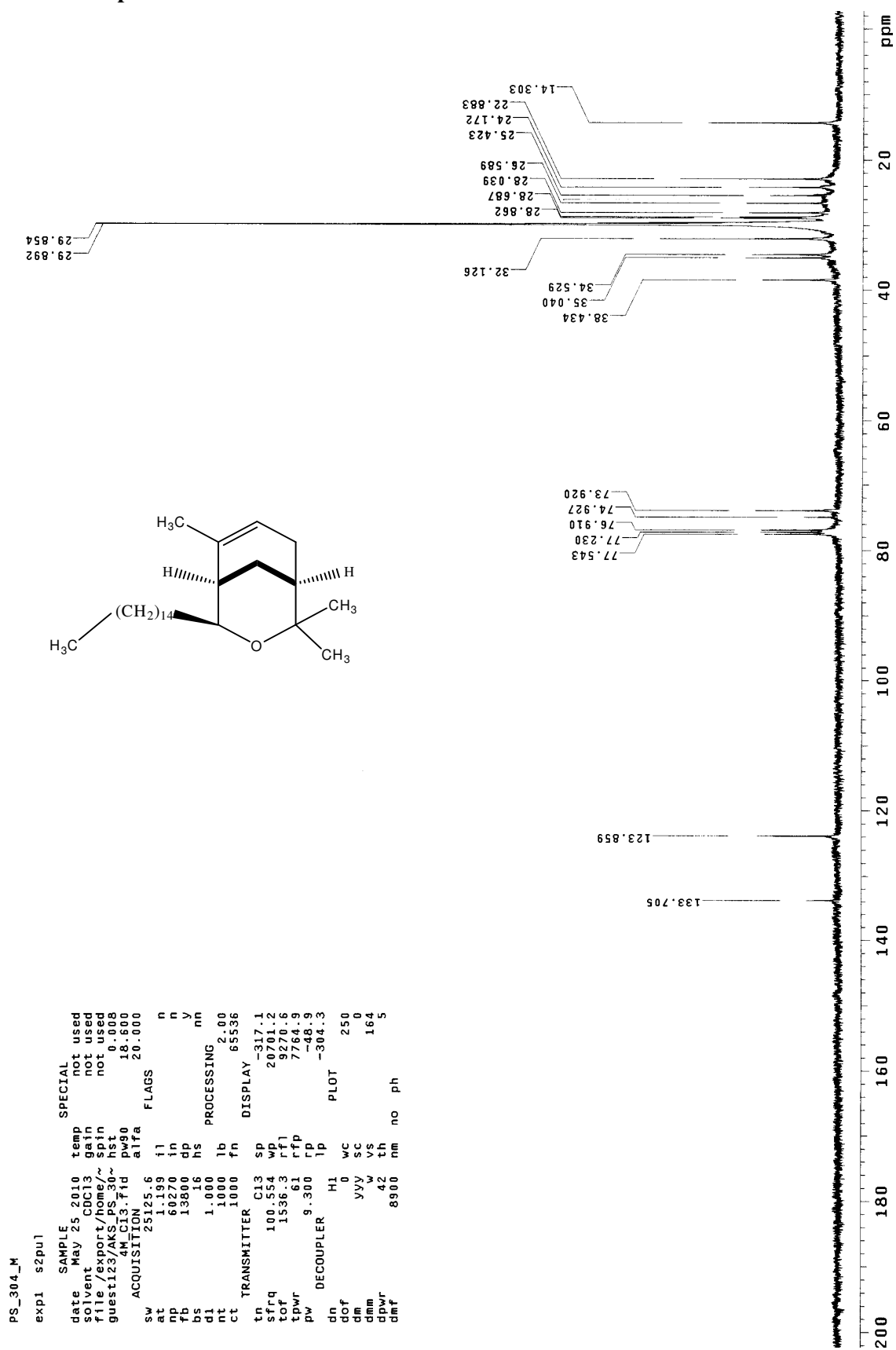
PS_302_M
exp1  szpu1
date  SAMPLE
    Jun 1 2010
solvent  CDC13
file  CDC13
sw  ACQUISITION
    at 25125.6
    np 60270
    fb 13800
    bs 16
    d1 1.000
    nt 4000
    ct 4000
    SPECIAL
    temp not used
    gain not used
    spfn not used
    hst 0.008
    pw90 18.600
    alfa 20.000
    FLAGS
    n n
    y y
    nn nn
    PROCESSING
    lb 2.00
    fn 65536
    DISPLAY
    sp -646.1
    wp 21361.4
    rfl 9269.0
    rfp 7764.9
    rp -64.8
    lp -271.4
    DECOUPLER
    H1
    dof 0
    dm yyy
    dmm w
    dpwr 42
    dmr 8900
    nm no ph
    250
    0
    22
    4
    
```



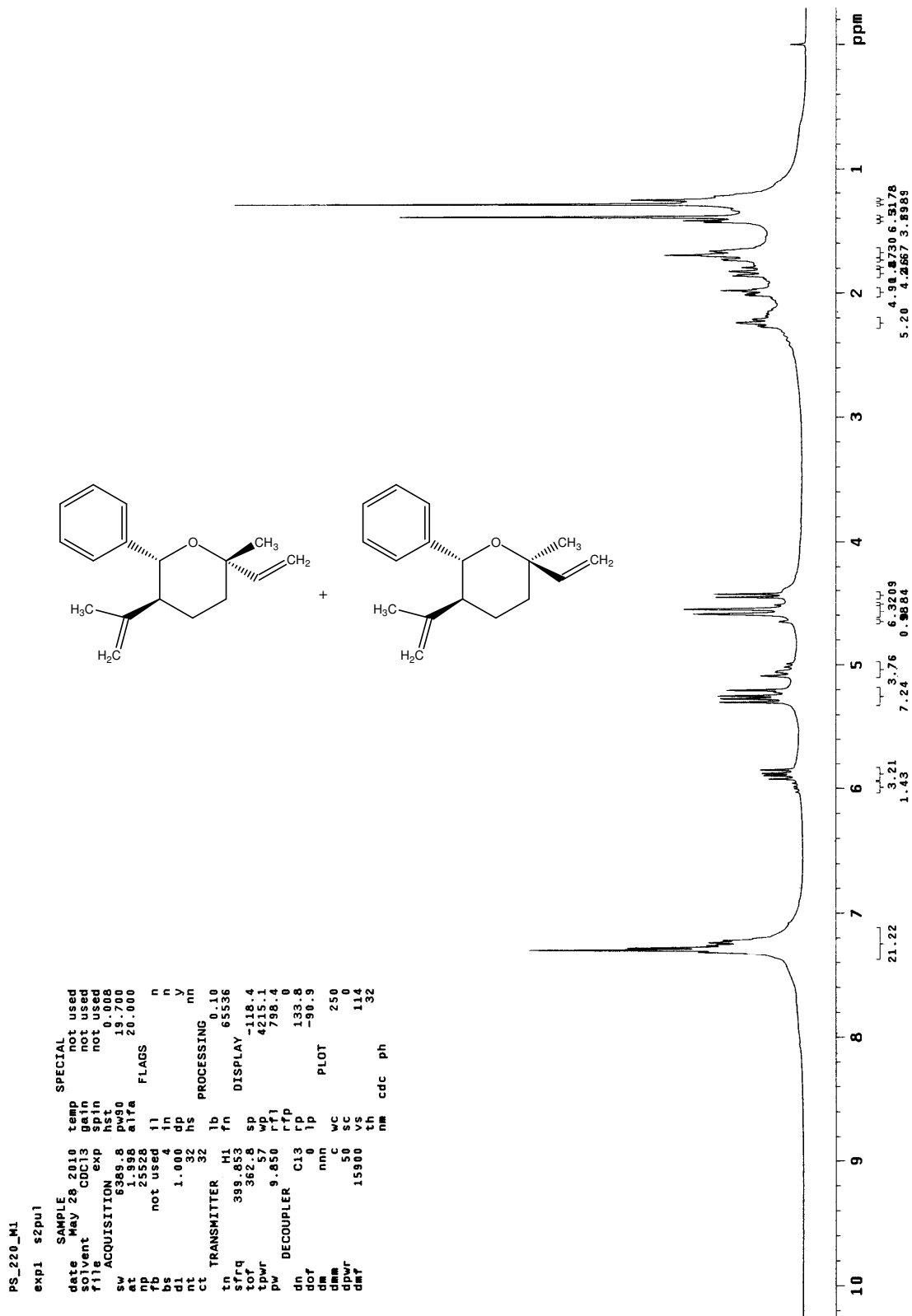
¹H NMR spectra of 3r



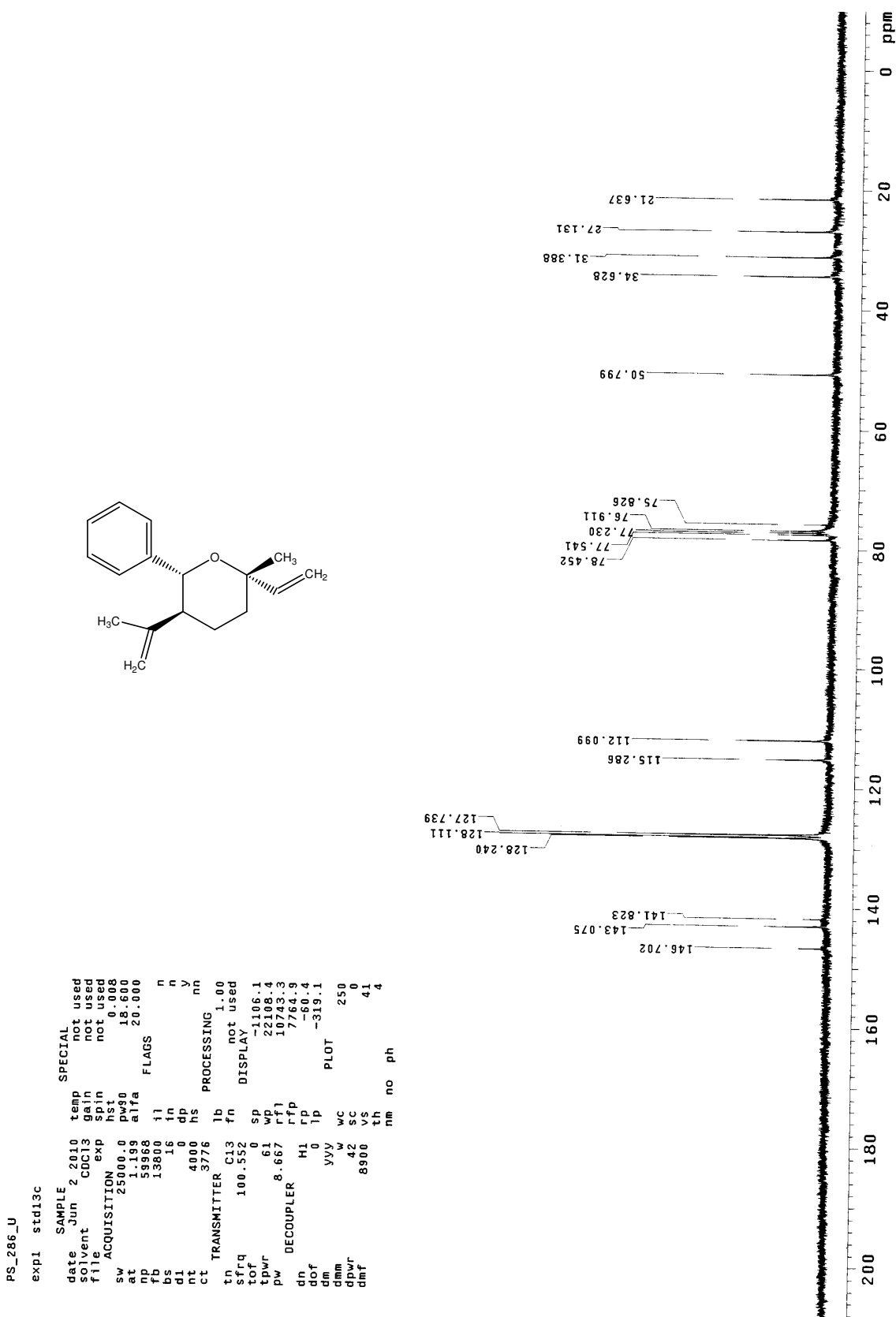
¹³C NMR spectra of 3r



¹H NMR spectra of 4a & 5a



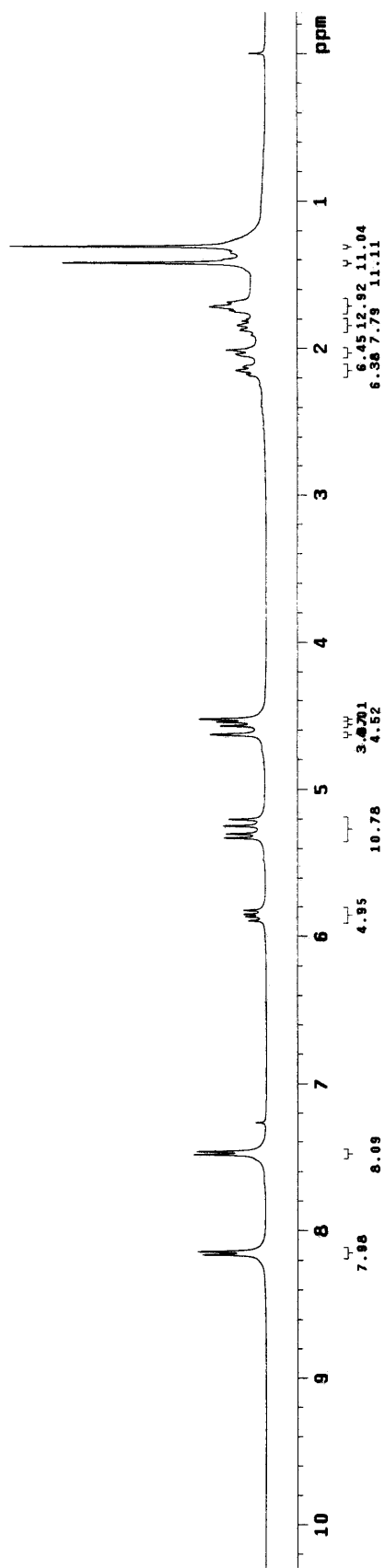
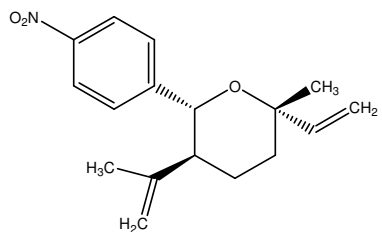
¹³C NMR spectra of 4a



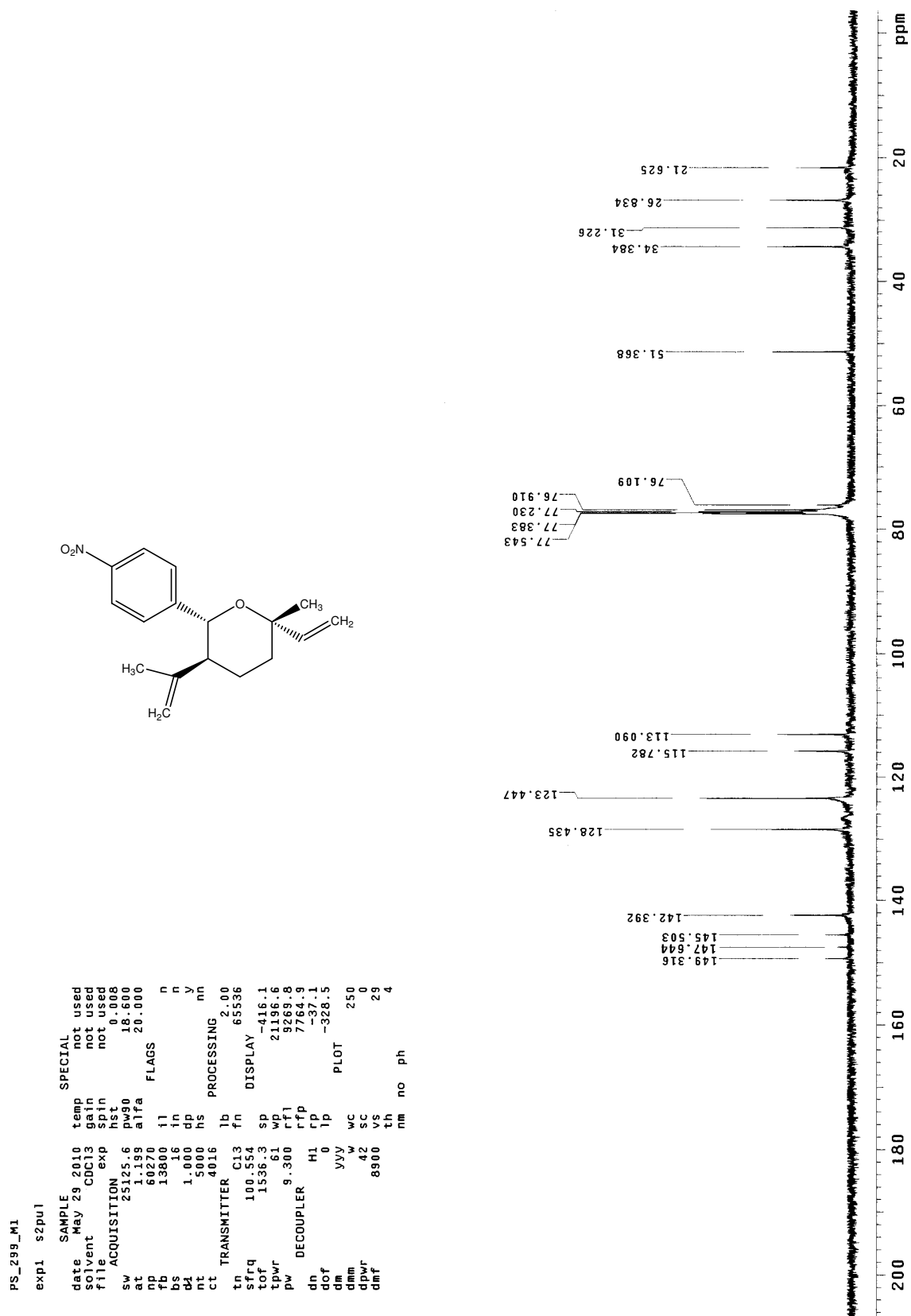
¹H NMR spectra of 4e

