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Journal of Organic Chemistry

Manuscript No. JO020136A

Synthesis, Stability, Spectroscopic and Electronic Properties of Three Benzocyclohepta[*a*]azulenylium Ions

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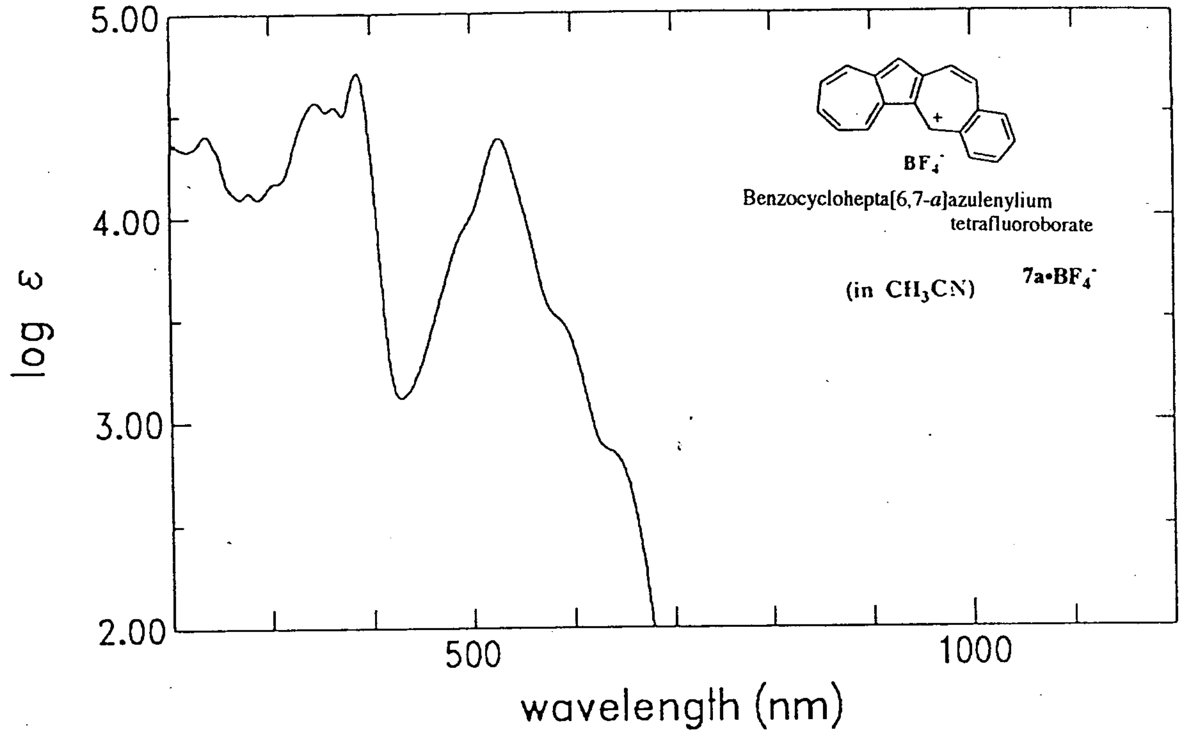
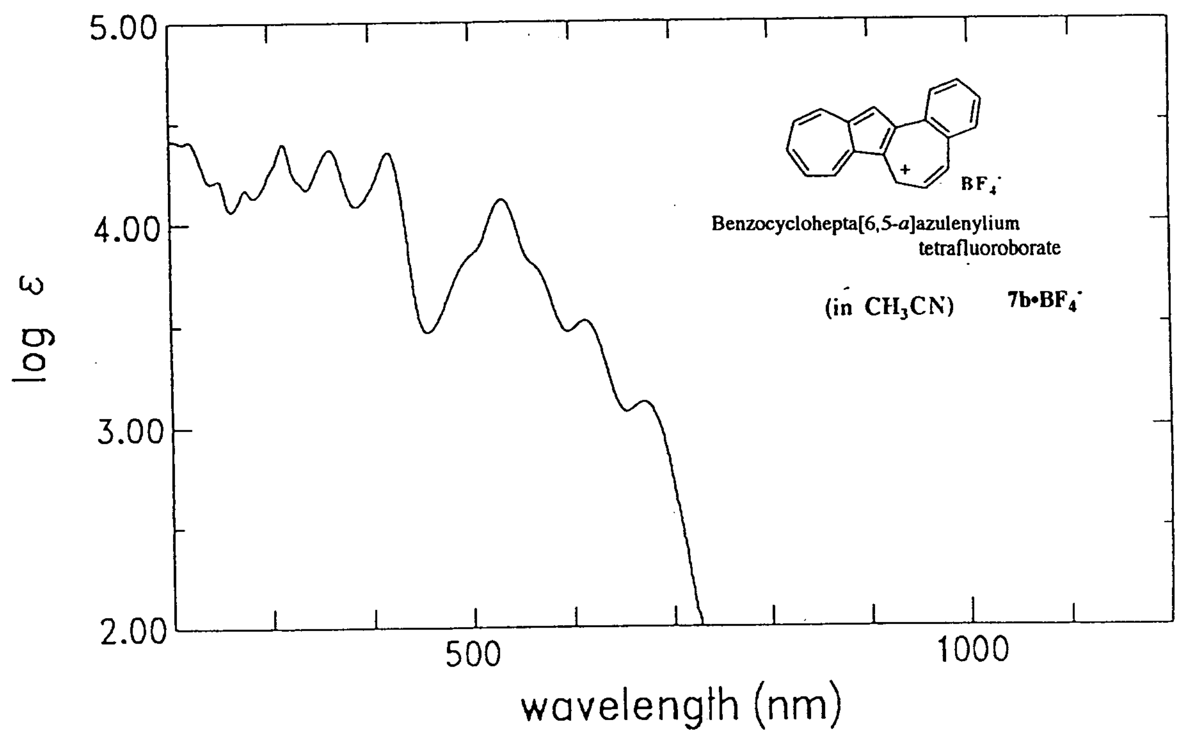
Supporting Information Available

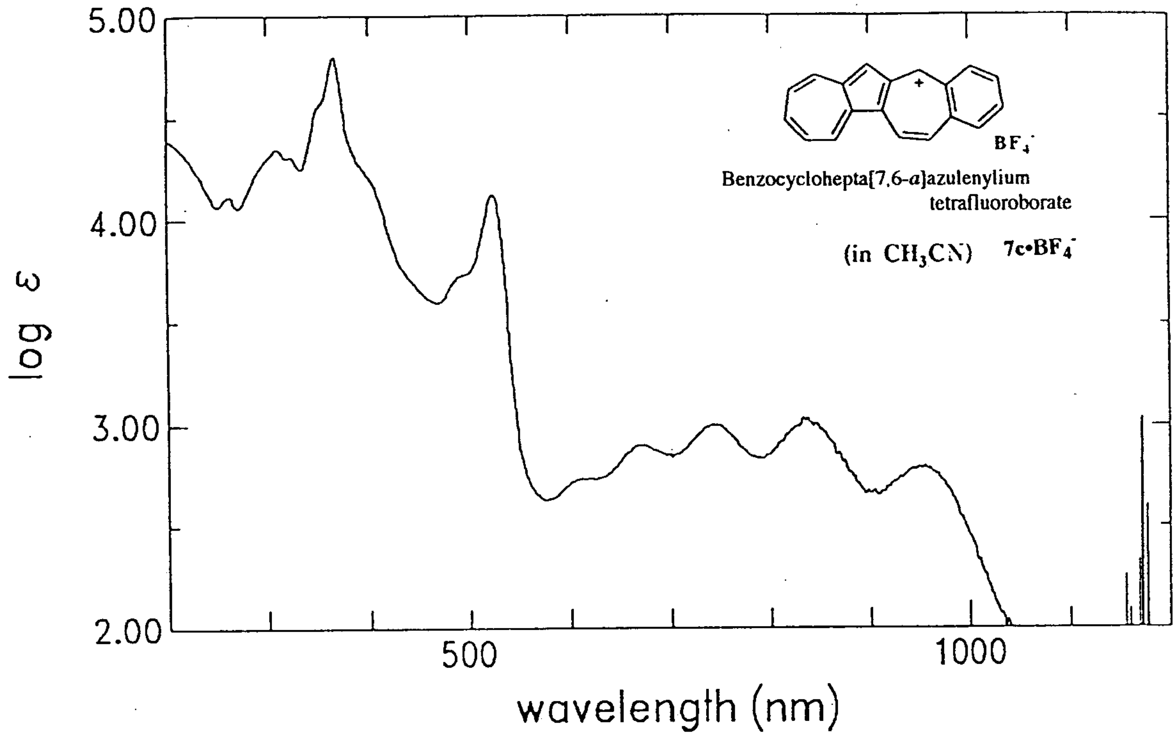
(^{1}H NMR, ^{13}C NMR, and electronic spectra for **7a-c•BF$_4^-$**, **4•BF$_4^-$**, **25•BF$_4^-$**, and **8a,b** and ^{1}H-^{1}H COSY spectra of **7a-c•BF$_4^-$** and **8a,b**.)

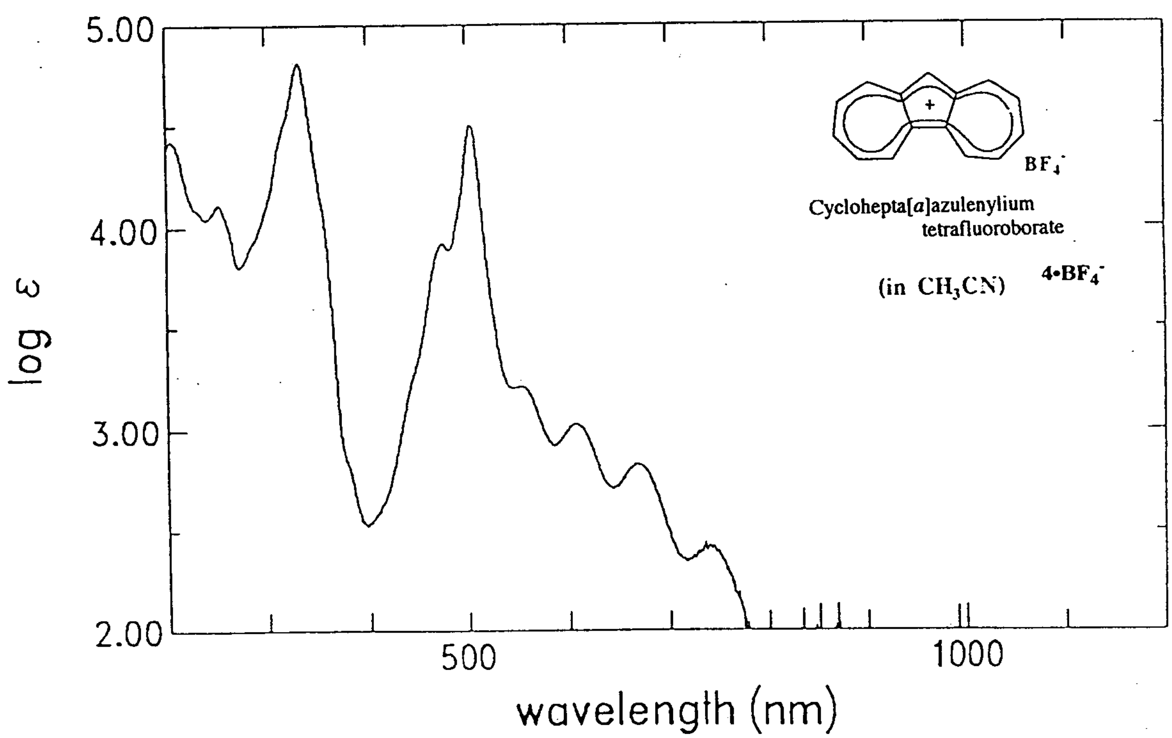


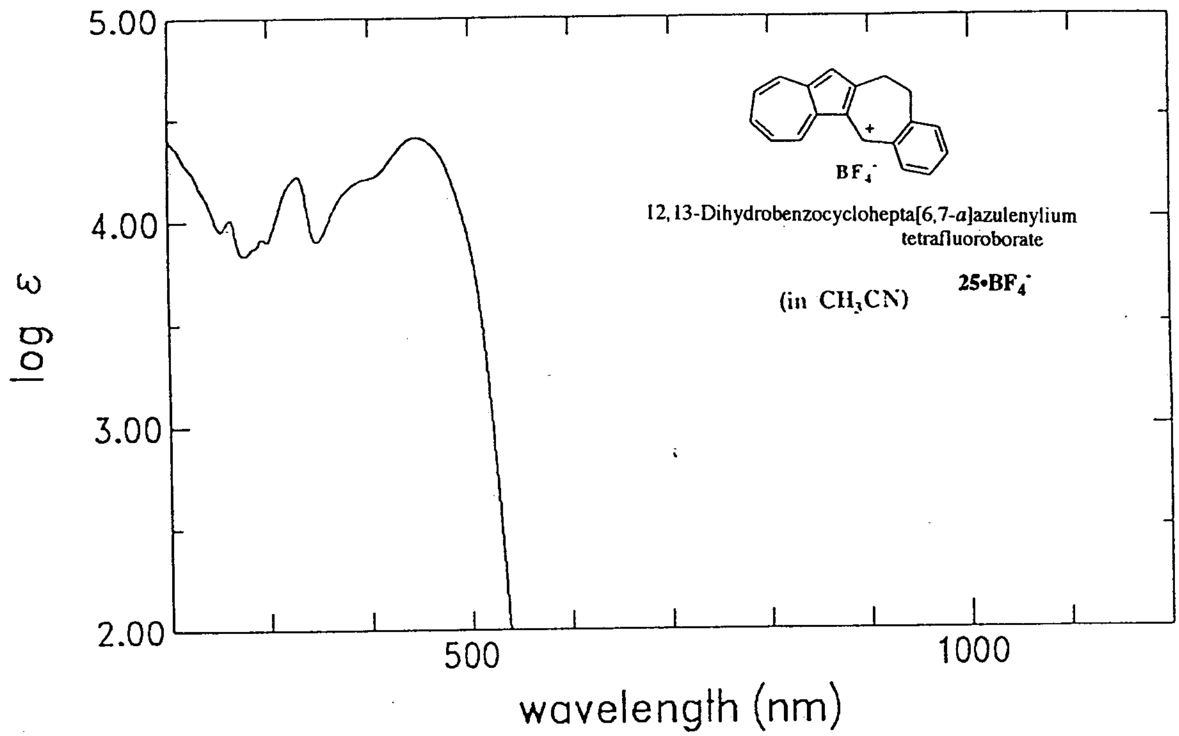
5.00
4.00
3.00
2.00
log ε
500
1000
wavelength (nm)
BF$_4^-$
Benzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate
(in CH_3CN)
7a•BF$_4^-$

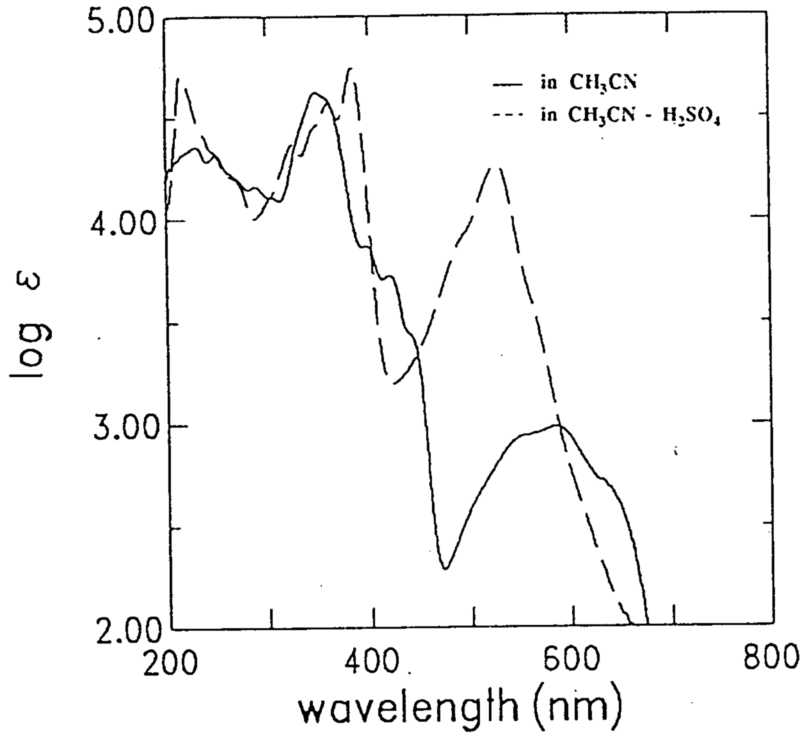


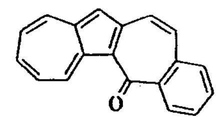
5.00
4.00
3.00
2.00
log ε
500
1000
wavelength (nm)
BF$_4^-$
Benzocyclohepta[6,5-*a*]azulenylium tetrafluoroborate
(in CH_3CN)
7b•BF$_4^-$


