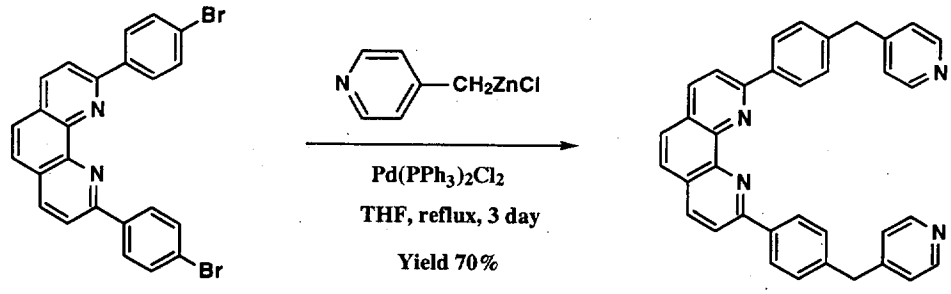
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 1

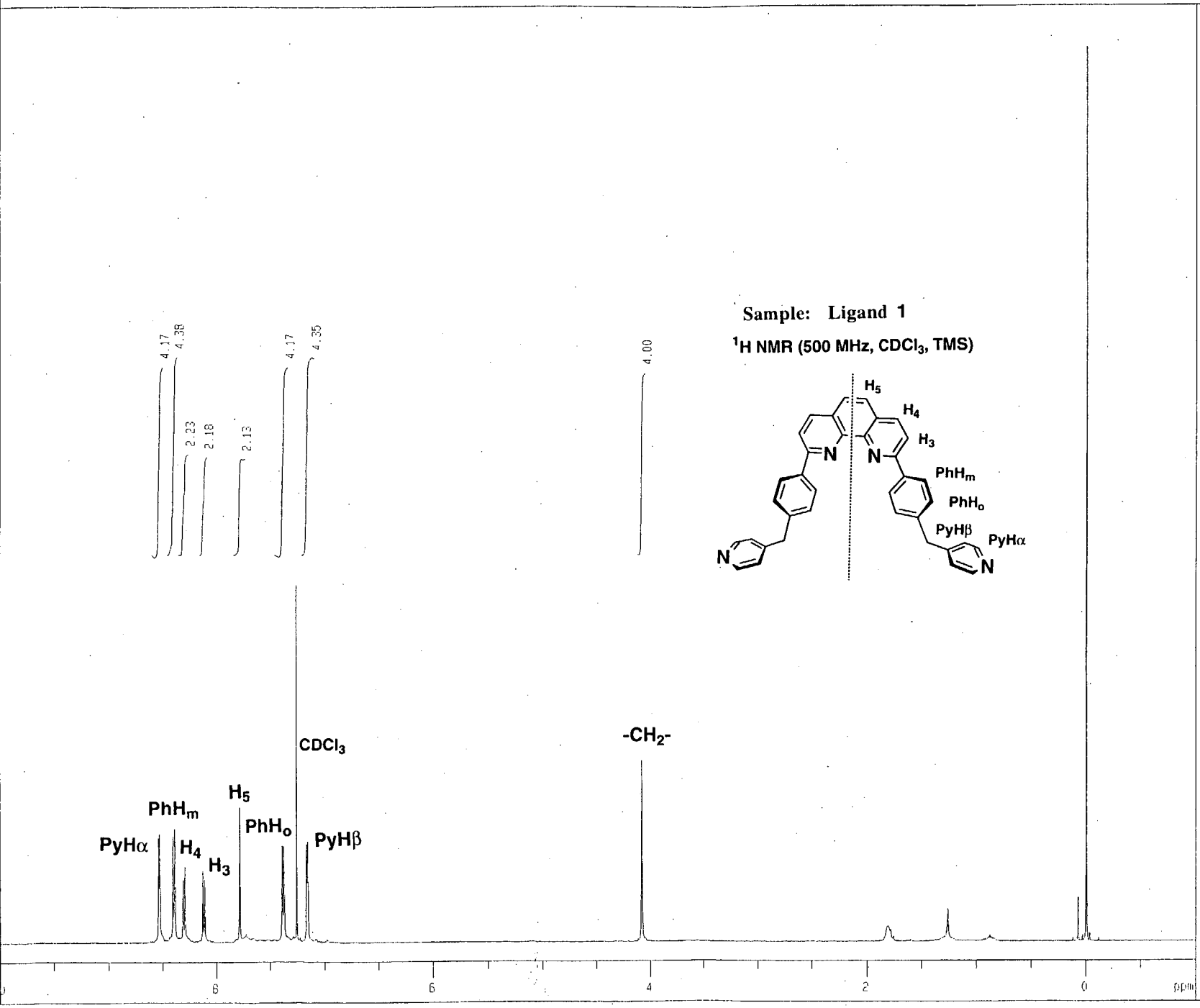
The synthesis of 2,9-bis{4-[(4-pyridyl)methyl]phenyl}-1,10-phenanthroline



To a THF (80 mL) solution of diisopropylamine (3.7 mL, 26.4 mmol), *n*-BuLi (16.5 mL, 26.4 mmol, 1.6 M in hexane) was added at 0 °C over 5 min. After the reaction mixture was stirred for 10 min at 0 °C, 4-methyl pyridine (2.3 mL, 24 mmol) was added at that temperature, then the mixture was stirred for 15 min at 0 °C. A THF solution of $ZnCl_2$ (53 mL, 26.4 mmol, 0.5 M in THF) was added at 0 °C, then unsoluble material was formed. To this mixture, $PdCl_2(PPh_3)_2$ (350 mg, 0.5 mmol) and 2,9-bis(4-bromophenyl)-1,10-phenanthroline (1.96 g, 4.00 mmol) were added, then a color of the solution turned into purple. The reaction mixture was stirred for 3 days at reflux temperature (85 °C). After the mixture was cooled down to room temperature, ethylenediamine (5 mL) and H_2O (10 mL) were added and stirred for 3 h. The solution was extracted with chloroform (100 mL x 2) and then the combined organic layer was dried over $MgSO_4$, filtered, and evaporated to driness to give a crude product (3.64 g). The crude product was purified by column chromatography (silica gel, $CHCl_3$: 2% MeOH) to give the titled compound as pale yellow crystal (1.44 g, 2.8 mmol, 70% yield).

^1H NMR (500 MHz, $CDCl_3$, TMS as internal standard) δ 8.53 (d, J = 5.9 Hz, 4 H, Py*Hα*), 8.40 (d, J = 8.3 Hz, 4 H, Ph*Hm*), 8.31 (d, J = 8.3 Hz, 2 H, H_4 and H_7), 8.12 (d, J = 8.3 Hz, 2 H, H_3 and H_8), 7.79 (s, 2 H, H_5 and H_6), 7.39 (d, J = 8.3 Hz, 4 H, Ph*Ho*), 7.16 (d, J = 5.9 Hz, 4 H, Py*Hβ*), 4.08 (s, 4 H, CH_2); ^{13}C NHR (126 MHz, $CDCl_3$, TMS as internal standard) δ 156.50 (*C*q), 149.92 (*C*H), 149.90 (*C*q), 146.14 (*C*q), 140.18 (*C*q), 138.14 (*C*q), 136.96 (*C*H), 129.67 (*C*H), 128.08 (*C*H), 127.94 (*C*q), 126.04 (*C*H), 124.30 (CH), 119.93 (*C*H), 41.03 (CH_2); IR (KBr, cm^{-1}) 3646.2, 3586.4, 3333.7, 3282.6, 1621.1, 1608.5, 1586.3, 1490.9, 1435.9, 840.9, 739.7, 558.4.; mp 89.0 - 91.5 °C; HR-MS (EI) Calcld for $C_{36}H_{26}N_4(M^+)$, 514.2178. Found 514.2171.

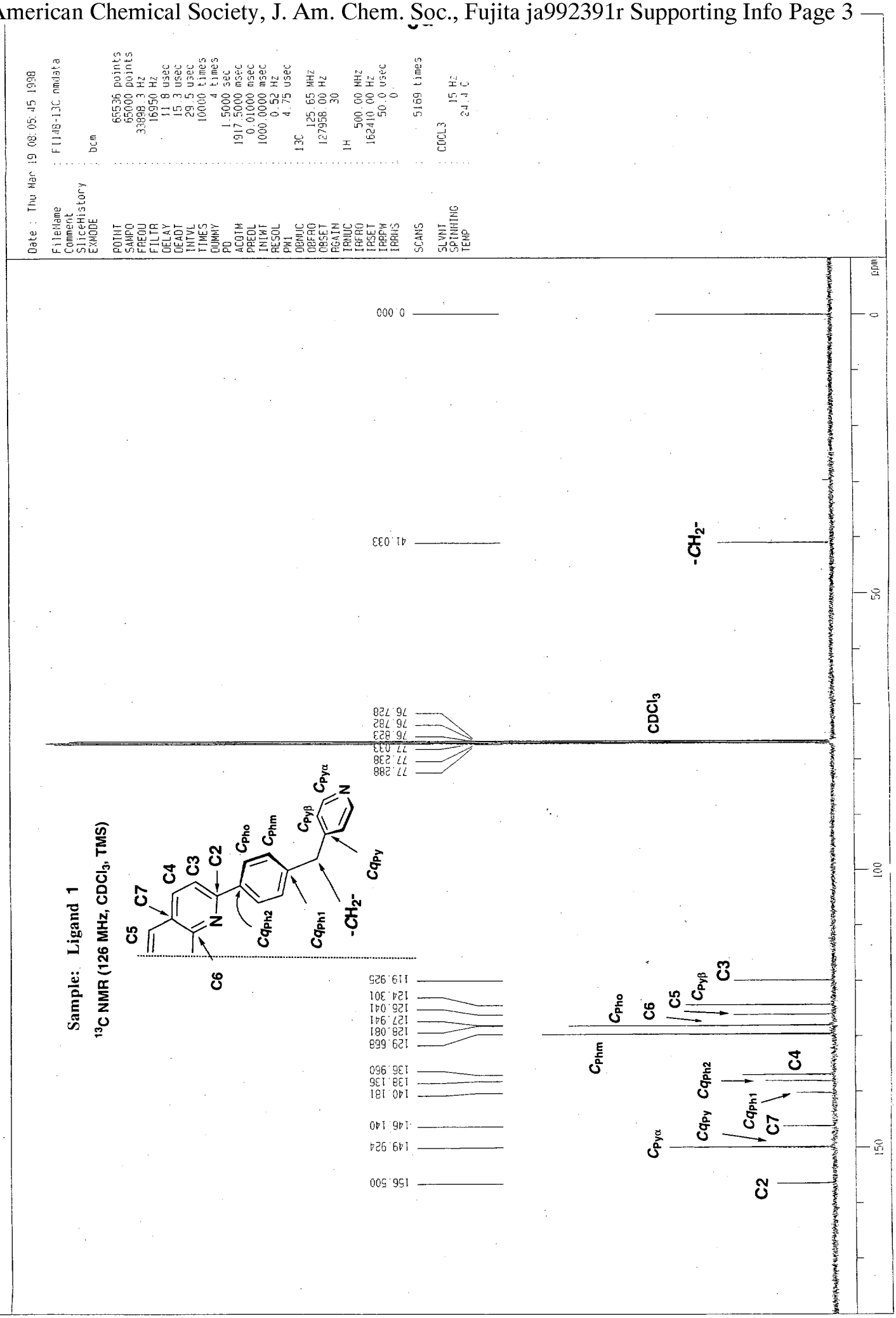
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 2

