

Supporting Information

Stable Ion Study of Benzo[a]pyrene (BaP) derivatives; 7,8-Dihydro-BaP, 9,10-Dihydro-BaP and its 6-Halo Derivatives, 1- and 3-Methoxy-9,10-Dihydro- BaP-7(8*H*)-one, as well as the Proximate Carcinogen BaP 7,8-Dihydrodiol and its Dibenzoate, Combined with a Comparative DNA Binding Study of Regioisomeric (1, 4, 2) Pyrenylcarbinols

Takao Okazaki,^a Kenneth K. Laali,^{*a} Barbara Zajc,^{b,c} Mahesh K. Lakshman,^b Subodh Kumar,^d William M. Baird,^e Wan-Mohaiza Dashwood^e

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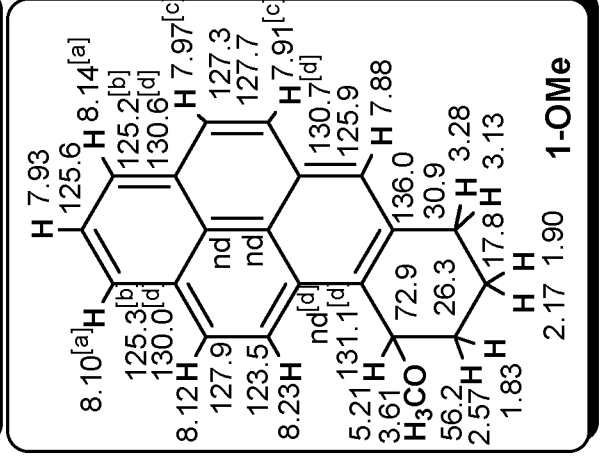
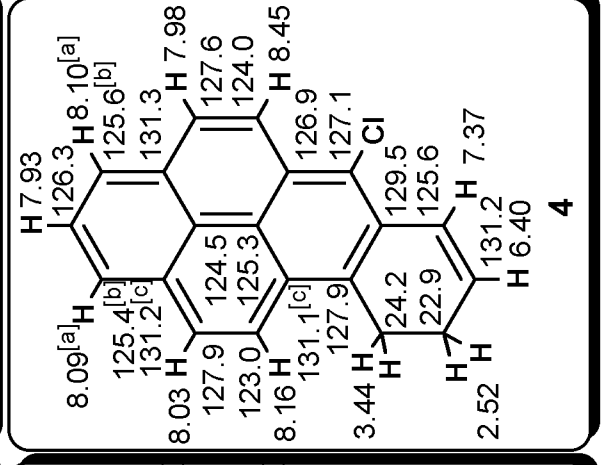
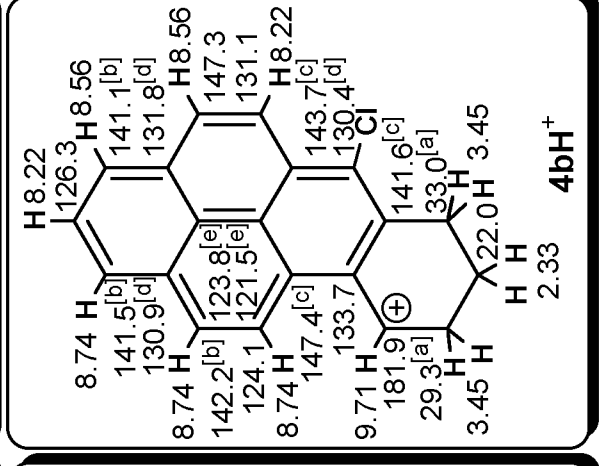
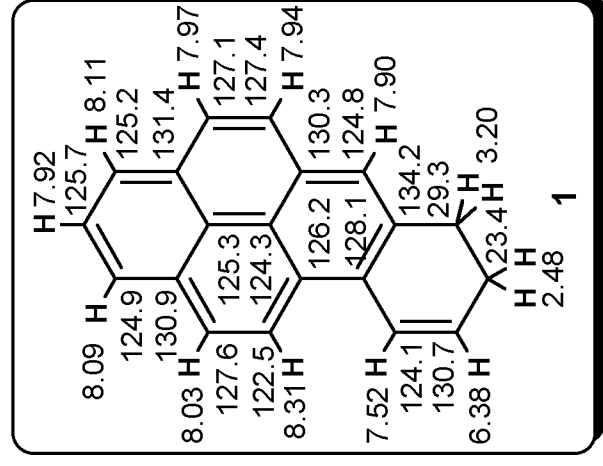
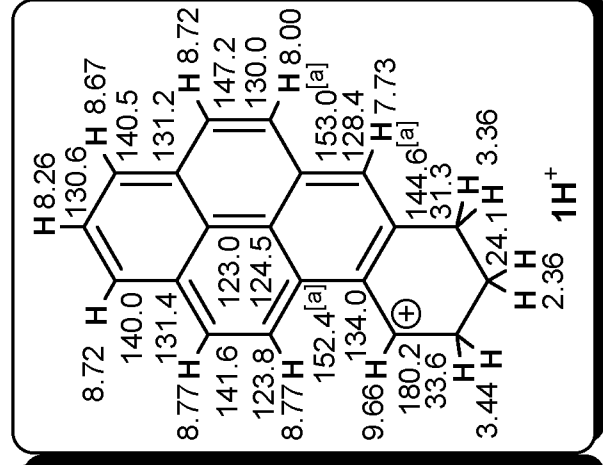
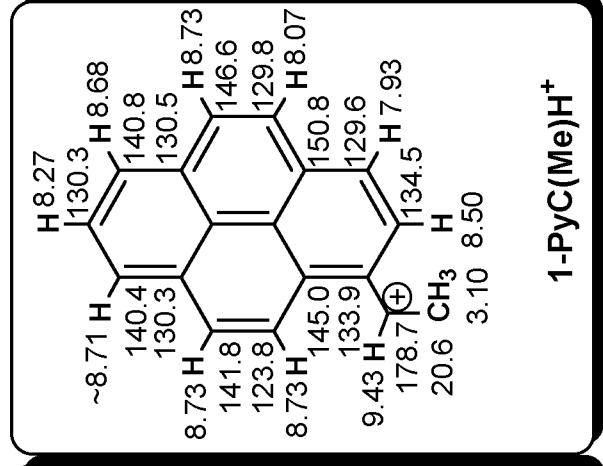
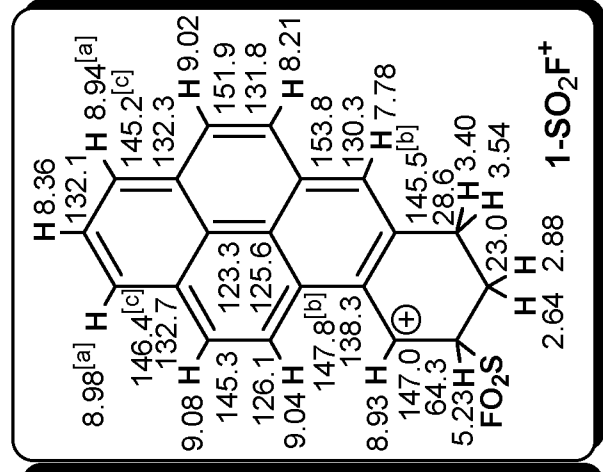


