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]

		Page
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}	S2-3
Chart S1.	^{1}H NMR spectrum for the protonation of **1**.	S4
Chart S2.	^{13}C NMR spectrum for the protonation of **1**.	S5
Chart S3.	HETCOR chart for the protonation of **1**.	S6
Chart S4.	H/H COSY chart for the protonation of **1**.	S7
Chart S5.	^{1}H NMR spectrum for the protonation of **6**. Origin of the broad-hump around 12 ppm in the ^{1}H NMR spectrum of $\mathbf{6H_2}^{2+}$ is uncertain; it exhibited temperature dependency and was significantly broader than the FSO_3H peak. This peak was not observed in the case of $\mathbf{7H_2}^{2+}$ (see proton spectrum in Chart S8; the COH^+ signal at δ 14.50 is not shown).	S8
Chart S6.	^{13}C NMR spectrum for the protonation of **6**.	S9
Chart S7.	H/H COSY chart for the protonation of **6**.	S10
Chart S8.	^{1}H NMR spectrum for the protonation of **7.** The COH^+ signal at δ 14.50 is not shown.	S11
Chart S9.	^{13}C NMR spectrum for the protonation of **7**.	S12
Chart S10.	H/H COSY chart for the protonation of **7**.	S13
Table S1.	Electronic Energies (E), Zero Point Energies (ZPE) and Relative Energies (Δ(E+ZPE)) Obtained from DFT Calculations at the B3LYP/6-31G(d)// B3LPY/6-31G(d) level.	S14

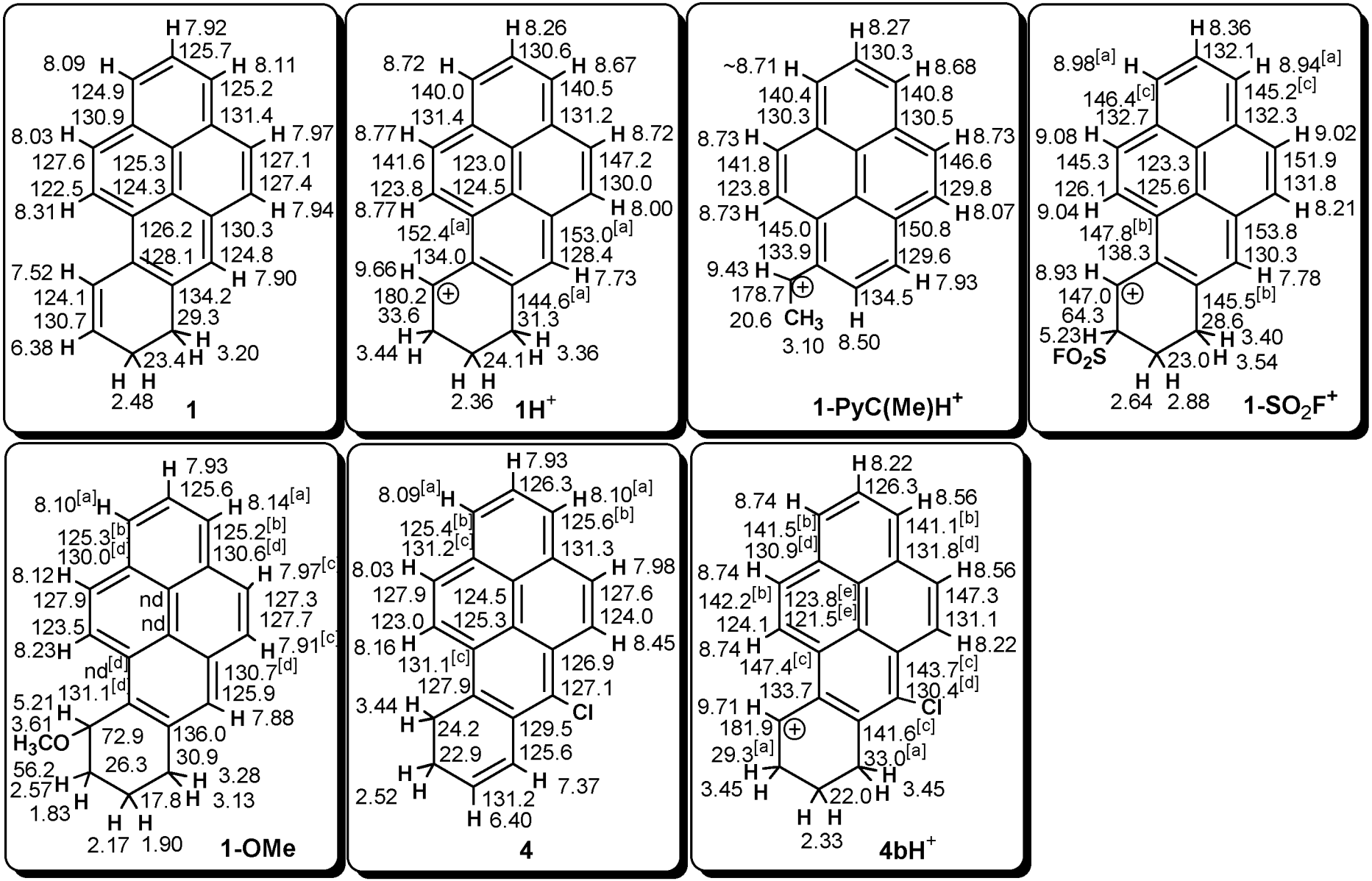


Figure S1. NMR data for the substrates and their persistent carbocations.
(NMR data for 1-(1-pyrenyl)ethyl cation are included for comparison)
{superscripts [a], [b], [c], [d], and [e] denote interchangeable assignments. nd: not detected}