```

PS_299H
exp1 s2pu1
SAMPLE
date Dec 17 2010
solvent CDC13
file CDC13
ACQUISITION
sw 6389.8
at 1.898
np 25528
fb not used
bs 8
di 1.000
nt 100
ct TRANSMITTER H1
tn 399.853
sfrq 362.8
tof 57
tpwr 9.650
pw DECOUPLER C13
dn 0
dm 0
dimm C
dpmf 50
dnt 15900
SPECIAL
temp not used
gain not used
spin not used
hst 0.008
pws0 19.700
alfa 20.080
FLAG
n
y
nm
0.10
65536
DISPLAY
-122.1
4240.2
793.7
109.5
-88.1
250
45
25
nm cdc ph
    
```



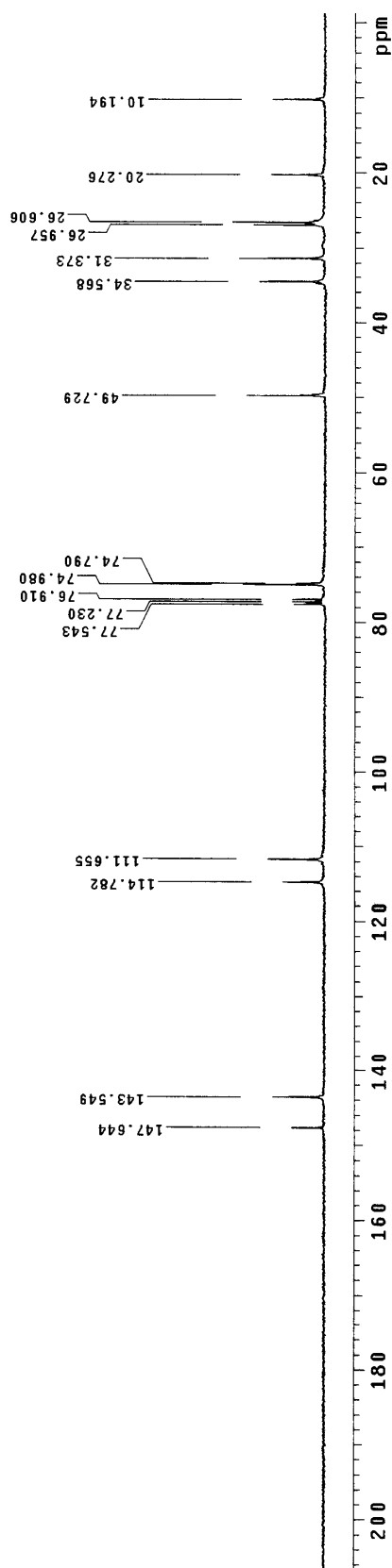
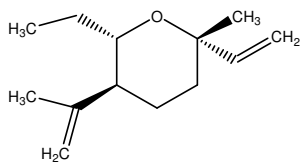
¹³C NMR spectra of 4e



¹³C NMR spectra of 4n

```

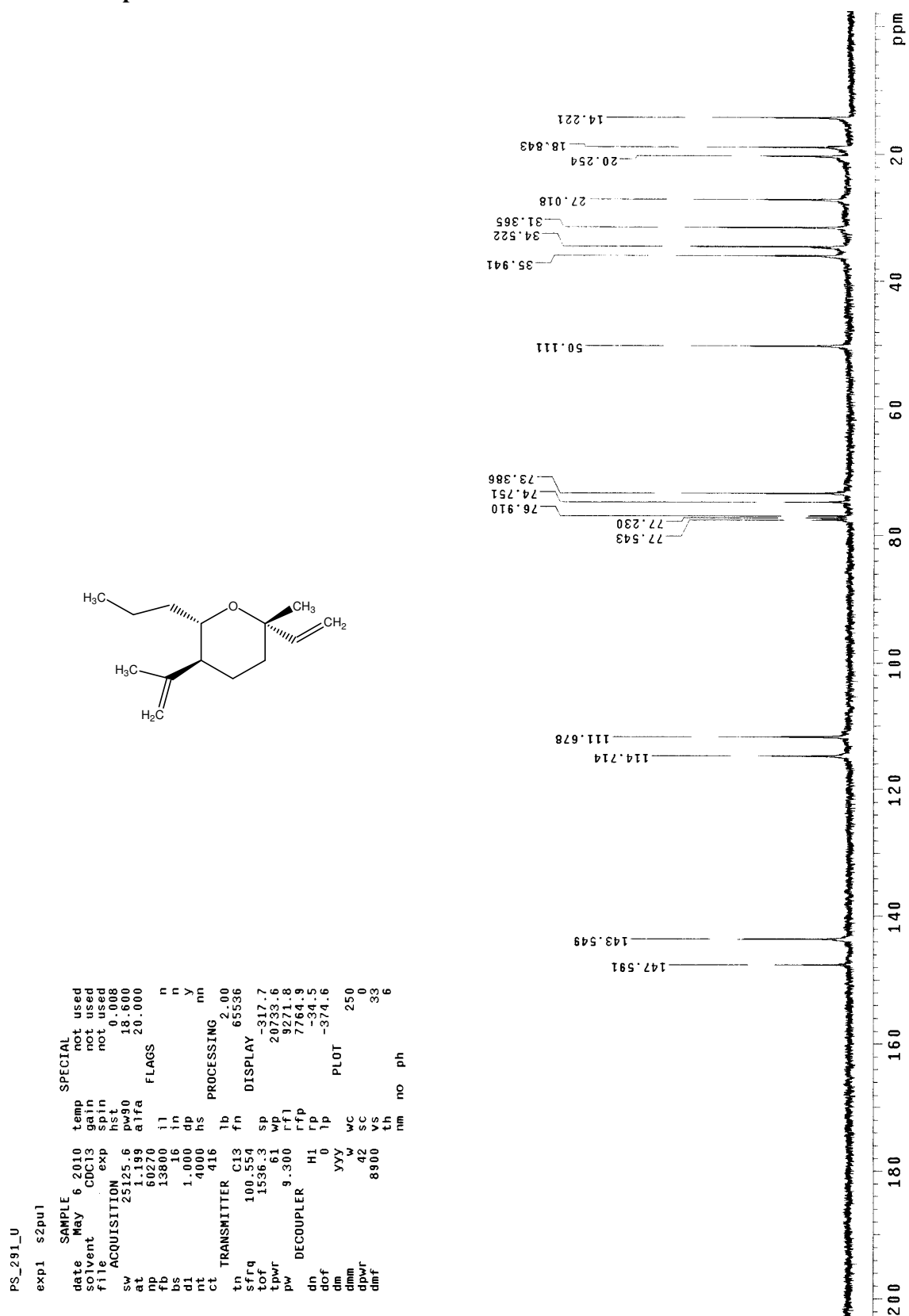
PS_221_U
exp1 s2pul
SAMPLE
date Dec 24 2009 temp not used
solvent CDCl3 gain not used
file /export/home/~ spin not used
asaikria/PS_221_U_1~ hst 0.000
pw30 18.000
alpha 20.000
ACQUISITION
sw 25125.6
at 1.188 l1
np 60270 ln
fb 13800 dn
bs 16 hs
d1 1.000
nt 5000 lb
ct 2920 fn
PROCESSING
ct 85536
DISPLAY
tn -185.8
sfrq 100.554 wp
tof 1536.3 rfl
tpwr 61 rfp
pw 9.300 rp
DECOUPLER
dn HI
dof 0 wc
dm YYY sc
dmm w vs
dpwr 42 th
dmf 8900 nm no ph
    