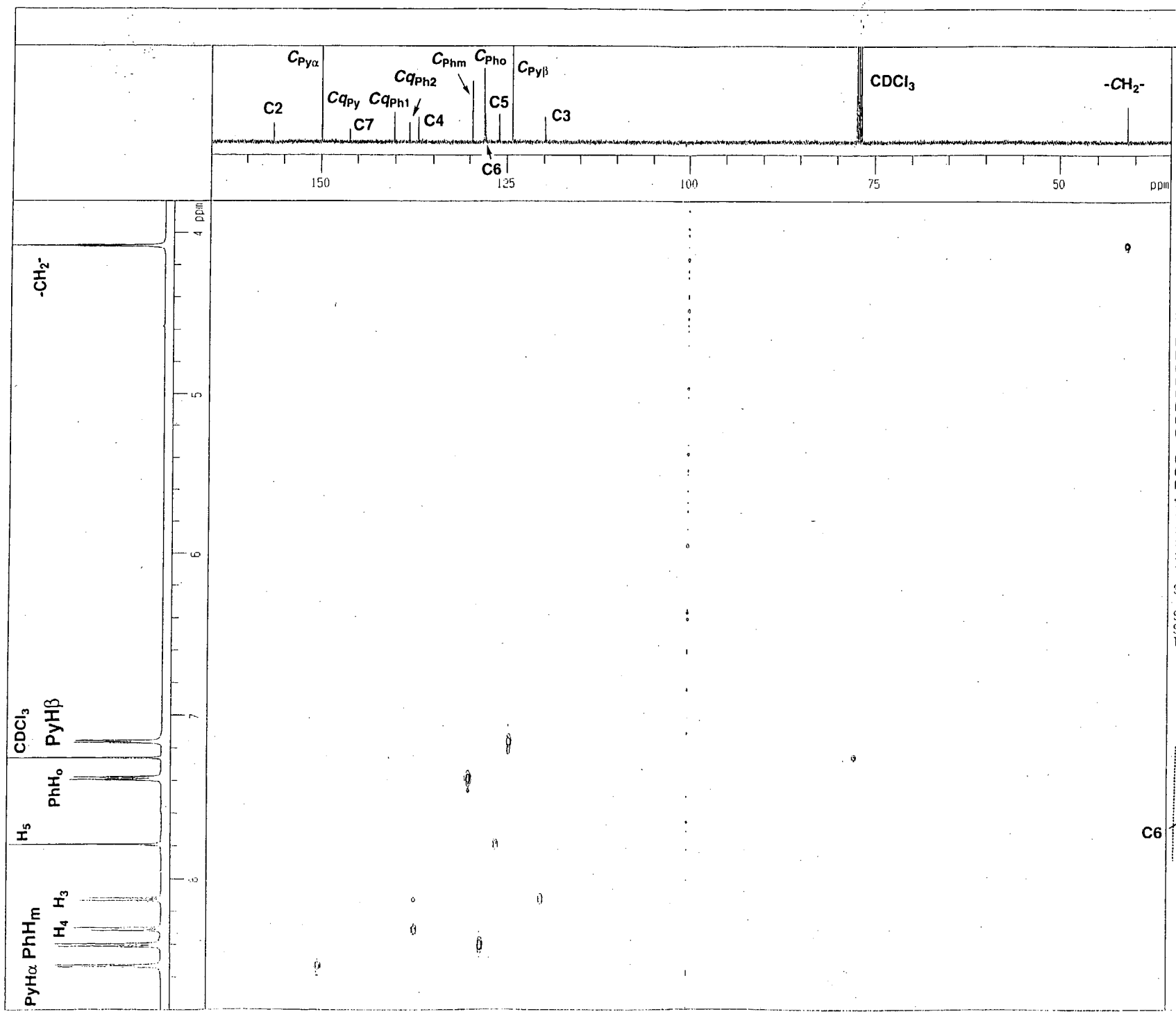


Date : Thu Mar 19 03:01:36 1998

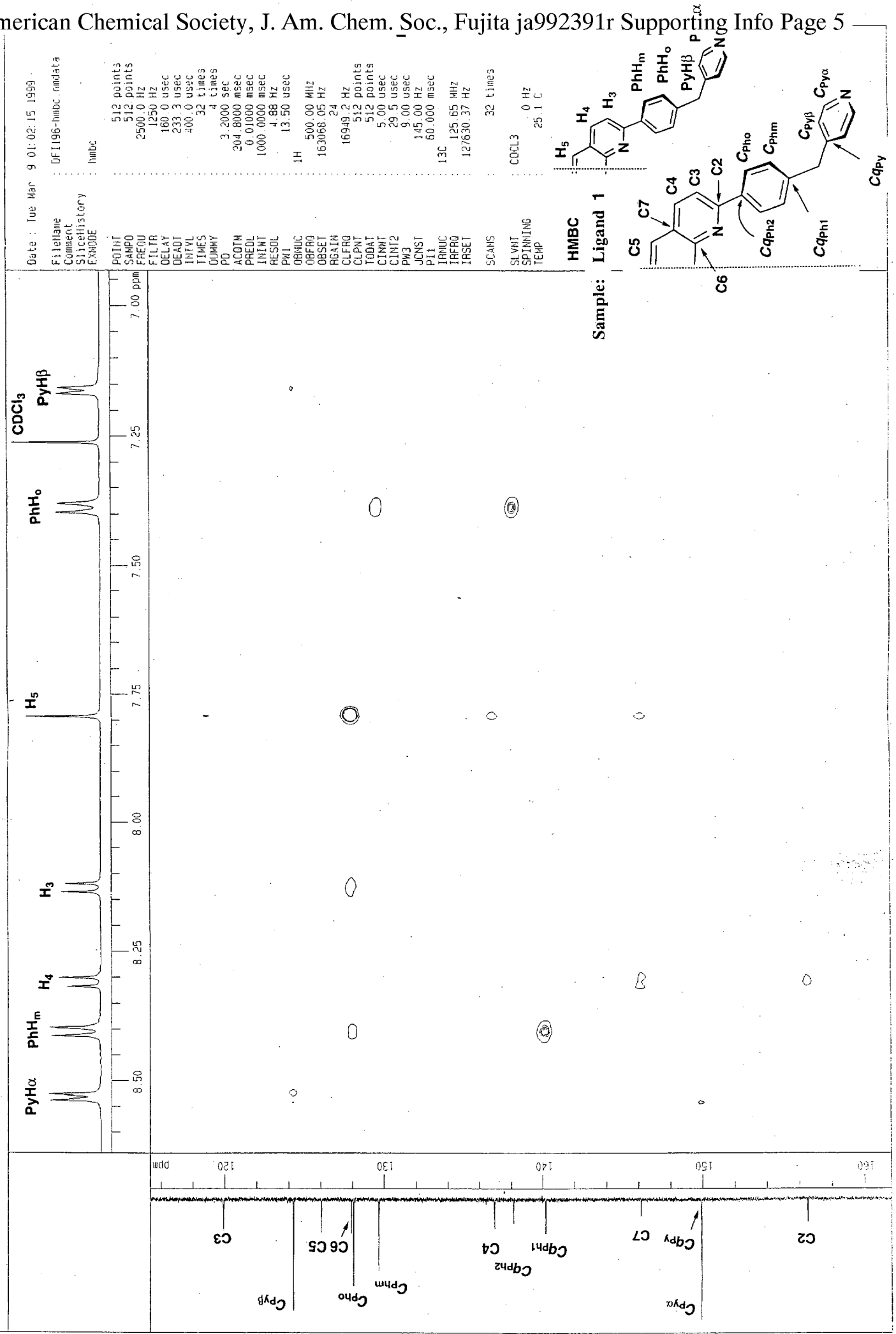
FileName	:	FI148-4.nmdata
Comment	:	
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	8000.0 Hz
FILTR	:	4000 Hz
DELAY	:	50.0 usec
DEADT	:	71.8 usec
INTVL	:	125.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	2.9000 sec
ACQTM	:	4096.0000 msec
PREDL	:	0.01000 msec
ININT	:	1000.0000 msec
RESOL	:	0.24 Hz
PW1	:	6.40 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162410.00 Hz
RGAIN	:	25
SCANS	:	32 times
SLVNT	:	CDCL3
SPINNING	:	16 Hz
TEMP	:	22.8 C

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 3



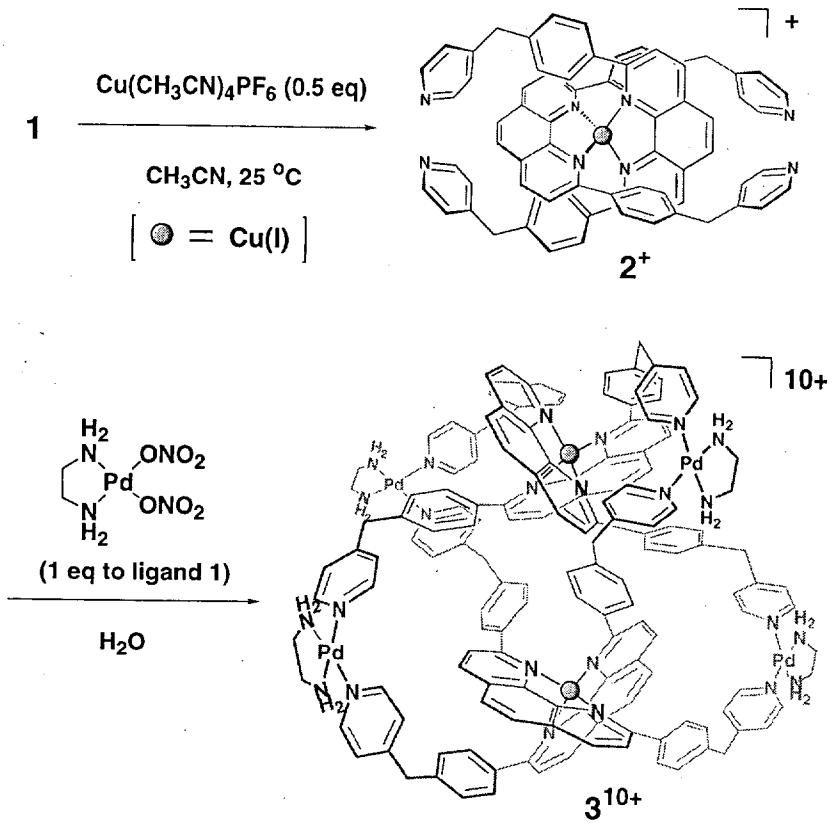


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 4


Sample: Ligand 1
HMBC
Date : Tue Mar 9 01:02:15 1999
Filename DFI196-hmbc nmrdata
Comment
SliceHistory
EXMODE hmbc
PyHα PhHm H4 H3 H5 PhHo CDCl3 PyHβ
7.00 ppm
7.25
7.50
7.75
8.00
8.25
8.50
120
130
140
150
160
ppm
C3
CPyβ
CPho
C6 C5
CPhm
C4
CqPh2
CqPh1
C7
CqPy
CPyα
C2
H5
H4
H3
PhHm
PhHo
PyHβ
PyHα
C7
C4
C3
C2
CPho
CPhm
CPyβ
CPyα
C5
N
CqPh2
CqPh1
CqPy
C6

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 6

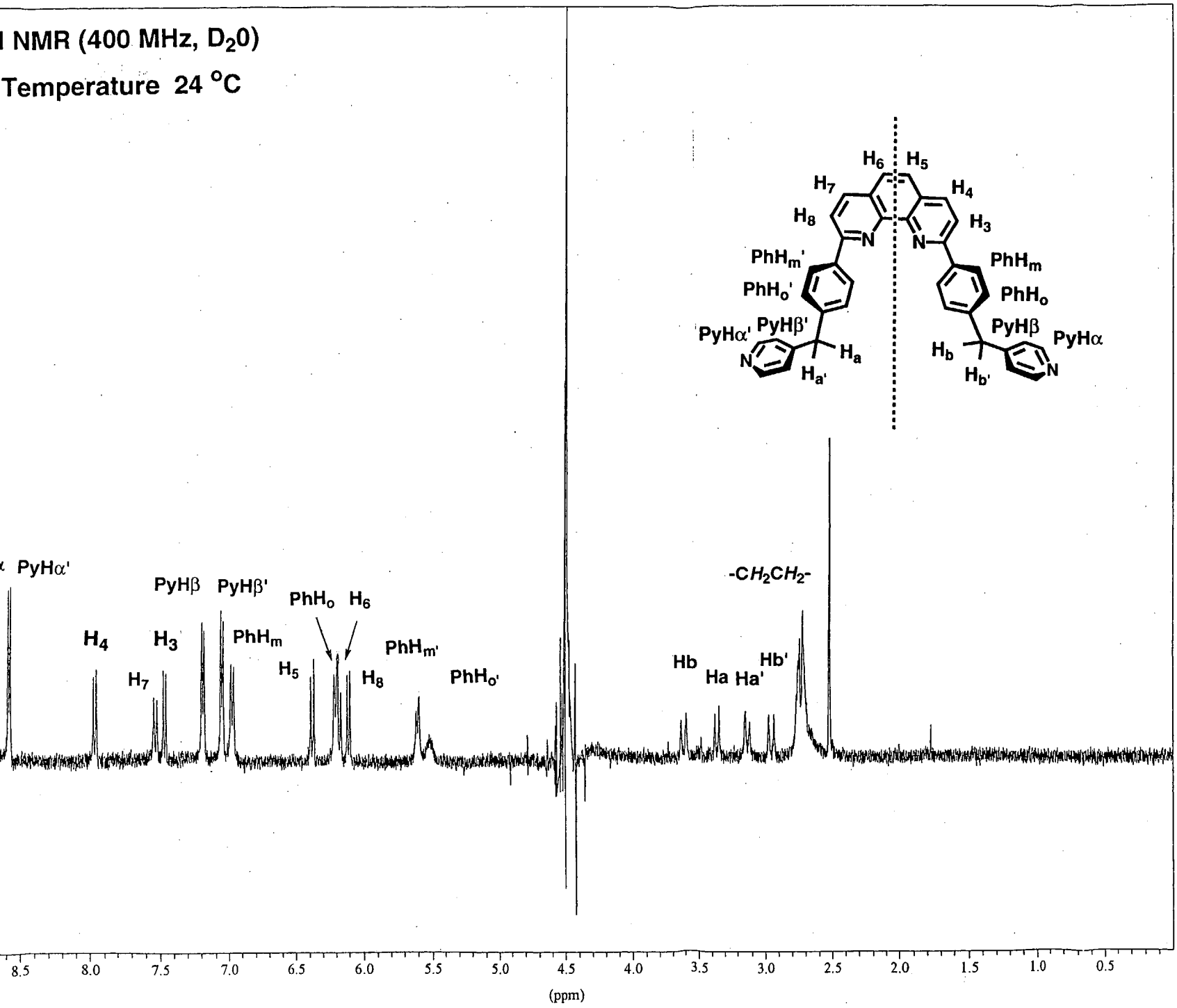
Synthesis of Doubly Interlocking [2]Catenane



To a acetonitrile solution (0.5 mL) of 1,10-bis(4-(4-pyridylmethyl)phenyl)-phenanthroline **1** (31 mg, 0.06 mmol), tetrakis(acetonitrile)copper(I) hexafluoro-phosphate (11 mg, 0.03 mmol) was added at 25 °C under Argon atmosphere. This red brown solution was stirred for 20 min to give the catenane precursor **2**. To the reaction mixture, an aqueous solution (1 mL) of ethylenediamine palladium nitrate (18 mg, 0.06 mmol) was added at 25 °C. The mixture was stirred for 20 min. To the reaction mixture, an aqueous KPF_6 (0.3 M, 2 mL) was added to give red-brown precipitates, and then it was stirred for 4 h at room temperature. The red-brown solids were filtered, dried to give the titled compound (60 mg, 92%).

Physical data of catenane $\mathbf{3}^{10+}$ (as PF_6 salt): ^{1}H NMR (400 MHz, D_2O, 80 °C, TMS as internal standard) δ 8.73 (d, J = 6.4 Hz, 4 H, Py$H\alpha$), 8.53 (d, J = 6.4 Hz, 4 H, Ph$H\alpha'$), 8.03 (d, J = 8.3 Hz, 2 H, H_4), 7.57 (d, J = 8.3 Hz, 2 H, H_3), 7.31 (d, 2 H,

J = 8.0 Hz, H_7), 7.18 (d, J = 6.4 Hz, 4 H, Py$H\beta$), 7.01 (d, J = 6.4 Hz, 4 H, Py$H\beta'$), 6.99 (d, J = 8.3 Hz, 4 H, PhHm), 6.47 (d, J = 8.8 Hz, 2 H, H_5), 6.30 (d, J = 8.8 Hz, 2 H, H_6), 6.20 (d, J = 8.3 Hz, 4 H, PhHo), 6.06 (d, 2 H, J = 8.0 Hz, H_8), 5.60 (d, J = 8.0 Hz, 4 H, PhHm'), 5.50 (d, J = 7.8 Hz, 4 H, PhHo'), 3.58 (d, J = 15.6 Hz, 2 H, CHb), 3.37 (d, 2 H, J = 13.4 Hz, CHa), 3.12 (d, J = 13.4 Hz, 2 H,CHa), 2.89 (d, J = 15.6 Hz, 2 H, CHb'), 2.75 - 2.70 (broad two singlets, 8 H, -CH_2CH_2-); ^{13}C NMR (CD_3CN, 126 MHz,TMS as external standard); 154.91, 154.85, 151.24, 151.16, 142.37, 142.33, 139.01, 137.03, 136.95, 136.45, 136.28, 136.14, 129.13, 128.13, 127.65, 127.49, 127.32, 127.12, 126.64, 126.52, 126.48, 126.27, 125.42, 124.79, 124.41, 122.73, 39.99, 39.65, 39.47, 39.10. IR (KBr, cm^{-1}) 3021.3, 2939.3, 2922.9, 1596.9, 1587.3, 1569.0, 1558.4, 1489.9, 1414.7, 846.7, 792.7, 781.1, 749.3; ESI-MS (CH_3CN) *m/z* (relative intensity) 1289.1 {[**3** - $(PF_6^-)_3$]$^{3+}$, 47%}, 930.4 {[**3** - $(PF_6^-)_4$]$^{4+}$, 98%}, 715.3 {[**3** - $(PF_6^-)_5$]$^{5+}$, 100%. Anal. Calcd for $\mathbf{3}^{10+}$ $\cdot(H_2O)_{3.5}$, ($C_{76}H_{75}CuF_{30}N_{12}O_{3.5}P_5Pd_2$): C, 41.24; H, 3.41; N, 7.59.; Found: C, 40.89; H, 3.05; N, 7.54.