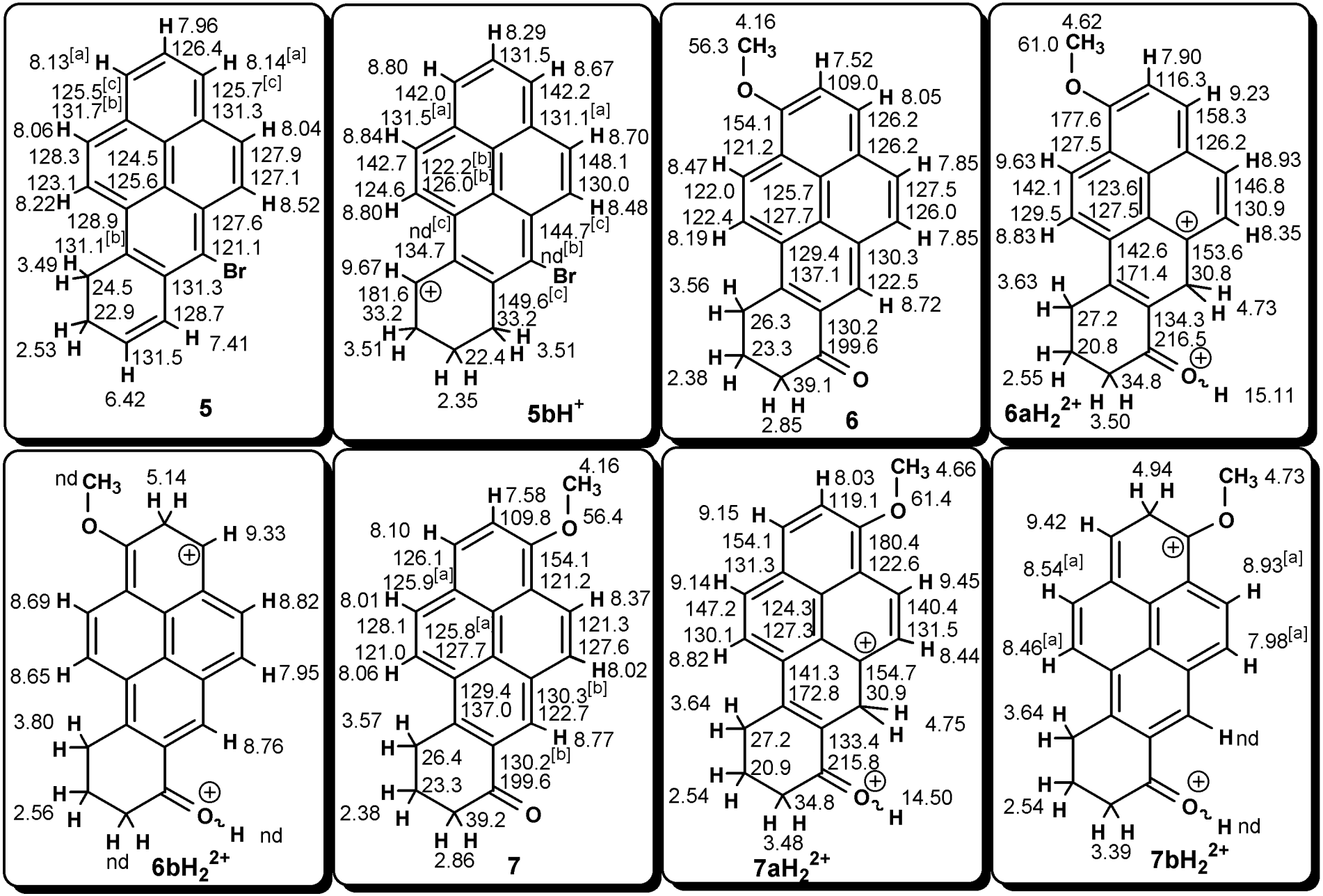


Figure S1,cont'd.

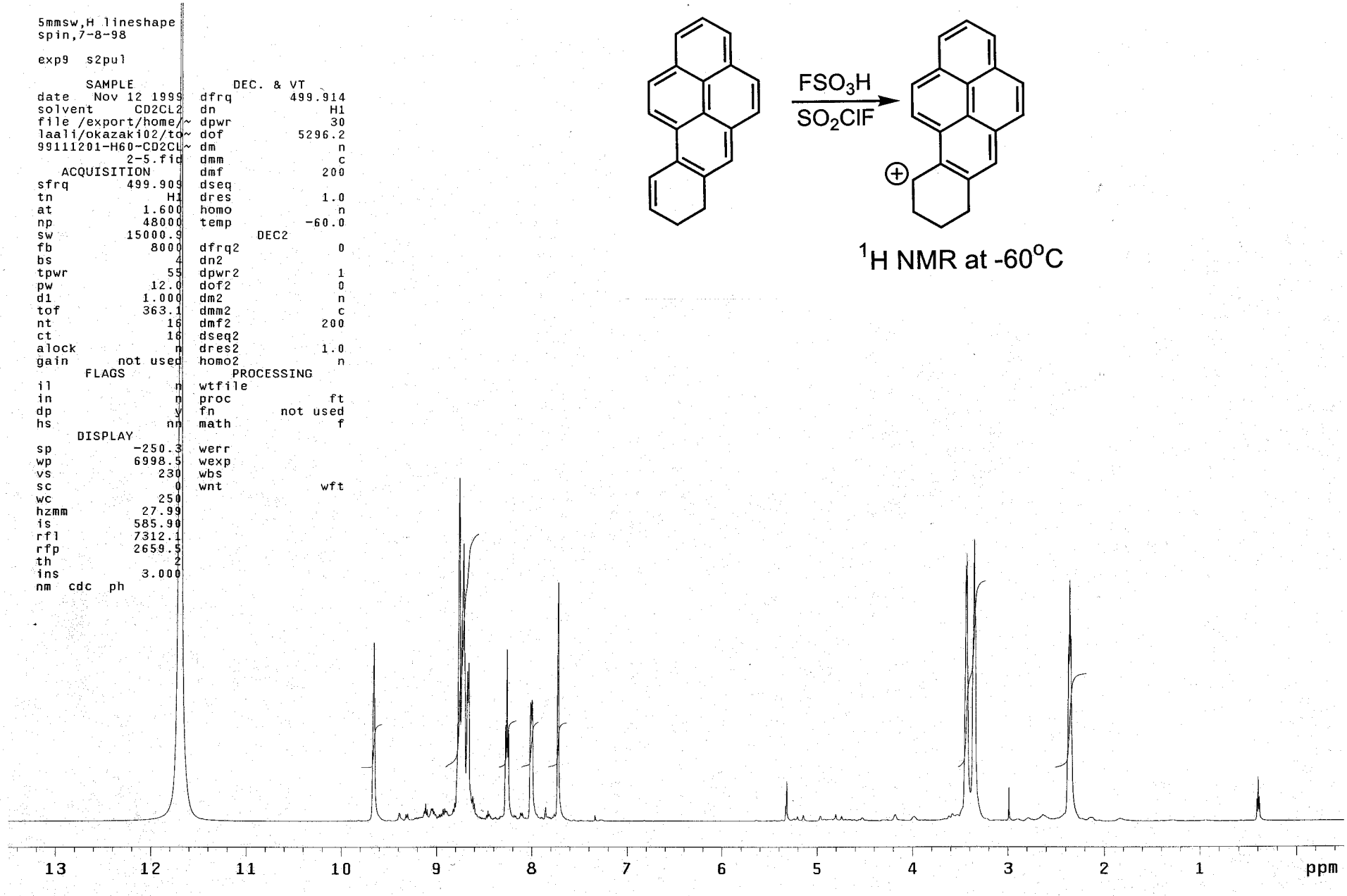
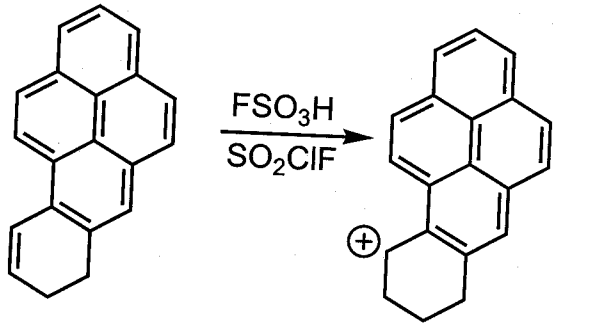