5.00
4.00
3.00
2.00
log ε
500
1000
wavelength (nm)
BF_4^-
Benzocyclohepta[7,6-*a*]azulenylium tetrafluoroborate
(in CH_3CN)
7c•BF_4^-


5.00
4.00
3.00
2.00
log ε
500
1000
wavelength (nm)
BF_4^-
Cyclohepta[*a*]azulenylium tetrafluoroborate
(in CH_3CN)
4•BF_4^-

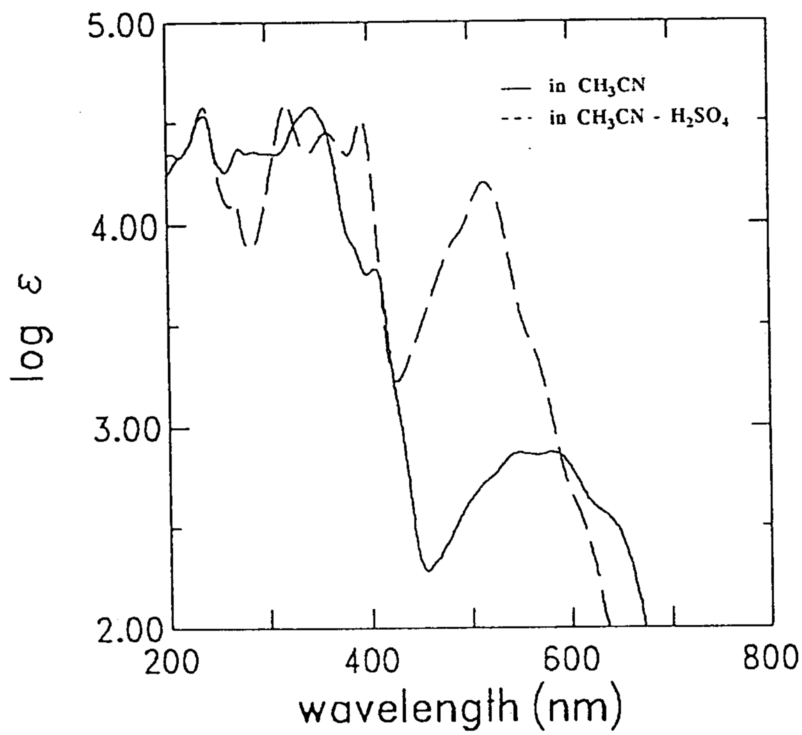

5.00
4.00
3.00
2.00
log ε
500
1000
wavelength (nm)
BF4-
12,13-Dihydrobenzocyclohepta[6,7-a]azulenylium tetrafluoroborate
25•BF4-
(in CH3CN)