*** Current Data Parameters ***

NAME	:	S6FI14VT
EXPNO	:	300
PROCNO	:	1

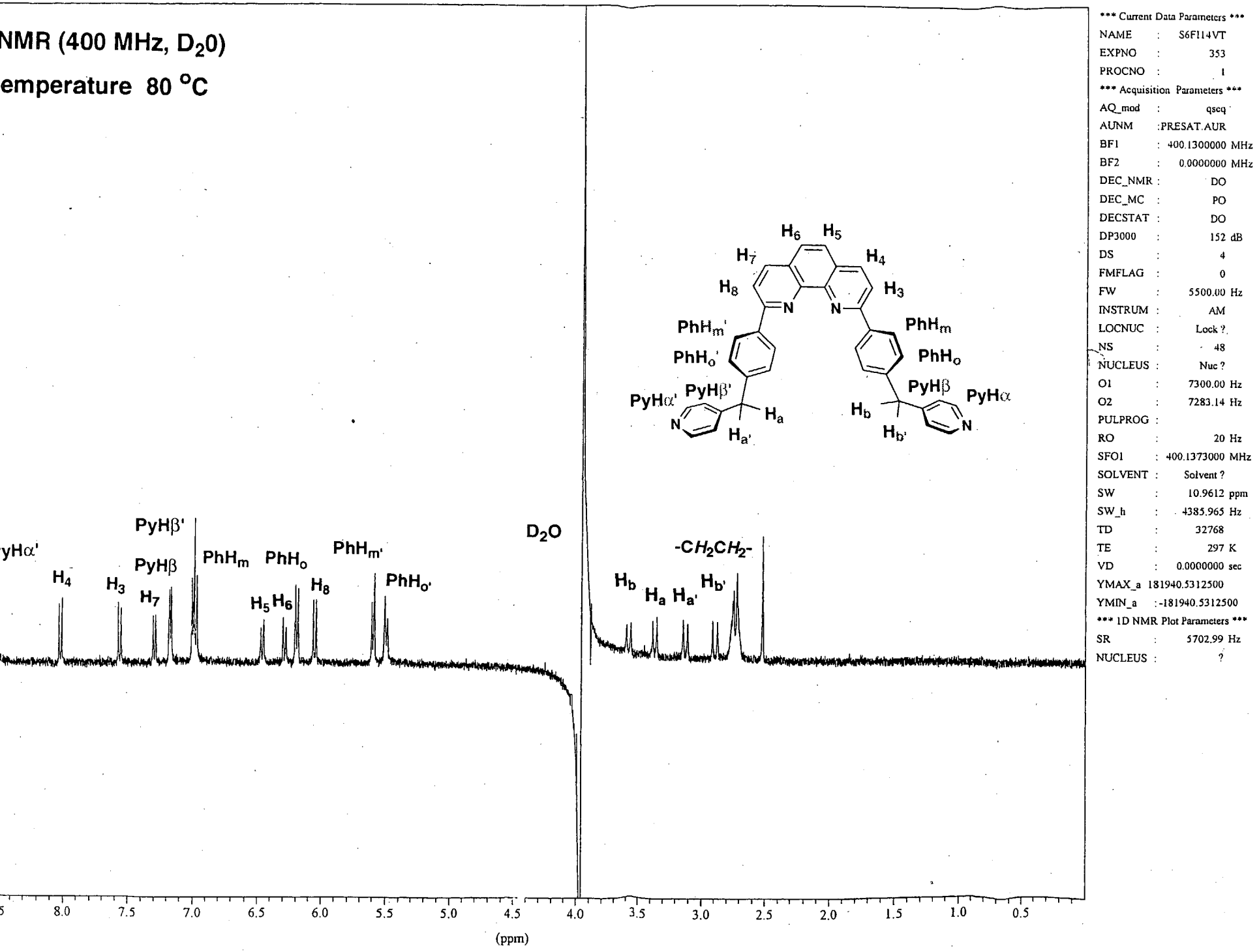
*** Acquisition Parameters ***

AQ_mod	:	qseq
AUNM		PRESAT.AUR
BF1	:	400.1300000 MHz
BF2	:	0.0000000 MHz
DEC_NMR		DO
DEC_MC	:	PO
DECSTAT		DO
DP3000	:	152 dB
DS	:	4
FMFLAG	:	0
FW	:	5500.00 Hz
INSTRUM		AM
LOCNUC	:	Lock ?
NS	:	72
NUCLEUS		Nuc ?
O1	:	7300.00 Hz
O2	:	7283.14 Hz
PULPROG		
RO	:	20 Hz
SFO1	:	400.1373000 MHz
SOLVENT		Solvent ?
SW	:	10.9612 ppm
SW_h	:	4385.965 Hz
TD	:	32768
TE	:	297 K
VD	:	0.0000000 sec
YMAX_a	:	680186.3125000
YMIN_a	:	-680186.3125000

*** 1D NMR Plot Parameters ***

SR	:	5485.08 Hz
NUCLEUS		?

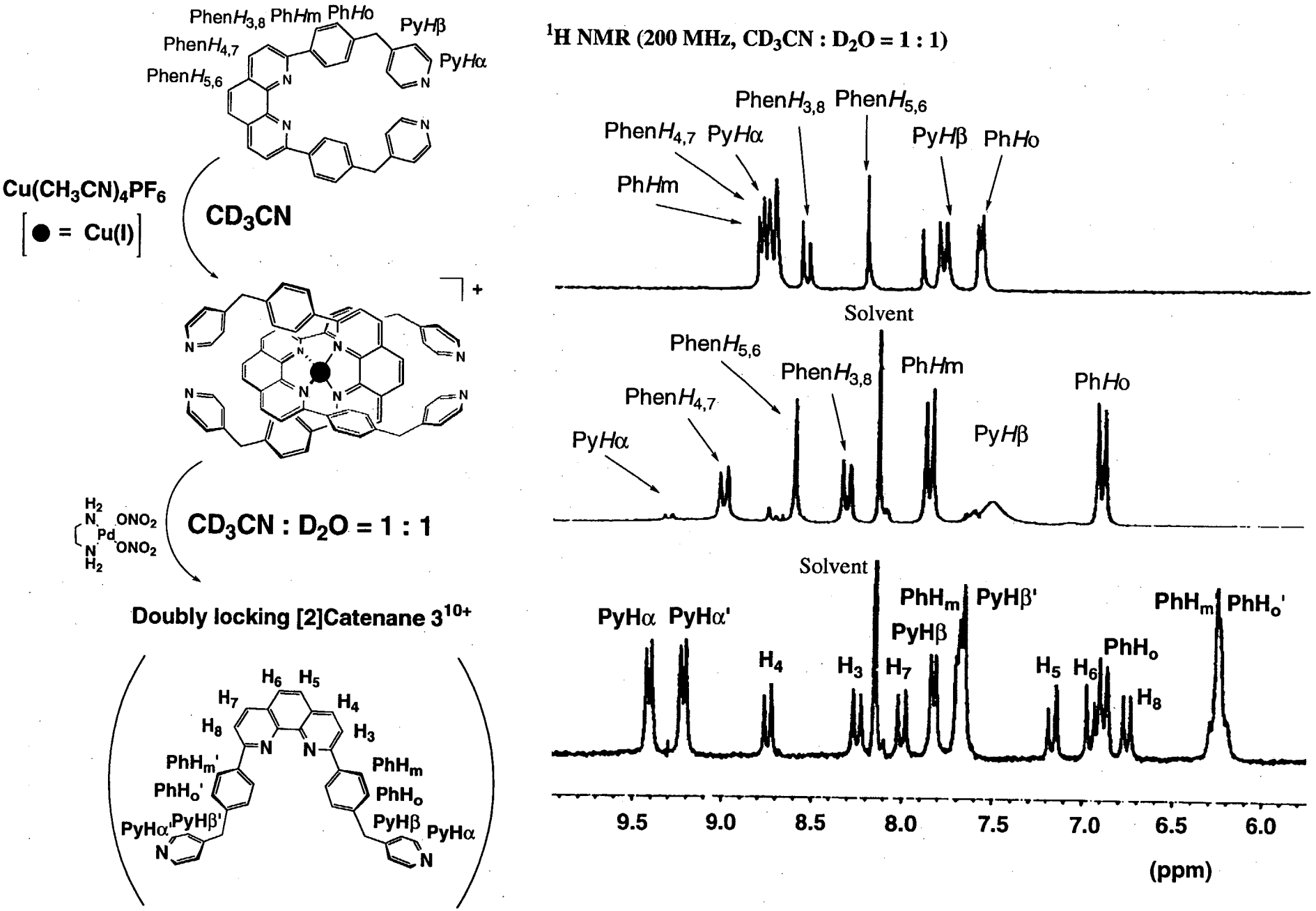
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 8




```
*** Current Data Parameters ***
NAME      :  S6F114VT
EXPNO     :  353
PROCNO    :  1
*** Acquisition Parameters ***
AQ_mod    :  qseq
AUNM      : PRESAT.AUR
BF1       :  400.1300000 MHz
BF2       :  0.0000000 MHz
DEC_NMR   :  DO
DEC_MC    :  PO
DECSTAT   :  DO
DP3000    :  152 dB
DS        :  4
FMFLAG    :  0
FW        :  5500.00 Hz
INSTRUM   :  AM
LOCNUC    :  Lock ?
NS        :  48
NUCLEUS   :  Nuc ?
O1        :  7300.00 Hz
O2        :  7283.14 Hz
PULPROG   :
RO        :  20 Hz
SFO1      :  400.1373000 MHz
SOLVENT   :  Solvent ?
SW        :  10.9612 ppm
SW_h      :  4385.965 Hz
TD        :  32768
TE        :  297 K
VD        :  0.0000000 sec
YMAX_a    : 181940.5312500
YMIN_a    : -181940.5312500
*** 1D NMR Plot Parameters ***
SR        :  5702.99 Hz
NUCLEUS   :  ?
```

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 9

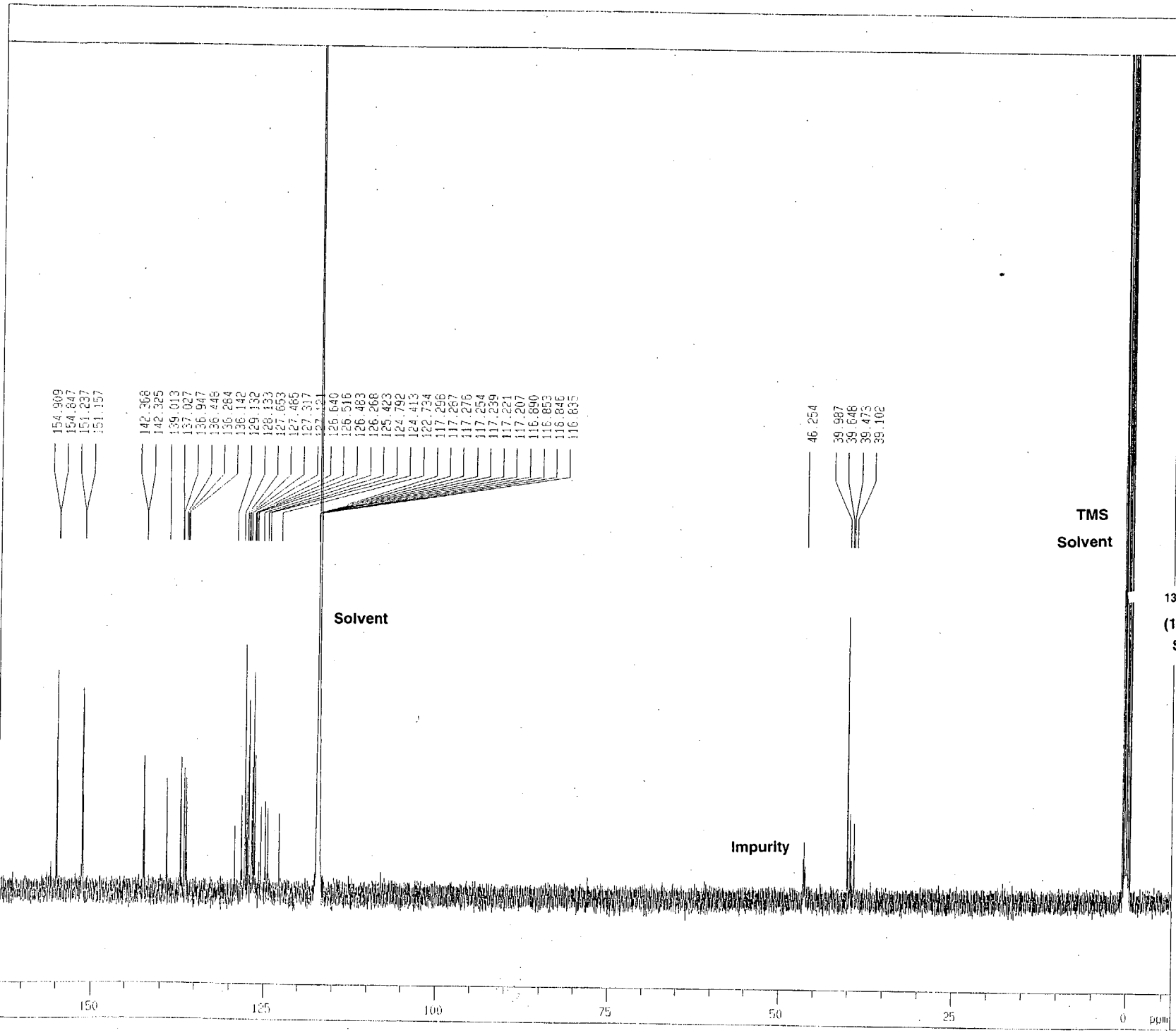
^{1}H NMR Experiment to the formation of the Doubly Locking [2]Catenane



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 10

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 11

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 12



Date : Wed May 27 10:04:37 1998

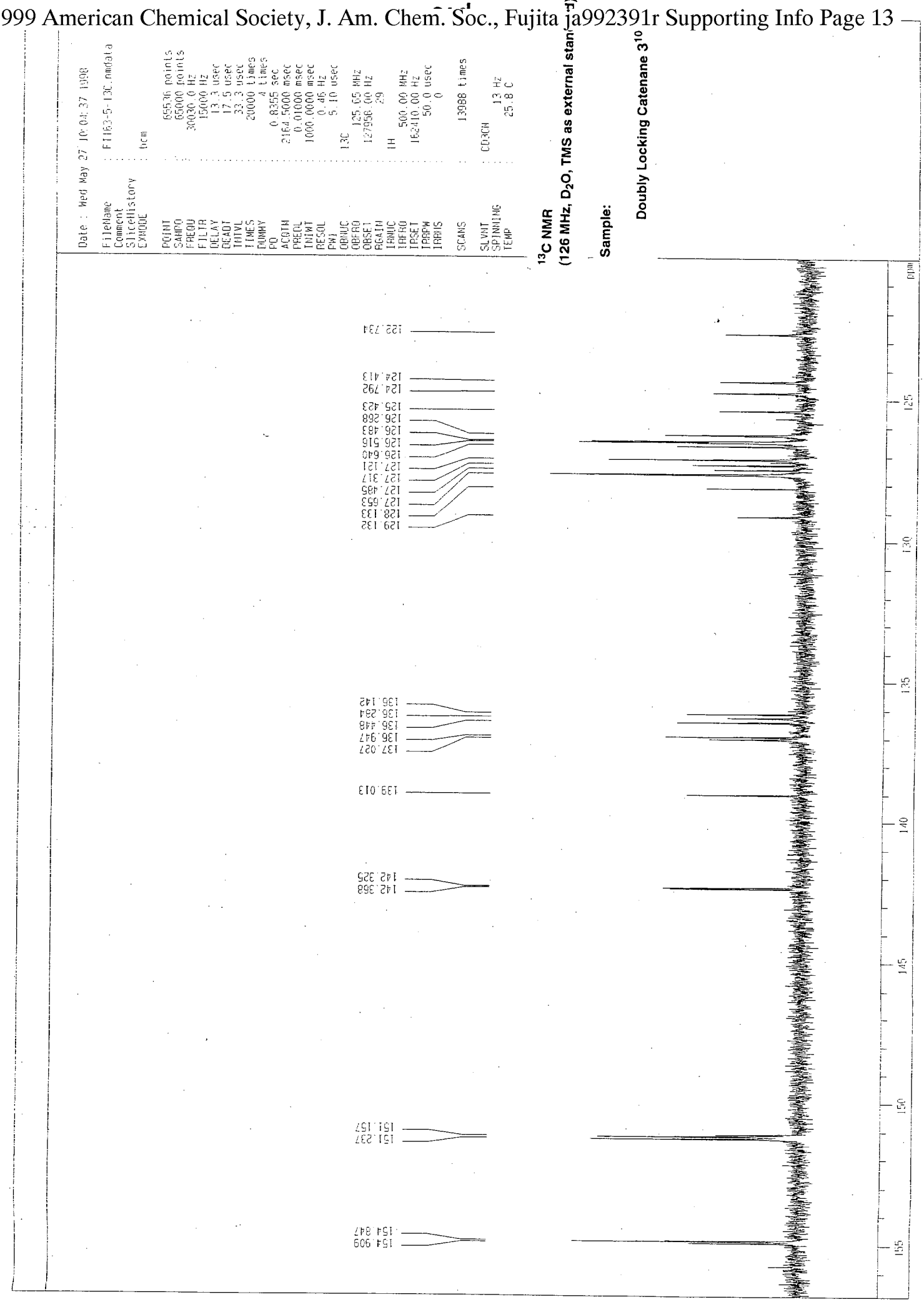
FileName	FI163-5-13C.nmdata
Comment	
SliceHistory	
EXMODE	bcm
POINT	65536 points
SAMPO	65000 points
FREQU	30030.0 Hz
FILTR	15000 Hz
DELAY	13.3 usec
DEADT	17.5 usec
INTVL	33.3 usec
TIMES	20000 times
DUMMY	4 times
PD	0.8355 sec
ACQTM	2164.5000 msec
PREDL	0.01000 msec
INIWT	1000.0000 msec
RESOL	0.46 Hz
PW1	5.10 usec
OBNUC	13C
OBFRQ	125.65 MHz
OBSET	127958.00 Hz
RGAIN	29
IRNUC	1H
IRFRQ	500.00 MHz
IRSET	162410.00 Hz
IRPW	50.0 usec
IRNS	0
SCANS	13988 times
SLVNT	CD3CN
SPINNING	13 Hz
TEMP	25.8 C