Figure S1. NMR data for the substrates and their persistent carbocations. (NMR data for 1-(1-pyrenyl)ethyl cation are included for comparison) {superscripts [a], [b], [c], [d], and [e] denote interchangeable assignments. nd: not detected}

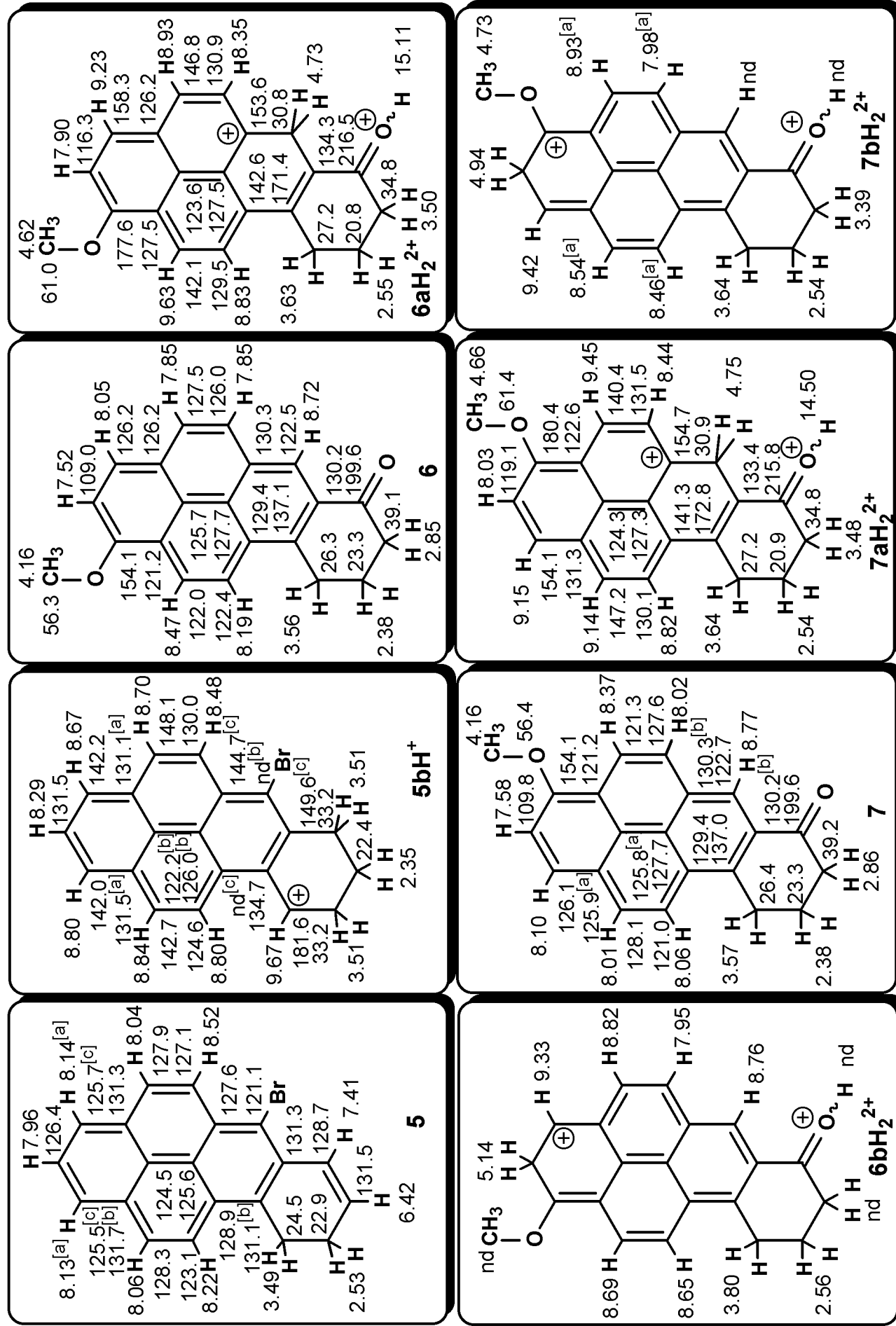
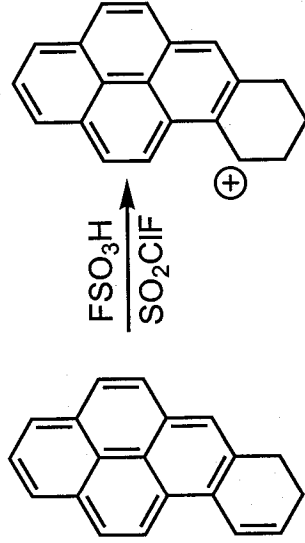


Figure S1, cont'd.

5mmsw,H_lineshape
spin,7-8-98
exp9 s2pu1

date Nov 12 1999
solvent CD2Cl2
file /export/home/~
laa11/okazaki102/10~
99111201-H60-CD2Cl2
2-5.fid
ACQUISITION
sfrq 499.909
tn 499.909
at 1.600
np 48000
sw 15000.5
fb 8000
bs 55
tpwr 12.0
pw 1.000
d1 363.1
tof 16
nt 16
ct 16
alock not used
gain not used
PROCCESSING
l1 n
in n
dp n
hs nm
sp -250.3
wp 6998.5
vs 230
sc 0
wc 250
hzmh 27.99
ls 585.90
rf1 7312.1
rfp 2659.5
th 3.000
nm cdc ph

DEC. & VT 499.914
dfrq dn H1
dn 30
dpwr 5296.2
dm 5
dmm C
dmc 200
dres 1.0
temp -60.0
DEC2
dfrq2 0
dn2 1
dpwr2 0
dm2 n
dmm2 C
dmc2 200
dres2 1.0
homo2 n
wfile n
proc n
fn not used
math f
werr
wexp
wbs
wnt
wft