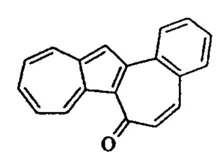




5*H*-Benzocyclohepta[6,7-*a*]azulen-5-one

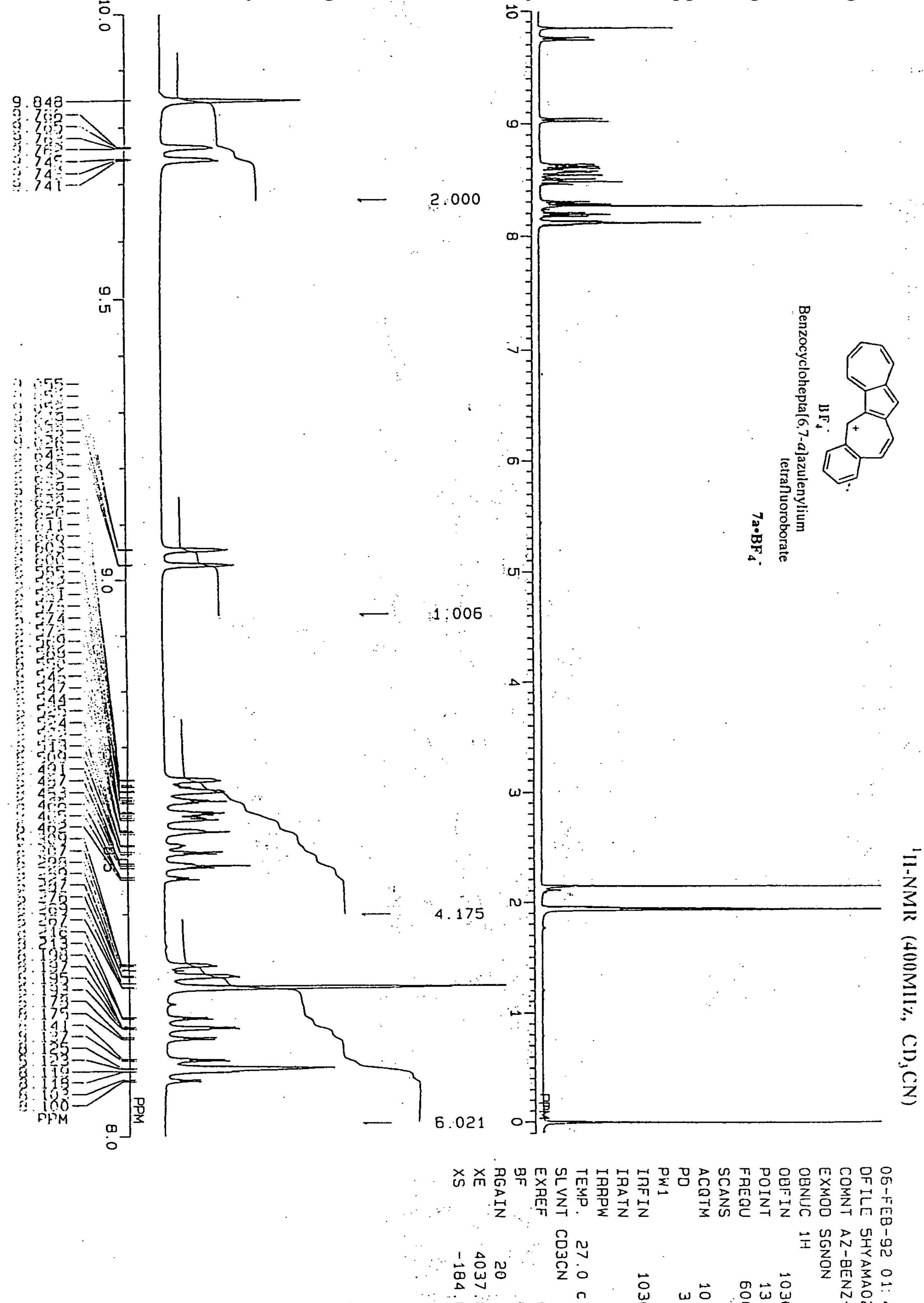
8a

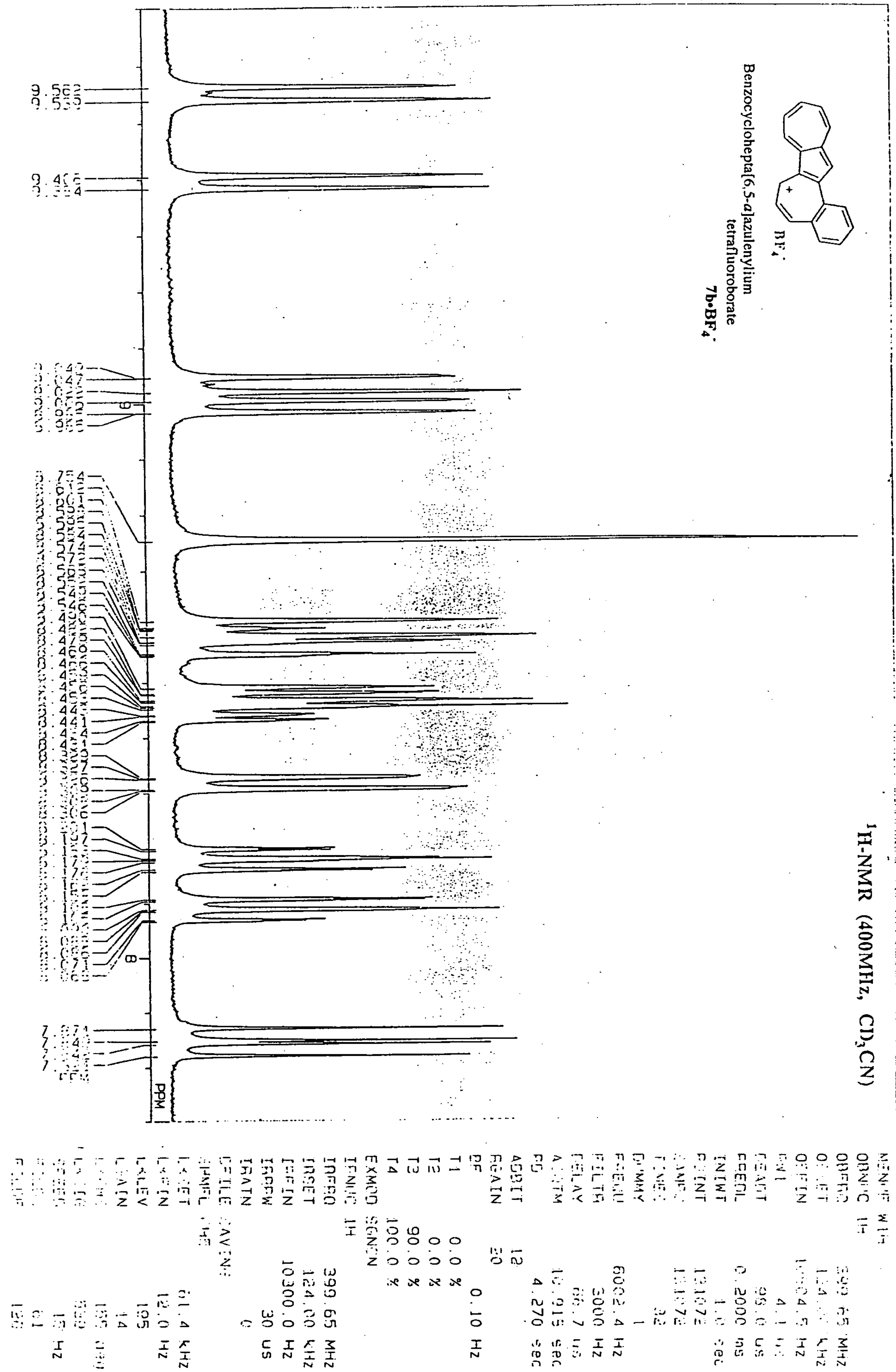


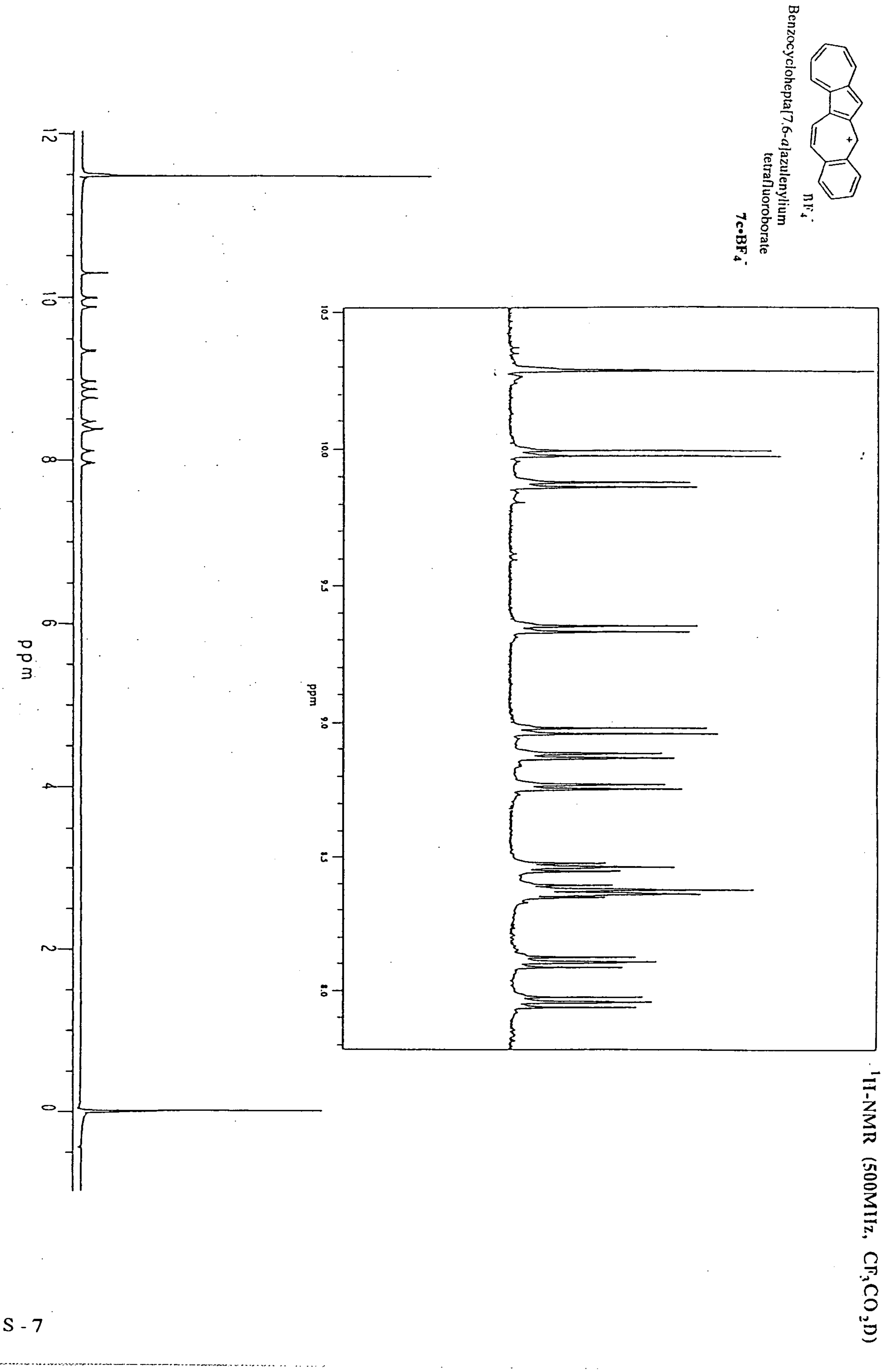


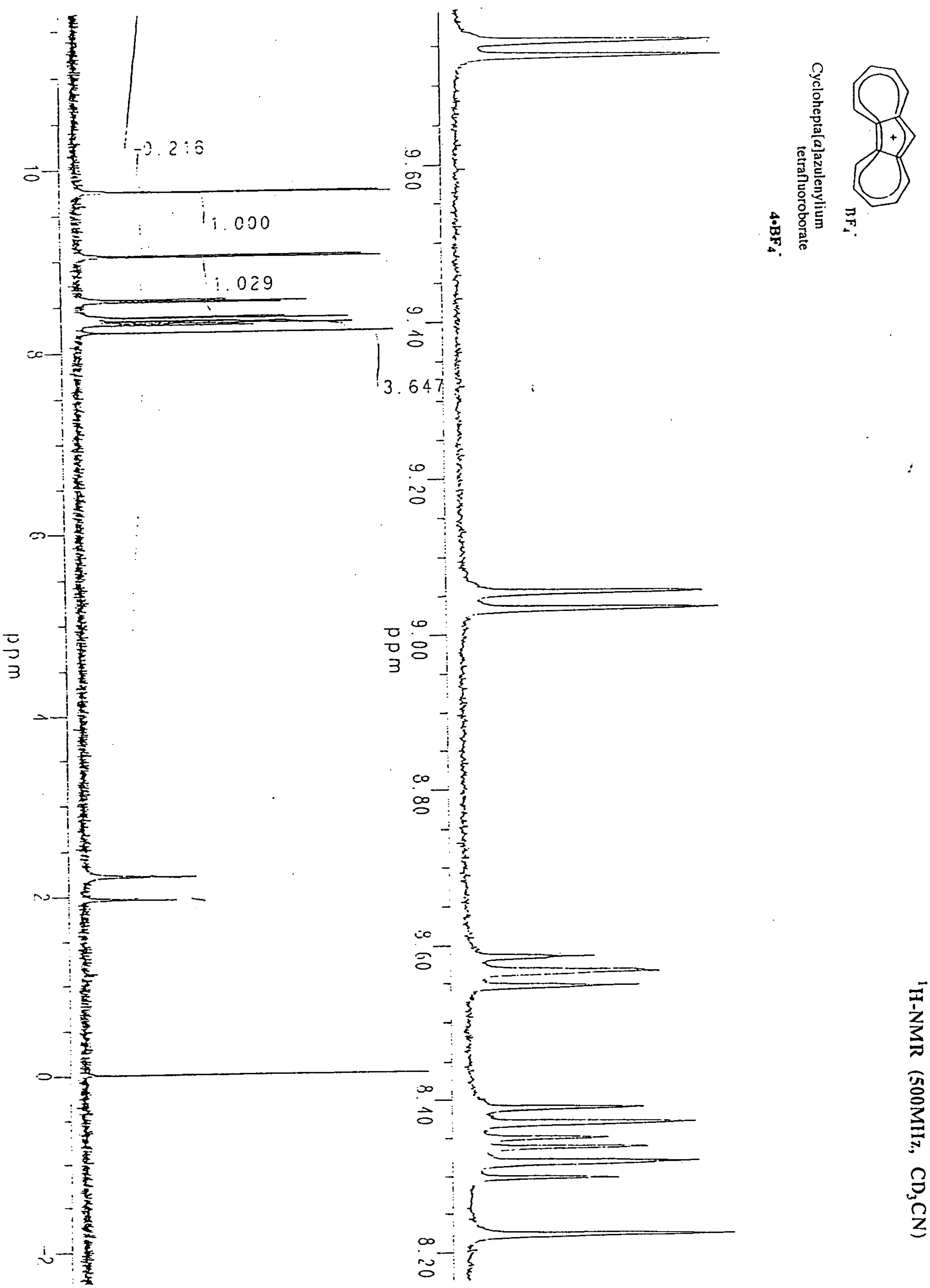
7*H*-Benzocyclohepta[6,5-*a*]azulen-7-one

8b


¹H-NMR (400MHz, CD3CN)
BF4-
Benzocyclohepta[6,7-a]azulenylium
tetrafluoroborate
7a•BF4-
2.000
1.006
4.175
6.021
06-FEB-92 01:45:01
DFILE SHYAMA02
COMNT AZ-BENZ-TR+
EXMOD SGNON
OBNUC 1H
OBFIN 10300.0 Hz
POINT 131072
FREQU 6002.4 Hz
SCANS 64
ACQTM 10.918 sec
PD 3.000 sec
PW1 6.3 us
IRFIN 10300.0 Hz
IRATN 0
IRRPW 30 us
TEMP. 27.0 c
SLVNT CD3CN
EXREF 0.00 pp.
BF 0.10 Hz
RGAIN 20
XE 4037.8030 Hz
XS -184.6875 Hz


Benzocyclohepta[6,5-*a*]azulenylium
tetrafluoroborate
7b•BF4⁻
¹H-NMR (400MHz, CD3CN)
PPM
11-AUG-91 13:56:07


BF4-
Benzocyclohepta[7,6-a]azulenylium
tetrafluoroborate
7c•BF4-
ppm
ppm
1H-NMR (500MHz, CF3CO2D)

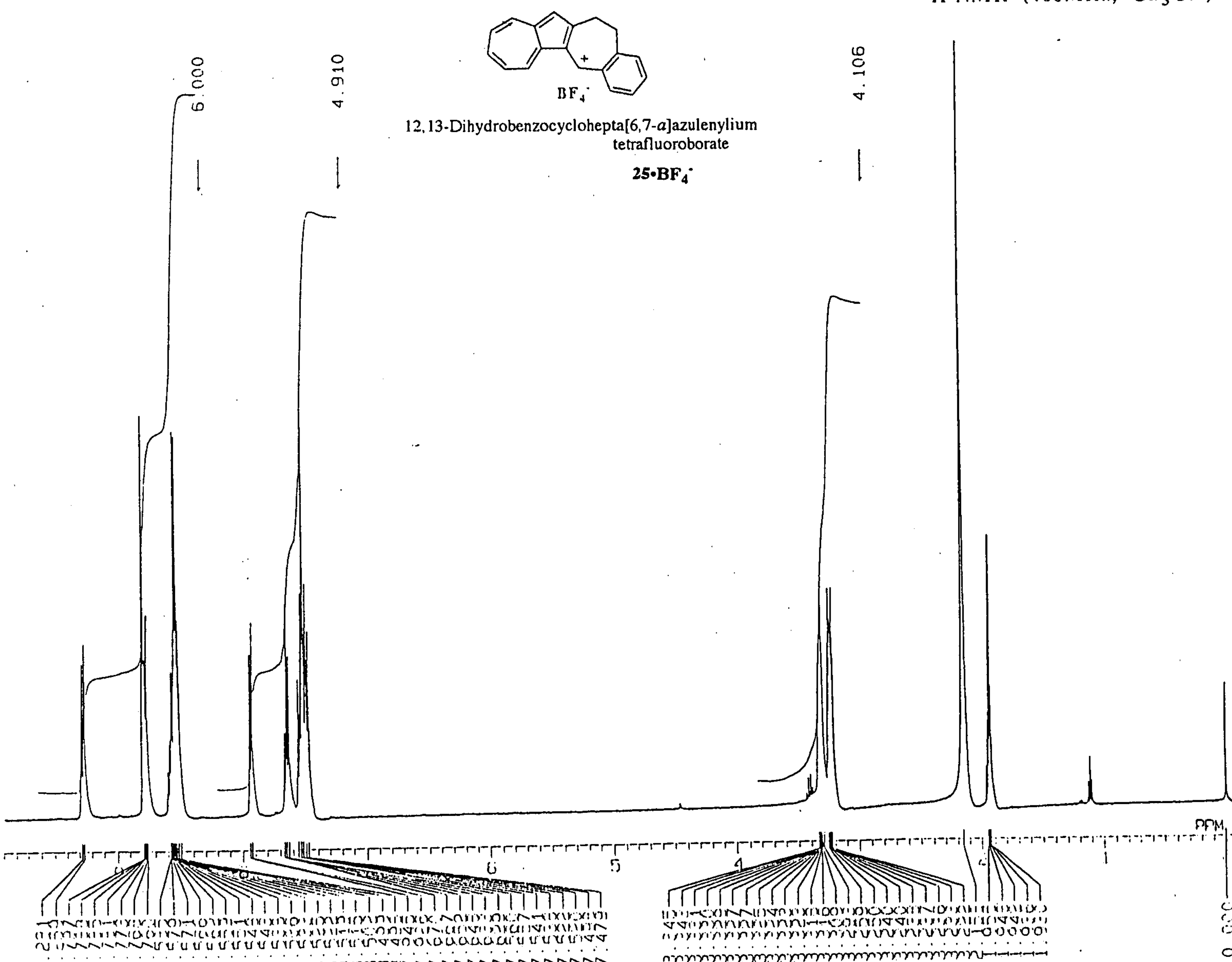


^{1}H-NMR (500MHz, CD_3CN)
BF_4^-
Cyclohepta[a]azulenylium
tetrafluoroborate
$4 \bullet BF_4^-$
9.60
9.40
9.20
9.00
8.80
8.60
8.40
8.20
ppm
0.216
1.000
1.029
3.647
10
8
6
4
2
0
-2
ppm

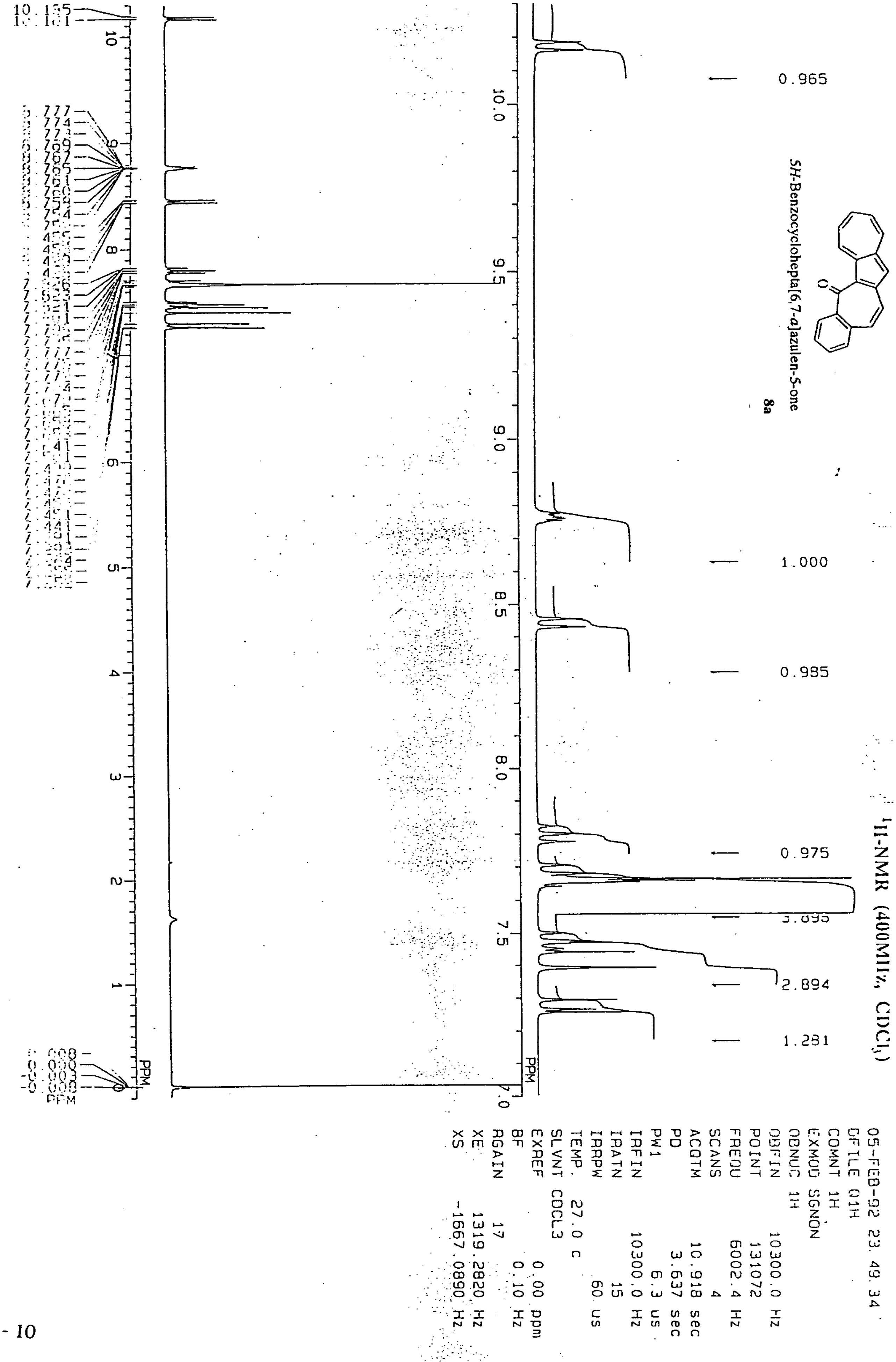
12,13-Dihydrobenzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate

25•BF$_4^-$

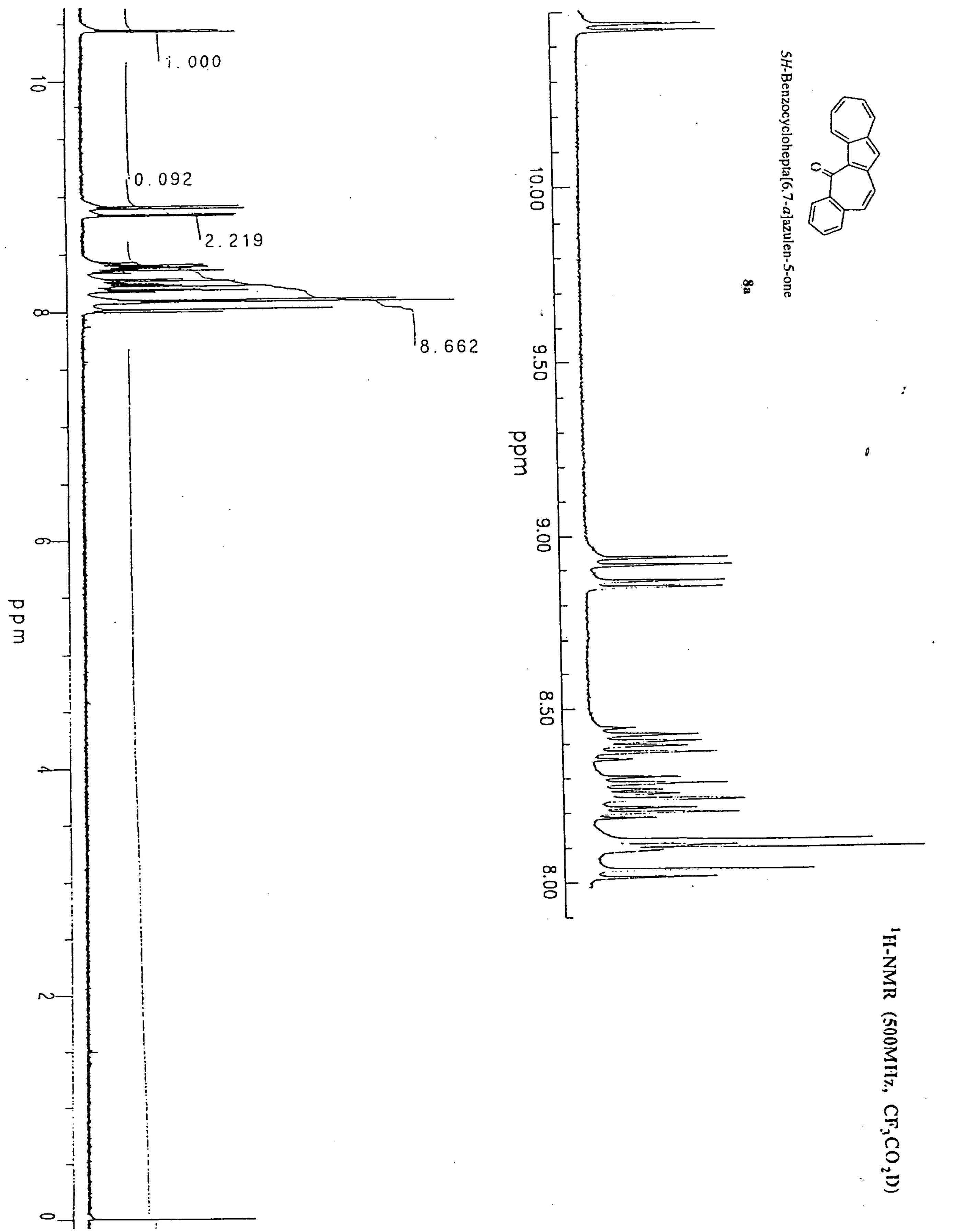
^{1}H-NMR (400MHz, CD_3CN)