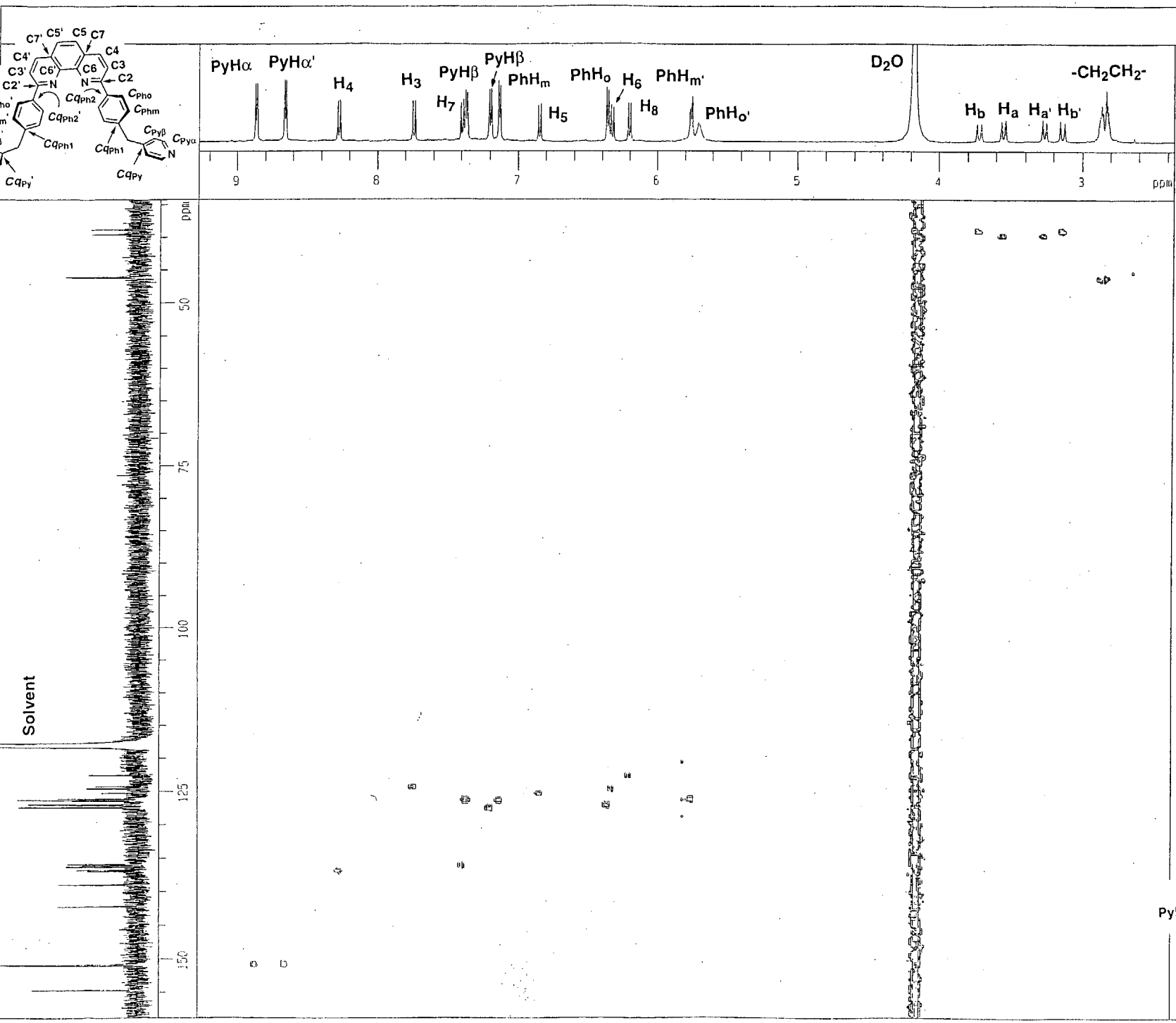
^{13}C NMR
(126 MHz, D_2O, TMS as external stand)
Sample:

Doubly Locking Catenane 3^{10+}

d12

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 13





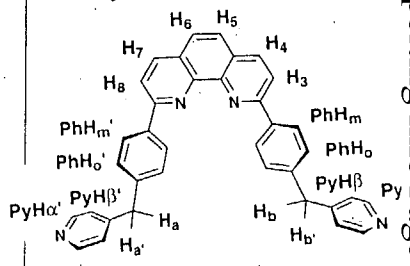
Date : Sat Jun 19 03:25:40 1999

FileName	2enhmqc.nmdata
Comment	
SliceHistory	
EXMODE	hmqc
POINT	512 points
SAMPO	512 points
FREQU	3468.6 Hz
FILTR	1750 Hz
DELAY	114.3 usec
DEADT	164.7 usec
INTVL	288.3 usec
TIMES	96 times
DUMMY	4 times
PD	1.5000 sec
ACQTM	147.6096 msec
PREDL	0.01000 msec
INIWT	1000.0000 msec
RESOL	6.77 Hz
PW1	13.50 usec
OBNUC	1H
OBFRQ	500.00 MHz
OBSET	162811.12 Hz
RGAIN	22
CLFRQ	15698.6 Hz
CLPNT	512 points
TODAT	512 points
CINWT	5.00 usec
CINT2	31.8 usec
PW3	9.00 usec
JCNST	145.00 Hz
IRNUC	13C
IRFRQ	125.65 MHz
IRSET	127487.86 Hz
IRRPW	46.0 usec
IRRNS	4
SCANS	96 times
SLVNT	CD3CN
SPINNING	0 Hz
TEMP	24.5 C

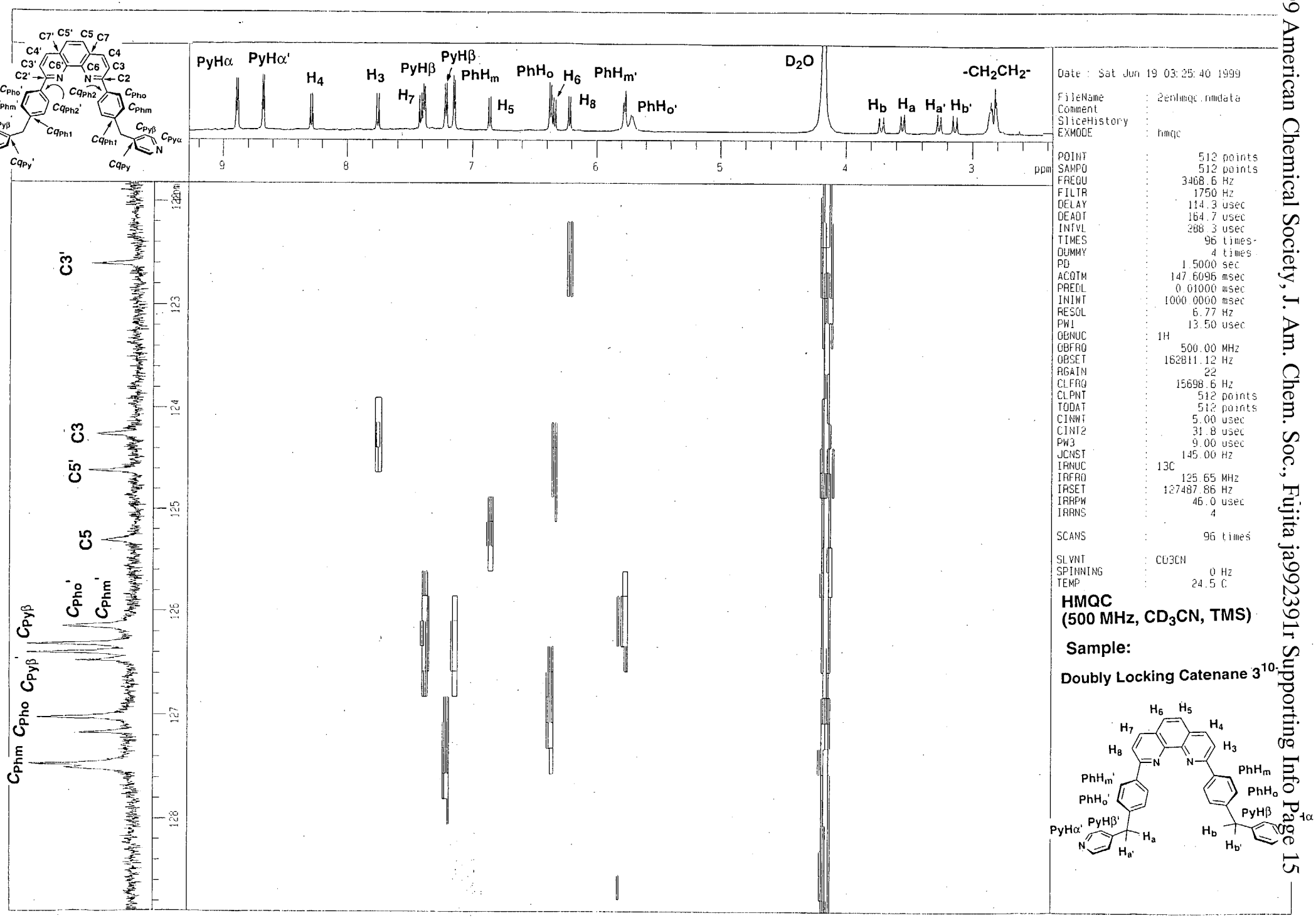
HMQC
(500 MHz, CD_3CN, TMS)

Sample:

Doubly Locking Catenane 3^{10+}

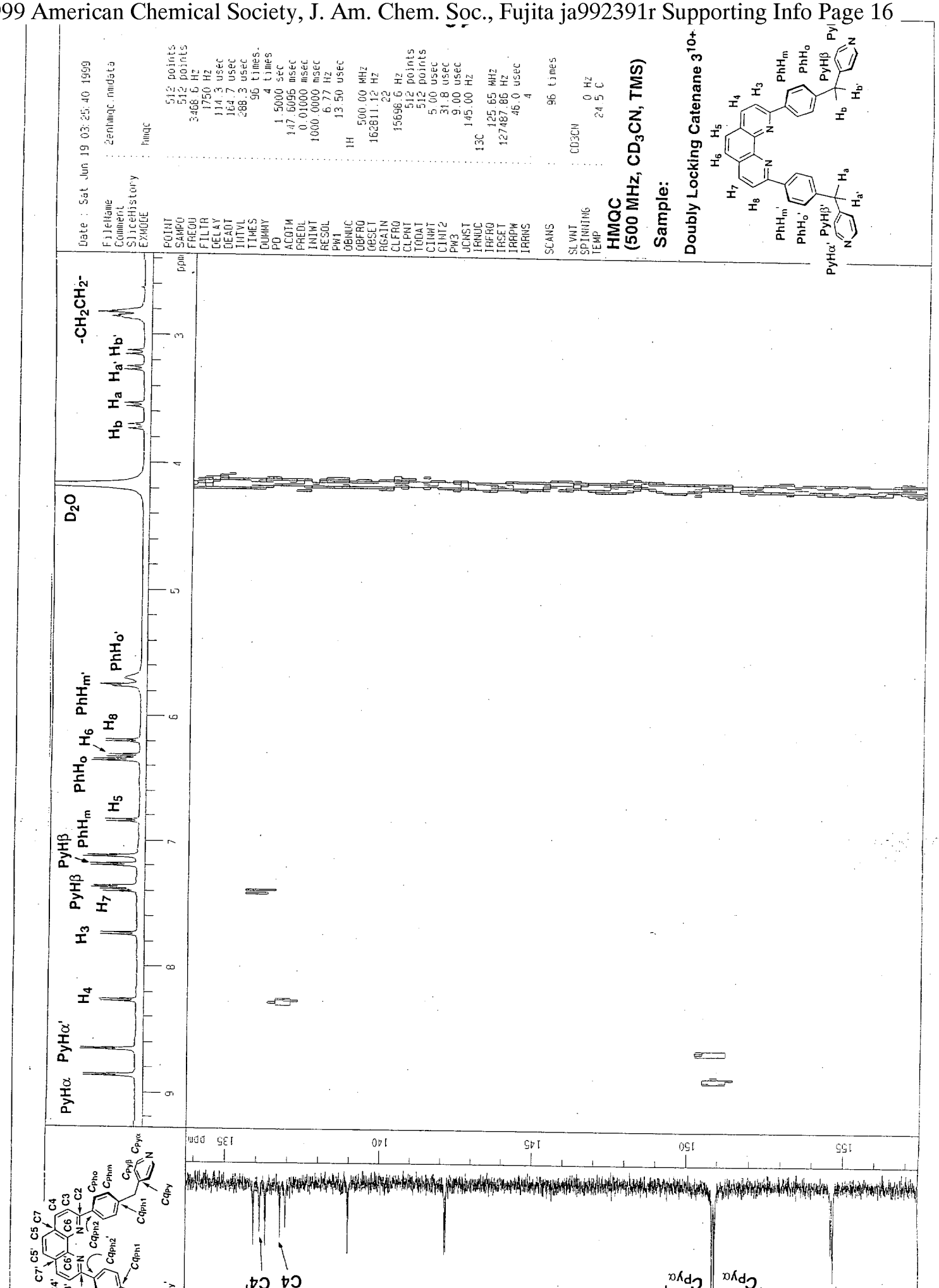


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 14

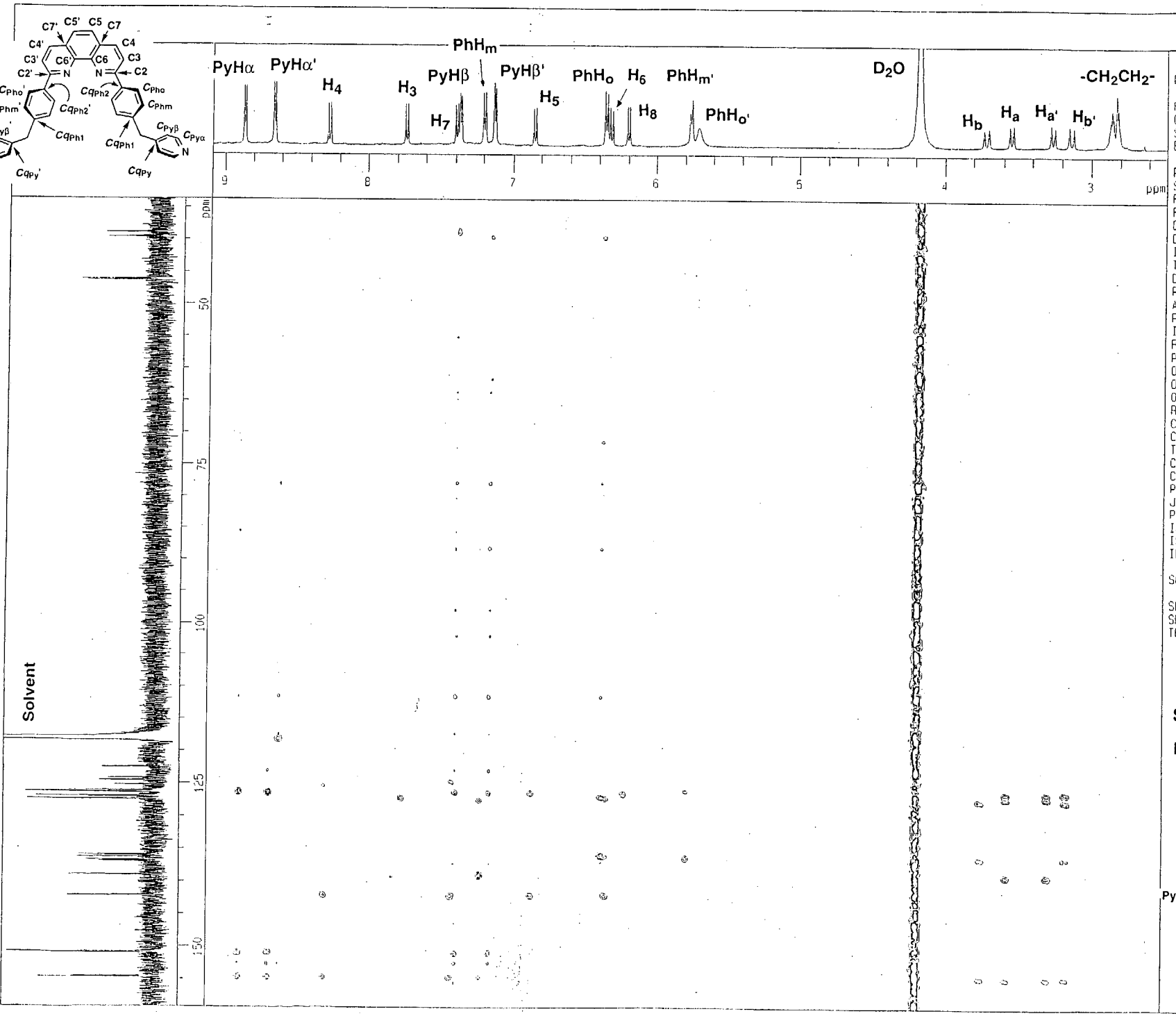


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 15

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 16



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 17



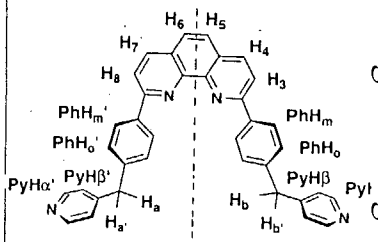
Date : Thu Jun 17 02:07:02 1999

FileName	2enhmbc.nmdata
Comment	
SliceHistory	
EXMODE	hmbc
POINT	512 points
SAMPO	512 points
FREQU	3311.3 Hz
FILTR	1650 Hz
DELAY	121.2 usec
DEADT	175.1 usec
INTVL	302.0 usec
TIMES	96 times
DUMMY	4 times
PD	1.3000 sec
ACQTM	154.6240 msec
PREDL	0.01000 msec
INIWT	1000.0000 msec
RESOL	6.47 Hz
PW1	13.50 usec
OBNUC	1H
OBFRQ	500.00 MHz
OBSET	162794.03 Hz
RGAIN	25
CLFRQ	15822.8 Hz
CLPNT	512 points
TODAT	512 points
CINNT	5.00 usec
CINT2	31.6 usec
PW3	9.00 usec
JCNST	145.00 Hz
PI1	60.000 msec
IRNUC	13C
IRFRQ	125.65 MHz
IRSET	127479.62 Hz
SCANS	96 times
SLVNT	CD3CN
SPINNING	0 Hz
TEMP	24.9 C

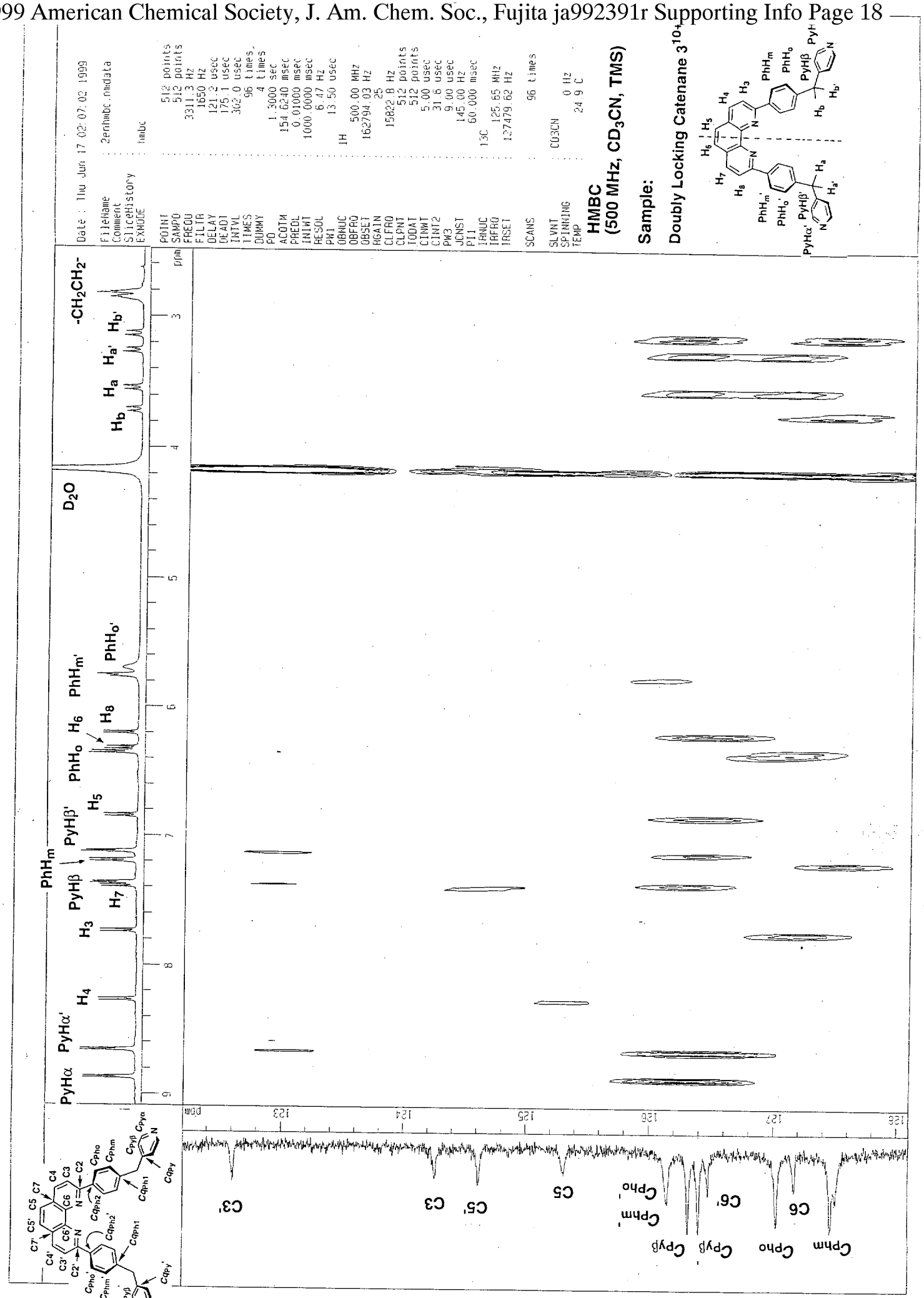
HMBC
(500 MHz, CD_3CN, TMS)

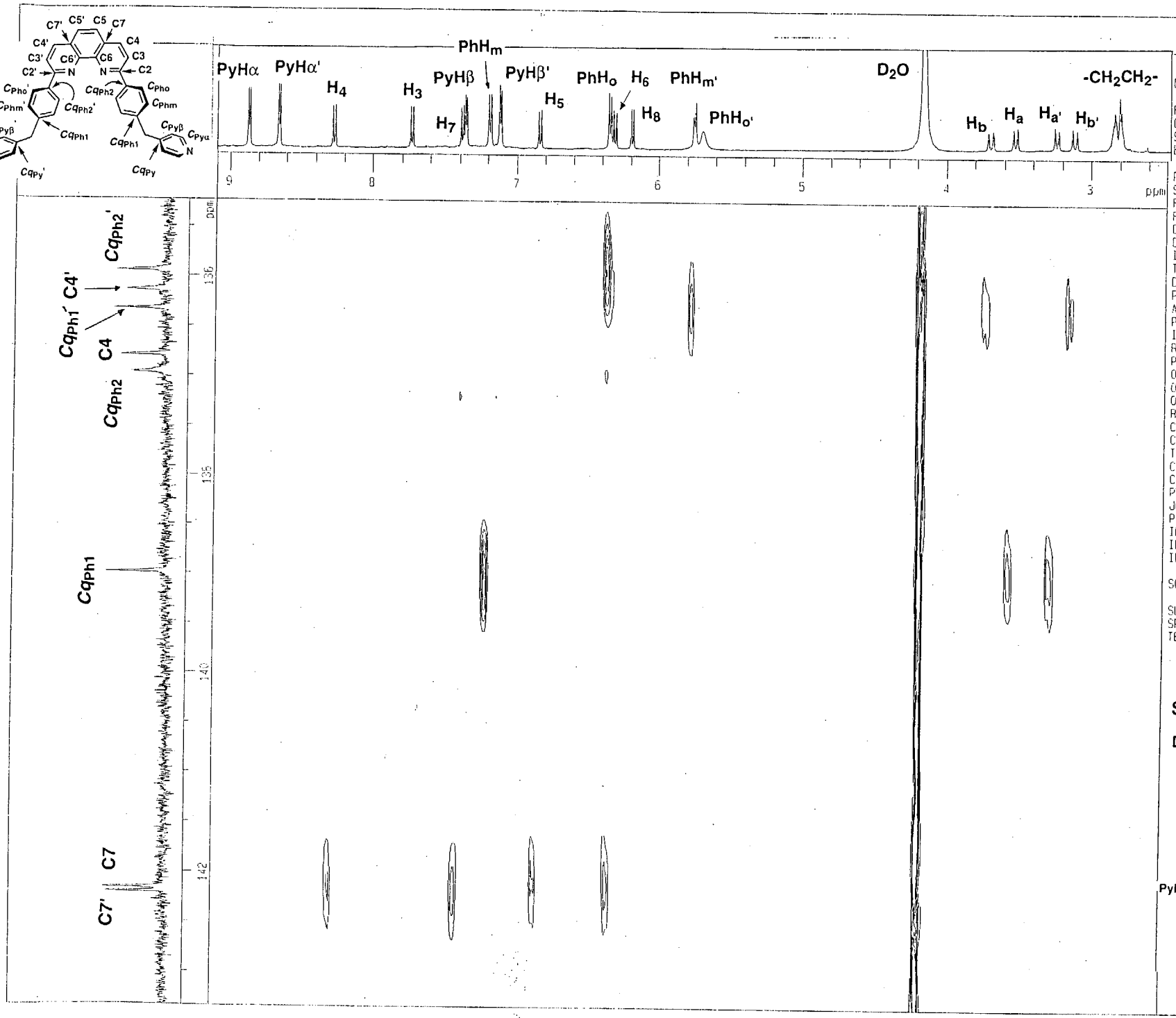
Sample:

Doubly Locking Catenane 3^{10}



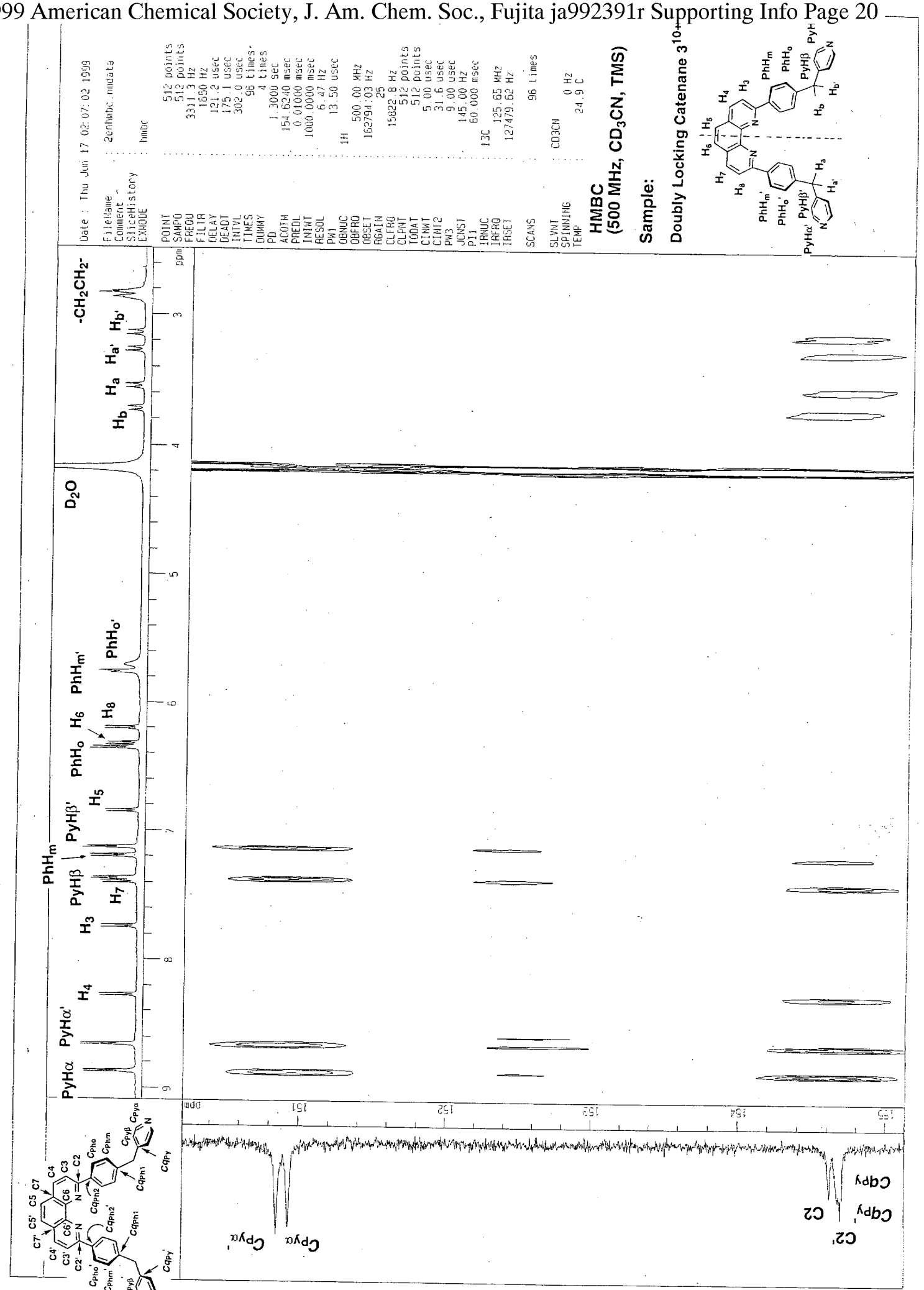
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 18