¹H NMR at -60°C

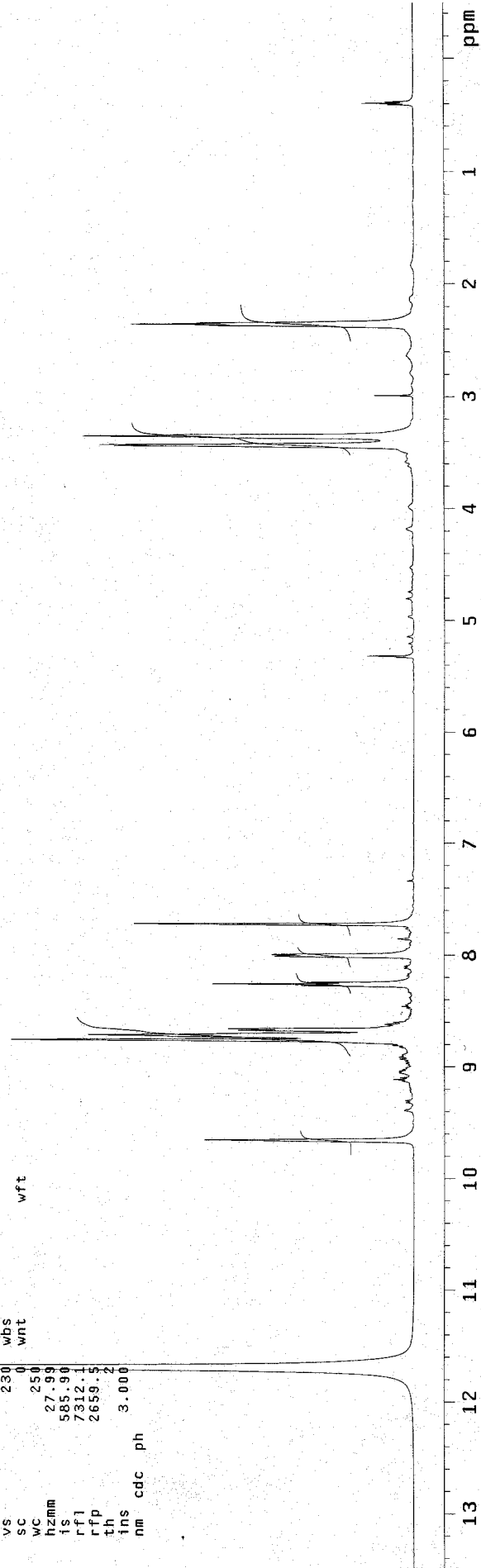
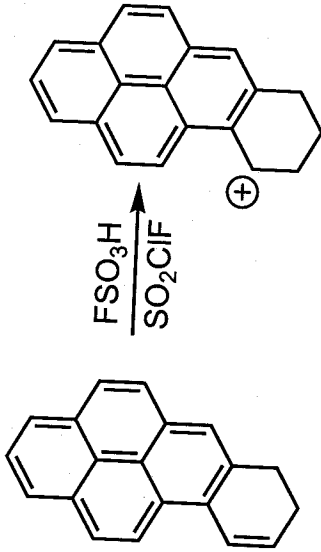


Chart S1. ¹H NMR spectrum for the protonation of **1**.

STANDARD CARBON PARAMETERS

```

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solvent CD2CL2 dn H1
file /export/home/~dpwr dpwr 35
laali/okazaki02/to~ dfr 0
99111201-C60-CD2CL~ dm nvy
2-5.fid dnm 10800
ACQUISITION dmf
sfrq 125.716 dseq 1
tn 1.0 C13 dres n
at 1.066 homo n
np 106560 temp -60.0
sw 50000.0 DECE 0
fb not used dfrq2 0
bs 4 dn2 1
tpwr 52 dpr2 0
pw 11.0 dot2 0
d1 0.500 dm2 n
d2 0.500 dnm2 c
tof 2423.4 dmf2 10000
nt 10000 dseq2 1.0
ct 96 dres2 n
alock s homo2 n
gain lb PROCESSING 2.00
il n wtfile n
in n proc ft
dp y fn not used
hs nn math f
DISPLAY
sp -628.9 werr
wp 25141.5 wexp
vs 46 whs
sc 0 wnt
wc 250
hzmm 100.57
is 4250.00
rfl 17343.1
rff 6788.2
th 3
ins 1.000
nm cdc ph
  
```



¹³C NMR at -60°C

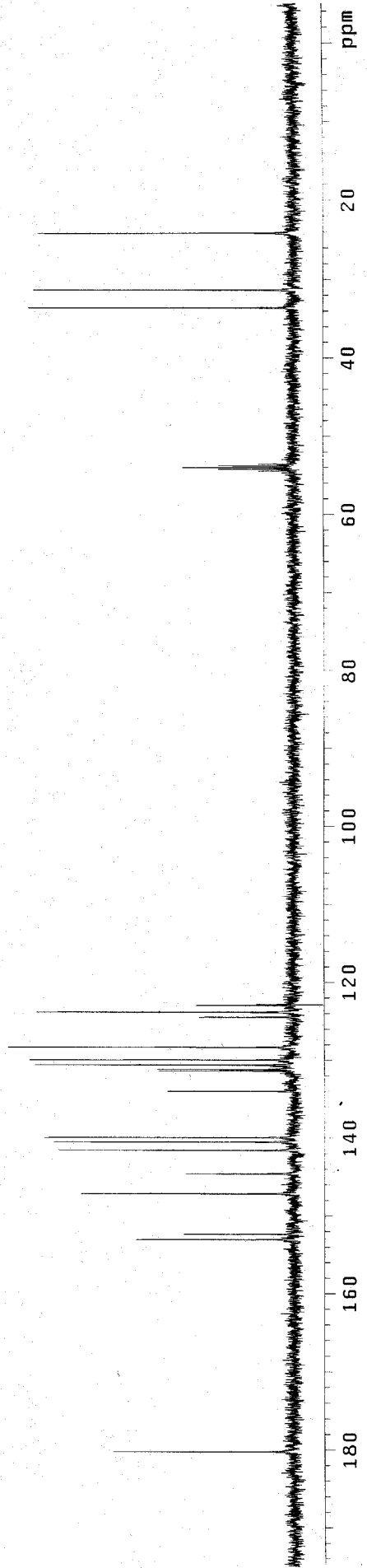


Chart S2. ¹³C NMR spectrum for the protonation of 1.

STANDARD CARBON PARAMETERS

Pulse Sequence: hetcor

Solvent: CD2CL2

Temp: -60.0 C / 213.2 K

User: 1-14-87

File: t099111201-HETCOR-CD2CL2-5

INOVA-500 "ksu500"