Chart S1. ^{1}H NMR spectrum for the protonation of **1**.

STANDARD CARBON PARAMETERS

exp8 s2pul

SAMPLE		DEC. & VT	
date	Nov 12 1999	dfrq	499.908
solvent	CD2CL2	dn	H1
file	/export/home/~	dpwr	35
laali/okazaki02/to~		dof	0
99111201-C60-CD2CL~		dm	nyy
	2-5.fid	dmm	w
ACQUISITION		dmf	10800
sfrq	125.716	dseq	
tn	C13	dres	1.0
at	1.066	homo	n
np	106560	temp	-60.0
sw	50000.0	DEC2	
fb	not used	dfrq2	0
bs	4	dn2	
tpwr	52	dpwr2	1
pw	11.0	dof2	0
d1	0.500	dm2	n
d2	0.500	dmm2	c
tof	2423.4	dmf2	10000
nt	10000	dseq2	
ct	96	dres2	1.0
alock	s	homo2	n
gain	60	PROCESSING	
FLAGS		lb	2.00
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-628.9	werr	
wp	25141.5	wexp	
vs	46	wbs	
sc	0	wnt	
wc	250		
hzmm	100.57		
is	4250.00		
rfl	17343.1		
rfp	6788.2		
th	3		
ins	1.000		
nm cdc ph			



^{13}C NMR at -60°C

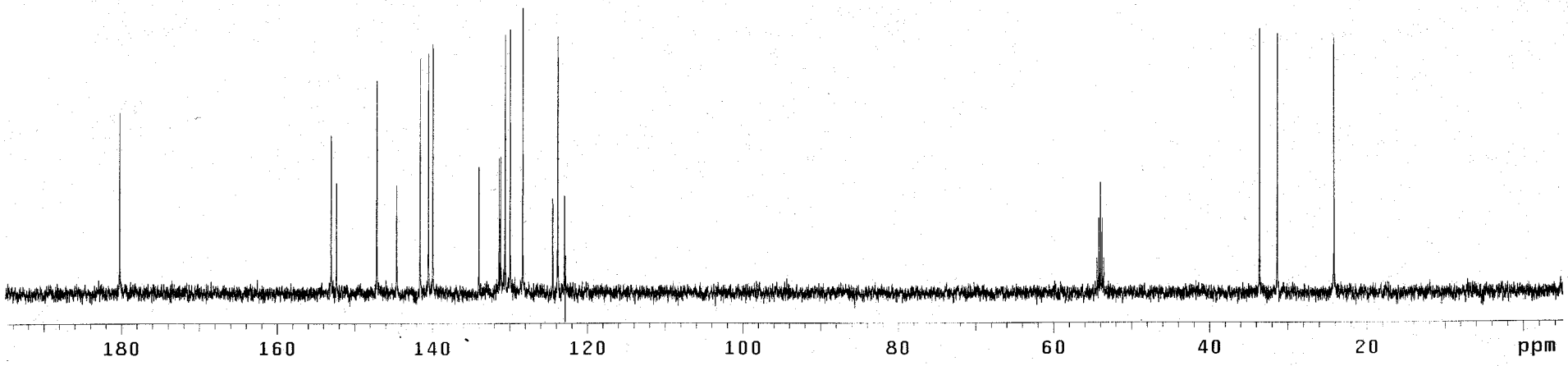


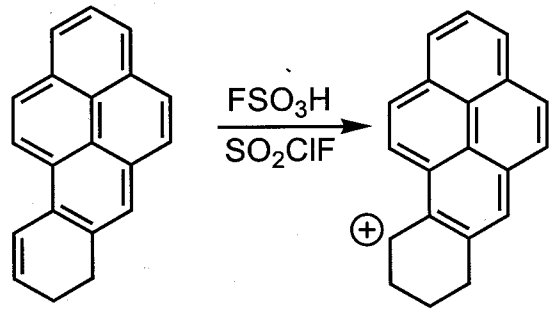
Chart S2. ^{13}C NMR spectrum for the protonation of **1**.

STANDARD CARBON PARAMETERS

Pulse Sequence: hetcor

Solvent: CD2CL2
Temp. -60.0 C / 213.2 K
User: 1-14-87
File: to99111201-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