```



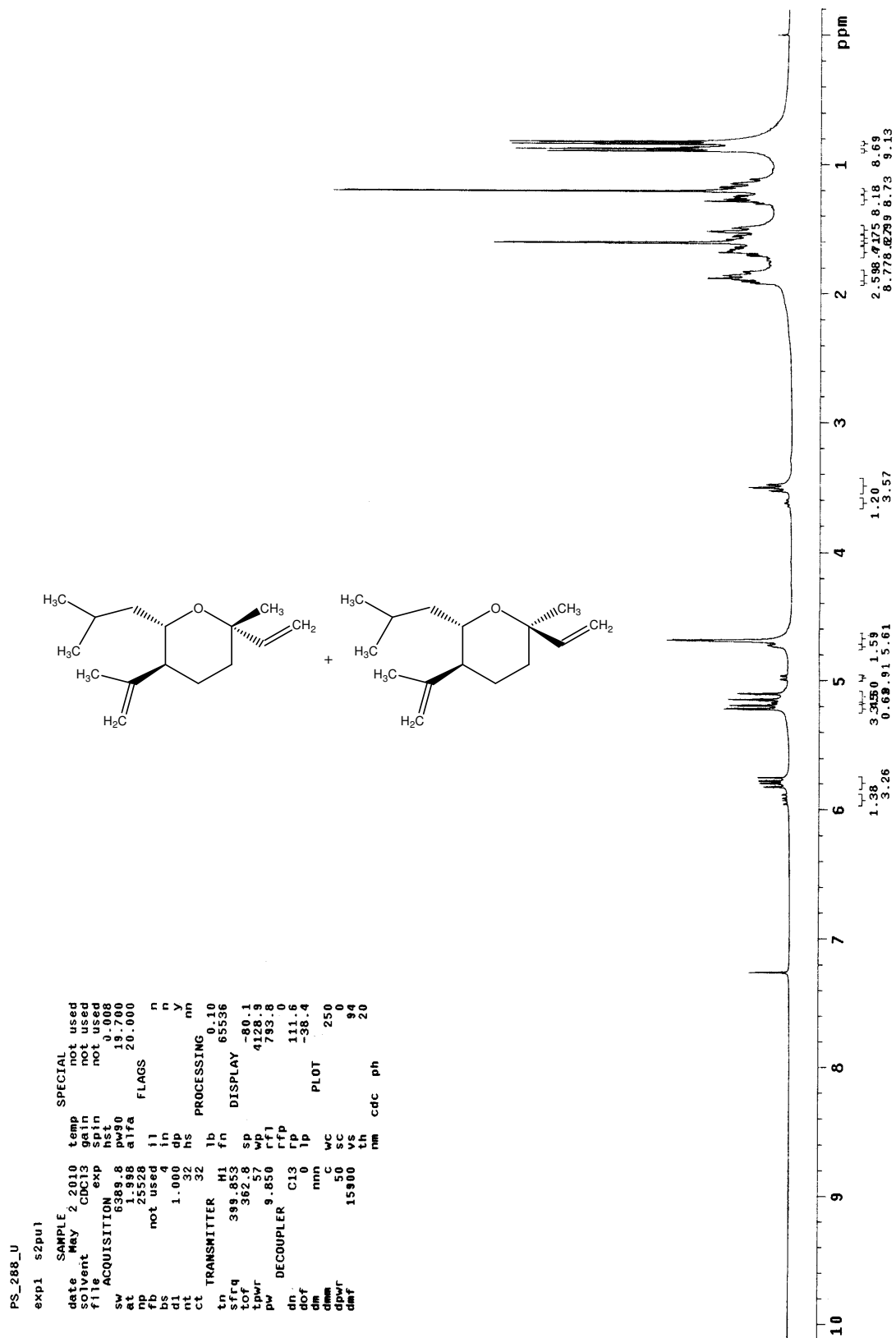
¹H NMR spectra of 4o & 5o



¹³C NMR spectra of 4o



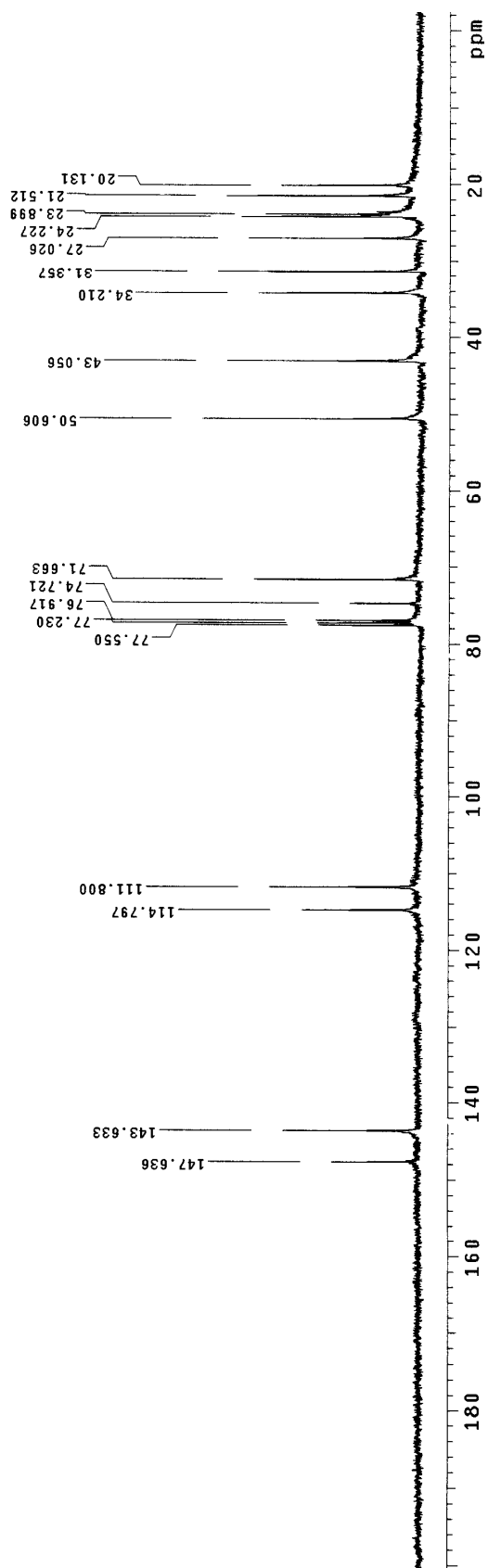
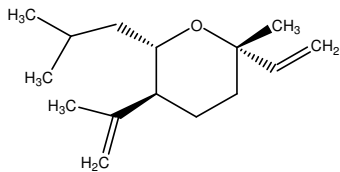
¹H NMR spectra of 4p & 5P



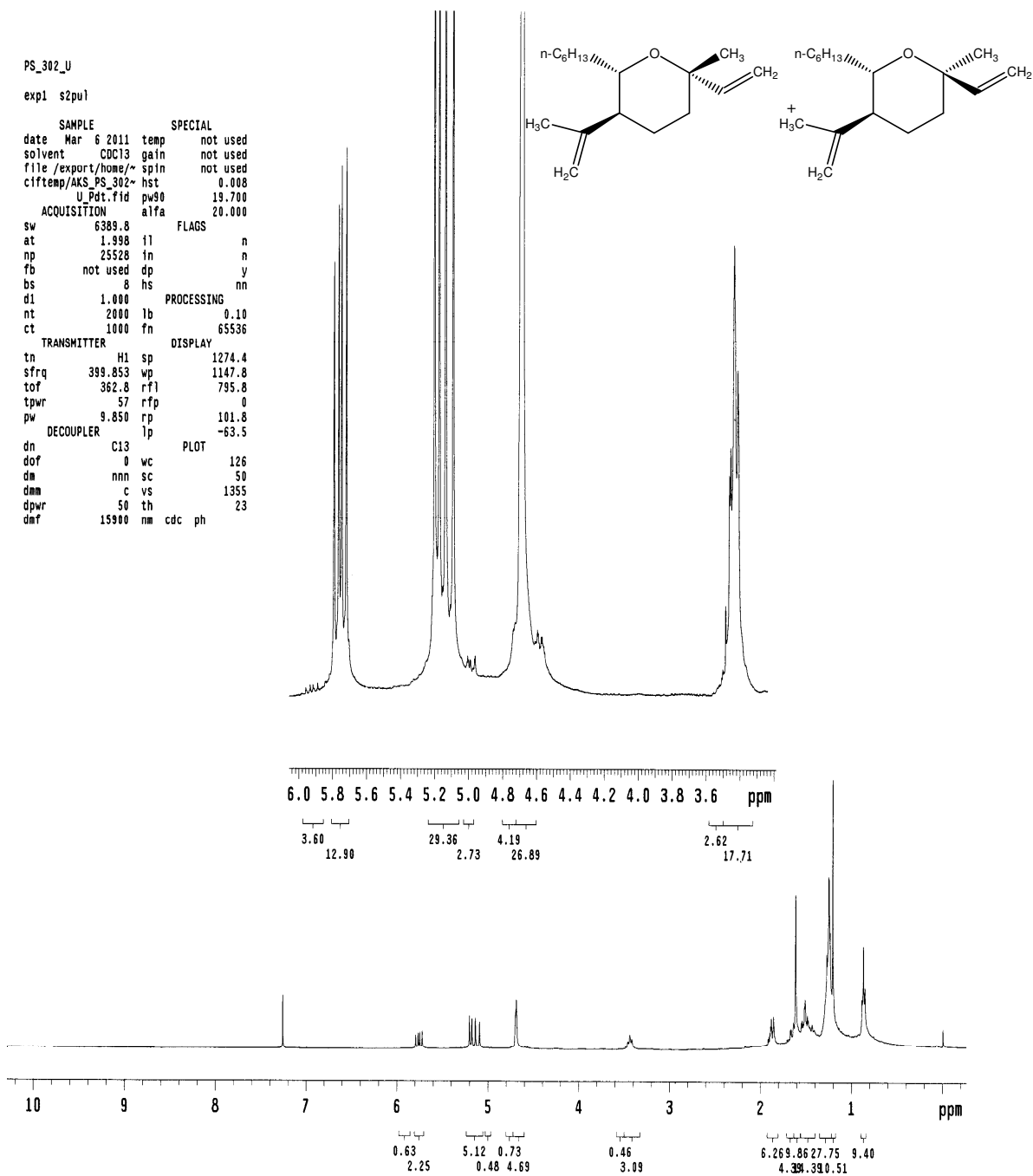
¹³C NMR spectra of 4p

```

PS_216M
exp1 s2pul1
date Dec 20 2009
solvent CDCl3
f1file CDC13
sw 23125.6
at 50275
pb 15670
rb 15610
d1 1.000
d2 10000
nt 16000
Ct 16000
tn 2.00
sfrq 100.554
tof 1536.3
tpwr 61
pw 9.300
dn DECOUPLER
dof H1
dm 0
dmm VVY
dppr W
dmf 42
8900
nm no ph
SPECIAL
temp not used
gain not used
spin not used
nst 0.008
pw90 18.000
alpha 20.000
FLAGS
n
y
m
PROCESSING
lb 2.00
fn 65536
DISPLAY
sp -250.2
wp 20568.7
rf1 9270.3
rfp 7764.9
rp -88.6
lp -271.4
PLOT
wc 250
sc 0
vs 35
th 10
    