PULSE SEQUENCE: hetcor

Relax. delay 0.800 sec

Acq. time 0.163 sec

Width 24509.8 Hz

2D Width 6680.0 Hz

16 repetitions

128 increments

OBSERVE C13, 125.7013210 MHZ

DECOUPLE H1, 499.9090206 MHZ

Power 35 dB

on during acquisition

off during delay

WALTZ-16 modulated

DATA PROCESSING

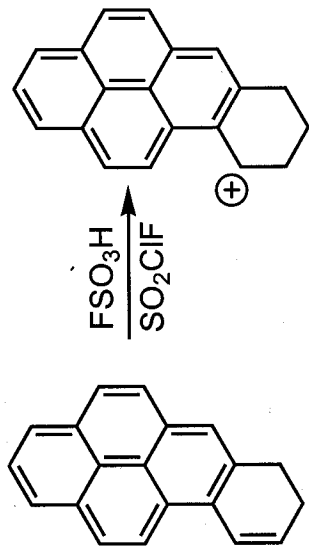
Sine bell 0.042 sec

F1 DATA PROCESSING

Sine bell 0.020 sec

FT size 8192 x 1024

Total time 34 min, 2 sec



HETCOR at -60°C

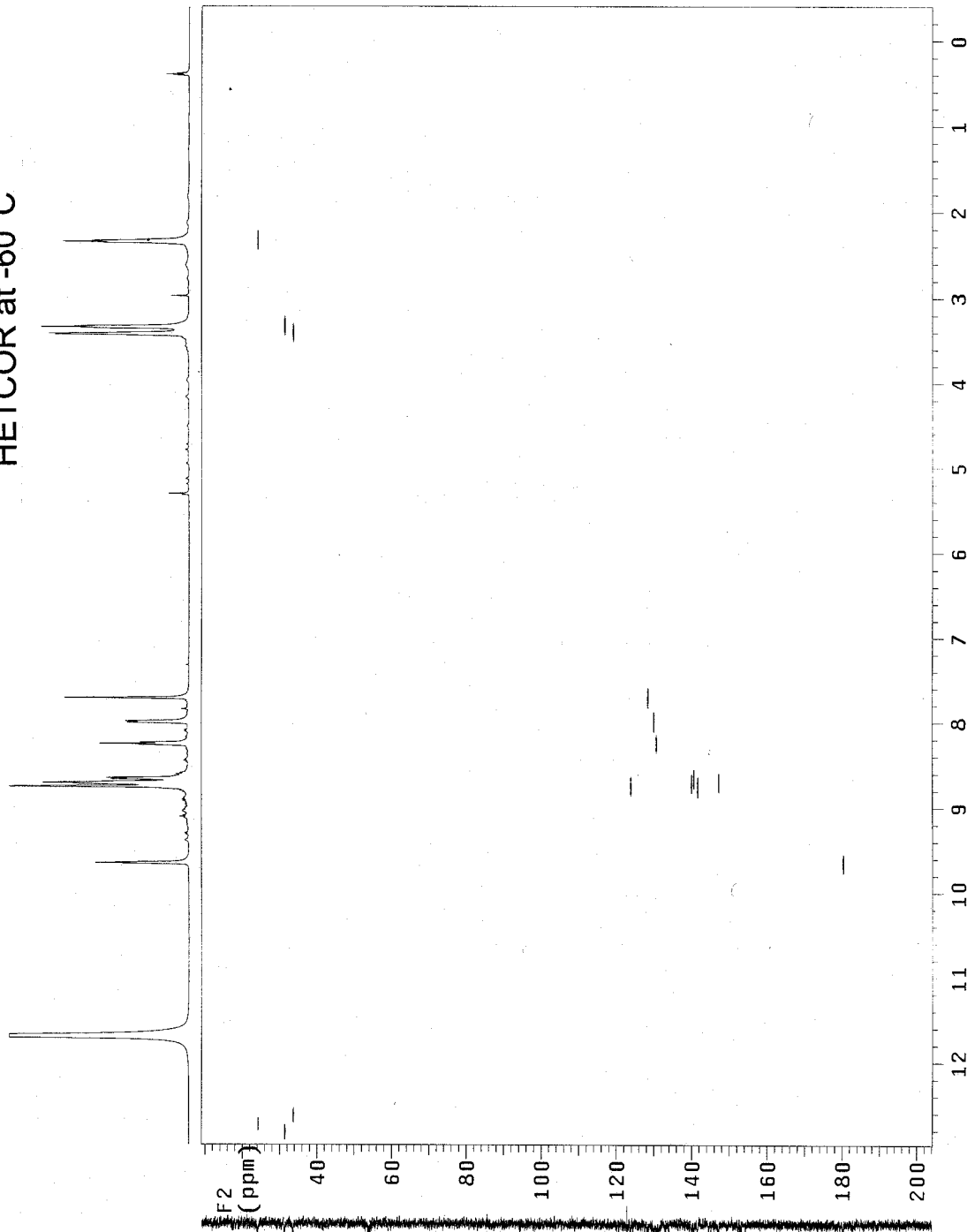


Chart S3. HETCOR chart for the protonation of 1.

okazaki/cation

Pulse Sequence: relayh

Solvent: CD2CL2
Temp. -60.0 C / 213.2 K
File: to99111201-COSY-CD2C12-5
INDVA-500 "ksu500"

PULSE SEQUENCE: relayh

Relax. delay 0.400 sec

COSY 90-90

Acq. time 0.599 sec

Width 6679.5 Hz

2D Width 6679.5 Hz

4 repetitions

128 increments

OBSERVE H1, 499.9058785 MHz

DATA PROCESSING

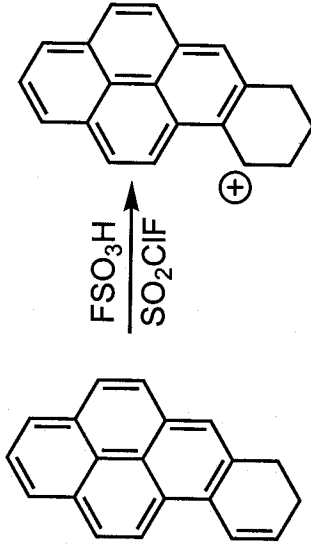
Sine bell 0.295 sec

F1 DATA PROCESSING

Sine bell 0.009 sec

FT size 8192 x 1024

Total time 8 min, 43 sec



H/H COSY at -60°C

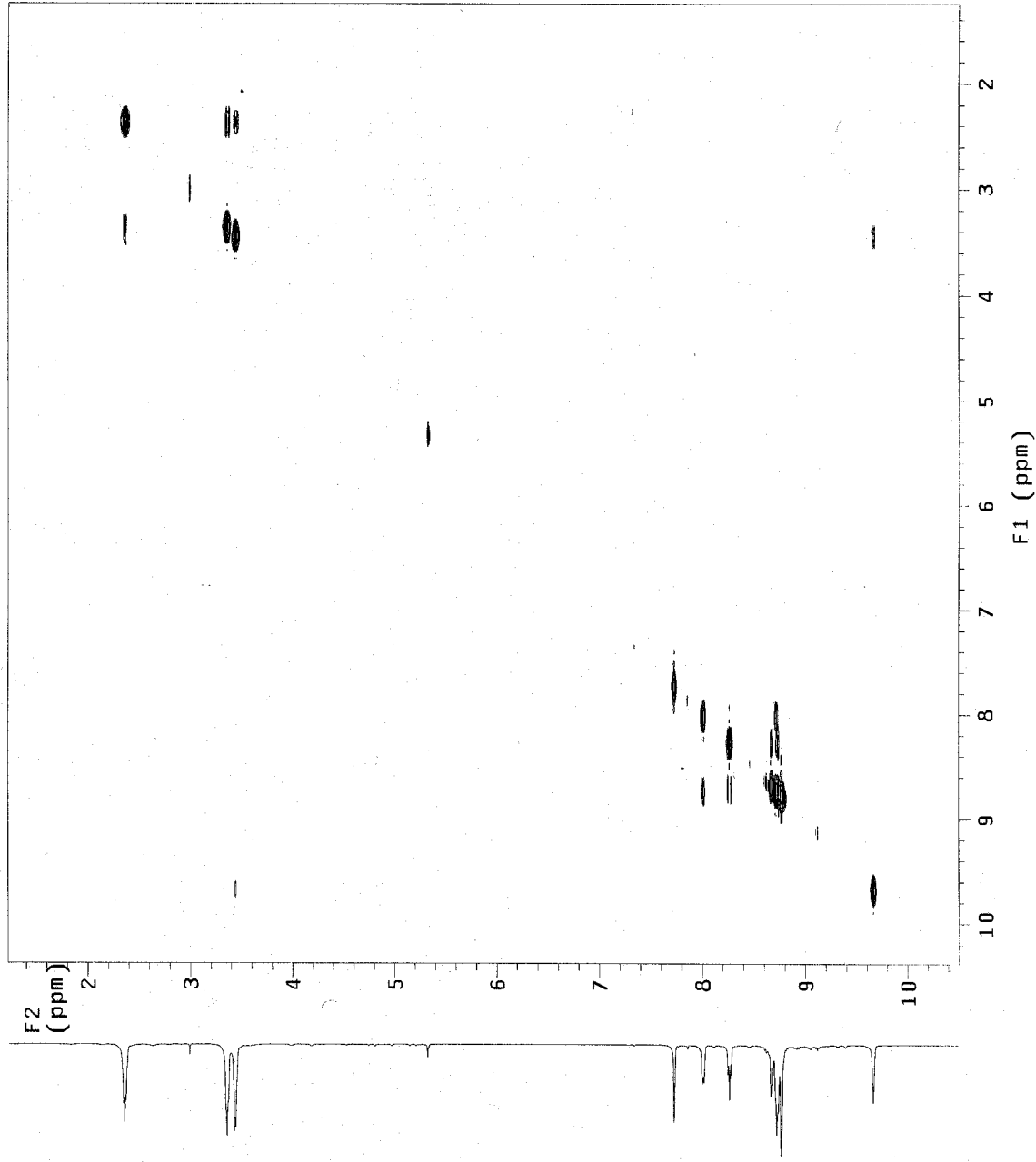


Chart S4. H/H COSY chart for the protonation of 1.