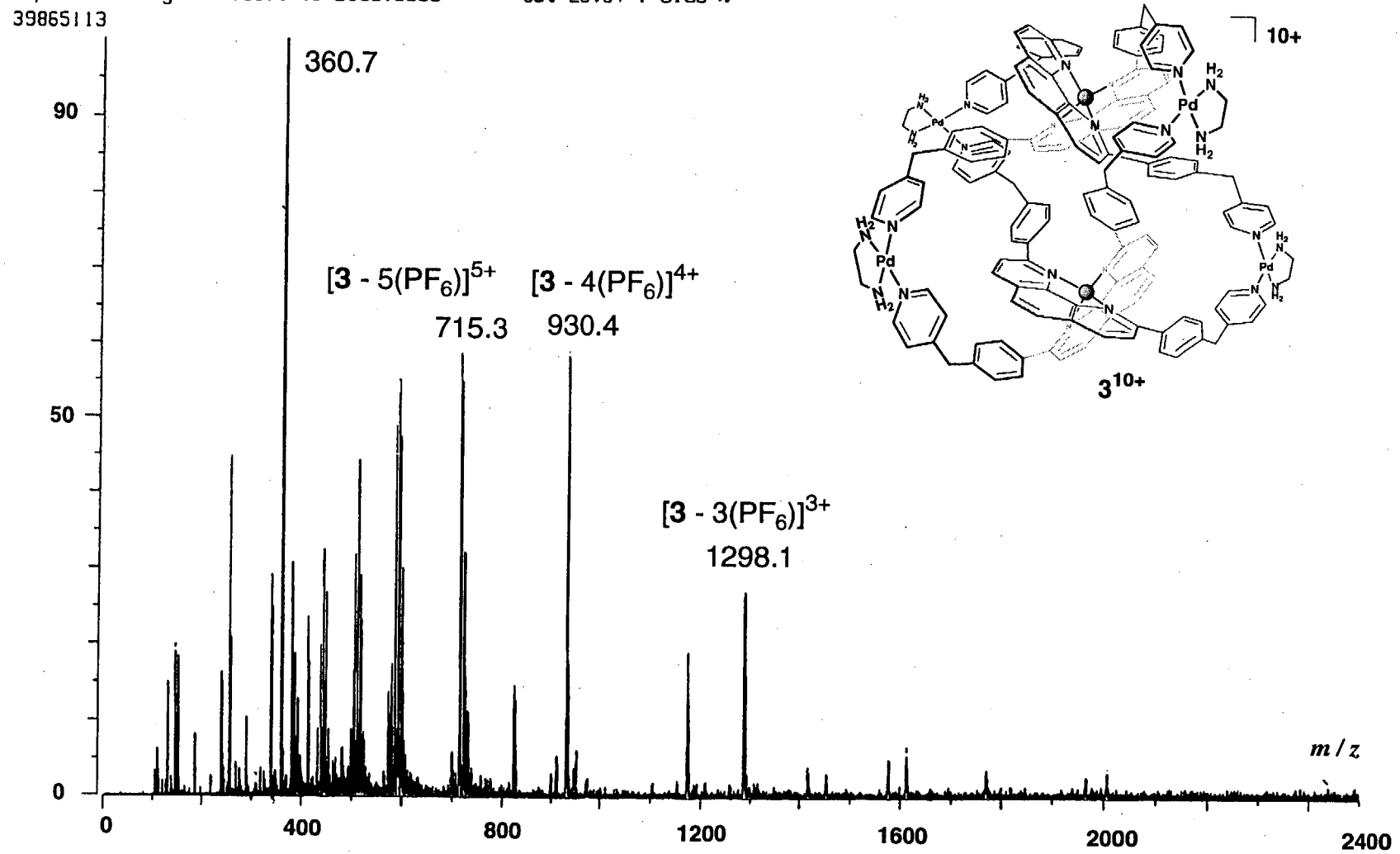


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 19

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 20



[Mass Spectrum]
Data : ESI-990203-DFI-180-006 Date : 03-Feb-1999 15:19
Sample:
Note : -
Inlet : Direct Ion Mode : ESI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 14.25 min Scan# : (1,82)
BP : m/z 360.7481 Int. : 46.36
Output m/z range : 0.0000 to 2500.0000 Cut Level : 0.00 %



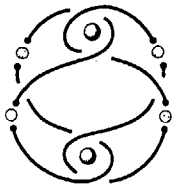
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 21

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 22

1H S/N

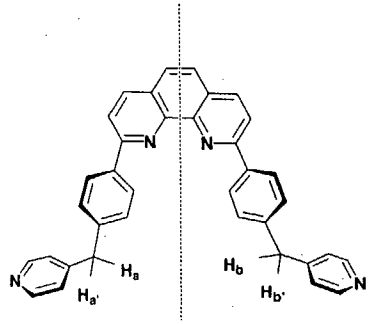
^{1}H NMR (500 MHz, D_2O:CD_3OD = 2 : 1)

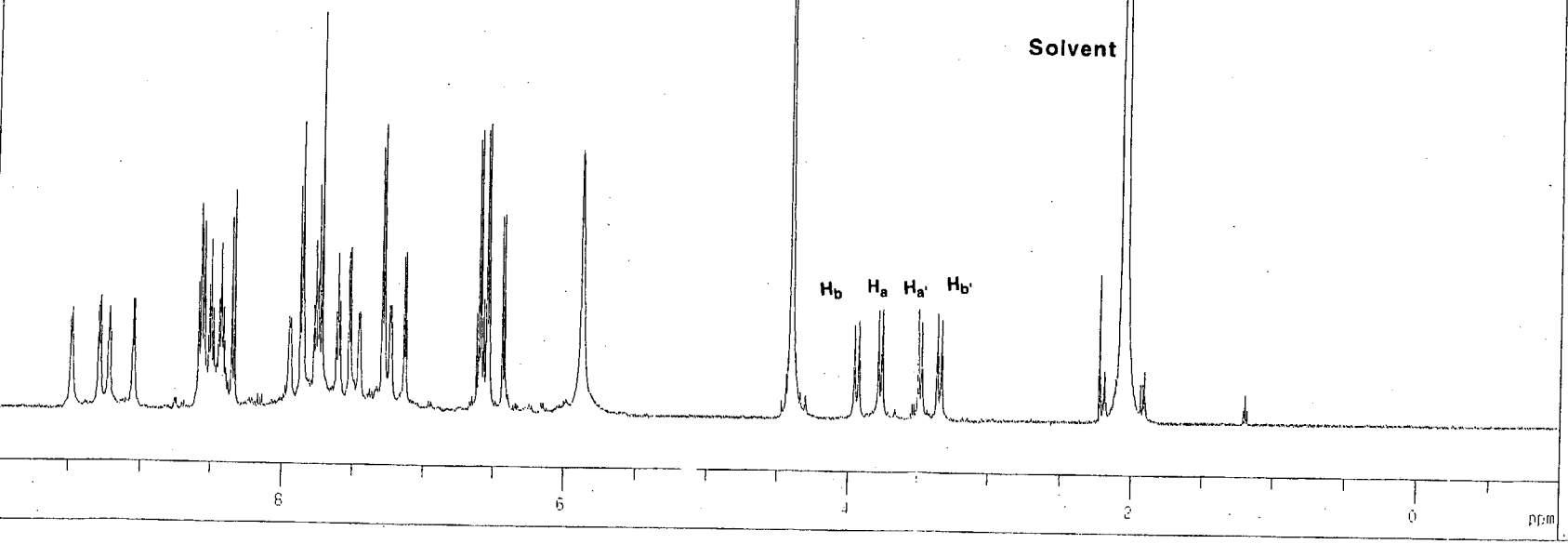
Sample: Doubly locking [2]catenane



● = Cu(I)

⊙ = 2,2'-(bipy)Pd$(NO_3)_2$

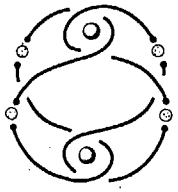





```
Date : Fri Dec 11 13:11:17 1998

FileName        : LoadingFID.nmdata
Comment         : 1H S/N
SliceHistory    :
EXMODE          : non

POINT           :     32768 points
SAMPO           :     32768 points
FREQU           :    8000.0 Hz
FILTR           :      4000 Hz
DELAY           :      50.0 usec
DEADT           :      71.8 usec
INTVL           :     125.0 usec
TIMES           :       200 times
DUMMY           :         1 times
PD              :    2.9000 sec
ACQTM           :  4096.0000 msec
PREDL           :    0.01000 msec
INIWT           :  1000.0000 msec
RESOL           :      0.24 Hz
PW1             :      6.40 usec
OBNUC           : 1H
OBFRQ           :    500.00 MHz
OBSET           :  162410.00 Hz
RGAIN           :        24

SCANS           :        75 times

SLVNT           : D2O
SPINNING        :        15 Hz
TEMP            :      24.2 C
```

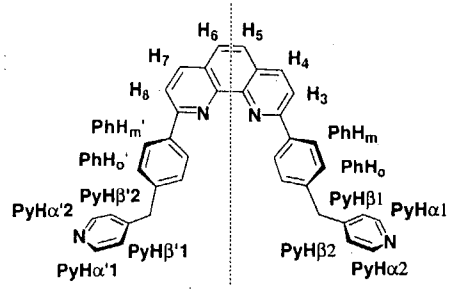
^{1}H NMR (500 MHz, D_2O:CD_3OD = 2 : 1)

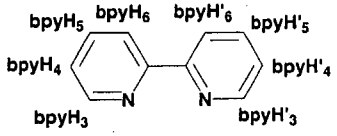
Sample: **Doubly locking [2]catenane**

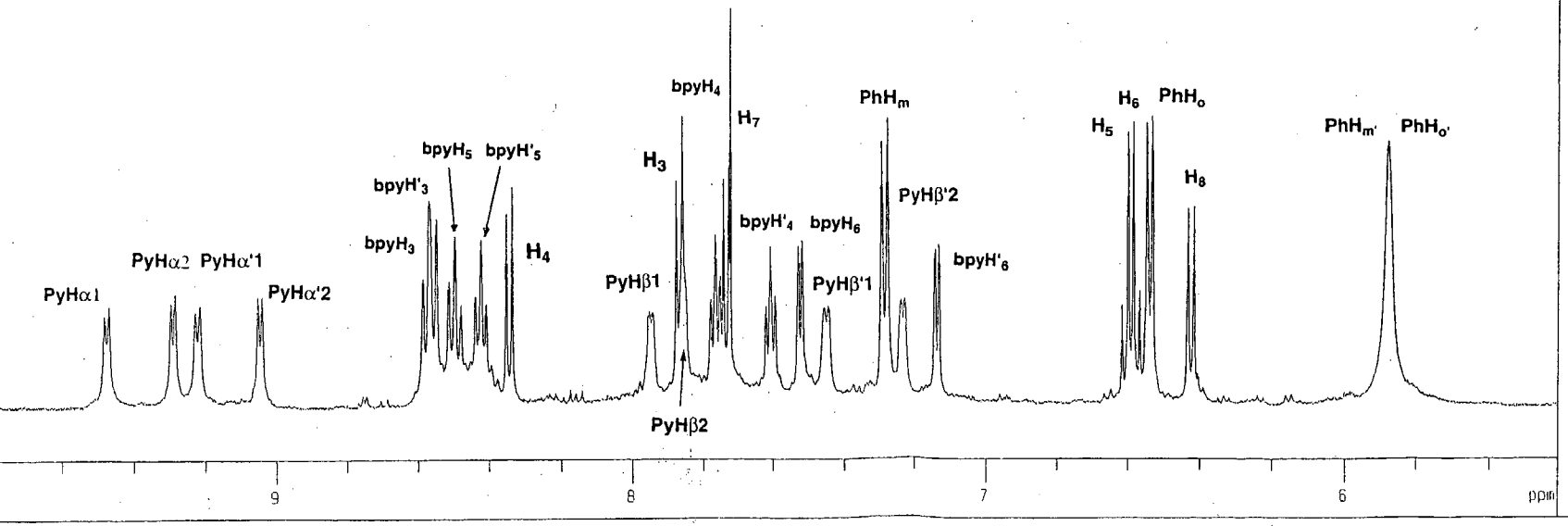


○ = Cu(I)

◎ = 2,2'-(bipy)Pd(NO_3)$_2$

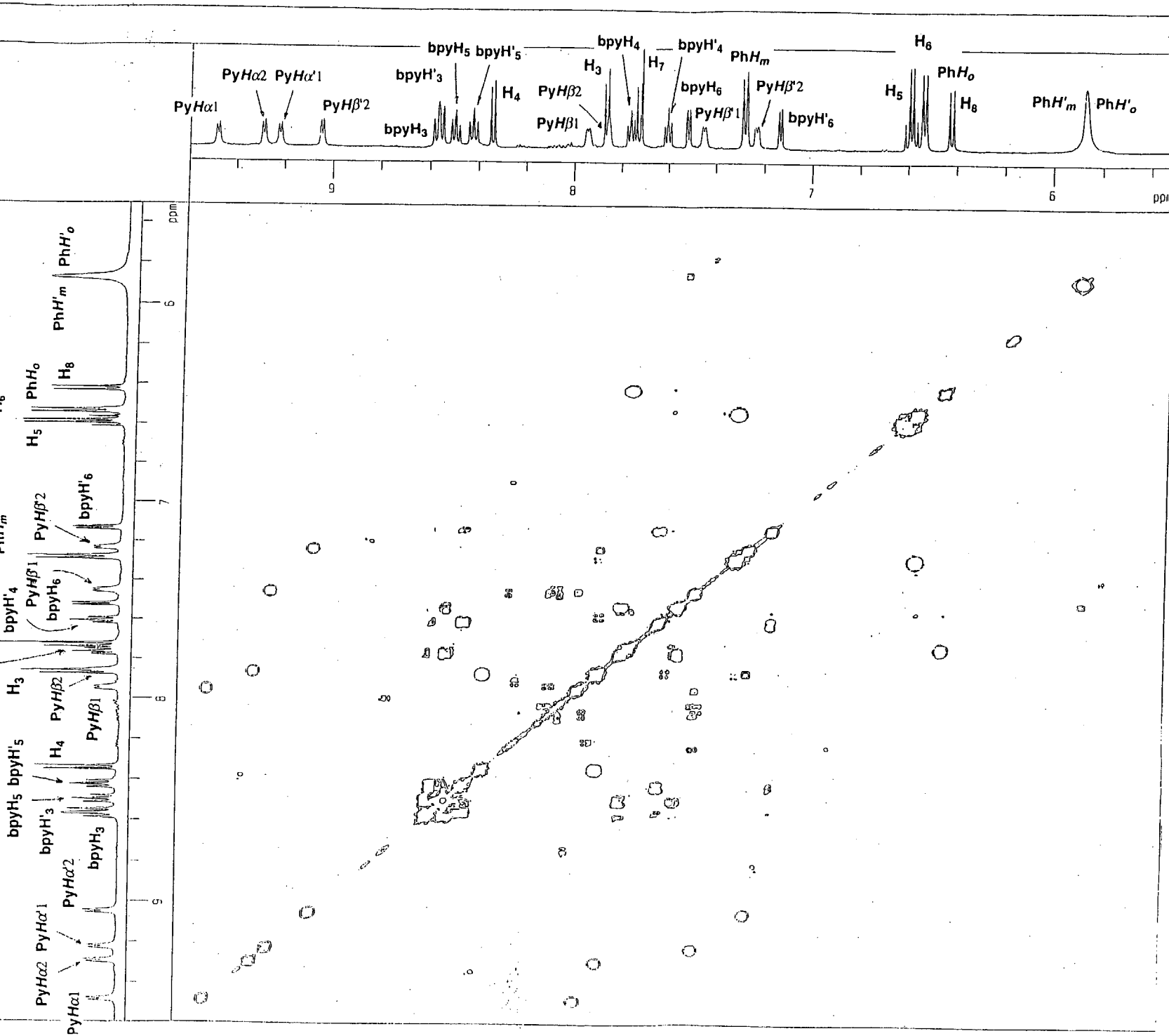







```
Date : Fri Dec 11 13:11:17 1998

FileName        : .LoadingFID.nmdata
Comment         : 1H S/N
SliceHistory    :
EXMODE          : non

POINT           :      32768 points
SAMPO           :      32768 points
FREQU           :     8000.0 Hz
FILTR           :       4000 Hz
DELAY           :       50.0 usec
DEADT           :       71.8 usec
INTVL           :      125.0 usec
TIMES           :        200 times
DUMMY           :          1 times
PD              :     2.9000 sec
ACQTM           :  4096.0000 msec
PREDL           :     0.0100 msec
INIWT           :  1000.0000 msec
RESOL           :       0.24 Hz
PW1             :       6.40 usec
OBNUC           : 1H
OBFRQ           :     500.00 MHz
OBSET           :  162410.00 Hz
RGAIN           :         24

SCANS           :         75 times

SLVNT           : D2O
SPINNING        :         15 Hz
TEMP            :       24.2 C
```

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 23

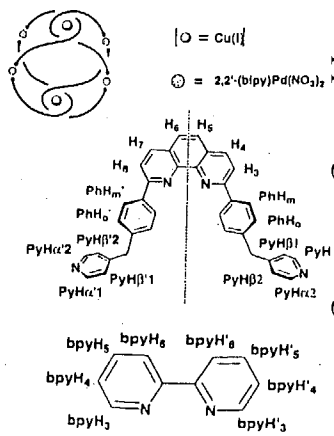


Date : Wed Dec 16 18:53:52 1998

FileName	dfi168HH.nmdata
Comment	
SliceHistory	
EXMODE	cosy
POINT	512 points
SAMPO	512 points
FREQU	2048.8 Hz
FILTR	1000 Hz
DELAY	200.0 usec
DEADT	293.3 usec
INTVL	488.1 usec
TIMES	16 times
DUMMY	4 times
PD	0.7501 sec
ACQTM	249.9072 msec
PREDL	0.01000 msec
INIWT	1000.0000 msec
RESOL	4.00 Hz
PW1	13.50 usec
OBNUC	1H
OBFRQ	500.00 MHz
OBSET	165008.02 Hz
RGAIN	32
CLFRQ	2048.8 Hz
CLPNT	512 points
TODAT	512 points
CINNT	5.00 usec
CINTV	488.1 usec
PW2	13.50 usec
IRNUC	1H
IRFRQ	500.00 MHz
IRSET	162410.00 Hz
IRATN	511
SCANS	16 times
SLVNT	D2O
SPINNING	15 Hz
TEMP	24.4 C