```



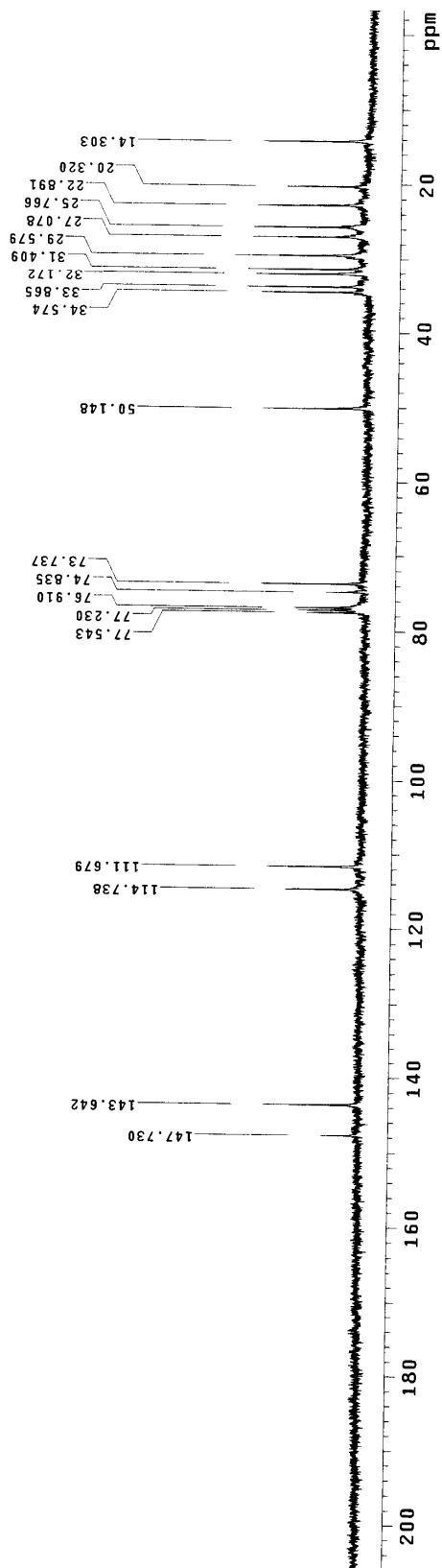
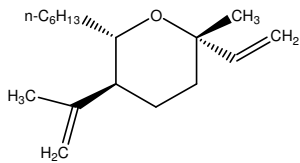
¹H NMR spectra of 4q & 5q



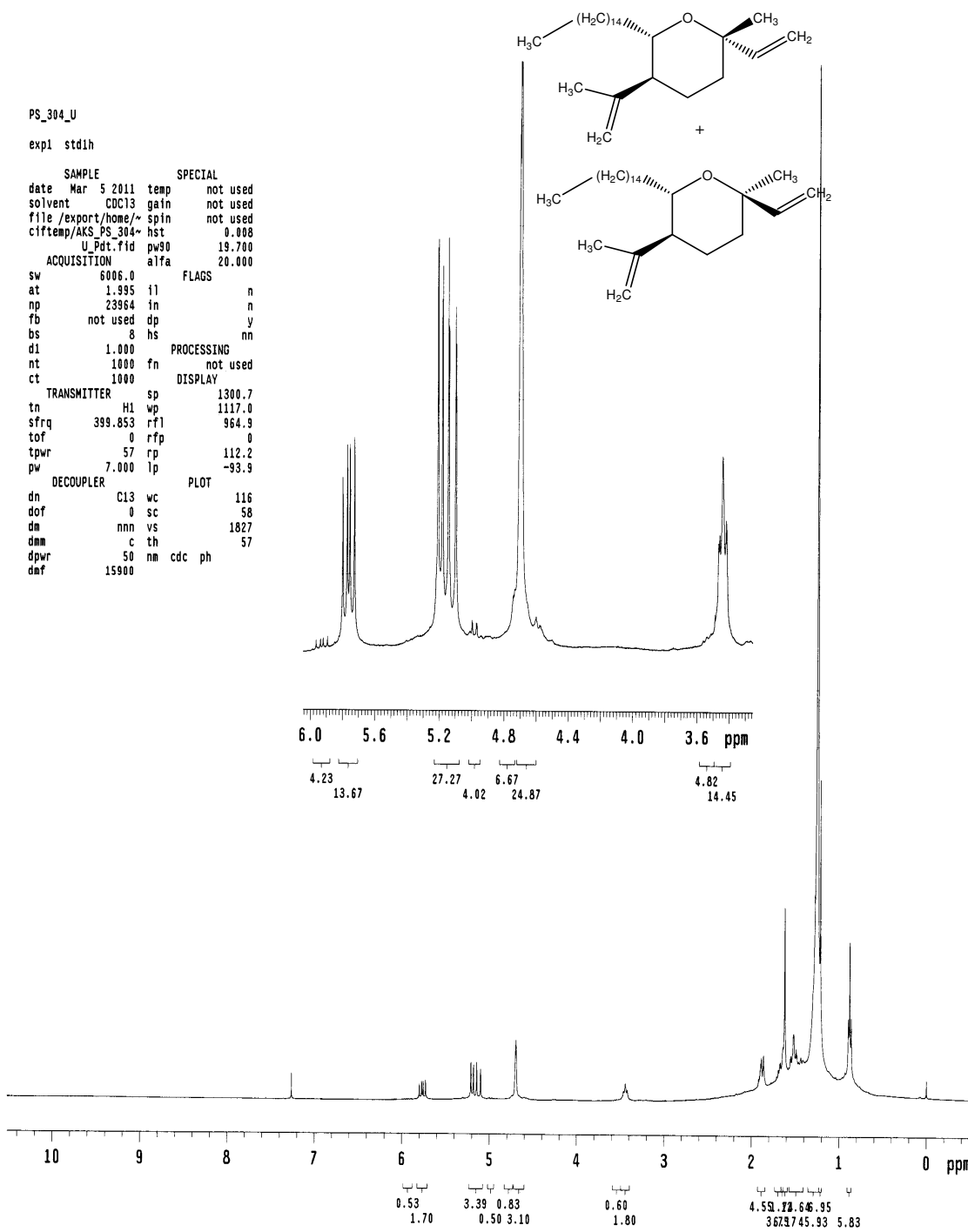
¹³C NMR spectra of 4q

```

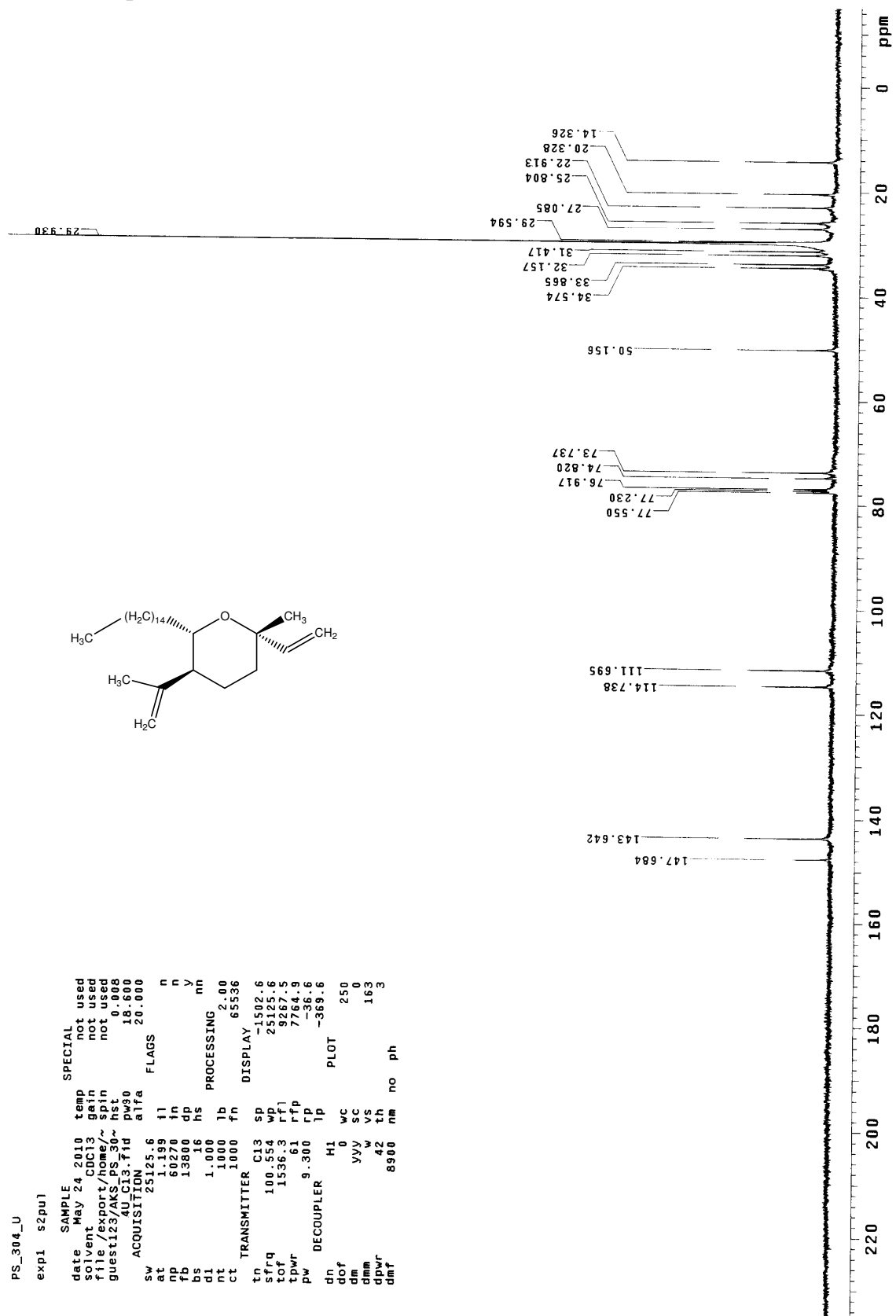
PS_302_U
exp1 s2pu1
SAMPLE
date May 31 2010
solvent CDCl3
file not used
sw ACQUISITION exp not used
at 25125.6 hz n
np 60270 t1 20.000
fb 19800 t1 n
bs 16 t1 n
d1 1.000 dp n
nt 4000 hs n
ct 1056
TRANSMITTER
tn C13
strq 100.554 fb 2.00
tof 1536.3 fn 65536
tpwr 61 sp -413.8
pw 9.300 rfl 21262.5
d1 DECOUPLER H1 rfp 9267.5
dof 0 rp -57.5
dmm yyy w PLOT -322.6
dmm w WC 250
dpr 42 SC 0
dmf 8900 t1 21
nm no ph 5
    
```



¹H NMR spectra of 4r & 5r