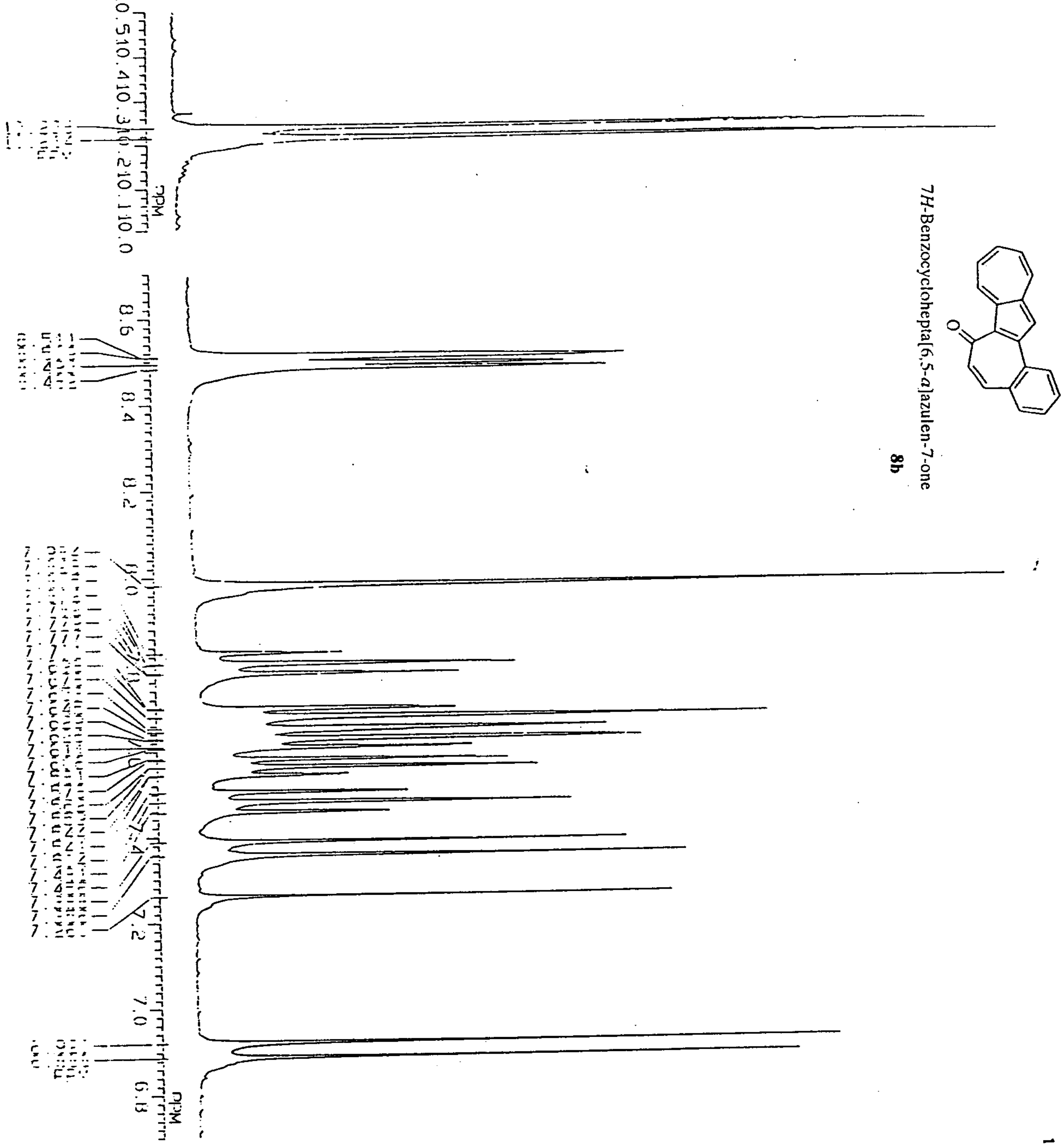


15-JUL-92	13.45:51
MENUF	W1H
OBNUC	1H
OBFRQ	399.65 MHz
OBSET	124.00 kHz
OBFIN	10804.5 Hz
PW1	4.1 us
DEADT	98.0 us
PREDL	0.2000 ms
INIWT	1.0 sec
POINT	131072
SAMPO	131072
TIMES	64
DUMMY	1
FREQU	6002.4 Hz
FILTR	3000 Hz
DELAY	66.7 us
ACQTM	10.918 sec
PD	4.270 sec
ADBIT	12
RGAIN	20
BF	0.10 Hz
T1	0.0 %
T2	0.0 %
T3	90.0 %
T4	100.0 %
EXMOD	SGNON
IRNUC	1H
IRFRQ	399.65 MHz
IRSET	124.00 kHz
IRFIN	10300.0 Hz
IRRPW	30 us
IRATN	0
DFILE	SAVING
SHMFL	CH5
LKSET	61.4 kHz
LKFIN	12.0 Hz
LKLEV	215
LGAIN	15
LKPHS	111 deg
LKSIG	468
SPEED	15 Hz
FILDC	54
FILDF	6



5H-Benzocyclohepta[6,7-a]azulen-5-one
8a
¹H-NMR (400MHz, CDCl₃)
0.965
1.000
0.985
0.975
2.894
1.281
10.0
9.5
9.0
8.5
8.0
7.5
7.0
PPM
05-FEB-92 23.49.34
DFILE 01H
COMNT 1H
EXMOD SGNON
OBNUC 1H
OBFIN 10300.0 Hz
POINT 131072
FREQU 6002.4 Hz
SCANS 4
ACQTM 10.918 sec
PD 3.637 sec
PW1 6.3 us
IRFIN 10300.0 Hz
IRATN 15
IRRPW 60 us
TEMP. 27.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 17
XE 1319.2820 Hz
XS -1667.0890 Hz


5H-Benzocyclohepta[6,7-a]azulen-5-one
8a
1H-NMR (500MHz, CF3CO2D)
10.00
9.50
9.00
8.50
8.00
ppm
1.000
0.092
2.219
8.662
10
8
6
4
2
0
ppm



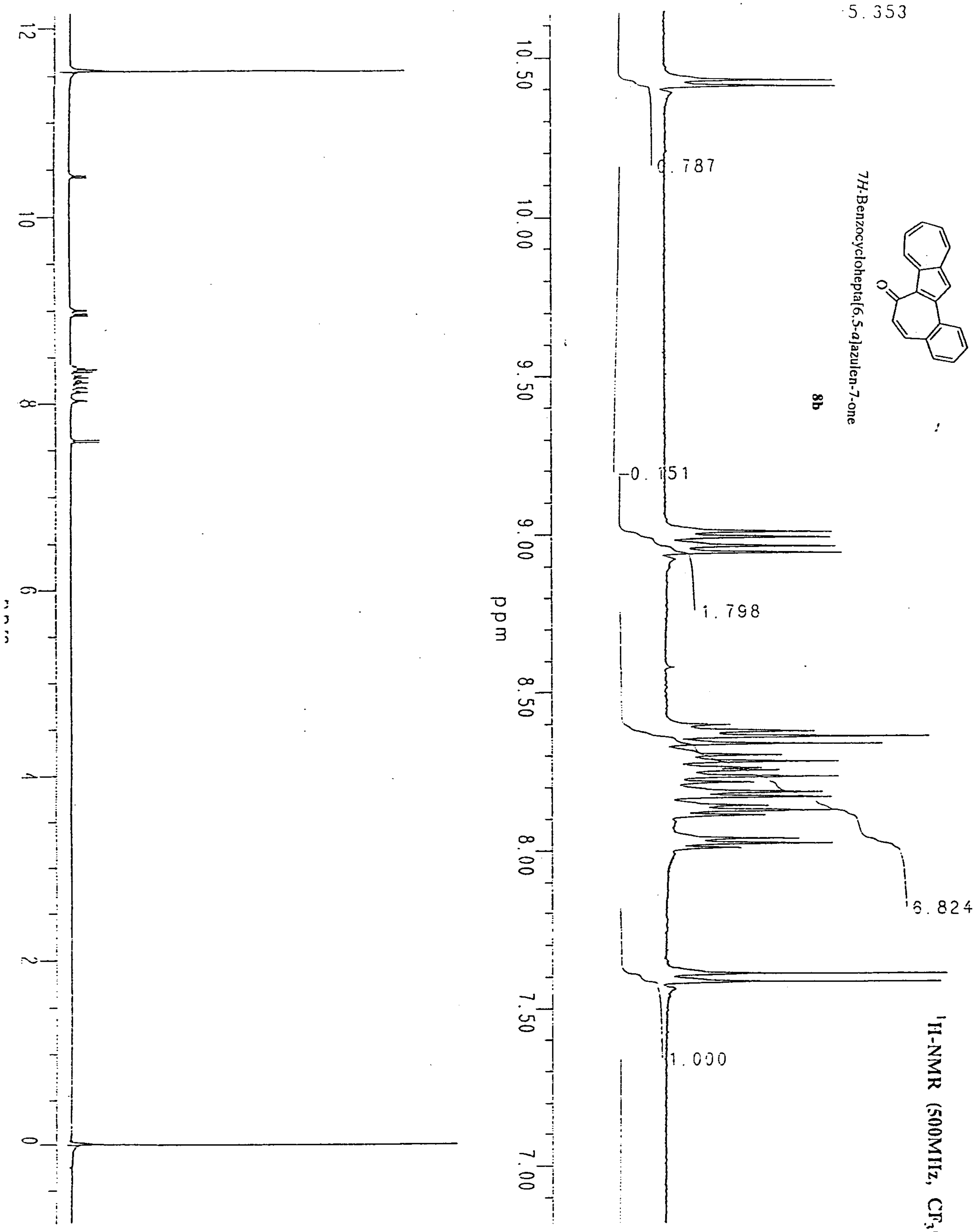
7H-Benzocyclohepta[6,5-*a*]azulen-7-one

8b

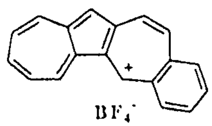
^{1}H-NMR (400MHz, $CDCl_3$)

7H-Benzocyclohepta[6,5-a]azulen-7-one

8b



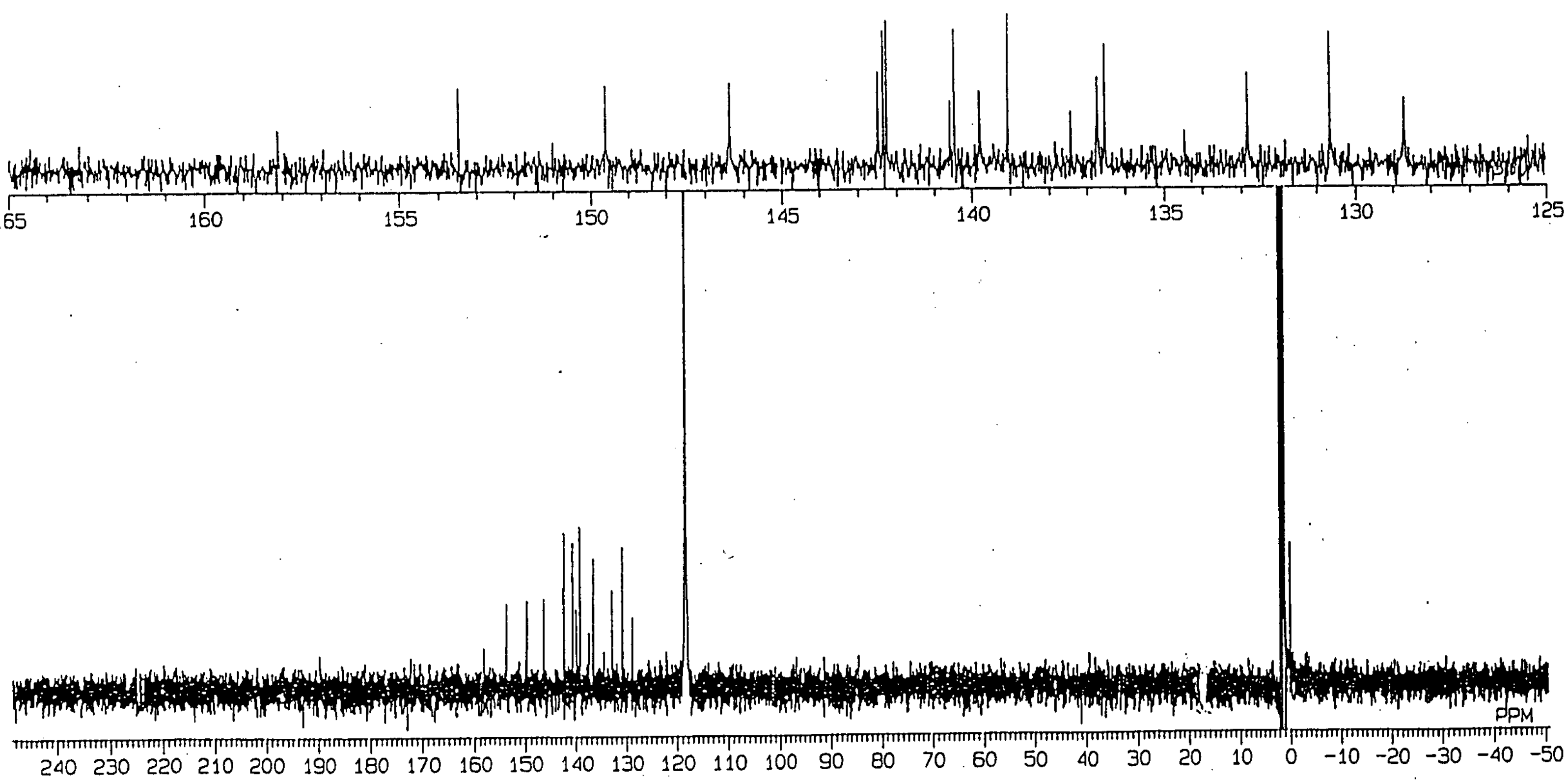
^{1}H-NMR (500MHz, CF_3CO_2D)



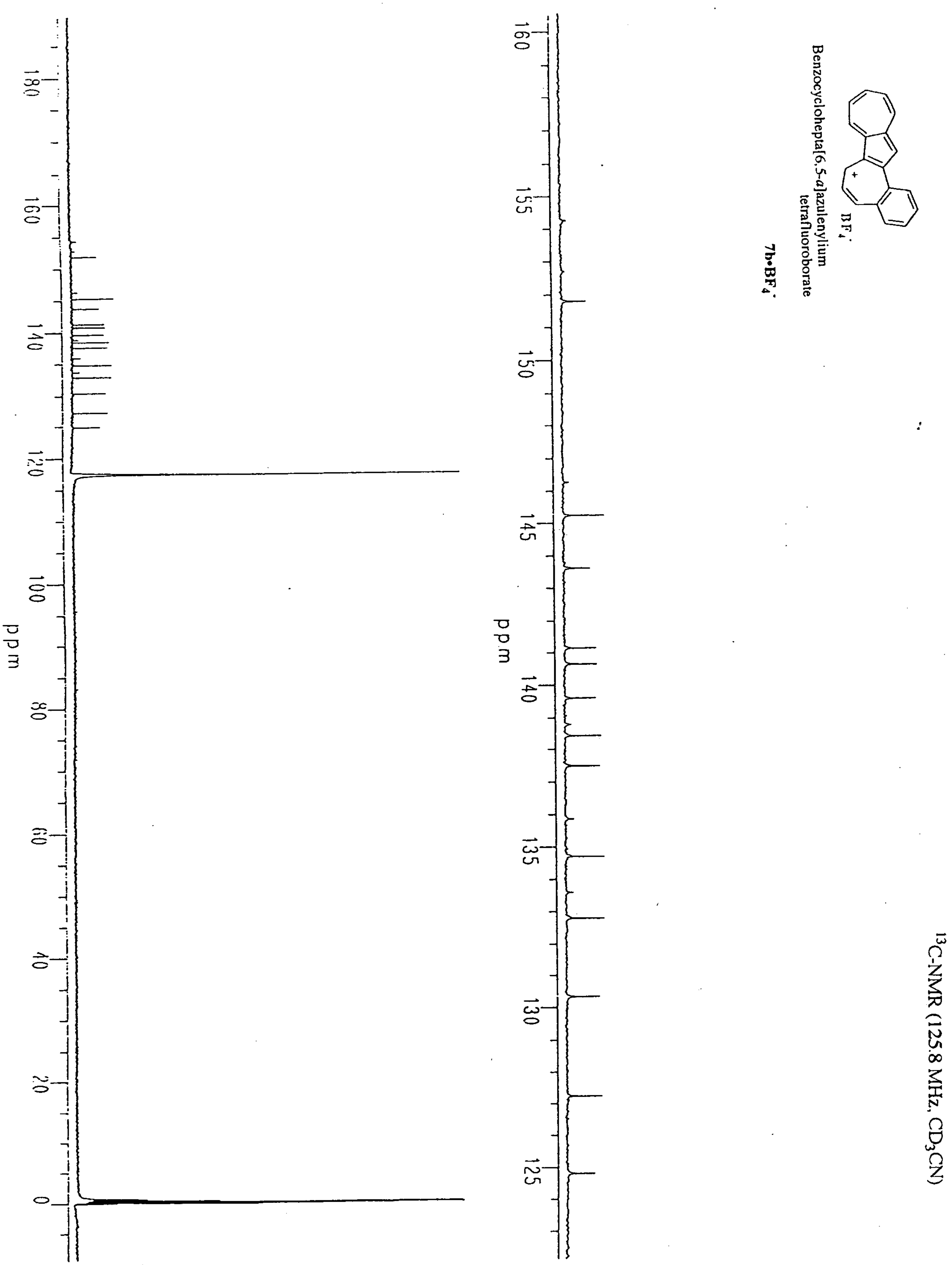
Benzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate

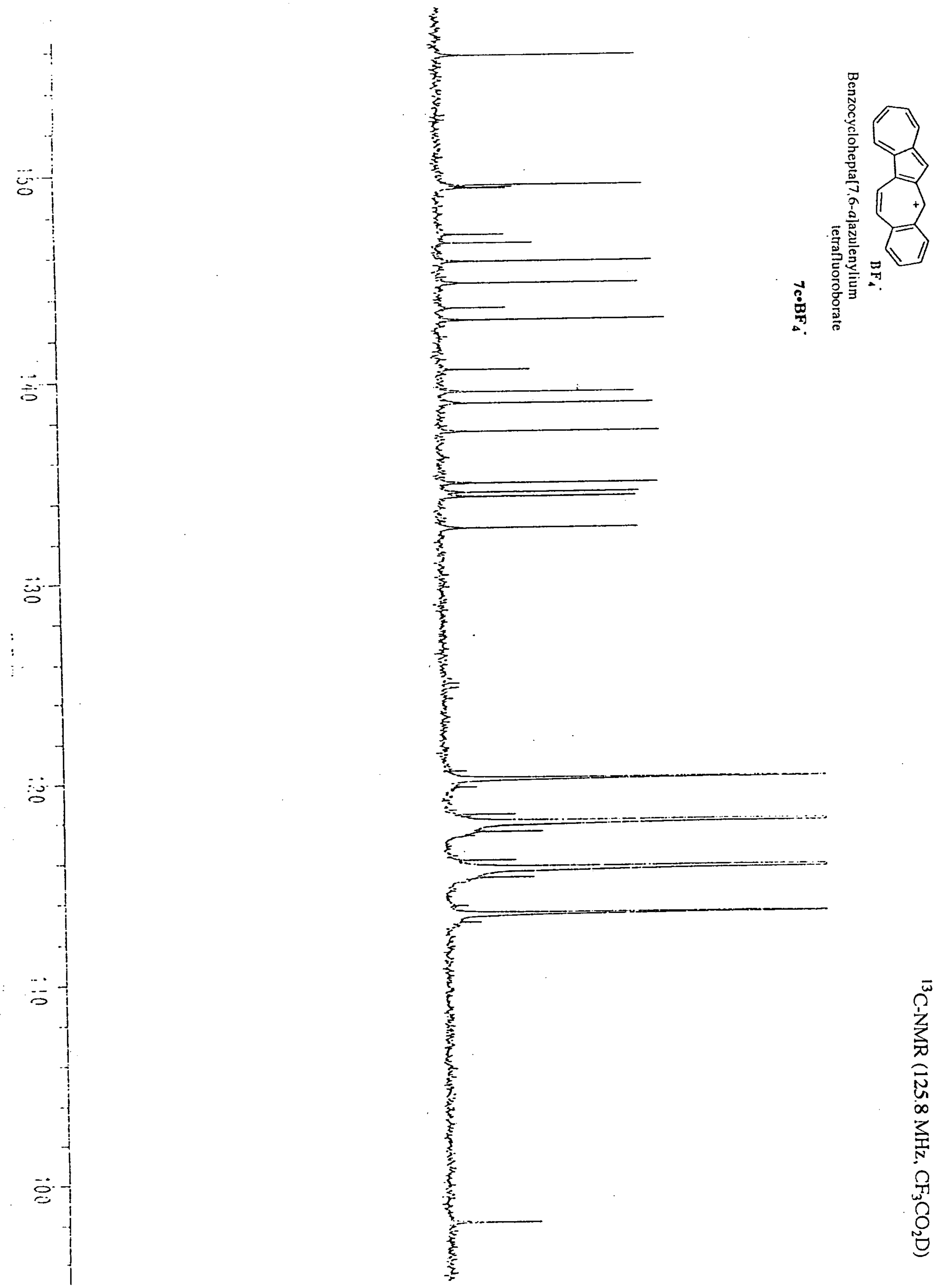
7a•BF_4^-

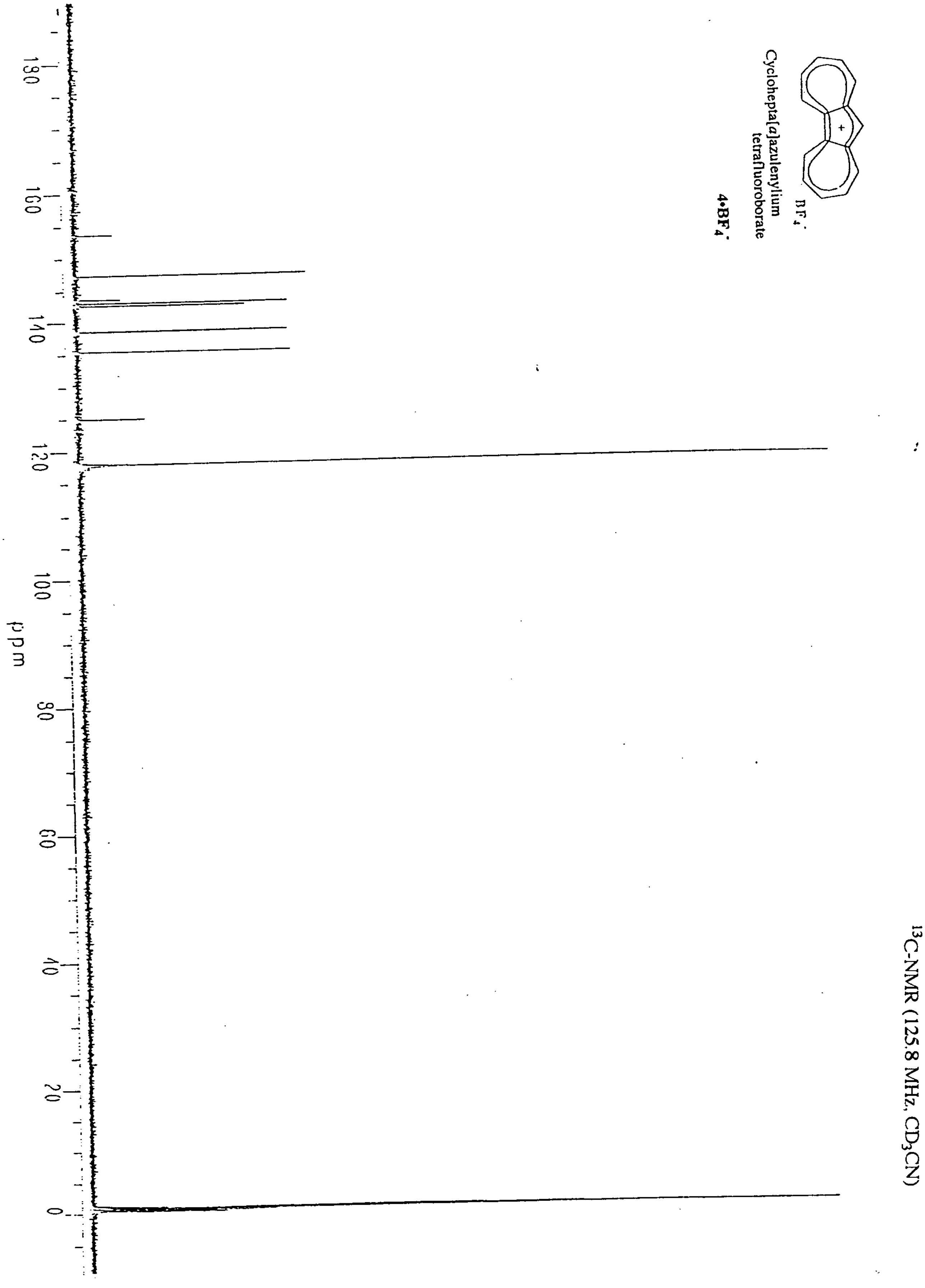
^{13}C-NMR (100.4 MHz, CD_3CN)



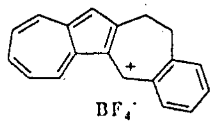
06-FEB-92 05: 19. 25	
DFILE	Q13C
COMNT	AZ-BENZ-TR+
EXMOD	SGBCM
OBNUC	13C
OBFIN	10244.0 Hz
POINT	32768
FREQU	30120.5 Hz
SCANS	2048
ACQTM	0.544 sec
PD	1.456 sec
PW1	4.5 us
IRFIN	10300.0 Hz
IRATN	22
IRRPW	50 us
TEMP.	27.0 c
SLVNT	CD3CN
EXREF	1.30 ppm
BF	0.10 Hz
RGAIN	26
XE	4021.0100 Hz
XS	-4624.7090 Hz


BF4-
Benzocyclohepta[6,5-a]azulenylium
tetrafluoroborate
7b•BF4-
13C-NMR (125.8 MHz, CD3CN)
160
155
150
145
140
135
130
125
ppm
180
160
140
120
100
80
60
40
20
0
ppm


BF_4^-
Benzocyclohepta[7,6-*a*]azulenylium
tetrafluoroborate
7c•BF_4^-
^{13}C-NMR (125.8 MHz, CF_3CO_2D)
150
140
130
120
110
100

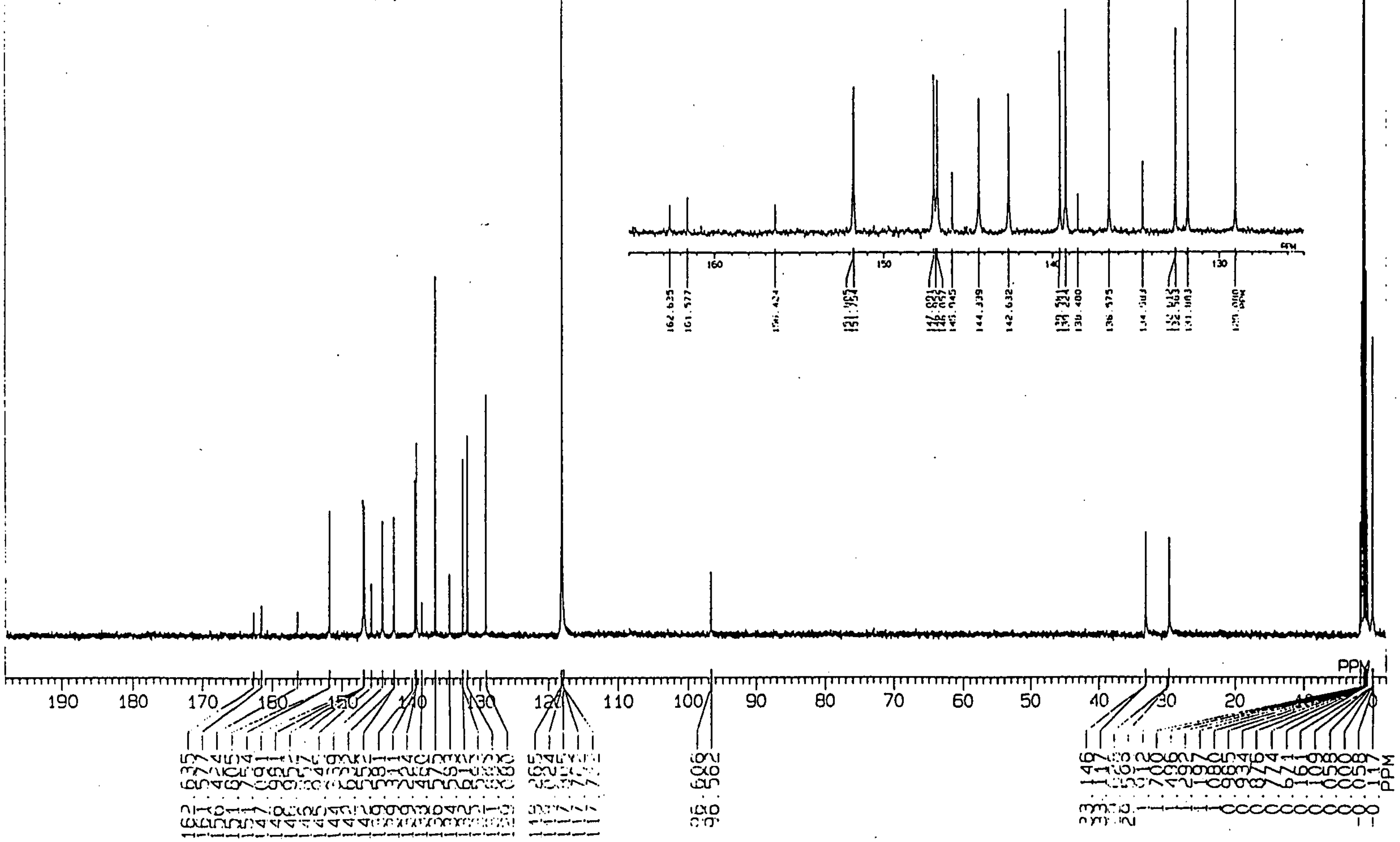

BF_4^-
Cyclohepta[a]azulenylium
tetrafluoroborate
$4{\bullet}BF_4^-$
^{13}C-NMR (125.8 MHz, CD_3CN)
180
160
140
120
100
80
60
40
20
0
ppm

^{13}C-NMR (100.4 MHz, CD_3CN)