5mmsw, H lineshape
spin, 7-8-98

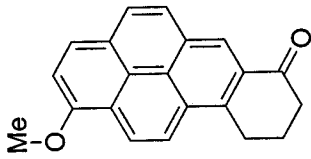
exp9 s2pu1

SAMPLE DEC. & VT
date Feb 17 2000 dfrq
solvent CD2CL2 dn
file /export/home/~
laali/okazaki104/to~ dpwr 30
00021706-H703-CD2C~ dm
L2-5.fid dmm
L2-5.fid dmf 200

ACQUISITION
sfrq 499.910 dseq
tn H1 dres
at 1.384 homo n
np 32000 temp
sw 11562.4 DEC2
fb 6000 dfrq2 0
bs 4 dn2 1
tpwr 55 dpwr2 1
pw 12.0 dof2 0
dl 1.000 dmZ n
tof 1918.9 dmm2 c
nt 16 dmi2 200
ct 16 dseq2
alock n dres2 1.0
gain not used homo2 n

PROCESSING
i1 n wfile
in n proc ft
dp y fn not used
hs nn math f

DISPLAY
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wp 6998.3 wexp
vs 616 wbs
sc 0 wnt
wc 250
hzmm 27.99
ls 1836.26
rf1 1380.1
rfp 0
th 2
ins 1.000
nm cdc ph



FSO₃H
SO₂ClF
→
¹H NMR at -70°C

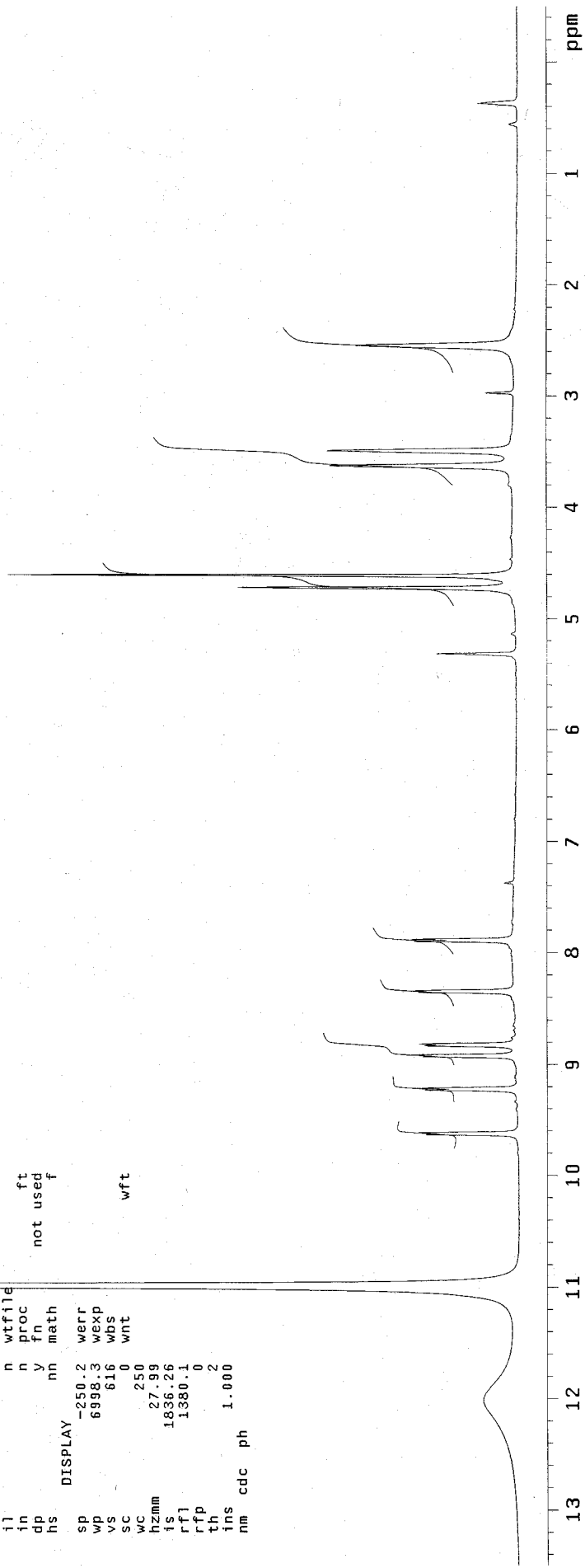


Chart S5. ¹H NMR spectrum for the protonation of 6.

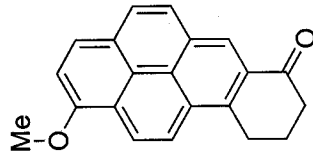
Origin of the broad-hump around 12 ppm in the ¹H NMR spectrum of 6H₂²⁺ is uncertain; it exhibited temperature dependency and was significantly broader than the FSO₃H peak. This peak was not observed in the case of 7H₂²⁺ (see proton spectrum in Chart S8; the COH⁺ signal at d 14.50 is not shown).

STANDARD CARBON PARAMETERS

```

exp8 s2pu1
SAMPLE DEC. & VT
date Feb 17 2000 dfrq
solvent CD2CL2 dn
file /export/home/~ dpwr 35
lsali/okazaki04/to~ dof 0
00021706-C70-CD2C1~ dm nvy
2-5.fid dmm 10800
ACQUISITION: dmf 10800
sfrq 125.716 dseq
tn C13 dres 1.0
at 0.640 homo n
np 64000 temp -70.0
sw 50000.0 DEC2
fb not used dfrq2 0
bs dn2 4
tpwr 52 dpwr2 1
pw 16.0 dof2 0
d1 0.500 dmm2 n
d2 0.500 dmm2 c
tof 2423.4 dmf2 10000
nt 10000 dseq2
ct 1328 dres2 1.0
homo2 n
gain not used lb PROCESSING
flags n wtfile 1.00
in n n
dp y n proc ft
hs nn math not used f
DISPLAY
sp -629.3 werr
wp 31424.9 wexp
vs 41 wbs
sc 0 wnt
wc 250
hzmm 125.70
is 4250.00
rfl 17352.5
rff 6787.9
th 6
ins 1.000
nm cdc ph

```



$\xrightarrow[\text{SO}_2\text{ClF}]{\text{FSO}_3\text{H}}$
 $^{13}\text{C NMR at } -70^\circ\text{C}$