^{1}H - ^{1}H COSY

Doubly locking [2]catenane



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 24

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 25

Date : Wed Jun 16 02:42:05 1999

FileName	13CcateDpy nmrdata
Comment	
SliceHistory	
EXMODE	bcm
POINT	32768 points
SAMPO	32768 points
FREQU	33898.3 Hz
FILTR	16950 Hz
DELAY	11.8 usec
DEADJ	15.0 usec
INTVL	29.5 usec
TIMES	25000 times
DUMMY	1 times
PD	2.0333 sec
ACQTM	966.6560 msec
PREDL	0.01000 msec
TNIWT	1000.0000 msec
RESOL	1.03 Hz
PW1	5.35 usec
13C	
OBNUC	
OBFRQ	125.65 MHz
OBSET	127958.00 Hz
AGAIN	28
1H	
TNUC	
IRFRQ	500.00 MHz
IRSET	162410.00 Hz
IRPW	50.0 usec
IRNS	0
SCANS	12768 times
SLVNT	CD3CN
SPINNING	14 Hz
TEMP	25.4 C

^{13}C NMR
(126 MHz, CD_3CN, TMS)

Sample:

Doubly Locking Catenane

TMS
Solvent
Solvent

40.470
41.293
124.380
125.525
125.704
125.770
125.918
126.156
126.749
127.547
128.098
128.591
128.616
129.044
129.175
129.225
129.521
129.603
129.800
129.825
130.516
137.598
137.623
137.927
138.330
138.552
140.156
140.173
143.817
143.907
143.924
144.006
151.047
151.244
152.141
152.299
156.213
156.287
157.373
157.389
157.414
157.726

ppm
0
25
50
75
100
125
150

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 26

Date : Wed Jun 16 02:42:05 1999

FileName	:	13Ccatebpy.nmdata
Comment	:	
SliceHistory	:	
EXMODE	:	bCM
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	33898.3 Hz
FILTR	:	16950 Hz
DELAY	:	11.8 usec
DEADT	:	15.0 usec
INTVL	:	29.5 usec
TIMES	:	25000 times
DUMMY	:	1 times
PD	:	2.0333 sec
ACQTM	:	966.6560 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	1.03 Hz
PW1	:	5.35 usec
OBNUC	:	13C
OBFRQ	:	125.65 MHz
OBSET	:	12795.00 Hz
RGAIN	:	28
IRNUC	:	1H
IRFRQ	:	500.00 MHz
IRSET	:	162410.00 Hz
IRPPW	:	50.0 usec
IRPWR	:	0
SCANS	:	12768 times
SLVNT	:	CD3CN
SPINNING	:	14 Hz
TEMP	:	25.4 C

^{13}C NMR
(126 MHz, CD_3CN, TMS)

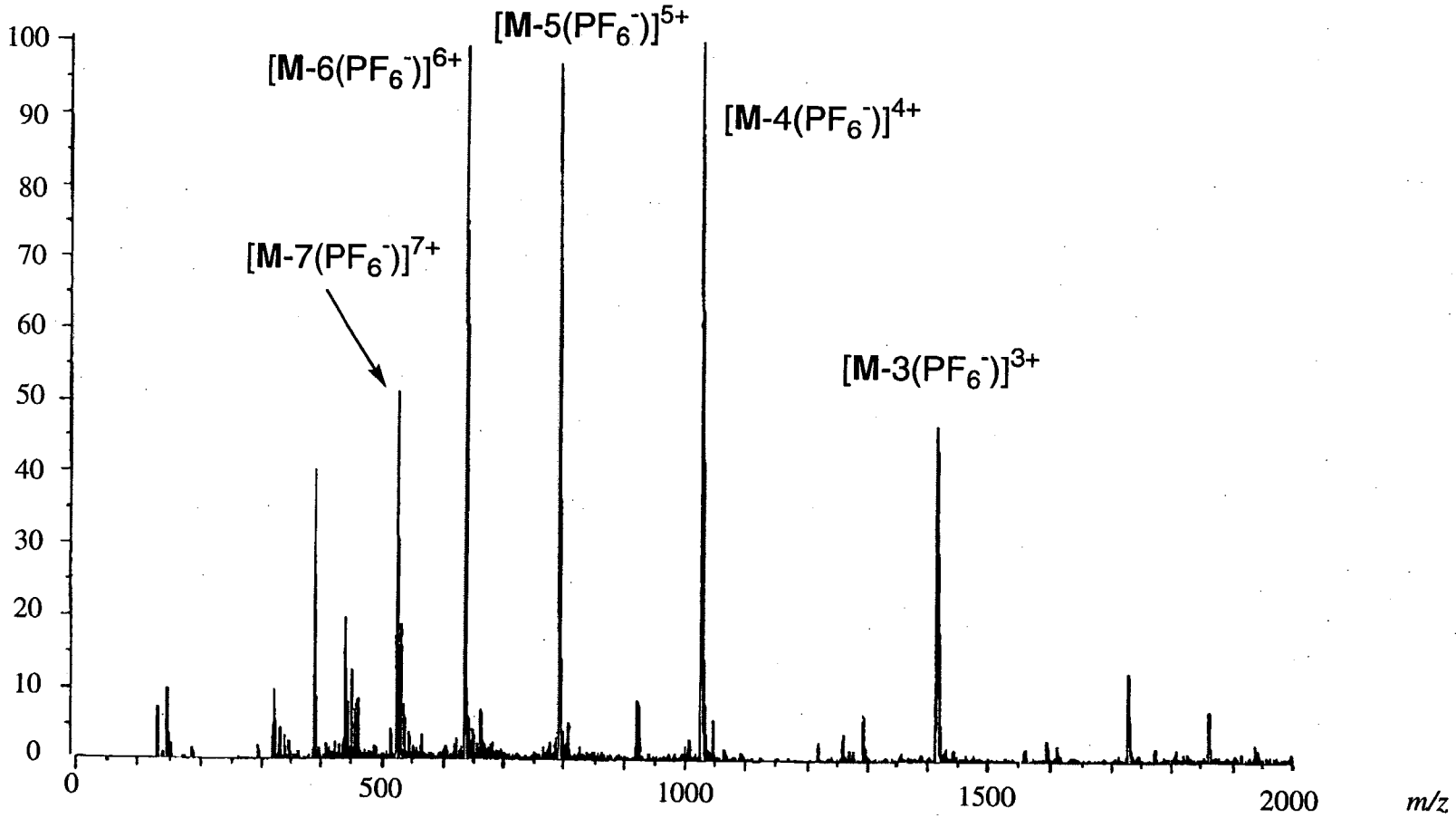
Sample:

Doubly Locking Catenane

High Resolution ESI-MS of Doubly locking [2]Catenane, bipy-protencetd analog

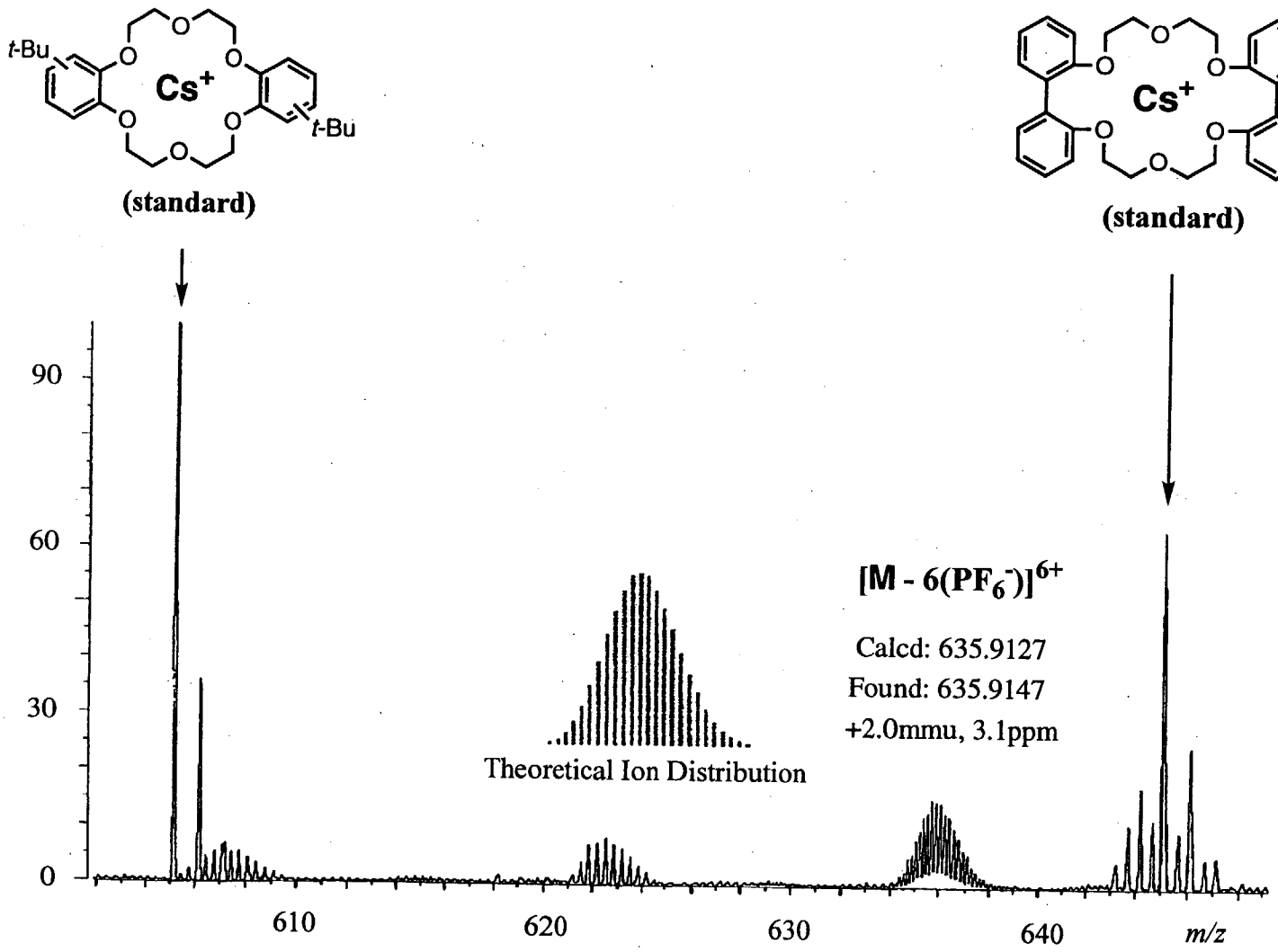
Formula: $[C_{184}H_{136}Cu_2N_{24}Pd_4]^{10+} \bullet 10(PF_6^-) = M^{10+} \bullet 10(PF_6^-)$