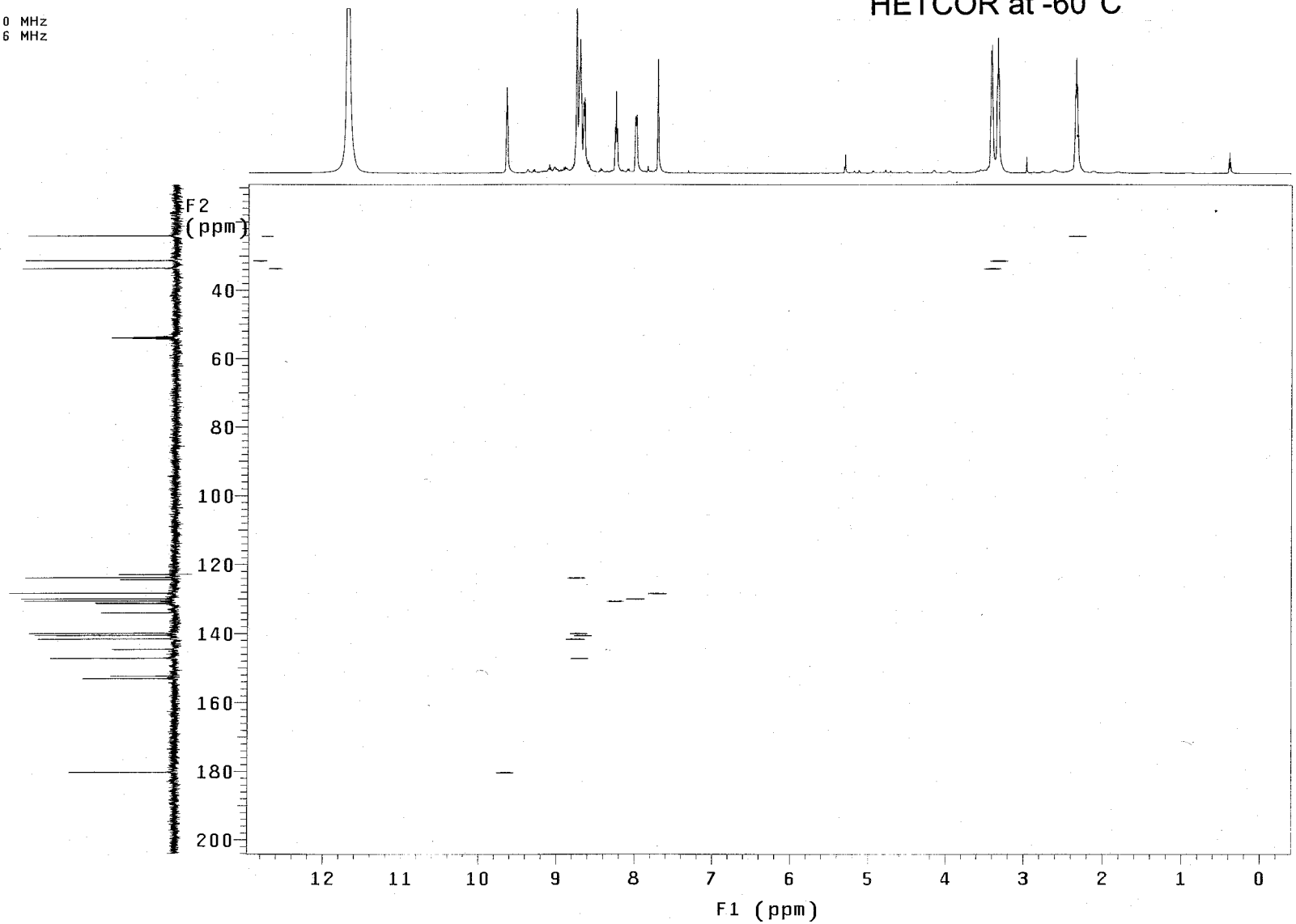
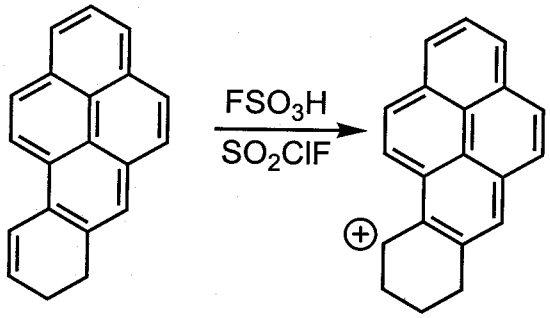


Chart S3. HETCOR chart for the protonation of **1**.

okazaki/cation

Pulse Sequence: relayh
Solvent: CD2Cl2
Temp. -60.0 C / 213.2 K
File: to99111201-COSY-CD2Cl2-5
INOVA-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