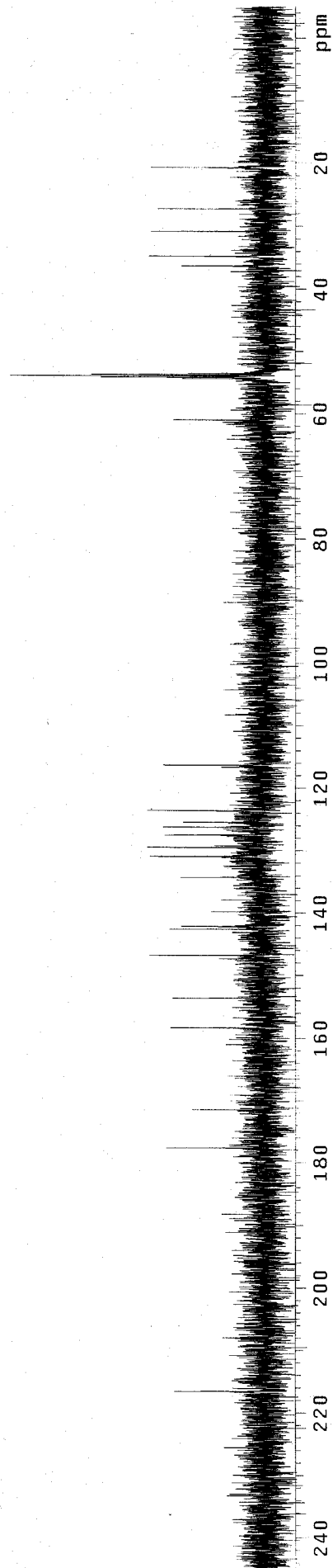


Chart S6. $^{13}\text{C NMR}$ spectrum for the protonation of **6**.

okazaki/cation

Pulse Sequence: relayh

Solvent: CD2Cl2

Temp. -70.0 C / 203.2 K

File: to00021706-COSY70-CD2Cl2-5

INOVA-500 "ksu500"

PULSE SEQUENCE: relayh

Relax. delay 0.400 sec

COSY 90-90

Acq. time 0.449 sec

Width 4490.3 Hz

2D Width 4490.3 Hz

4 repetitions

128 increments

OBSERVE H1, 499.9058794 MHz

DATA PROCESSING

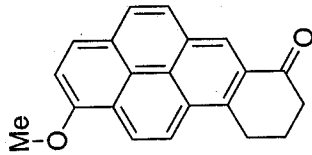
Sine bell 0.224 sec

F1 DATA PROCESSING

Sine bell 0.014 sec

FT size 4096 X 512

Total time 7 min, 28 sec



$\xrightarrow[\text{SO}_2\text{ClF}]{\text{FSO}_3\text{H}}$ H/H COSY at -70°C

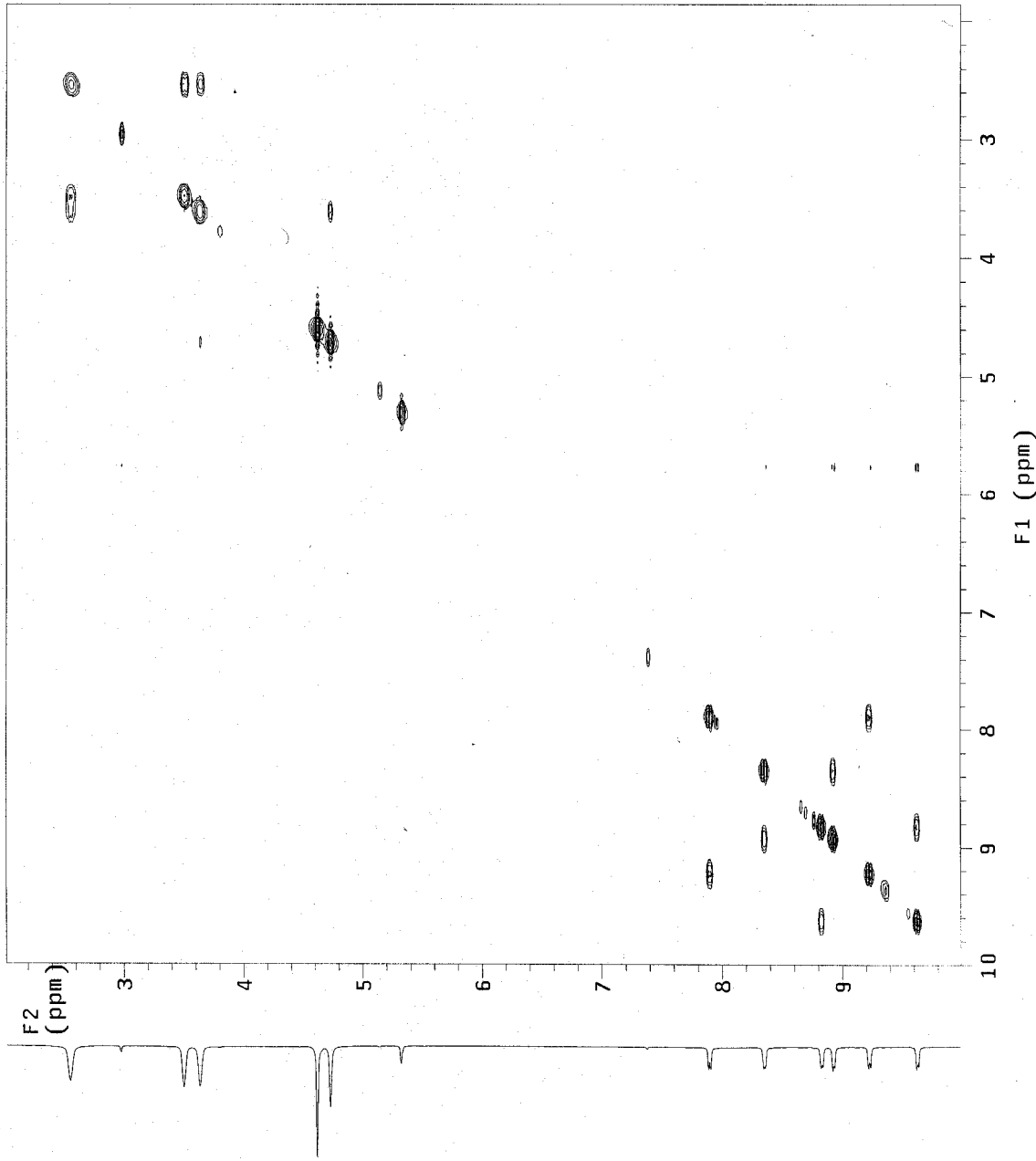


Chart S7. H/H COSY chart for the protonation of **6**.