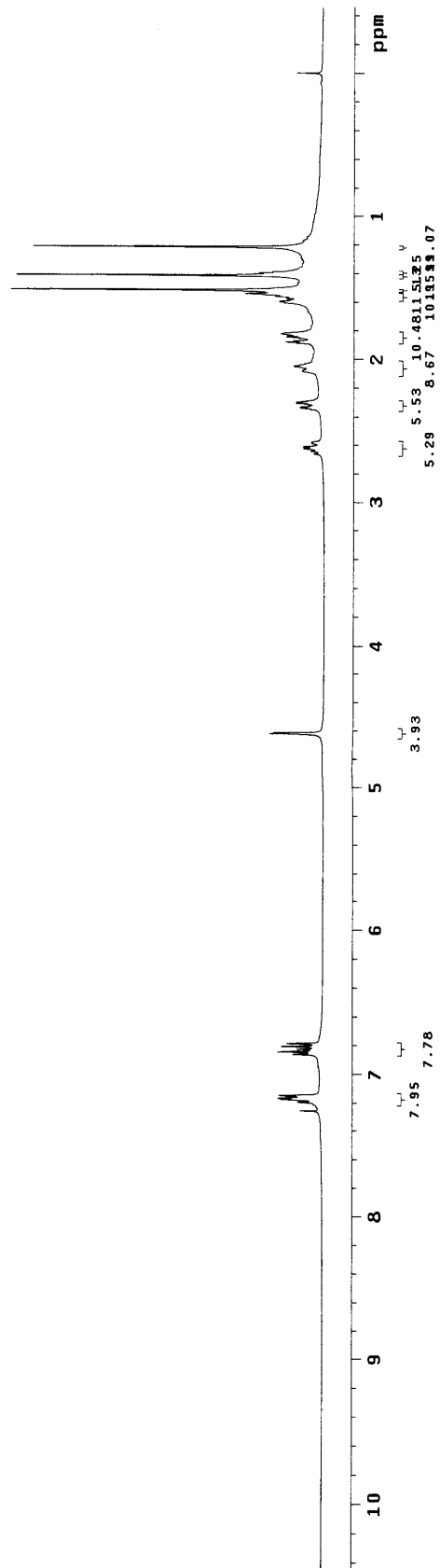
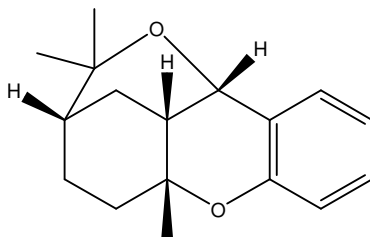


¹³C NMR spectra of 4r

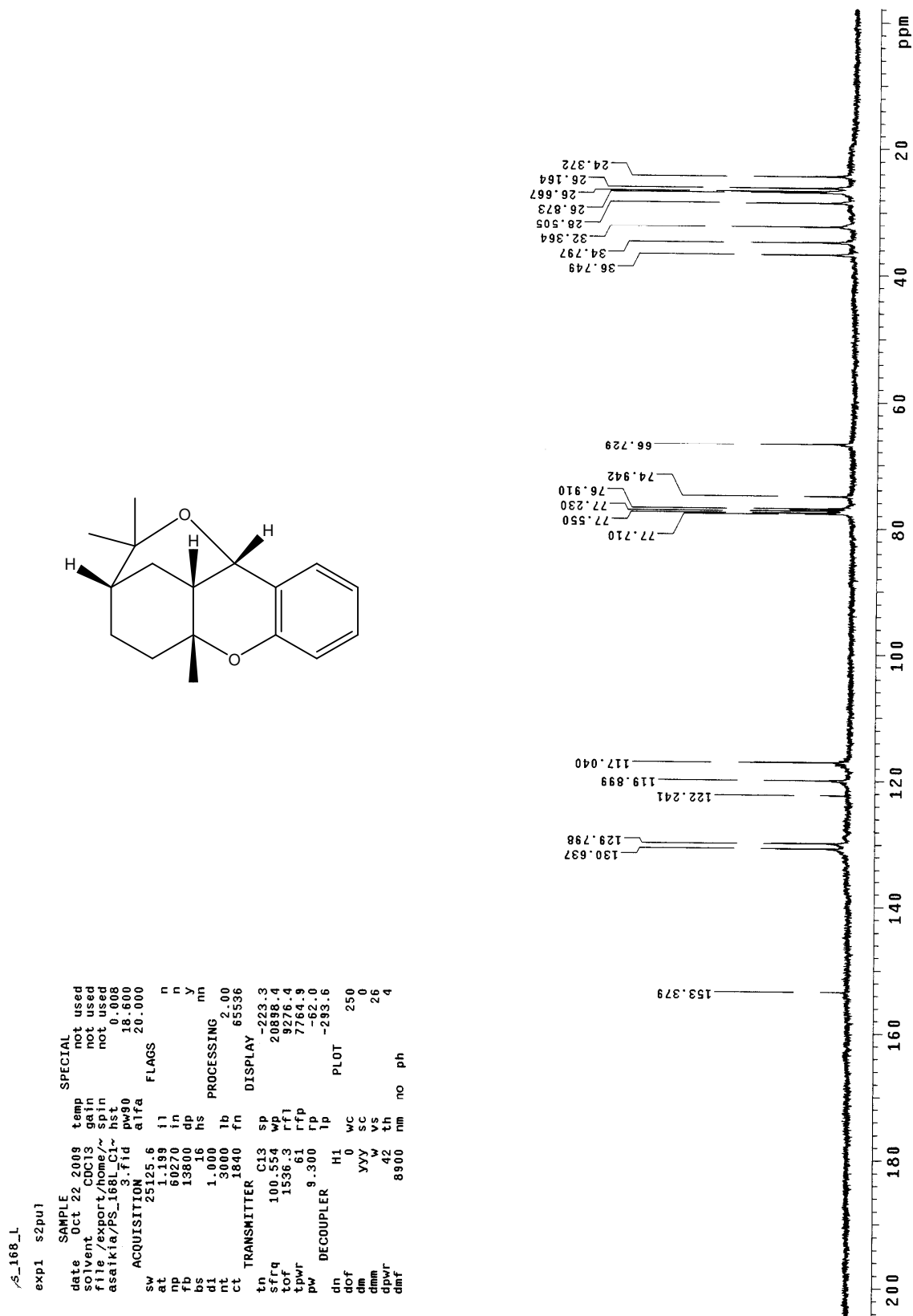


¹H NMR spectra of 15

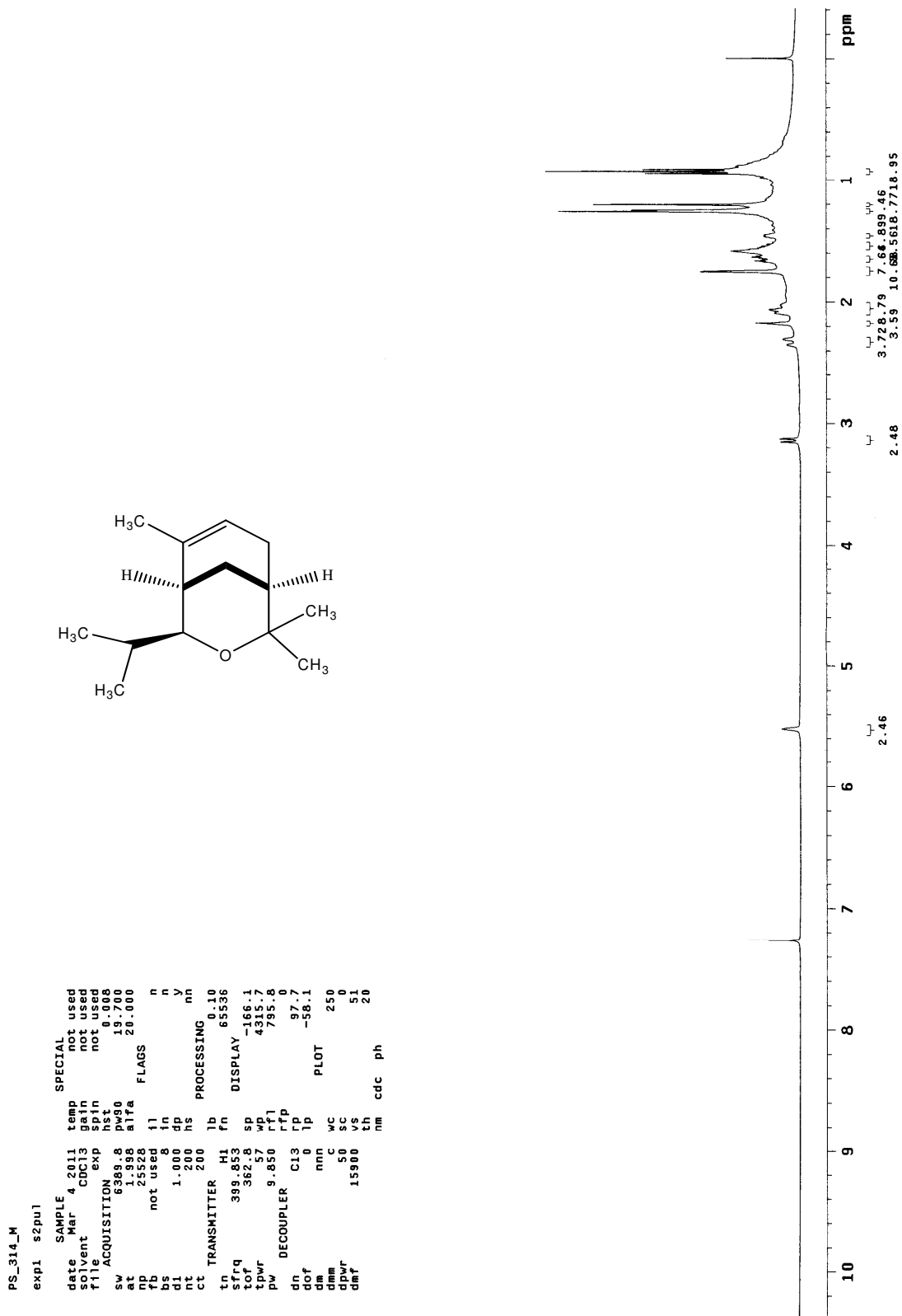
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PS_i68_L
exp1 s2pu1
date SAMPLE 4 2011
solvent var C6Cl3
file C6Cl3
ACQUISITION exp
sw 6389.8 hst 0.008
at 1.998 pw90 19.700
rs 2528 alfa 20.000
np not used fl n
pb not used h n
bs 1.000 dp v
d1 200 hs
ct TRANSMITTER 200
tn 0.10
sfrq 399.853 fn 65536
tof 362.9 sp -184.7
cpwr 9.850 wfl 4974.6
pw DECOUPLER C13 rfp 797.6
dn 103.2 rfp -68.8
dm 0 lp
dof nnn wc 250
dmm C
dpwr 50 sc 0
dmf 15900 vs 56
tn cdc ph 20
```