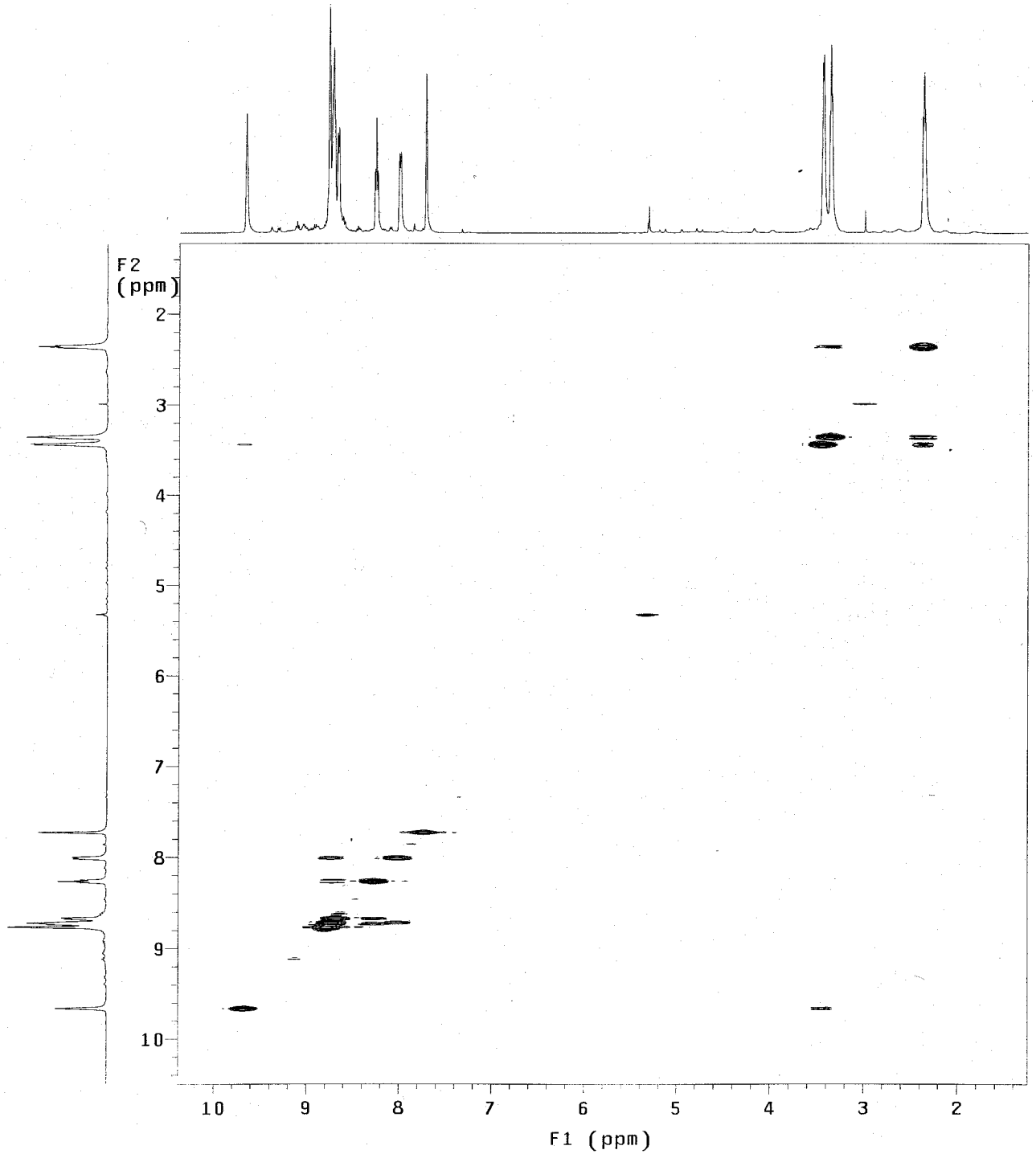


Chart S4. H/H COSY chart for the protonation of **1**.

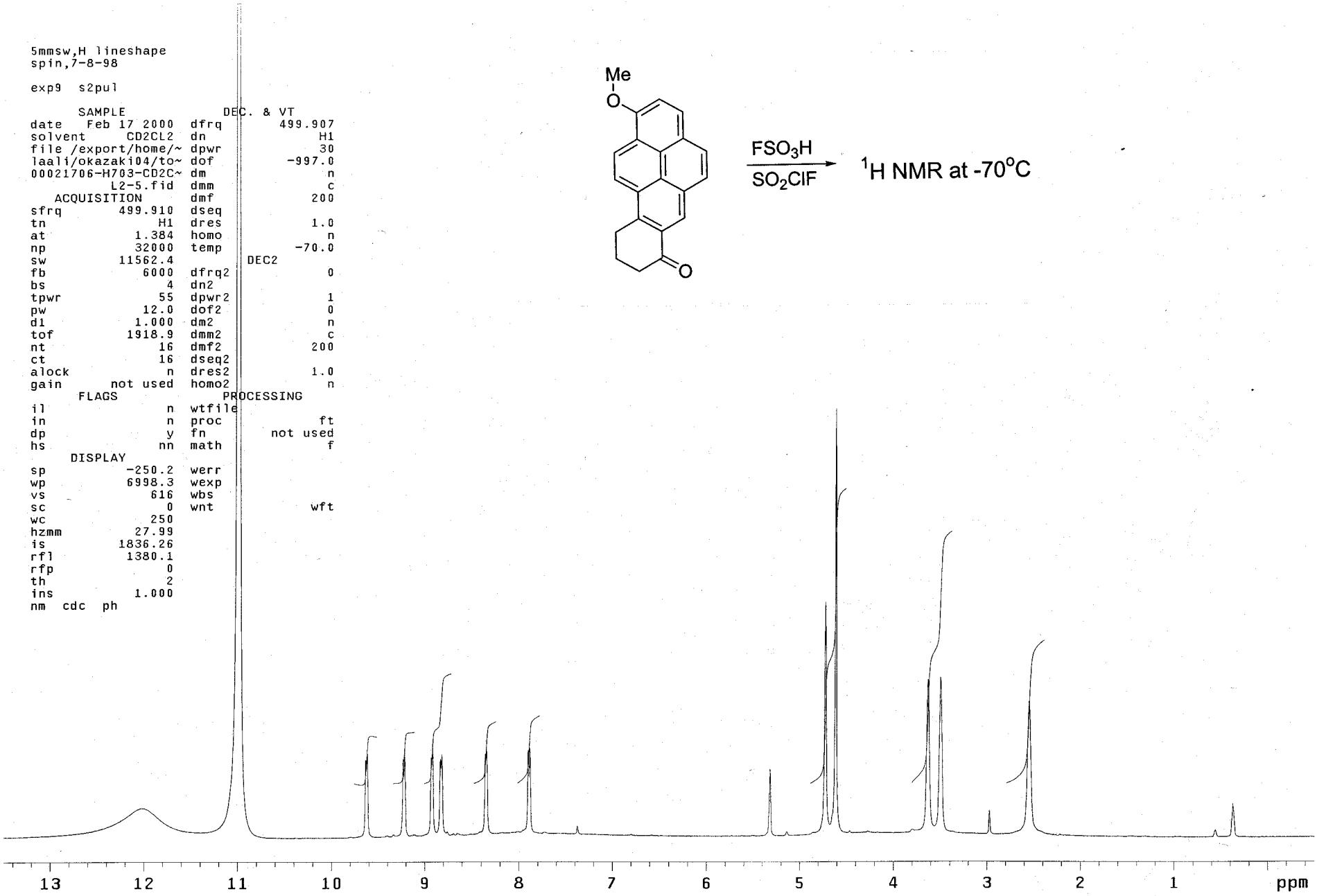


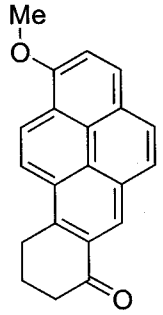
Chart S5. ^{1}H NMR spectrum for the protonation of **6**.

Origin of the broad-hump around 12 ppm in the ^{1}H NMR spectrum of $\mathbf{6H_2}^{2+}$ is uncertain; it exhibited temperature dependency and was significantly broader than the FSO_3H peak. This peak was not observed in the case of $\mathbf{7H_2}^{2+}$ (see proton spectrum in Chart S8; the COH^+ signal at d 14.50 is not shown).