S10

Smsw, H lineshape
spin, 7-8-98
exp9 s2pul

date Feb 18 2000
solvent C02CL2
file /export/home/...
00021802-H70-CD2Cl2

DEC. & VT
dfrq 499.910
dn H1
dpwr 30
dof 1343.5
dm n
dmm c
dseq 200

ACQUISITION
sfrq 499.910
tn H1
at 1.384
np 32000
sw 11562.4
fb 8000

dresq
homo n
temp -70.0
DEC2
dfrq2 0
dn2 4
tpwr 55
pw 0
dl 12.0
tof 1918.8

dm2 n
dmm2 c
nt 18
ct 16
dseq2 200
alock n
gain 1.0

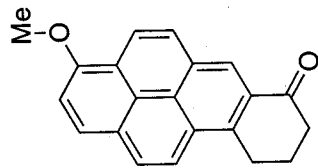
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in n
dp n
hs n

wtfile
proc ft
fn not used
math f

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wp 6498.6
vs 2116
sc 250
wc 250

hzmm
is 2236.99
rfl 4042.9
rffp 2659.5
th 2
ins 1.000
nm cdc ph

wft



FSO₃H
SO₂ClF
→
¹H NMR at -70°C

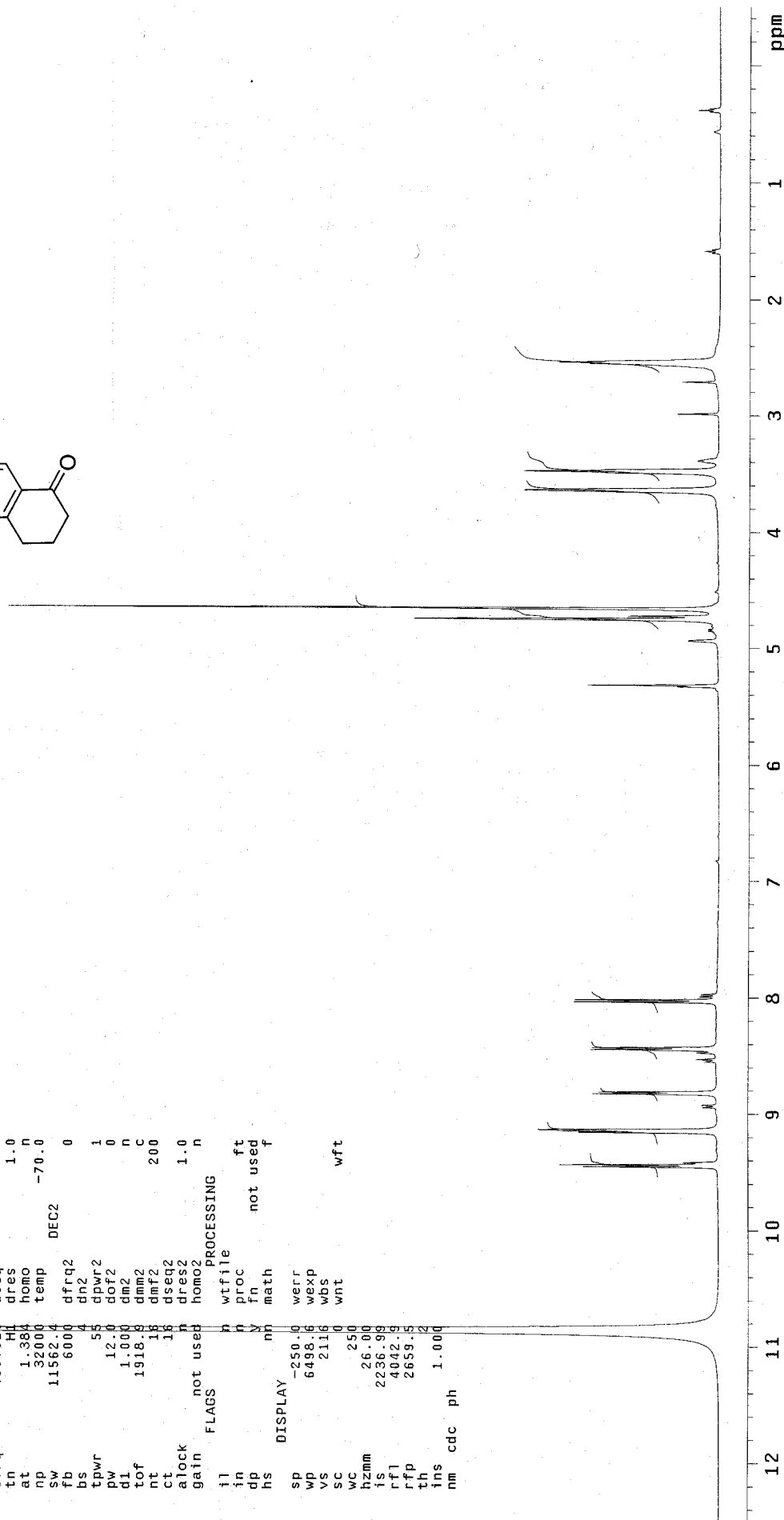


Chart S8. ¹H NMR spectrum for the protonation of 7.

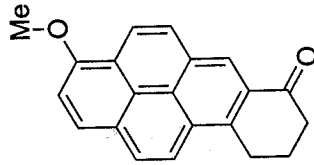
The COH⁺ signal at δ 14.50 is not shown.