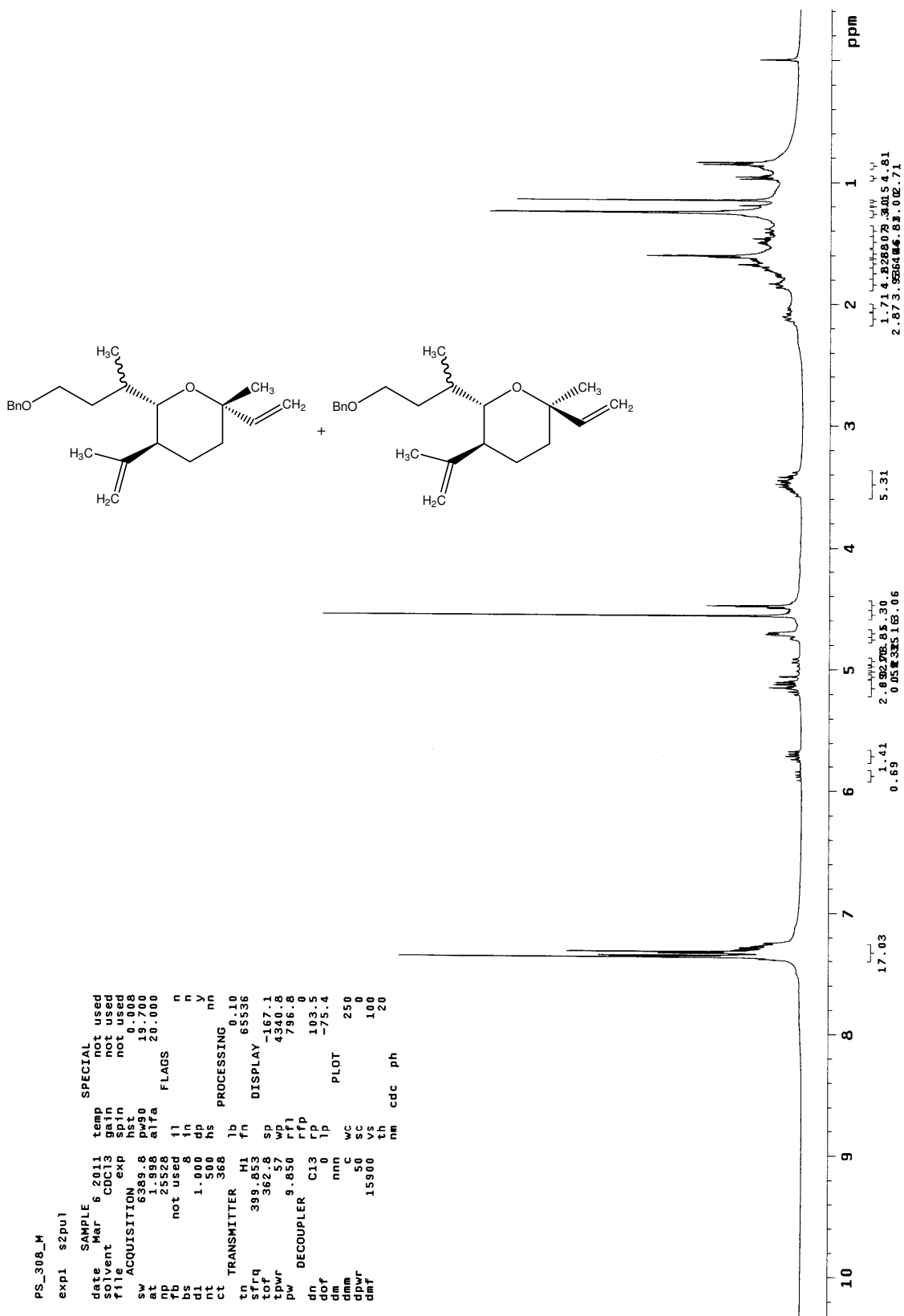
¹³C NMR spectra of 15



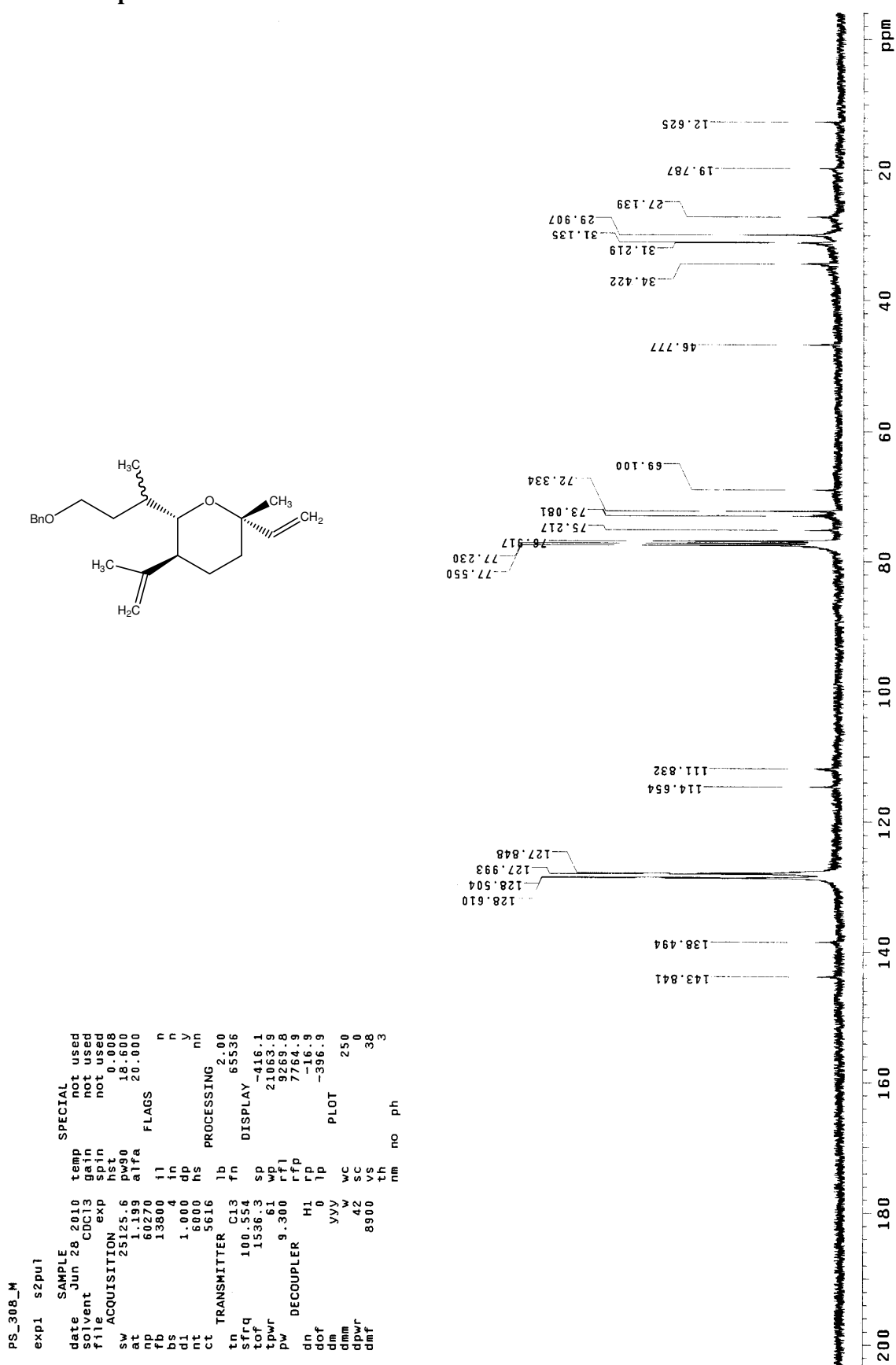
¹H NMR spectra of 17b



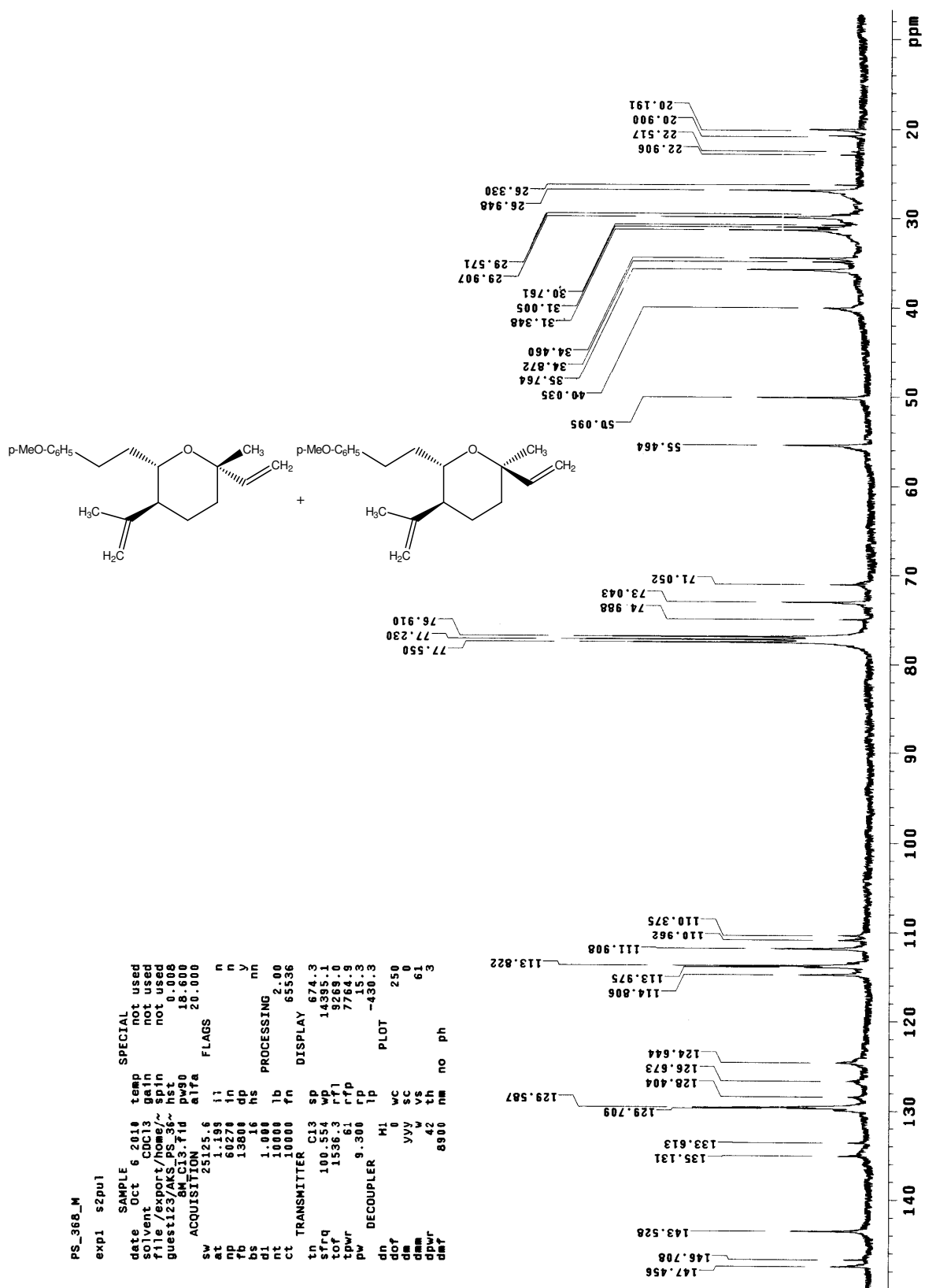
¹H NMR spectra of 18d & 19d



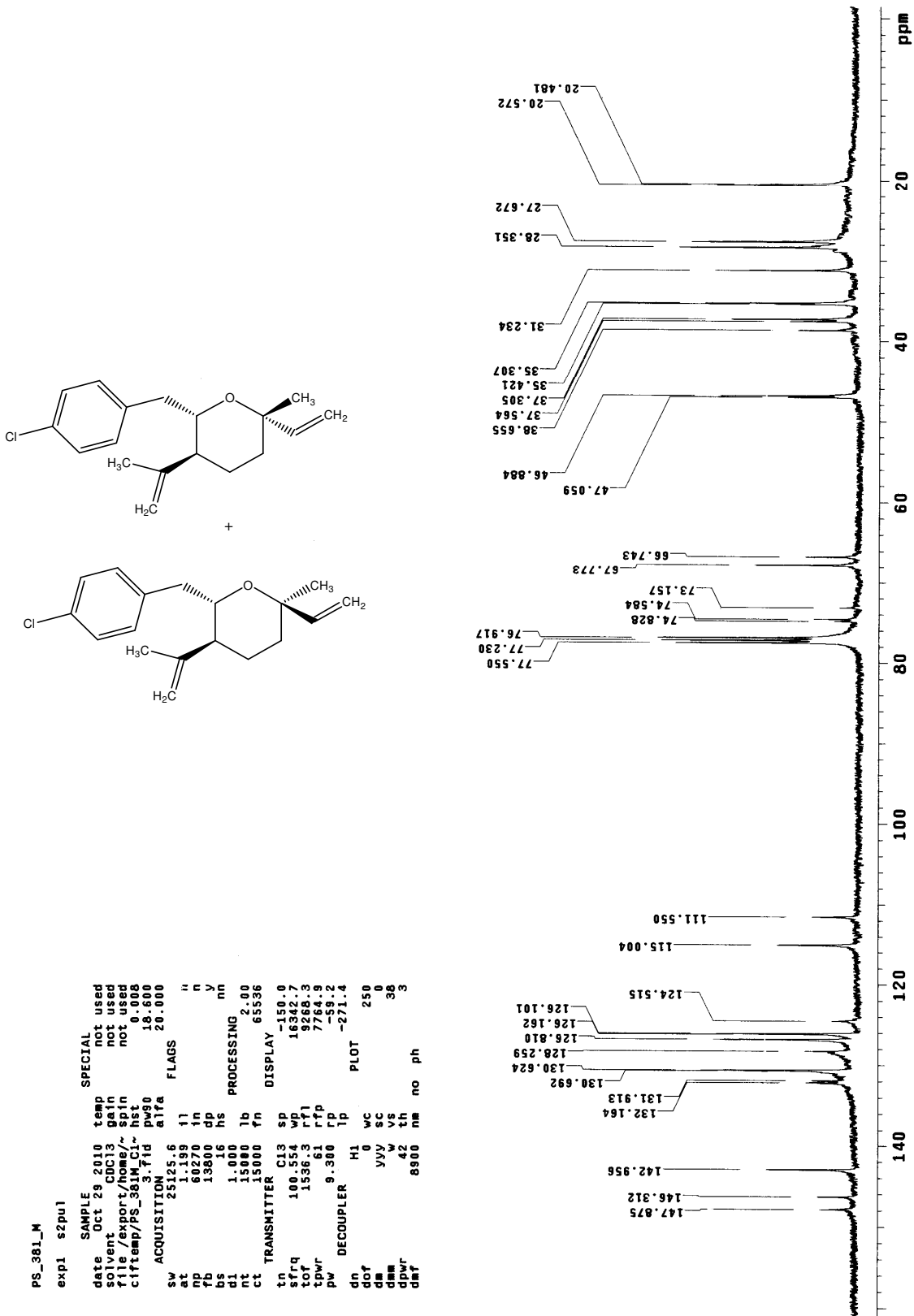
¹³C NMR spectra of 18d



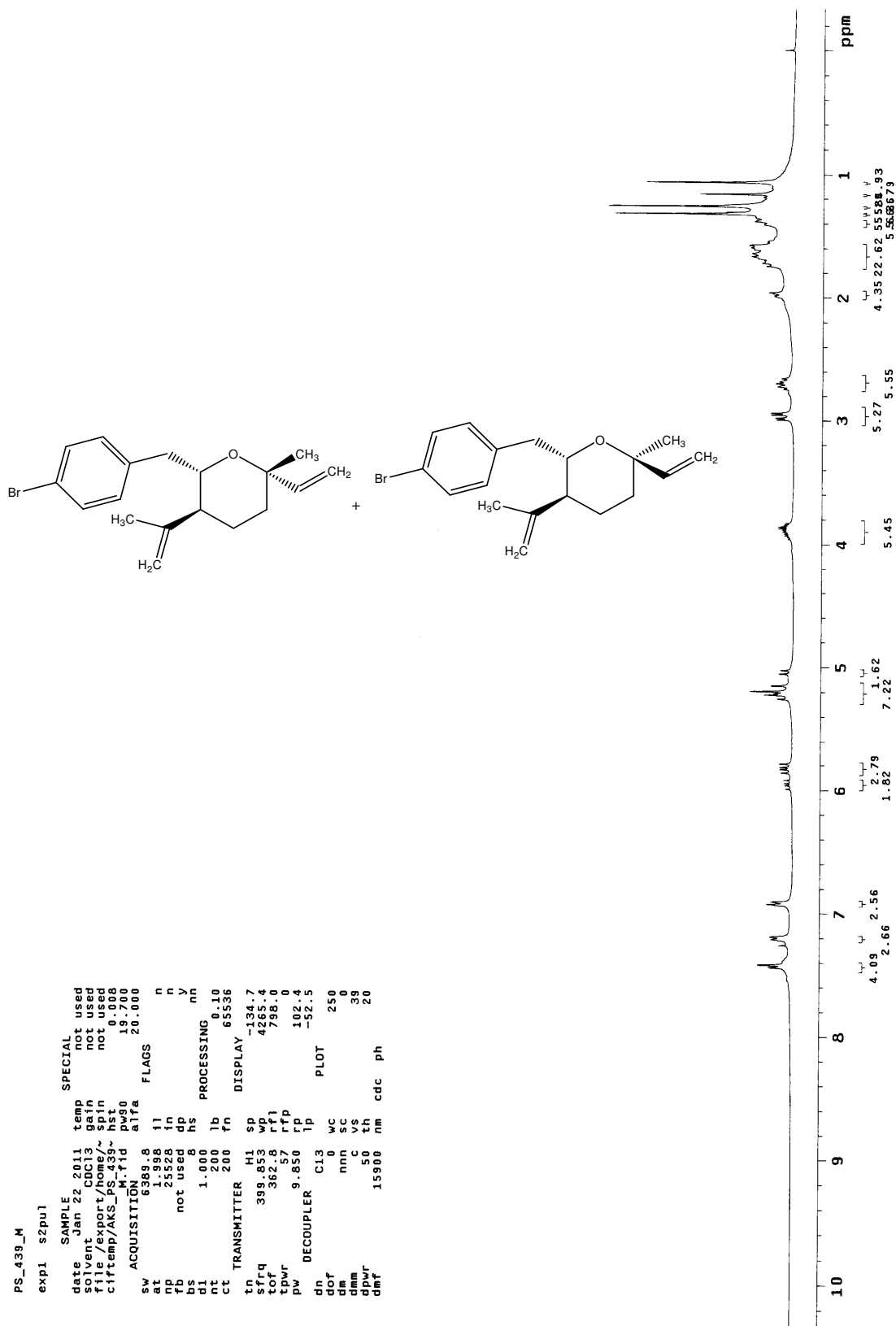
¹³C NMR spectra of 18e & 19e