12,13-Dihydrobenzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate

25•BF_4^-



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MENUF	J13C
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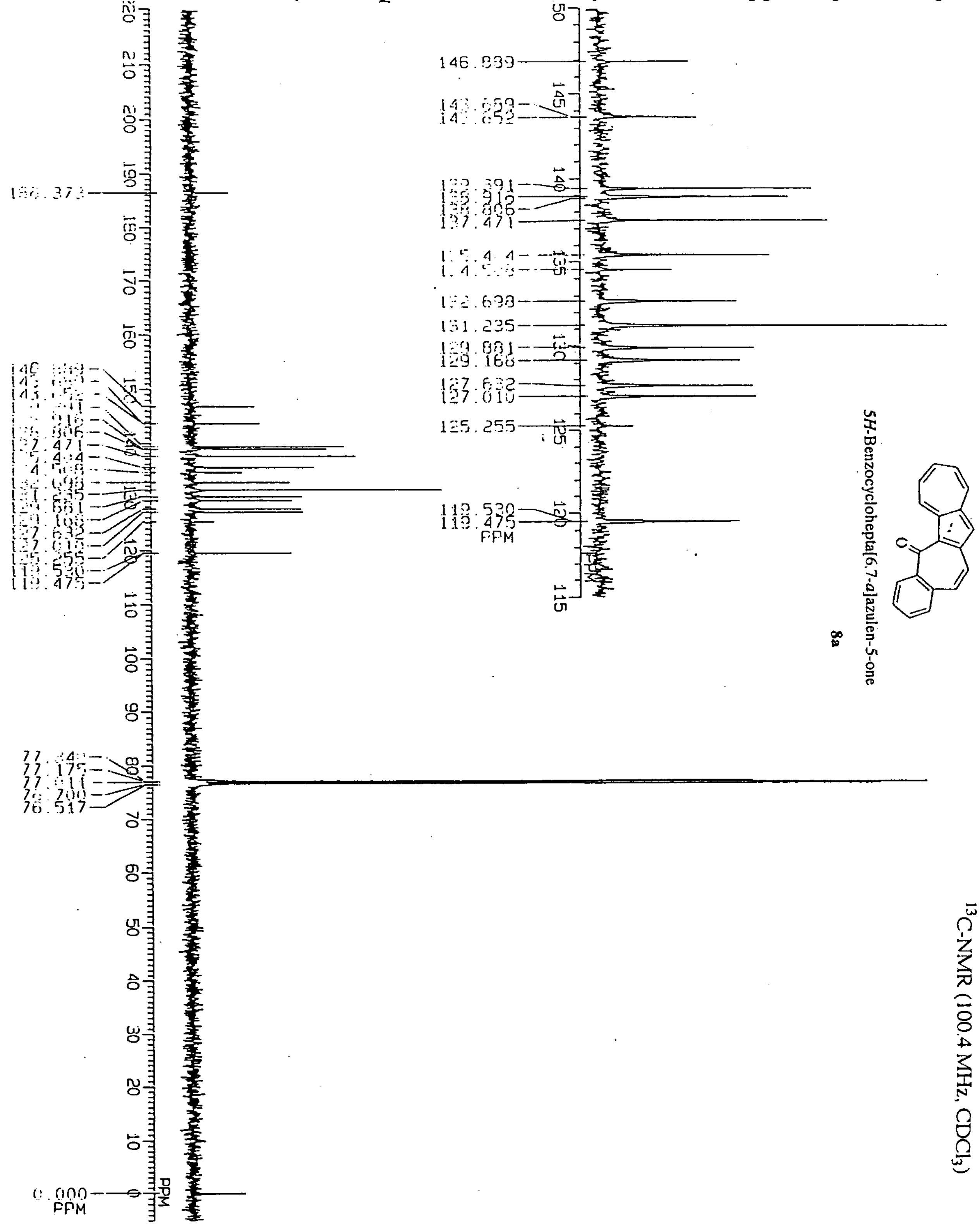
OBSET	125.00 kHz
OBFIN	10244.0 Hz
PW1	9.0 us
DEADT	20.5 us
PREDL	0.2000 ms
INIWT	1.0 sec
POINT	65536
SAMPO	65536
TIMES	4096
DUMMY	1
FREQU	24038.5 Hz
FILTR	12000 Hz
DELAY	16.7 us
ACQTM	1.363 sec
PD	0.800 sec
ADBIT	12
RGAIN	27
BF	1.00 Hz
T1	0.0 %
T2	0.0 %
T3	90.0 %
T4	100.0 %
EXMOD	SGBCM
IRNUC	1H
IRFRQ	399.65 MHz
IRSET	124.00 kHz
IRFIN	10300.0 Hz
IRRPW	50 us
IRATN	22
DFILE	SAVING
SHMFL	MU10
LKSET	61.4 kHz
LKFIN	12.0 Hz
LKLEV	230
LGAIN	15
LKPHS	117 deg
LKSIG	803
SPEED	15 Hz
FILDC	61
FILDF	64

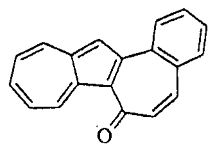
^{13}C-NMR (100.4 MHz, $CDCl_3$)

5*H*-Benzocyclohepta[6,7-*a*]azulen-5-one

8a



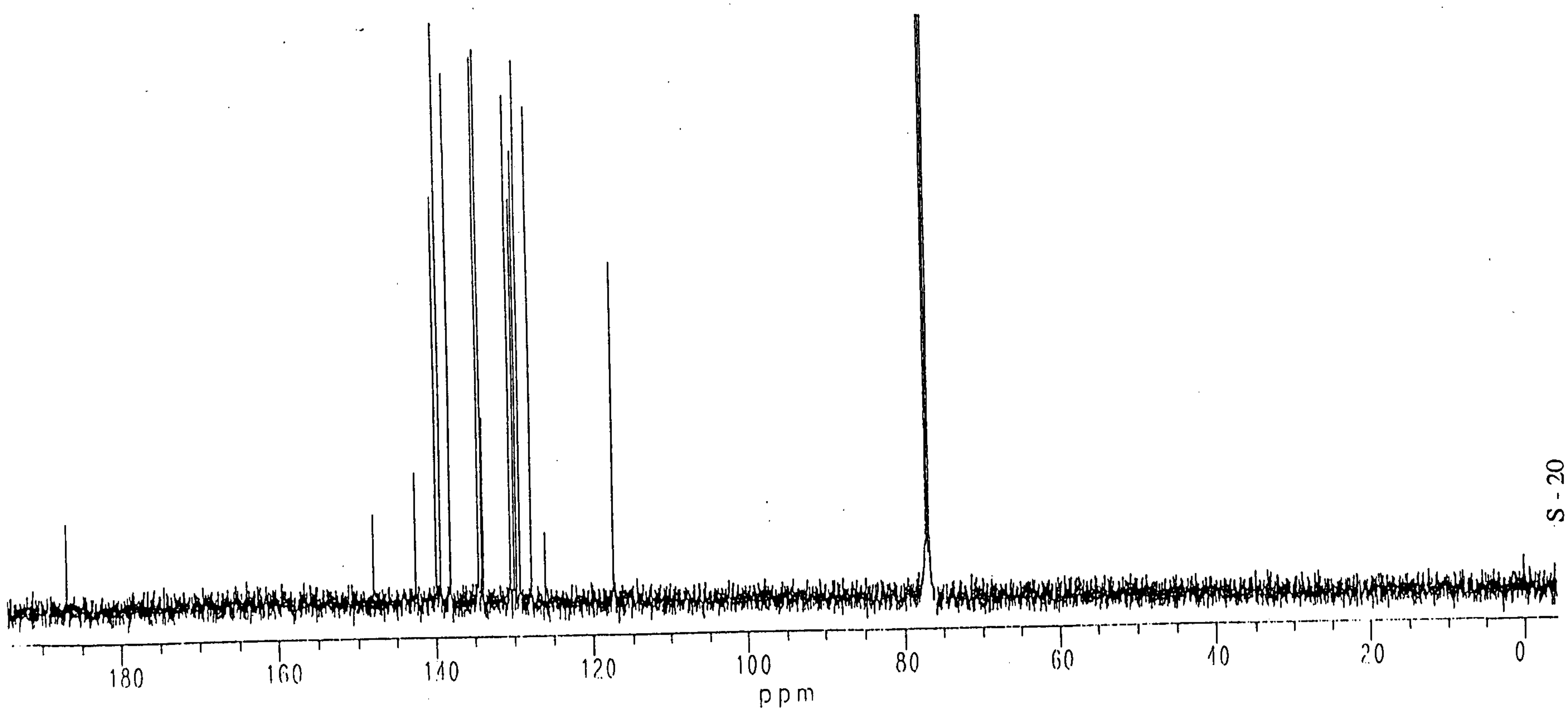
06-FEB-92 00:36:29
DFILE Q13C
COMNT COM
EXMOD SGBCM
OBNUC 13C
OBFIN 10244.[illegible] Hz
POINT 3270[illegible]
FREQU 30120.5 Hz
SCANS 809
ACQTM 0.544[illegible]
PD 1.456 sec
PW1 4.5 us
IRFIN 10300.0 Hz
IRATN 22
IRRPW 50 us
TEMP. 27.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 27
XE 22618.2100 Hz
XS -954.4502 Hz

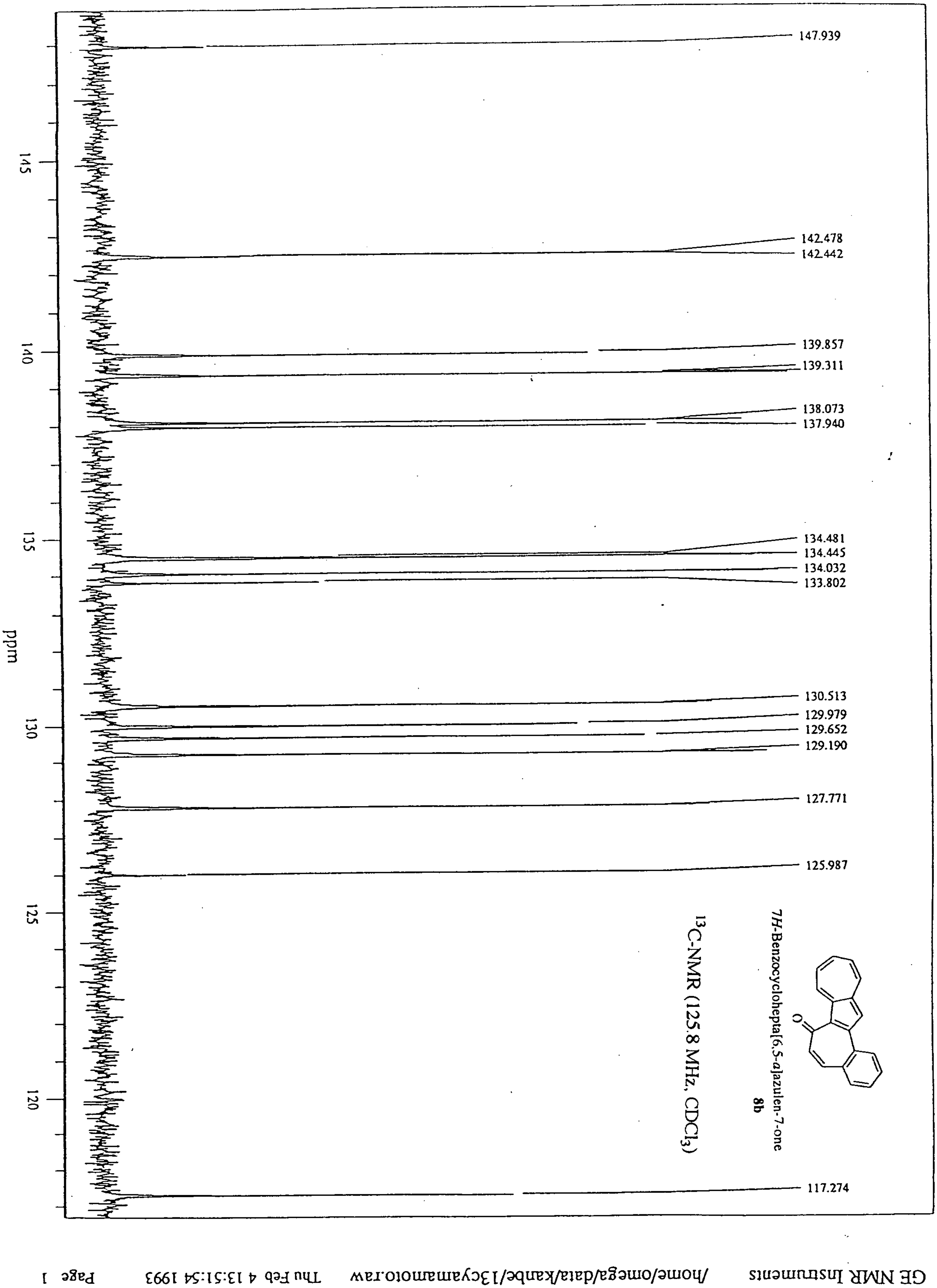


7*H*-Benzocyclohepta[6,5-*a*]azulen-7-one

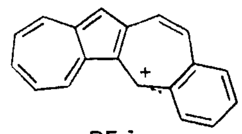
8b

^{13}C-NMR (125.8 MHz, $CDCl_3$)




147.939
142.478
142.442
139.857
139.311
138.073
137.940
134.481
134.445
134.032
133.802
130.513
129.979
129.652
129.190
127.771
125.987
117.274
145
140
135
130
125
120
ppm
O
7H-Benzocyclohepta[6,5-a]azulen-7-one
8b
13C-NMR (125.8 MHz, CDCl3)
GE NMR Instruments
/home/omega/data/kanbe/13cyamamoto.raw
Thu Feb 4 13:51:54 1993
Page 1

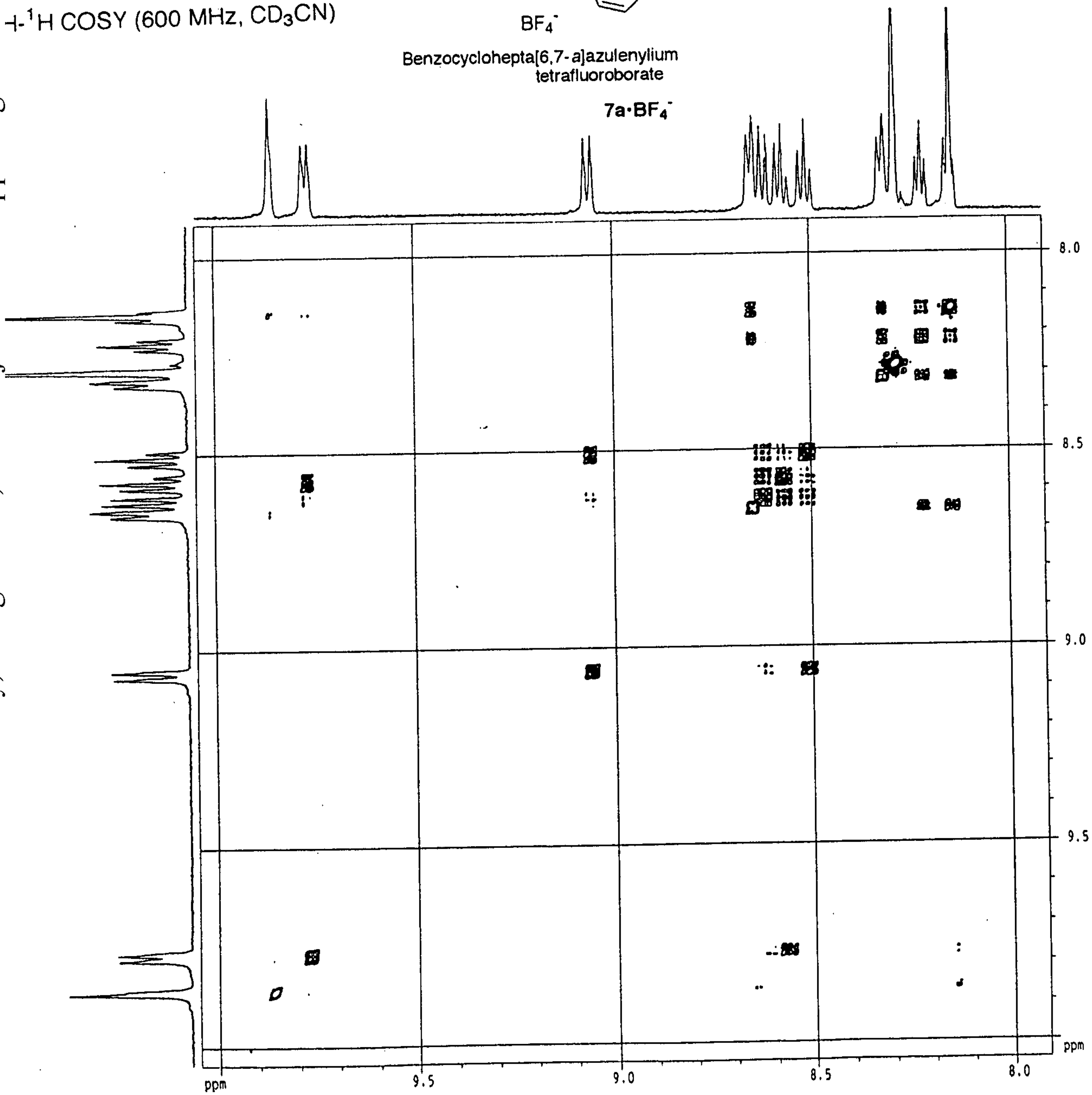
H-^{1}H COSY (600 MHz, CD_3CN)



BF_4^-

Benzocyclohepta[6,7-*a*]azulenylium tetrafluoroborate

7a·BF_4^-



Current Data Parameters

NAME	Oshibue
EXPNO	155
PROCNO	1

F2 - Acquisition Parameters

Date_	20020516
Time	19.10
INSTRUM	drx600
PROBHD	5 mm Multinu
PULPROG	cosygs
TD	2048
SOLVENT	DMSO
NS	2
DS	8
SWH	1280.738 Hz
FIDRES	0.625360 Hz
AQ	0.7995892 sec
RG	1024
DW	390.400 usec
DE	6.00 usec
TE	300.0 K
d0	0.00000300 sec
d13	0.00000300 sec
D1	1.32334101 sec
P1	10.40 usec
SFO1	600.1353890 MHz
NUC1	1H
PL1	-6.00 dB
P16	1000.00 usec
D16	0.00010000 sec
P0	10.40 usec
IN0	0.00078080 sec