STANDARD CARBON PARAMETERS

exp8 s2pul

SAMPLE		DEC. & VT	
date	Feb 17 2000	dfrq	499.908
solvent	CD2CL2	dn	H1
file	/export/home/~	dpwr	35
	laali/okazaki04/to~	dof	0
	00021706-C70-CD2Cl~	dm	nyy
	2-5.fid	dmm	w
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	4	dn2	
tpwr	52	dpwr2	1
pw	16.0	dof2	0
d1	0.500	dm2	n
d2	0.500	dmm2	c
tof	2423.4	dmf2	10000
nt	10000	dseq2	
ct	1328	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS		lb	1.00
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	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		
rfp	6787.9		
th	6		
ins	1.000		
nm cdc ph			



$\xrightarrow[SO_2ClF]{FSO_3H}$ ^{13}C NMR at -70°C

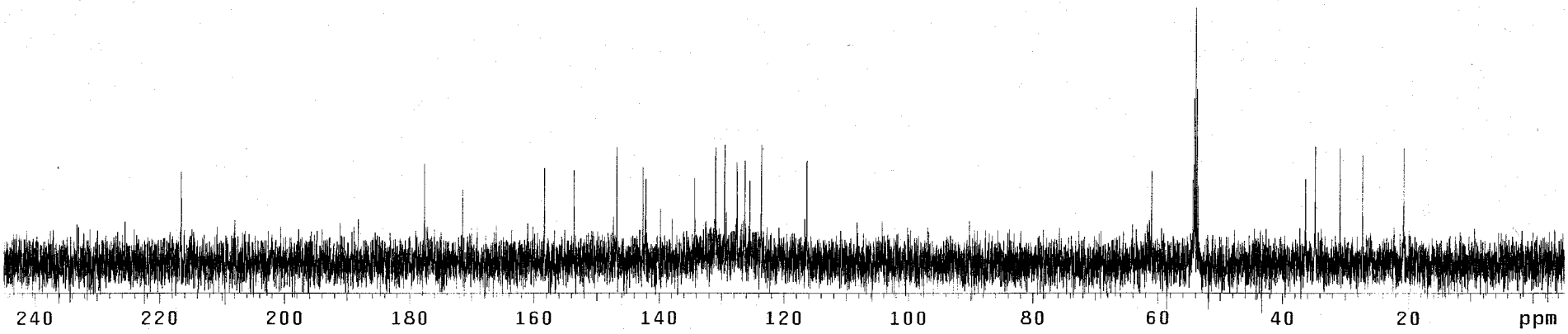


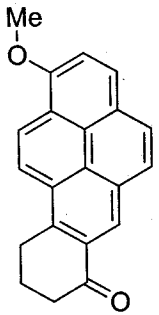
Chart S6. ^{13}C NMR spectrum for the protonation of **6**.

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



$\xrightarrow[SO_2ClF]{FSO_3H}$ H/H COSY at -70°C

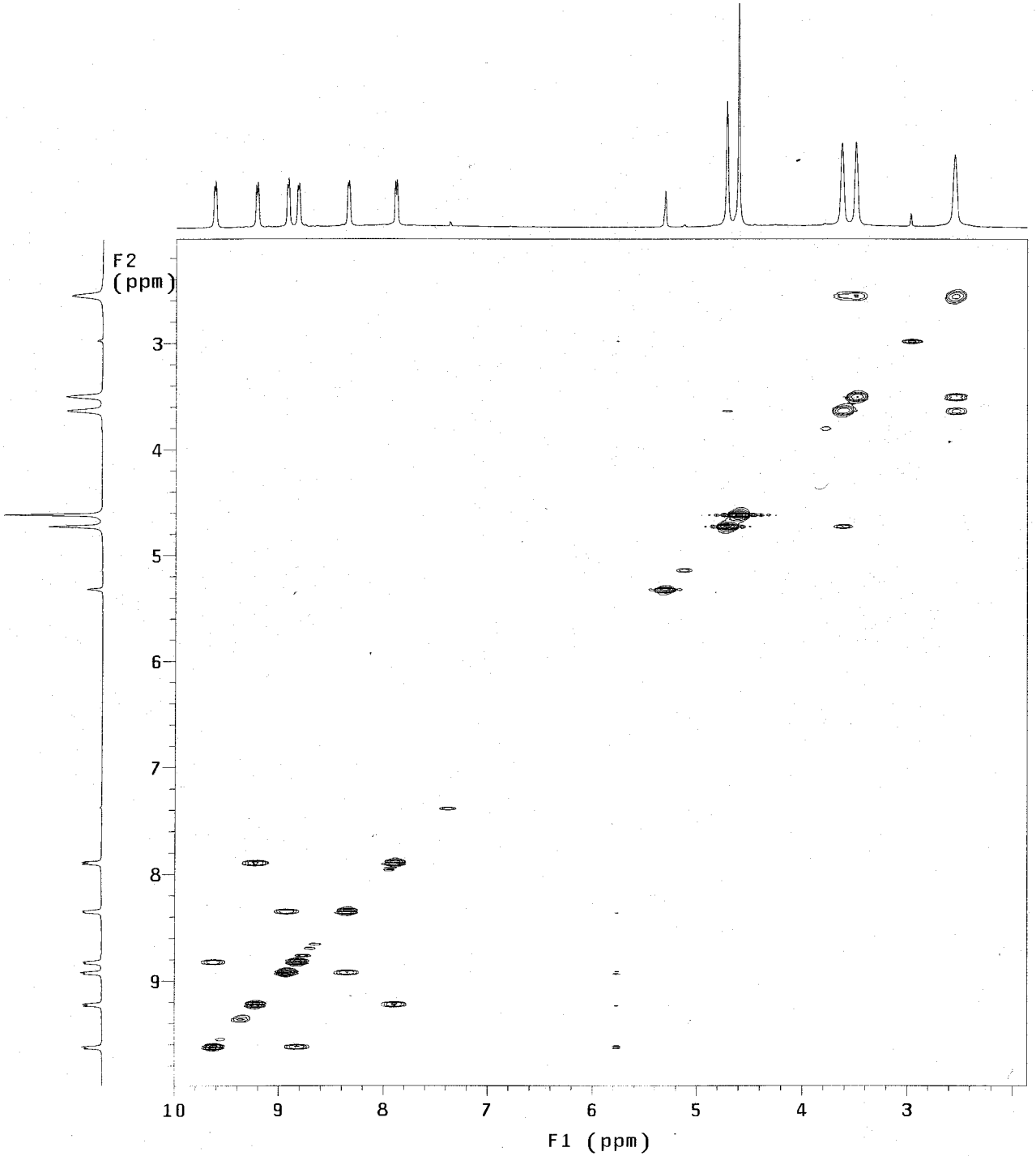


Chart S7. H/H COSY chart for the protonation of **6**.