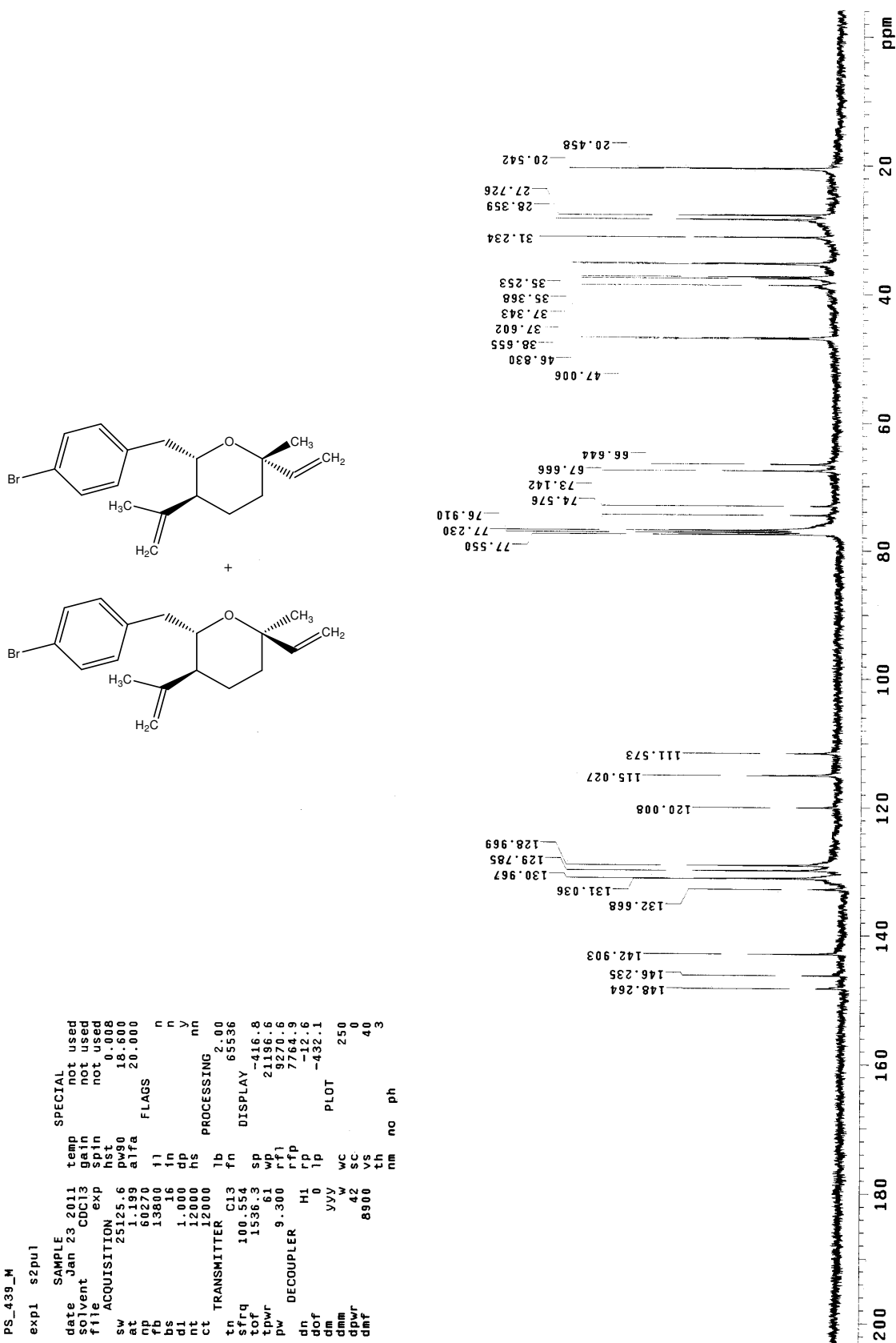
¹³C NMR spectra of 18f & 19f



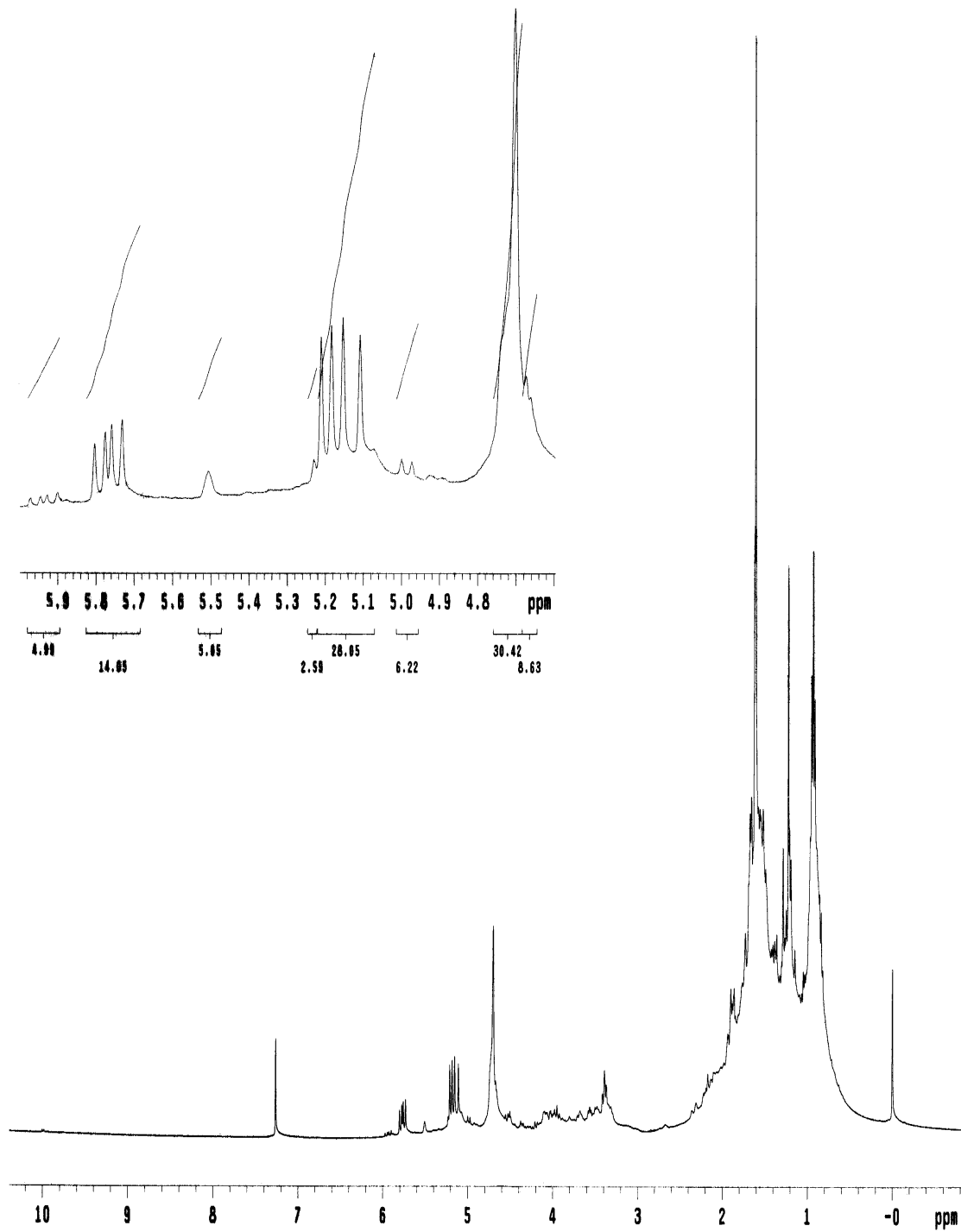
¹H NMR spectra of 18g & 19g



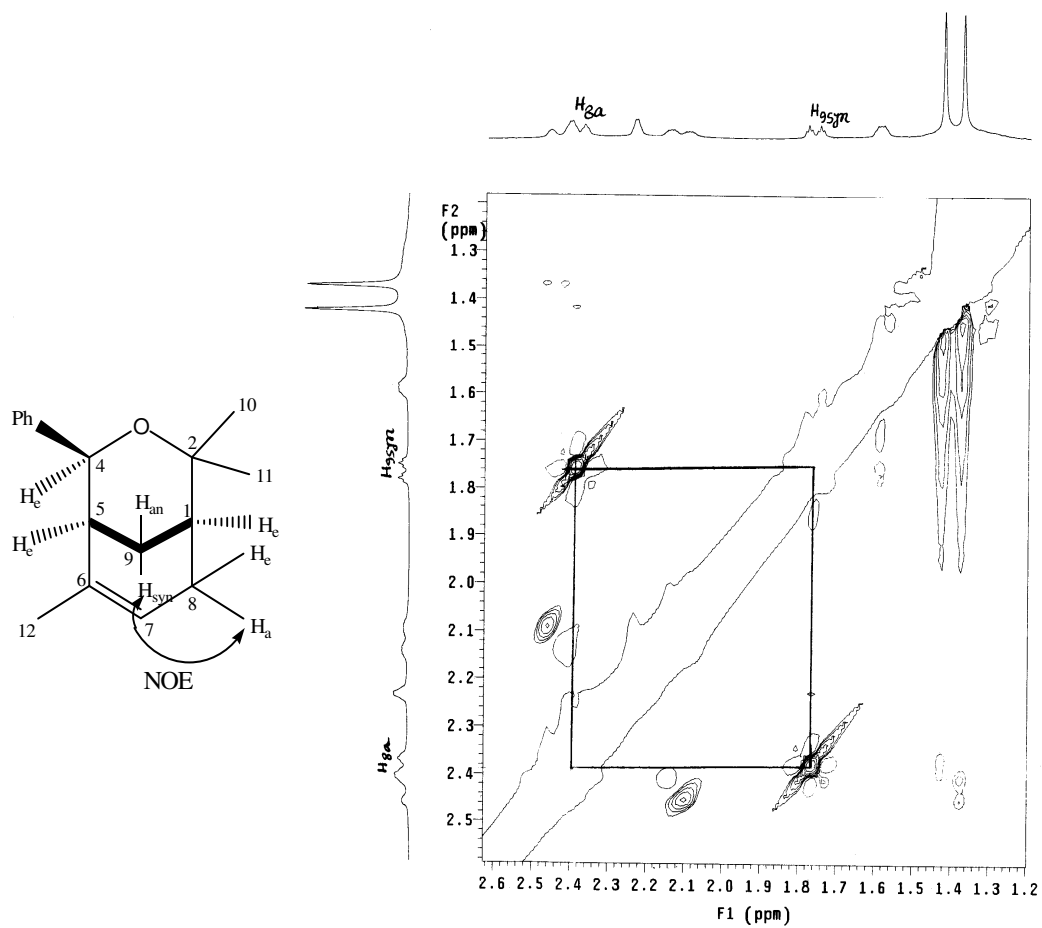
¹³C NMR spectra of 18g & 19g



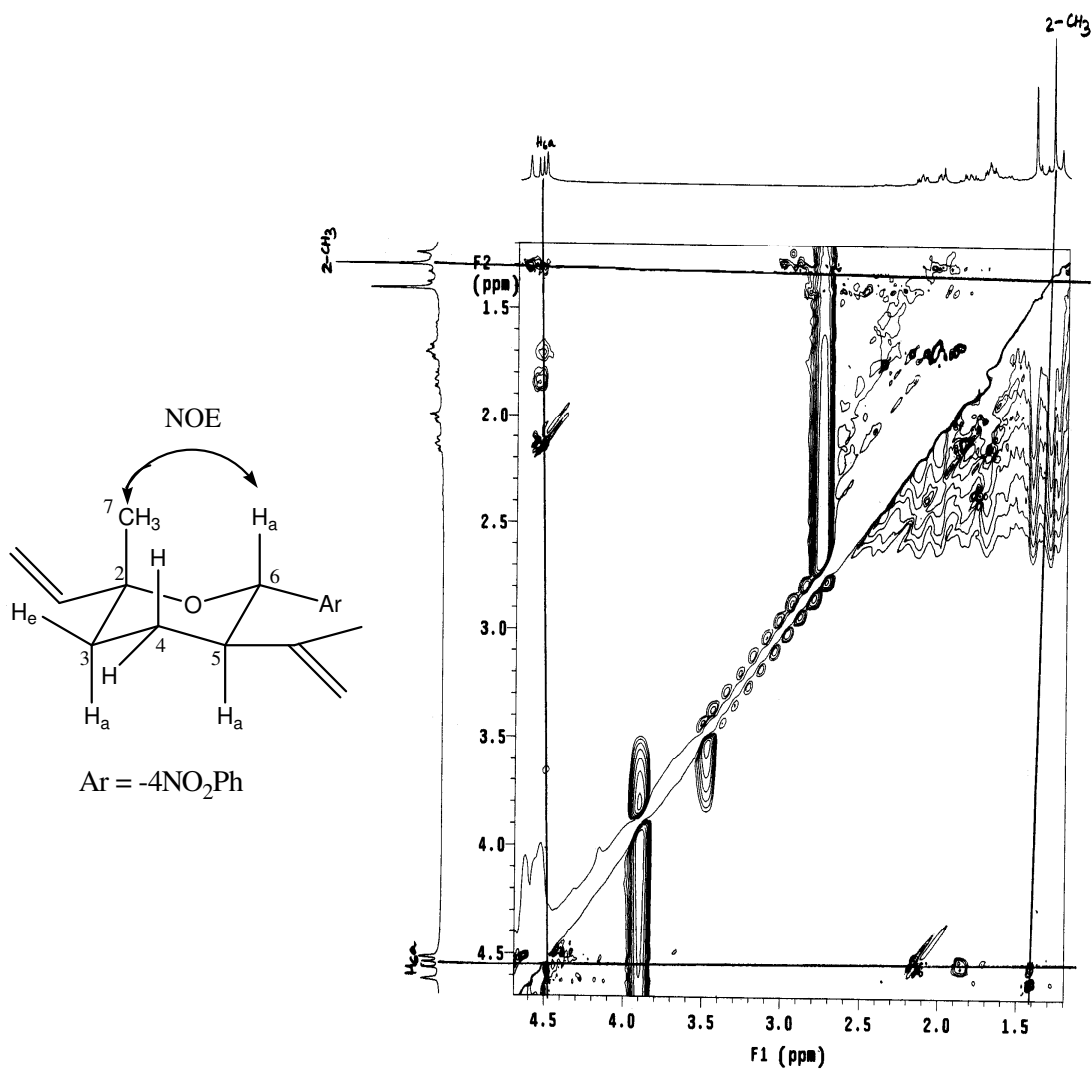
Crude ^1H NMR spectra showing 3n, 4n & 5n are in the ratio 1:3:1