F1 - Acquisition parameters

ND0	1
TD	256
SFO1	600.1354 MHz
FIDRES	5.002882 Hz
SW	2.134 ppm

F2 - Processing parameters

SI	1024
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

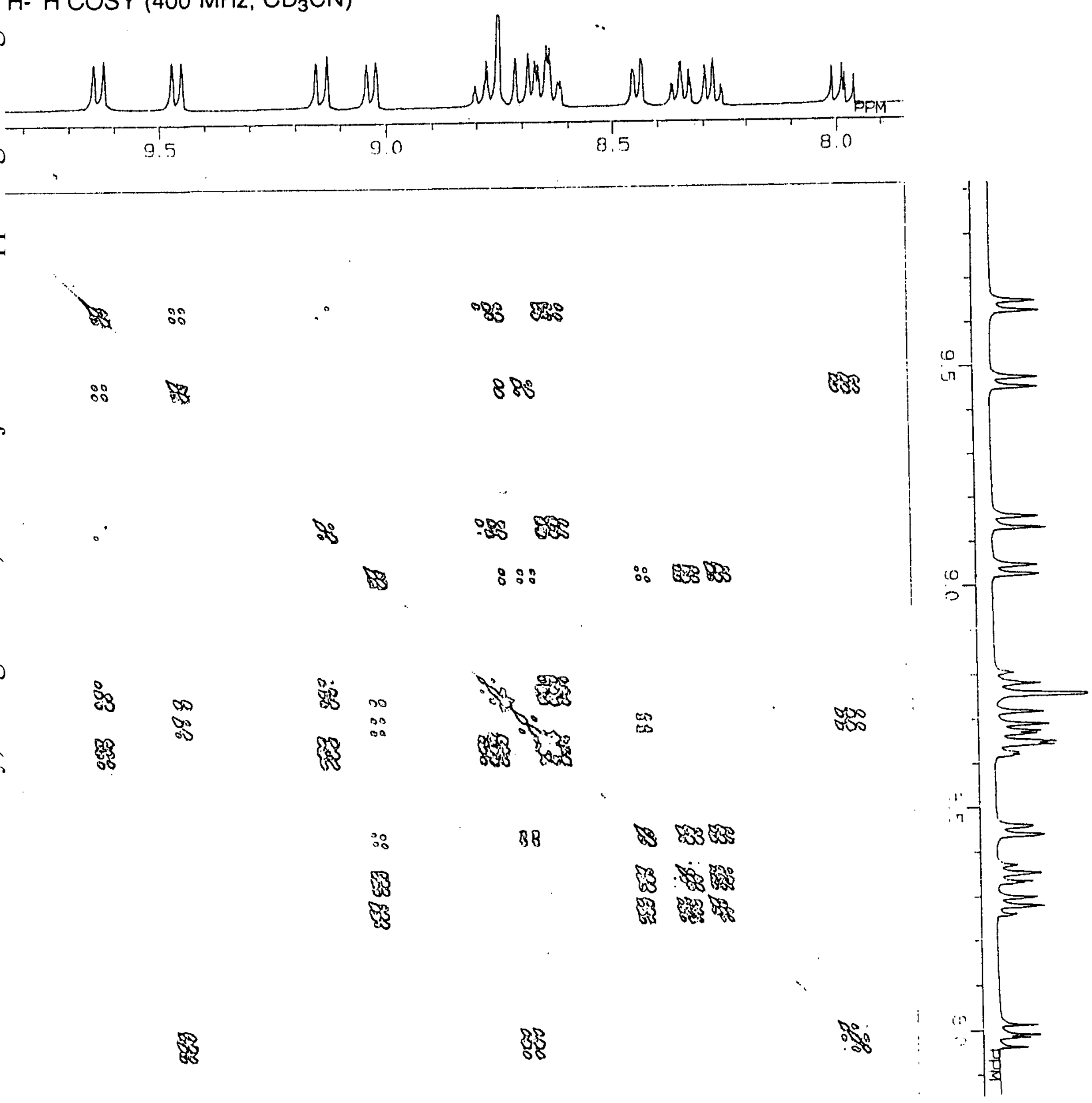
F1 - Processing parameters

SI	1024
MC2	QF
SF	600.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

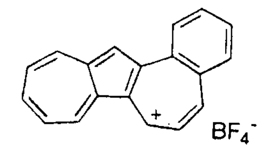
2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	10.047 ppm
F2LO	6029.36 Hz
F2PHI	7.913 ppm
F2HI	4748.62 Hz
F1PLO	10.047 ppm
F1LO	6029.36 Hz
F1PHI	7.913 ppm
F1HI	4748.62 Hz
F2PPMCM	0.10671 ppm/cm
F2HZCM	64.03689 Hz/cm
F1PPMCM	0.10671 ppm/cm
F1HZCM	64.03689 Hz/cm

H-^{1}H COSY (400 MHz, CD_3CN)

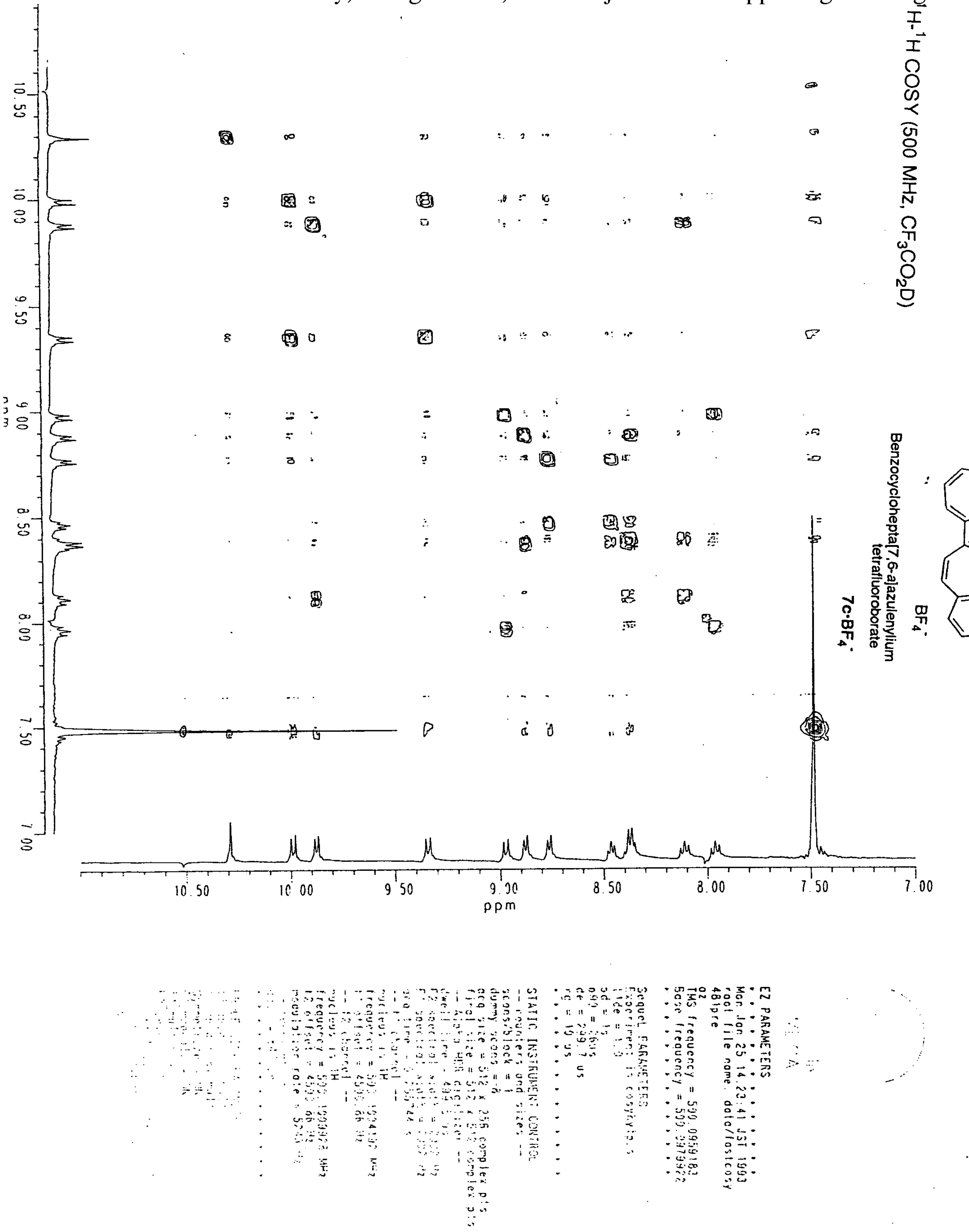


17-NOV-92 14: 22: 26	
DFILE 1HYAMA	
EXMOD SGNON	
COMNT 1H-NMR . CONDITION	
OBNUC 1H	
OBFIN	12307.8 Hz
OBATN	0
POINT	16384
FREQU	828.2 Hz
CLPNT	256
TODAT	9
CLFRQ	100.0 Hz
SCANS	4
ACQTM	9.891 sec
PD	4.270 sec
PW1	6.0 us
PW2	13.0 us
PW3	13.0 us
PI1	1.000 ms
PI2	1.000 ms
PI3	1.000 ms
IRNUC 1H	
IRFIN	10300.0 Hz
IRATN	0
IRRPW	30 us
TRNUC 1H	
TRFIN	0.0 Hz
TRATN	0
TRRPW	50 us
TEMP	27.0 c
SPEED	15 Hz
SLVNT CDCL3	
LOOP1	1
XS	-0.7971 Hz
CXS	-0.8088 Hz
XE	826.6083 Hz
CXE	826.6083 Hz
TH	100.00000
DEADT	747.0 us
DELAY	500.0 us
PREDL	0.2000 ms

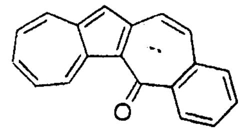


Benzocyclohepta[6,5-*a*]azulenylium tetrafluoroborate

7b·BF_4^-

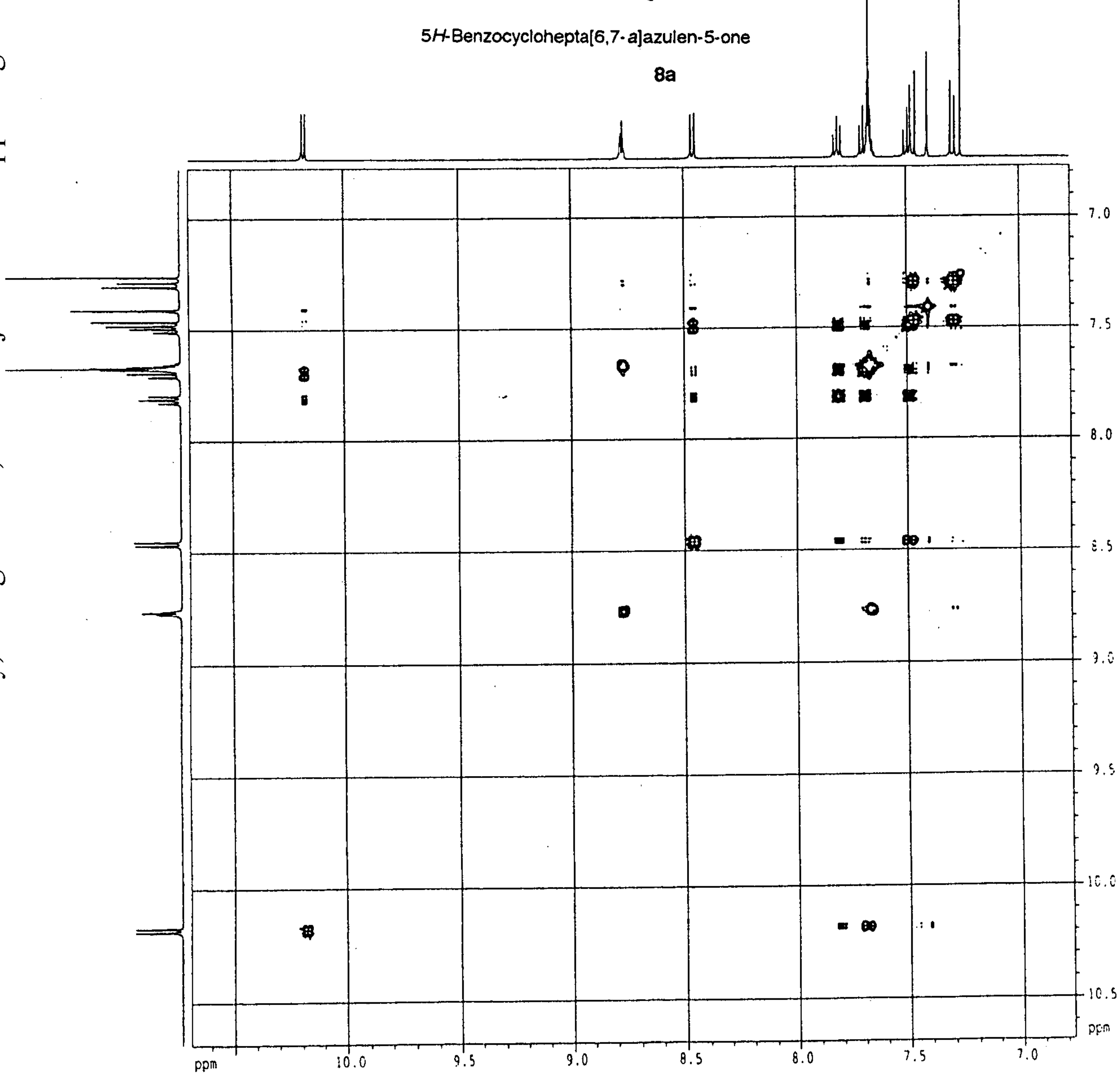

1H-1H COSY (500 MHz, CF3CO2D)
BF4-
Benzocyclohepta[7,6-a]azulenylium tetrafluoroborate
7c·BF4-
ppm
EZ PARAMETERS
STATIC INSTRUMENT CONTROL

-^{1}H COSY (600 MHz, $CDCl_3$)



5*H*-Benzocyclohepta[6,7-*a*]azulen-5-one

8a



Current Data Parameters

NAME	Oshibue
EXPNO	150
PROCNO	1

F2 - Acquisition Parameters

Date_	20020513
Time	18.28
INSTRUM	drx600
PROBHD	5 mm Multinu
PULPROG	cosygs
TD	2048
SOLVENT	DMSO
NS	1
DS	8
SWH	2349.624 Hz
FIDRES	1.147277 Hz
AQ	0.4358644 sec
RG	1448.2
DW	212.800 usec
DE	6.00 usec
TE	300.0 K
d0	0.00000300 sec
d13	0.00000300 sec
D1	1.68542695 sec
P1	10.40 usec
SFO1	600.1352576 MHz
NUC1	1H
PL1	-6.00 dB
P16	1000.00 usec
D16	0.00010000 sec
P0	10.40 usec
IN0	0.00042560 sec