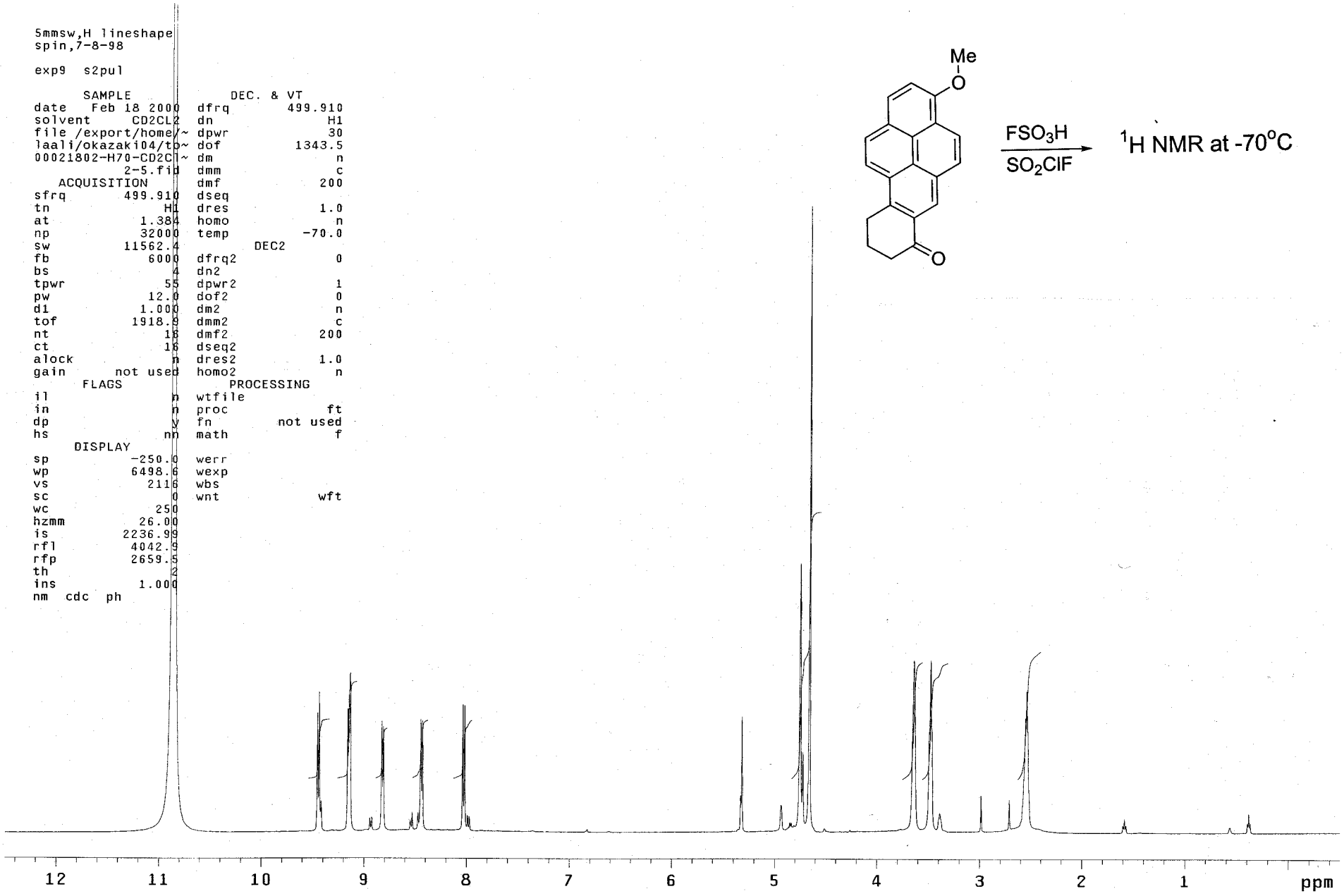


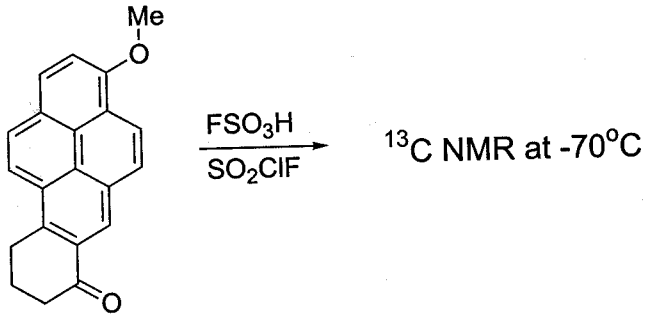
Chart S8. ^{1}H NMR spectrum for the protonation of **7**.

The COH^+ signal at δ 14.50 is not shown.

STANDARD CARBON PARAMETERS

exp8 s2pul

SAMPLE		DEC. & VT	
date	Feb 18 2000	dfrq	499.908
solvent	CD2CL2	dn	H1
file	/export/home/~	dpwr	35
	laali/okazaki04/to~	dof	0
	00021802-C70-CD2CL~	dm	nyy
	2-5.fid	dmm	w
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	4	dn2	
tpwr	52	dpwr2	1
pw	16.0	dof2	0
d1	0.500	dm2	n
d2	0.500	dmm2	c
tof	2423.4	dmf2	10000
nt	10000	dseq2	
ct	380	dres2	1.0
alock	n	homo2	n
gain	not used	PROCESSING	
FLAGS		lb	2.00
il	n	wtfile	
in	n	proc	ft
dp	y	fn	not used
hs	nn	math	f
DISPLAY			
sp	-629.8	werr	
wp	31424.9	wexp	
vs	44	wbs	
sc	0	wnt	
wc	250		
hzmm	125.70		
is	4250.00		
rfl	17348.3		
rfp	6787.9		
th	6		
ins	1.000		
nm cdc ph			