STANDARD CARBON PARAMETERS

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solvent CD2CL2 dn HI 35
file /export/home/~dpwr dpwr 0
laali/okazaki04/to~ dof 0
00021802-C70-CD2CL~ dm nvy w
2-5.fid dnm 10800
ACQUISITION
sfrq 125.716 dseq
tn C13 dres 1.0
at 0.640 homo n
np 64000 temp DEC2 -70.0
sw 50000.0 dfrq2 0
bs not used 4 dn2
tpwr 52 dpwr2 1
pw 16.0 dof2 0
d1 0.500 dm2 n
d2 0.500 dnm2 C
tof 2423.4 dmf2 10000
nt 10000 dseq2
ct 380 dres2 1.0
alock n homo2 n
gain not used lb PROCESSING 2.00
flags f1 n wifile
in n n
dp y n proc ft
hs nn math not used f
DISPLAY
sp -629.8 werr
wp 31424.9 wexp
vs 44 wbs
sc 0 wnt
wc 250
hzmm 125.70
ts 4250.00
rfl 17348.3
rff 6787.9
th 6
ins cdc ph 1.000
nm

```



FSO₃H
SO₂ClF
→
¹³C NMR at -70°C

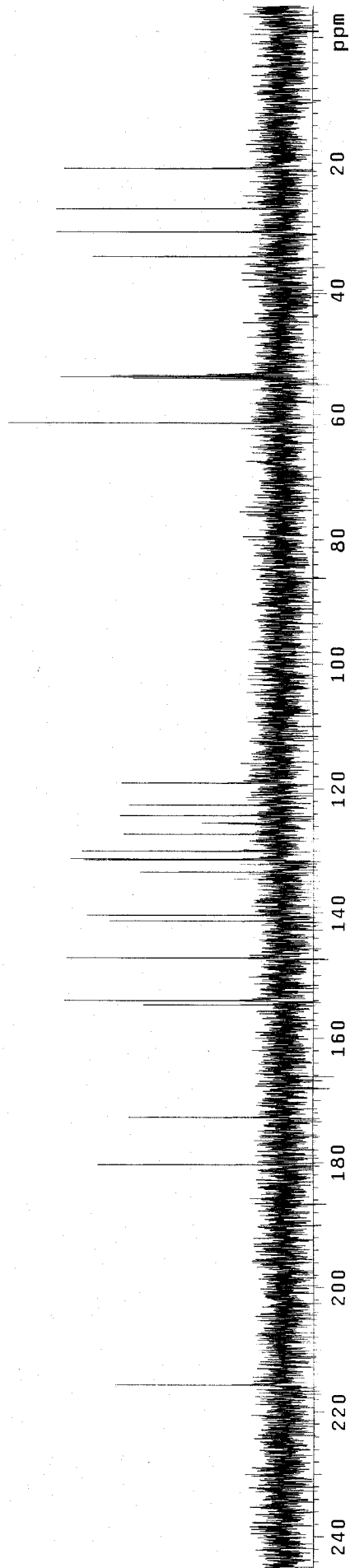


Chart S9. ¹³C NMR spectrum for the protonation of 7.

okazaki/cation

Pulse Sequence: relayh

Solvent: CD2Cl2

Temp. -70.0 C / 203.2 K

File: t00021802-COSY70-CD2Cl2-5

INOVA-500 "ksu500"

PULSE SEQUENCE: relayh

Relax delay 0.700 sec

COSY 90-90

Acq. time 0.243 sec

Width 4216.7 Hz

2D Width 4216.7 Hz

4 repetitions

128 increments

OBSERVE H1, 499.9058840 MHz

DATA PROCESSING

Sine bell 0.116 sec

F1 DATA PROCESSING

Sine bell 0.014 sec

FT size 2048 x 512

Total time 8 min, 17 sec

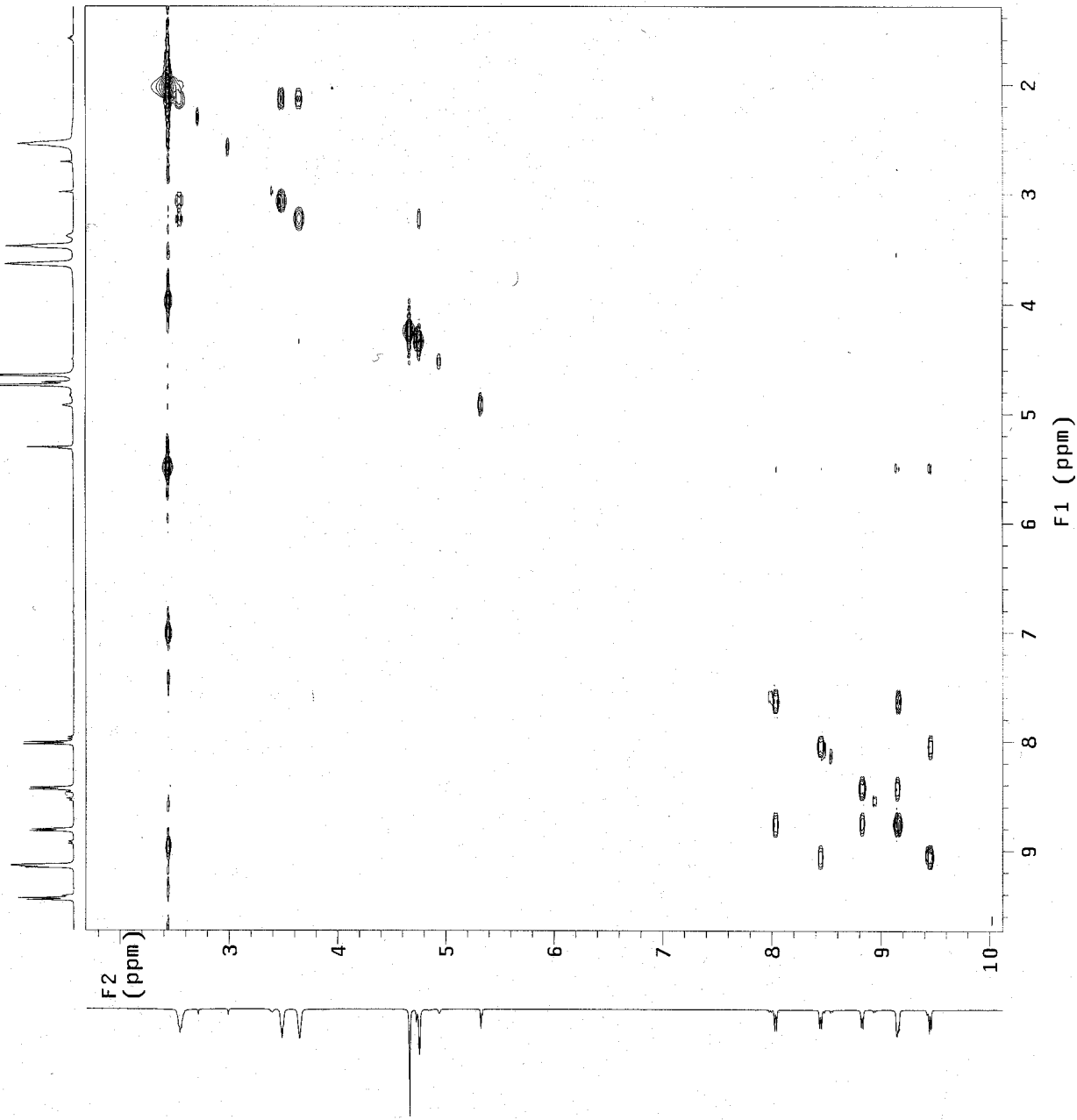
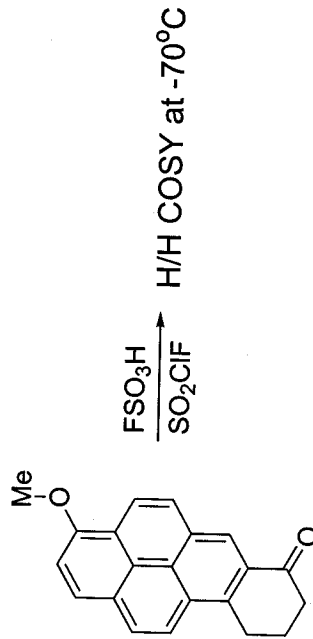


Chart S10. H/H COSY chart for the protonation of 7.

S13

Table S1. Electronic Energies (E), Zero Point Energies (ZPE) and Relative Energies ($\Delta(E+ZPE)$) Obtained from DFT Calculations at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level.

Compd	E, hartree ^a	ZPE, hartree ^a	E+ZPE, hartree ^a	$\Delta(E+ZPE)$, kcal/mol
2H⁺	-770.9690272	0.289719	-770.679308	
1H⁺	-770.9850750	0.290139	-770.694936	-9.8 ^b
3aH⁺	-3342.0581556	0.279515	-3341.778641	
3bH⁺	-3342.0757458	0.280124	-3341.795622	-10.7 ^c
4aH⁺	-1230.5476092	0.279807	-1230.267802	
4bH⁺	-1230.5649246	0.280329	-1230.284596	-10.5 ^d
5aH⁺	-870.1962905	0.281205	-869.915086	
5bH⁺	-870.2134295	0.281675	-869.931754	-10.5 ^e
6aH₂⁺	-960.9866305	0.339322	-960.647309	
6bH₂⁺	-960.9798675	0.338721	-960.641147	3.9 ^f
7aH₂⁺	-960.9829508	0.339178	-960.643772	
7bH₂⁺	-960.9832940	0.338743	-960.644551	-0.5 ^g
9aH⁺	-921.4010368	0.298625	-921.102412	
9bH⁺	-921.341218	0.294809	-921.046409	35.1 ^h

^a 1 hartree = 627.5096 kcal/mol. ^b Relative to **2H⁺**. ^c Relative to **3aH⁺**. ^d Relative to **4aH⁺**.

^e Relative to **5aH⁺**. ^f Relative to **6aH₂⁺**. ^g Relative to **7aH₂⁺**. ^h Relative to **9bH⁺**.