F1 - Acquisition parameters

ND0	1
TD	256
SFO1	600.1353 MHz
FIDRES	9.178219 Hz
SW	3.915 ppm

F2 - Processing parameters

SI	1024
SF	600.1300180 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

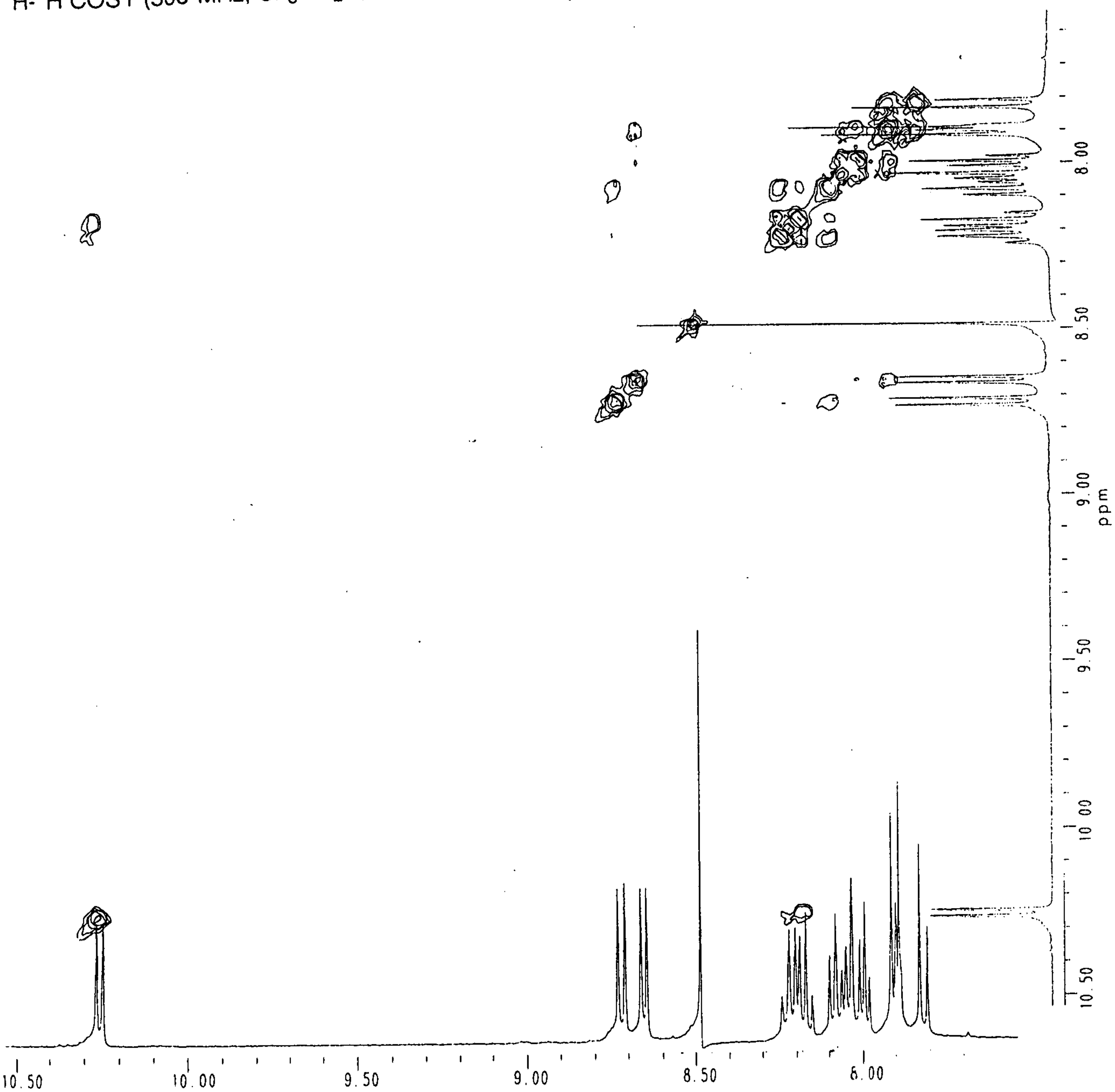
F1 - Processing parameters

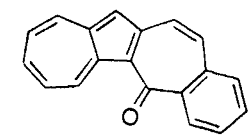
SI	1024
MC2	QF
SF	600.1300180 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	10.688 ppm
F2LO	6414.39 Hz
F2PHI	6.773 ppm
F2HI	4064.77 Hz
F1PLO	10.688 ppm
F1LO	6414.39 Hz
F1PHI	6.773 ppm
F1HI	4064.77 Hz
F2PPMCM	0.19576 ppm/cm
F2HZCM	117.48120 Hz/cm
F1PPMCM	0.19576 ppm/cm
F1HZCM	117.48120 Hz/cm

^{1}H-^{1}H COSY (500 MHz, CF_3CO_2D)





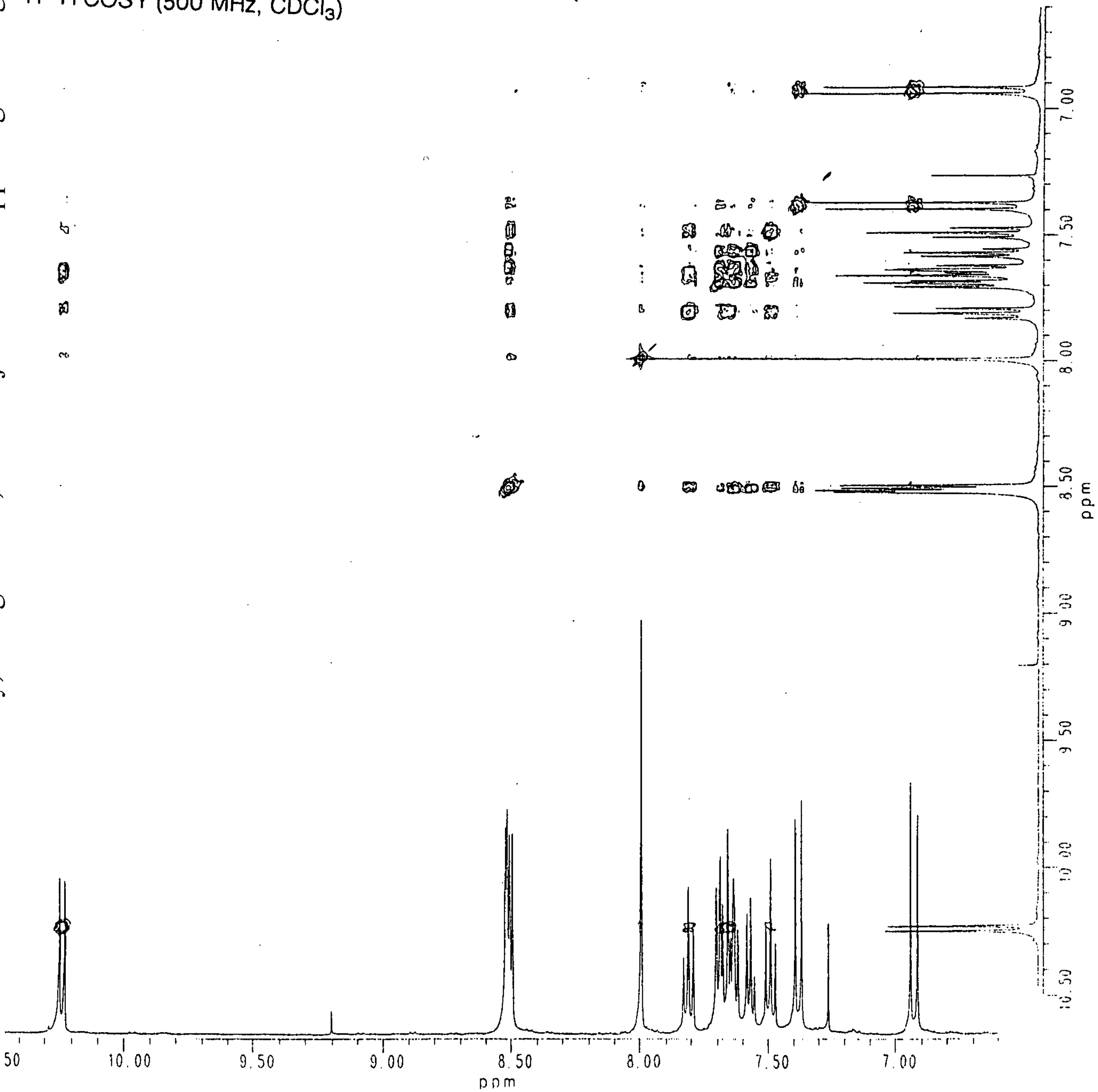
5*H*-Benzocyclohepta[6,7-*a*]azulen-5-one

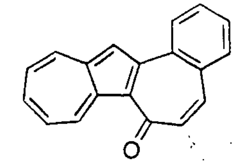
8a

GE NMR
OMEGA

```
EZ PARAMETERS
Tue Jan 18 13:10:04 JST 1994
root file name: data/cosy
tr1
heteroco
TMS frequency = 500.0940000
Base frequency = 500.0940000

Sequel PARAMETERS
Experiment is cosy.s
pd = 1sec
p90 = 12.5us
de = 399.9 us
rg = 10 us

STATIC INSTRUMENT CONTROL
-- counters and sizes --
scans/block = 16
dummy scans = 4
acq size = 256 x 256 complex pts
final size = 256 x 256 complex pts
-- Alpha HDR digitizer --
dwell time = 666.5 us
F2 spectral width = 1500.38 Hz
F1 spectral width = 1500.38 Hz
acq time = 0.170624 s
-- f1 channel --
nucleus is 1H
frequency = 500.0985208 MHz
f1 offset = 4520.8 Hz
-- f2 channel --
nucleus is 1H
frequency = 500.0962504 MHz
f2 offset = 4520.8 Hz
modulation rate = 5243 Hz
-- receiver --
gain = 3140.06

PROCESSING PARAMETERS
t1_apod = sinmult
t2_apod = sinmult
Symmetrize = ON
F1_phase = A: 81.6 B: 0
F1_magcalc = ON
t1_mult = 0.5
F1_level = ON
F2_level = ON
2d_type = magnitude
t2mult = 0.5
F1_reverse = ON
```

^{1}H-^{1}H COSY (500 MHz, $CDCl_3$)





7*H*-Benzocyclohepta[6,5-*a*]azulen-7-one

8a

GE NMR
OMEGA

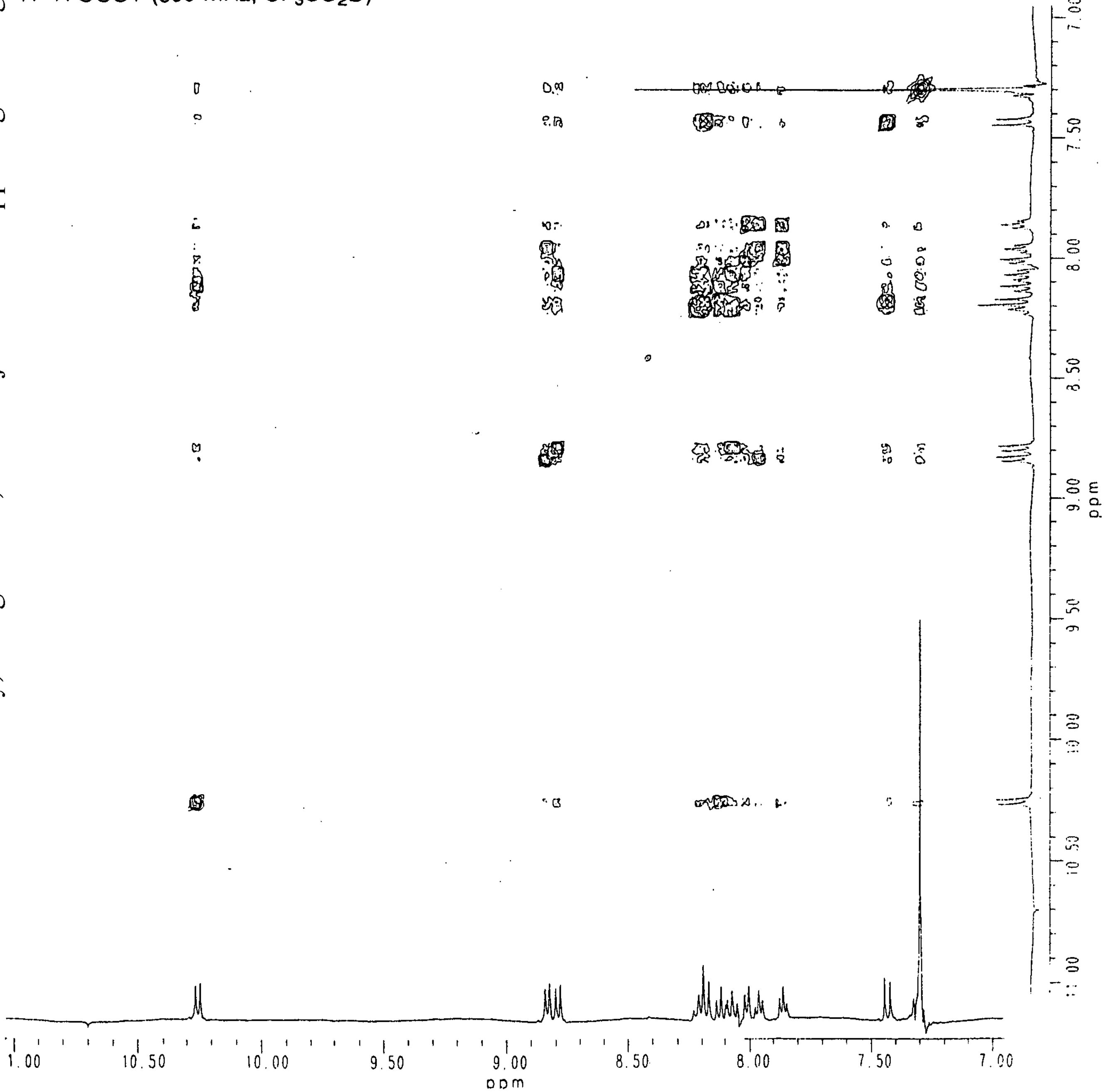
EZ PARAMETERS
Thu Feb 4 12:51:57 JST 1993
root file name: data/cosy
az-bz
cosy
TMS frequency = 500.0979922
Base frequency = 500.0979922

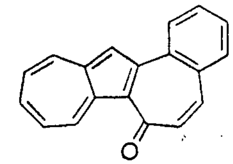
Sequel PARAMETERS
Experiment is cosy.s
pd = 1sec
p90 = 26us
de = 307.5 us
rg = 10 us

STATIC INSTRUMENT CONTROL
-- counters and sizes --
scans/block = 8
dummy scans = 4
acq size = 512 x 512 complex pts
final size = 512 x 512 complex pts
-- Alpha HDR digitizer --
dwell time = 512.5 us
F2 spectral width = 1951.22 Hz
F1 spectral width = 1951.22 Hz
acq time = 0.2624 s
-- f1 channel --
nucleus is 1H
frequency = 500.1022680 MHz
f1 offset = 4275.8 Hz
-- f2 channel --
nucleus is 1H
frequency = 500.1002426 MHz
f2 offset = 4275.8 Hz
modulation rate = 5243 Hz
-- receiver --
gain = 323.73

PROCESSING PARAMETERS
f1_apod = sinmult
f2_apod = sinmult
Symmetrize = ON
F1_phase = A: 215.6 B: 0
F1_magcalc = ON
f1_mult = 0.5
F2_level = ON
2d_type = magnitude
f2mult = 0.5
F1_reverse = ON

^{1}H-^{1}H COSY (500 MHz, CF_3CO_2D)





7*H*-Benzocyclohepta[6,5-*a*]azulen-7-one

8a

GE NMR
OMEGA

```
EZ PARAMETERS
• • • • • • • • • • • • • • •
Wed Feb  3 15:46:47 JST 1993
root file name: data/fastcosy
az-bz
mps
TMS frequency = 500.0979922
Base frequency = 500.0979922
• • • • • • • • • • • • • • •

Sequel PARAMETERS
Experiment is cosyhylp.s
fide = 1.0
pd = 1s
p90 = 26us
de = 292.5 us
rg = 10 us
• • • • • • • • • • • • • • •

STATIC INSTRUMENT CONTROL
-- counters and sizes --
scans/block = 2
dummy scans = 8
acq size = 512 x 512 complex pts
final size = 512 x 512 complex pts
-- Alpha HDR digitizer --
dwell time = 487.5 us
F2 spectral width = 2051.28 Hz
F1 spectral width = 2051.28 Hz
acq time = 0.2496 s
-- f1 channel --
nucleus is 1H
frequency = 500.1024932 MHz
f1 offset = 4501 Hz
-- f2 channel --
nucleus is 1H
frequency = 500.1024274 MHz
f2 offset = 4501 Hz
modulation rate = 5243 Hz
-- receiver --
gain = 844.18
• • • • • • • • • • • • • • •

PROCESSING PARAMETERS
i1_apod = sinmull
i2_apod = sinmull
Symmetrize = ON
f1_magcalc = ON
i1_mull = 0.5
f2_level = ON
t1_zerofill = 1 time
2d_type = hypercomplex
f2mull = 0.5
```