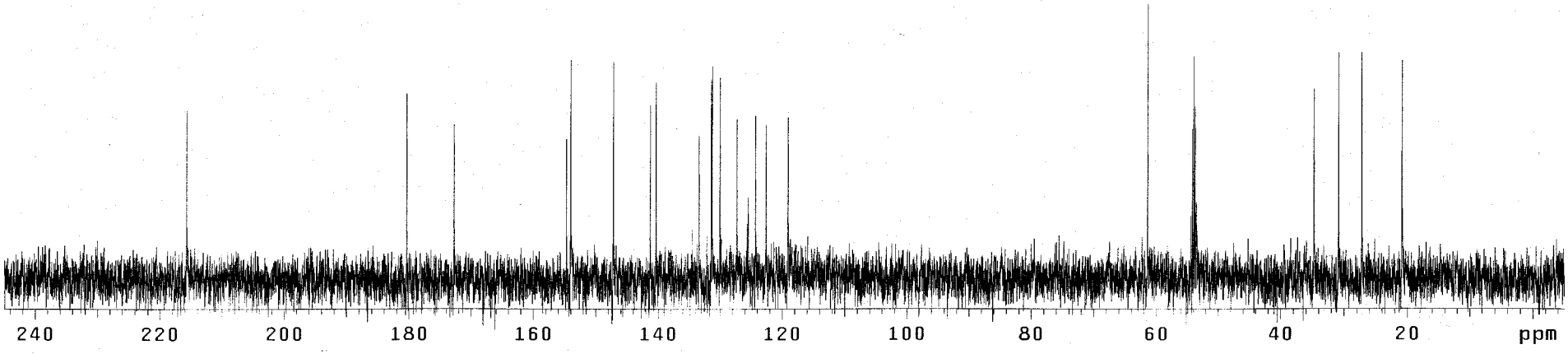


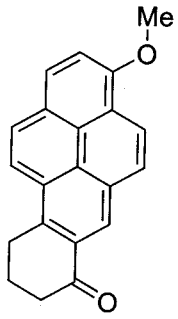
Chart S9. ^{13}C NMR spectrum for the protonation of **7**.

okazaki/cation

Pulse Sequence: relayh

Solvent: CD2CL2
Temp. -70.0 C / 203.2 K
File: to00021802-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



$\xrightarrow[SO_2ClF]{FSO_3H}$ H/H COSY at -70°C

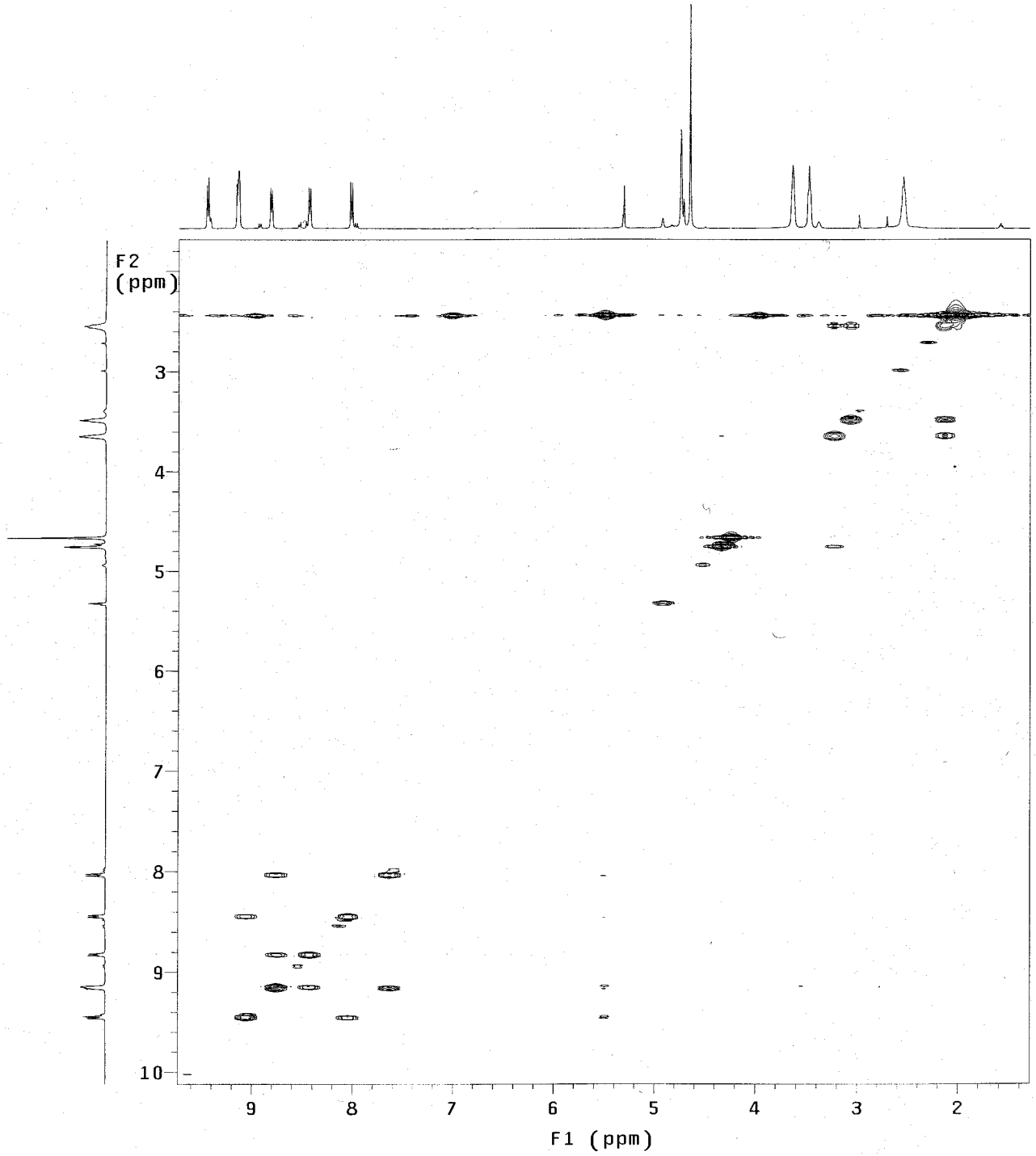


Chart S10. H/H COSY chart for the protonation of **7**.

Table S1. Electronic Energies (E), Zero Point Energies (ZPE) and Relative Energies (Δ(E+ZPE)) Obtained from DFT Calculations at the B3LYP/6-31G(d)//B3LPY/6-31G(d) level.

Compd	E, hartree[a]	ZPE, hartree[a]	E+ZPE, hartree[a]	Δ(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]
6aH$_2$ $^+$	-960.9866305	0.339322	-960.647309	
6bH$_2$ $^+$	-960.9798675	0.338721	-960.641147	3.9[f]
7aH$_2$ $^+$	-960.9829508	0.339178	-960.643772	
7bH$_2$ $^+$	-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 **6aH$_2$**$^+$. [g] Relative to **7aH$_2$**$^+$. [h] Relative to **9bH**$^+$.