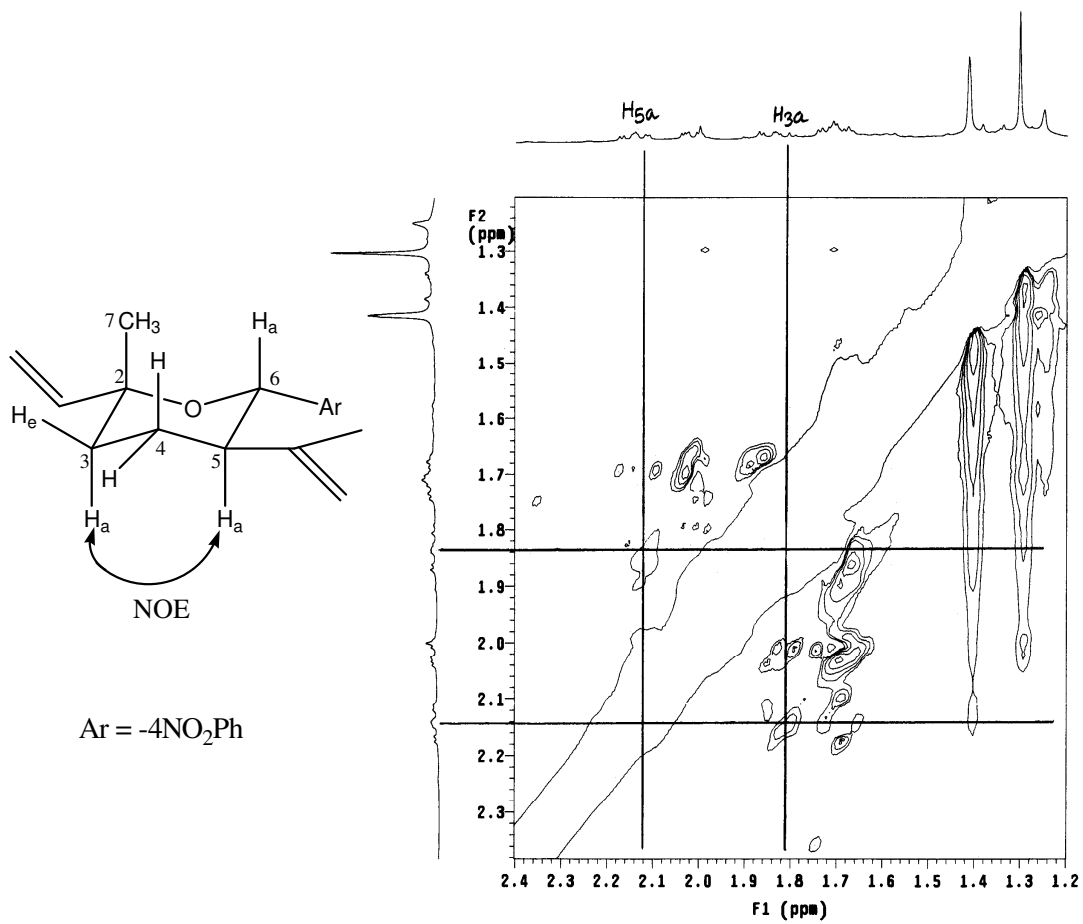
NOESY spectra of 3a



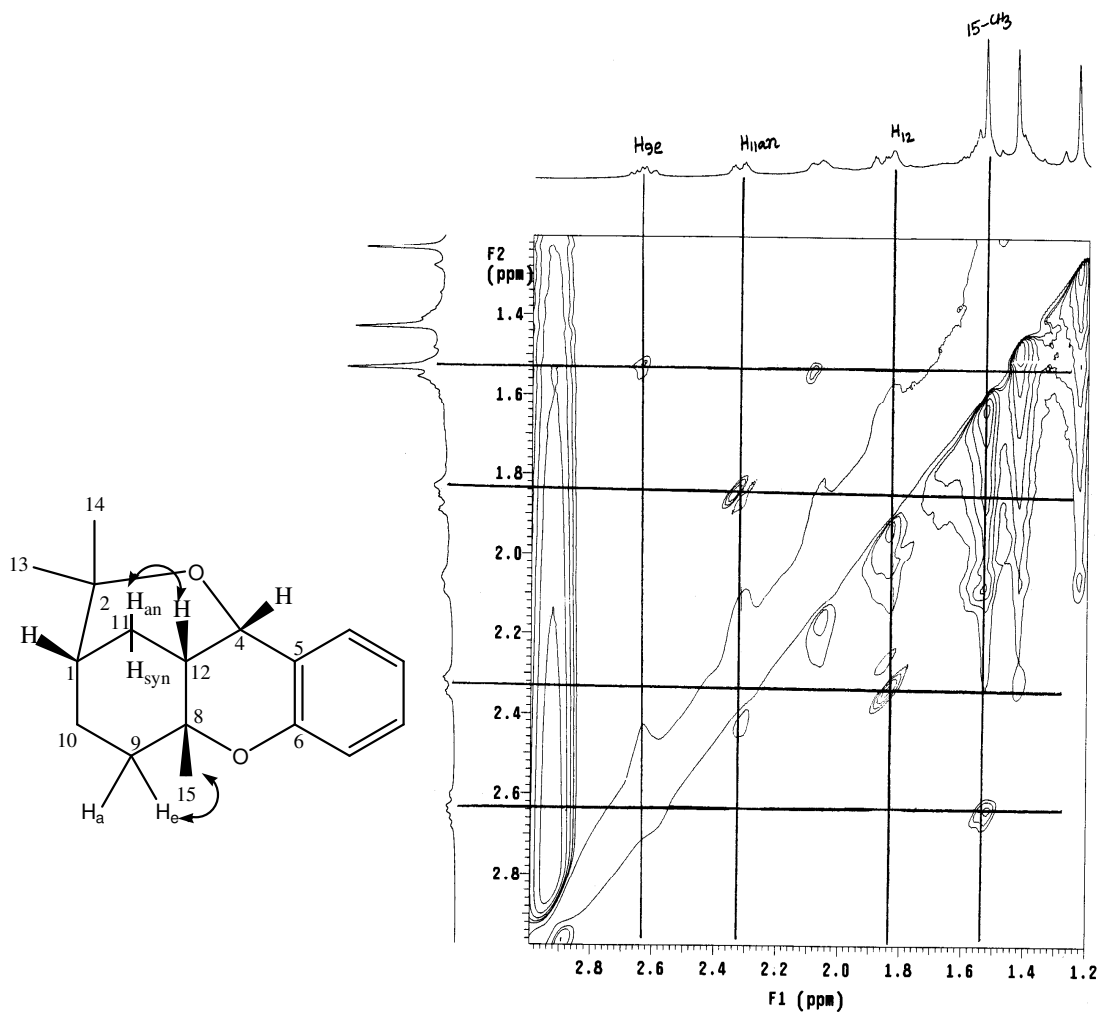
NOESY spectra of 4e



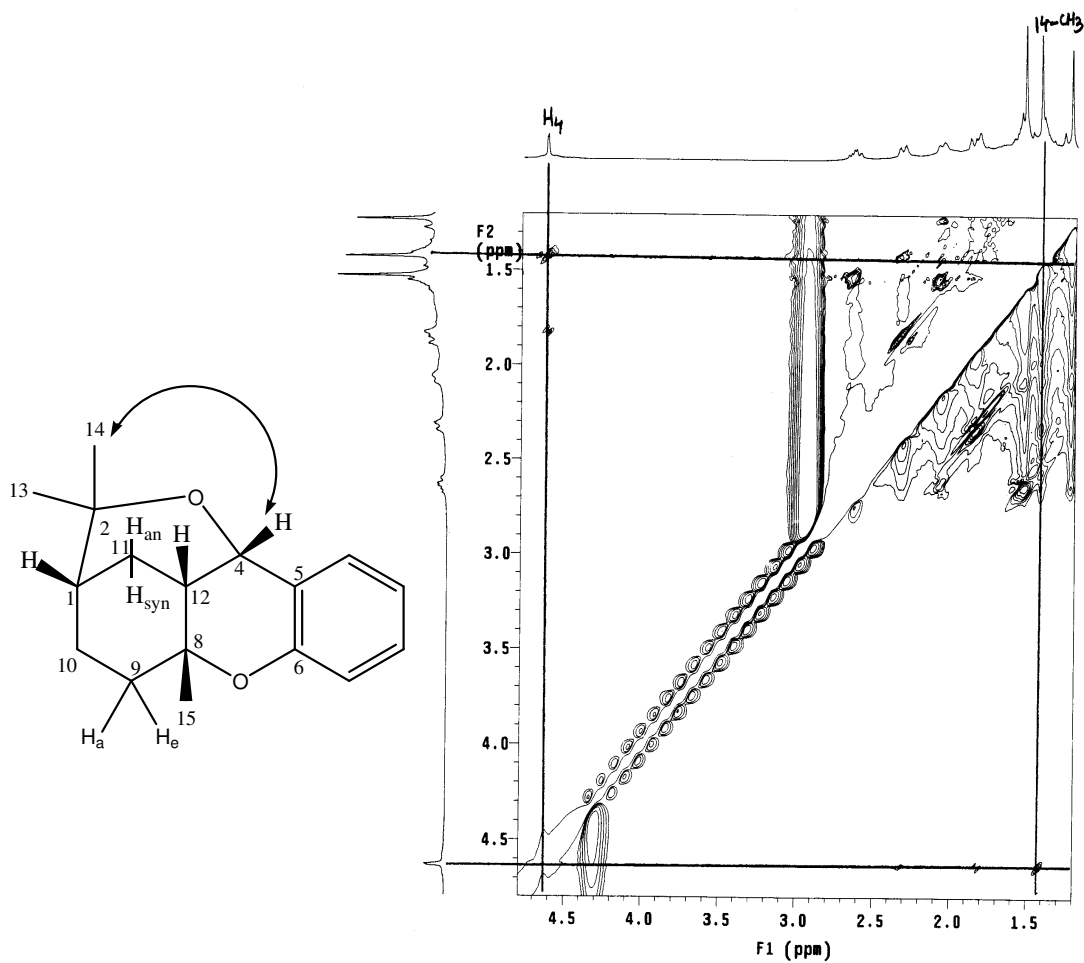
NOESY spectra of 4e



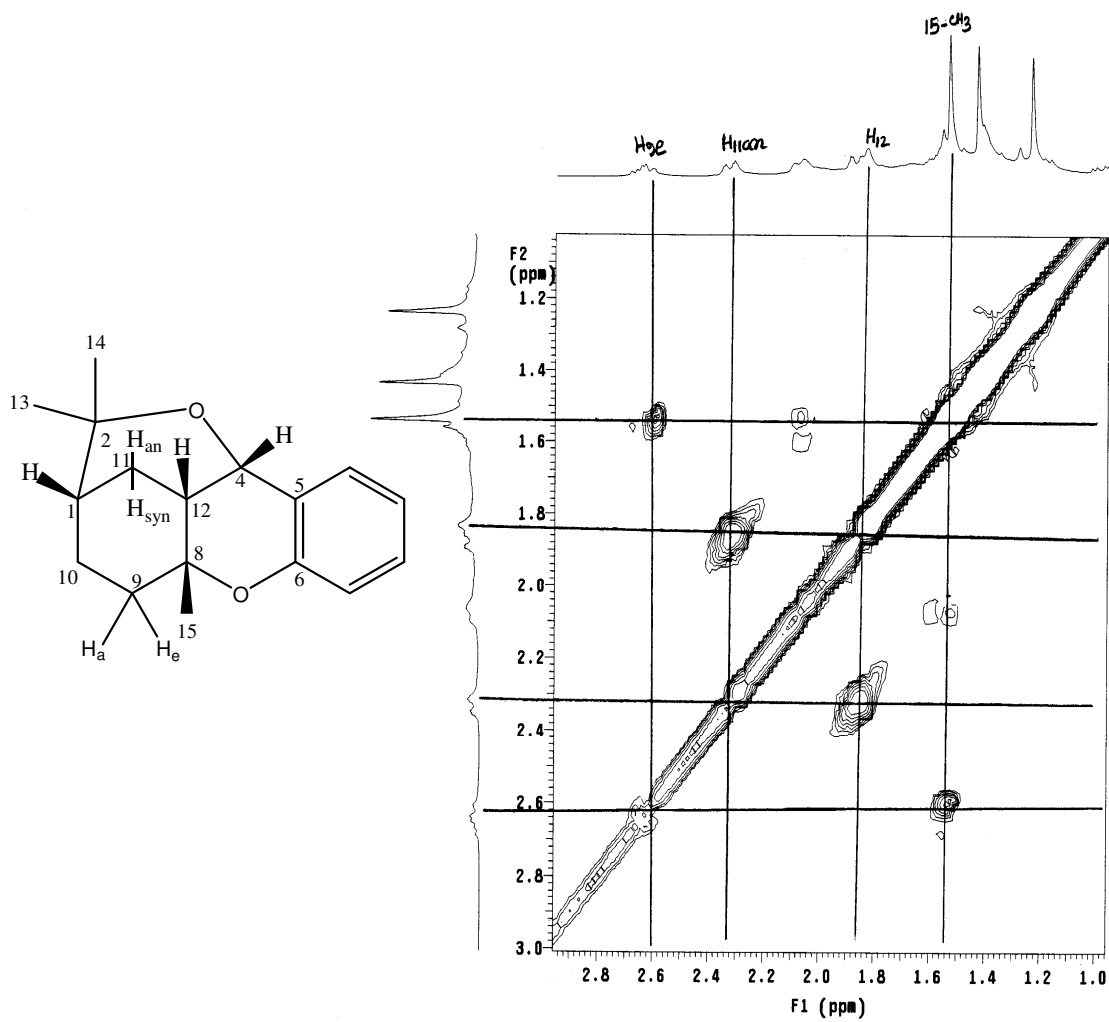
NOESY spectra of 15



NOESY spectra of 15



COSY spectra of 15



COSY spectra of 15