Molecular Weight: 4685.6784

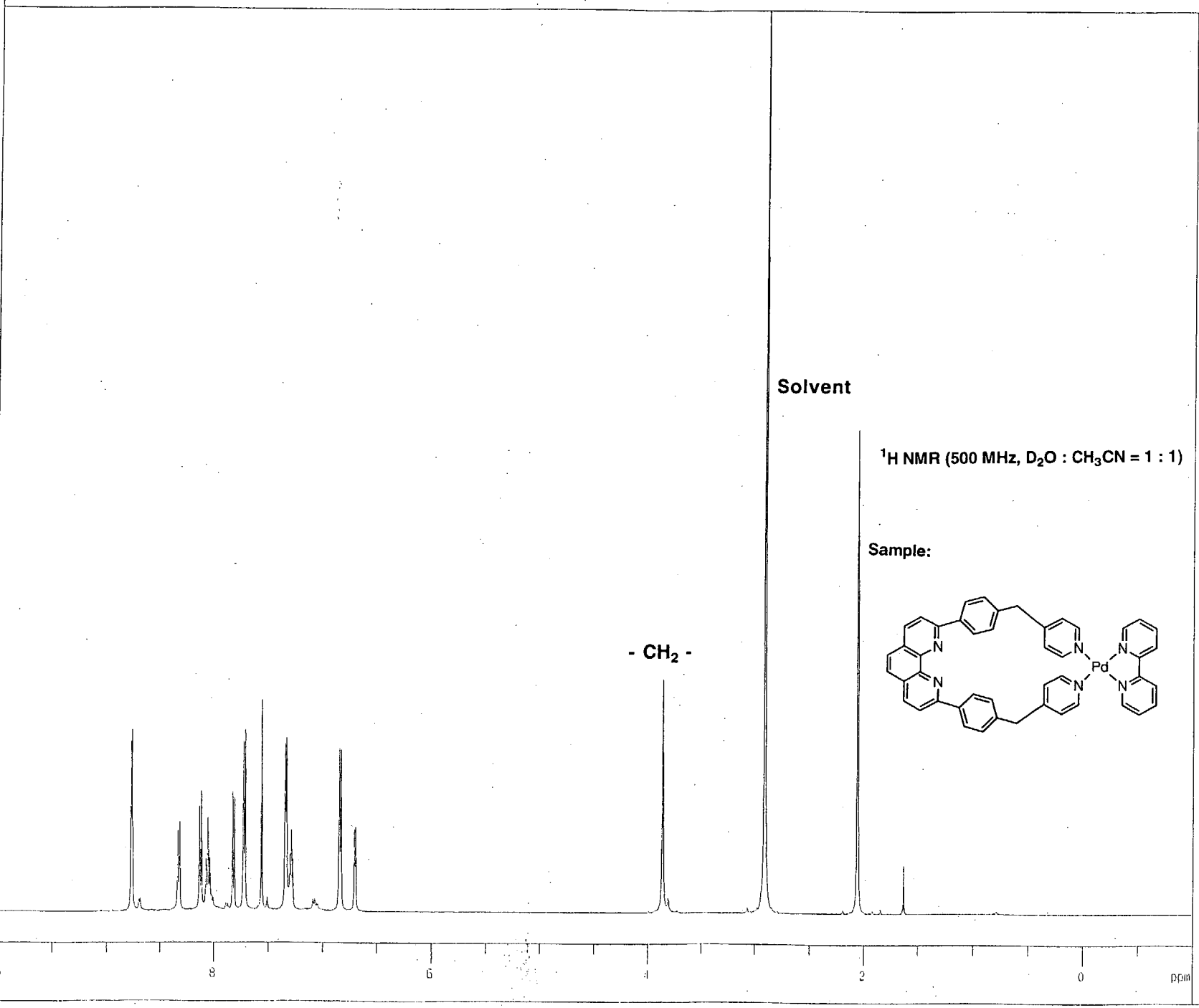


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 27

High Resolution ESI-MS of Doubly Locking [2]Catenane, bipy-protenceted analog



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 28



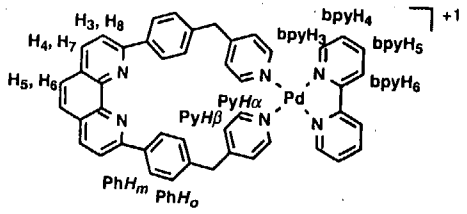
Date : Mon Dec 21 15:43:13 1998

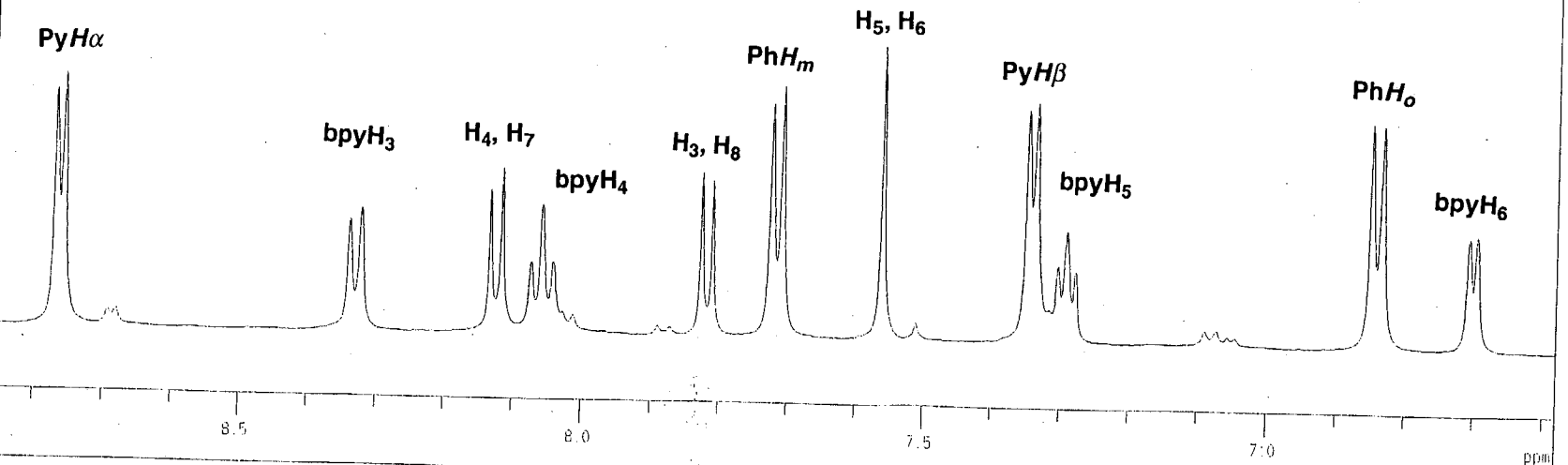
FileName	:	DFI168-HH.nmdata
Comment	:	
SliceHistory	:	
EXMODE	:	non
POINT	:	32768 points
SAMPO	:	32768 points
FREQU	:	8000.0 Hz
FILTR	:	4000 Hz
DELAY	:	50.0 usec
DEADT	:	71.6 usec
INTVL	:	125.0 usec
TIMES	:	32 times
DUMMY	:	1 times
PD	:	2.9040 sec
ACQTM	:	4096.0000 msec
PREDL	:	0.01000 msec
INIWT	:	1000.0000 msec
RESOL	:	0.24 Hz
PW1	:	6.75 usec
OBNUC	:	1H
OBFRQ	:	500.00 MHz
OBSET	:	162410.00 Hz
RGAIN	:	21
SCANS	:	32 times
SLVNT	:	DMSO
SPINNING	:	16 Hz
TEMP	:	24.6 C

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 29

^{1}H NMR (500 MHz, DMSO-d_6)

Sample:

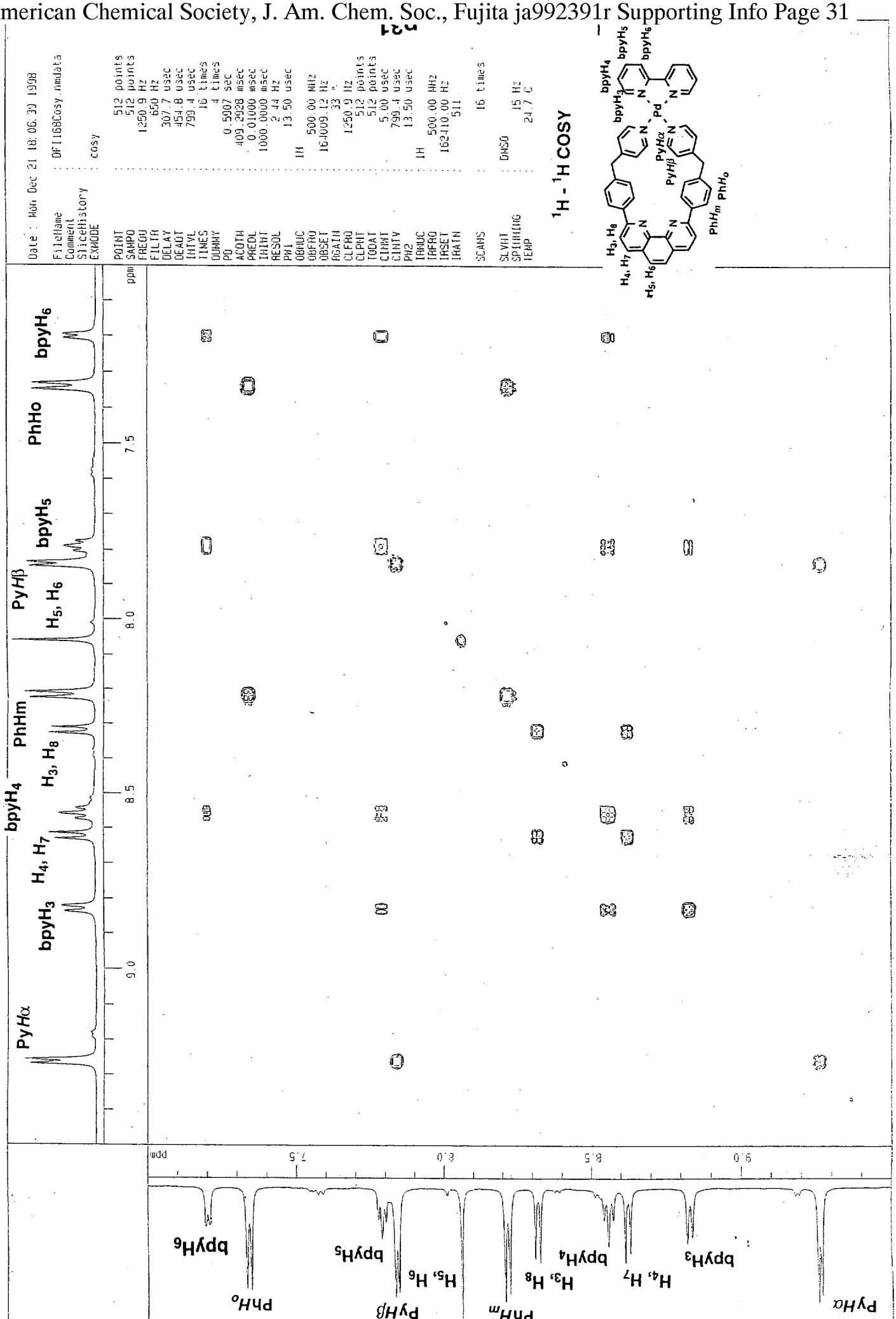




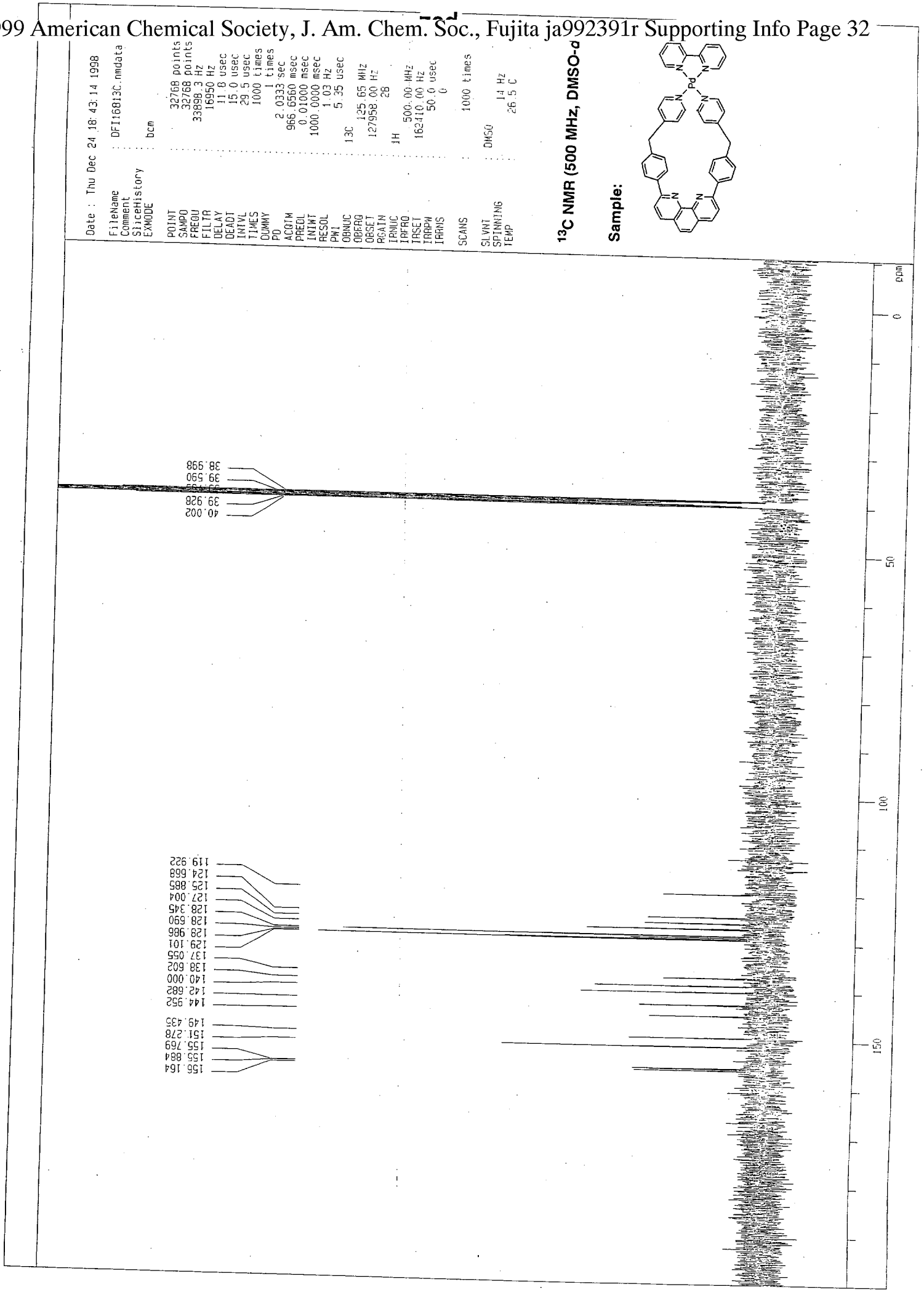

```
Date : Mon Dec 21 15:43:13 1998

FileName      : OFI166-HH.nmdata
Comment       :
SliceHistory  :
EXMODE        : non

POINT         :     32768 points
SAMPO         :     32768 points
FREQU         :    8000.0 Hz
FILTR         :      4000 Hz
DELAY         :      50.0 usec
DEADT         :      71.6 usec
INTVL         :     125.0 usec
TIMES         :        32 times
DUMMY         :         1 times
PD            :    2.9040 sec
ACQTM         : 4096.0000 msec
PREDL         :  0.01000 msec
INIWT         : 1000.0000 msec
RESOL         :      0.24 Hz
PW1           :      6.75 usec
OBNUC         : 1H
OBFRQ         :    500.00 MHz
OBSET         : 162410.00 Hz
RGAIN         :        21

SCANS         :        32 times

SLVNT         : DMSO
SPINNING      :        16 Hz
TEMP          :      24.6 C
```

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 30

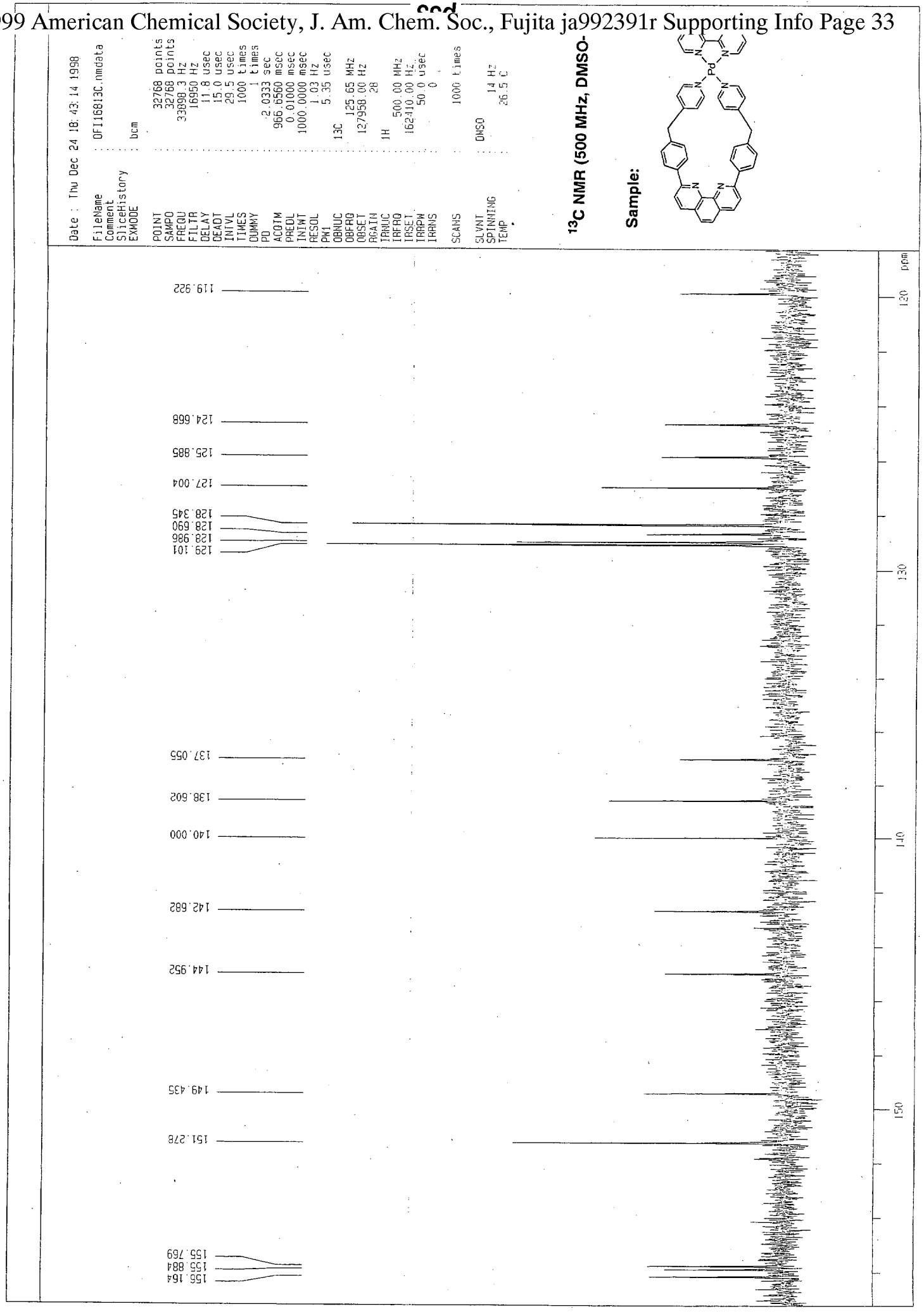
© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 31



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 32



© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 33

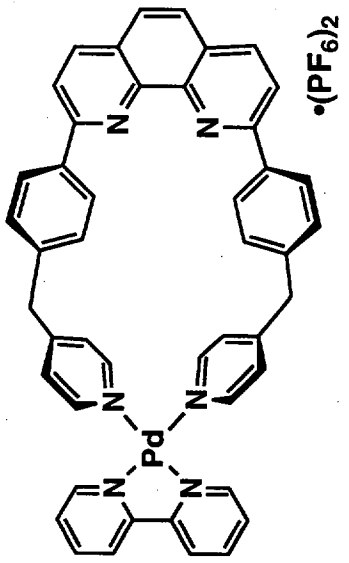


© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 34

[Mass Spectrum]
Data : ESI-990202-DFI-174-007
Sample:
Note : -
Inlet : Direct
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.95 min
BP : m/z 388.2125
Output m/z range : 0.0000 to 20000.0000
6246079

Date : 02-Feb-1999 18:25
Ion Mode : ESI+
Scan# : (1,7)
Int. : 84.67
Cut Level : 0.50 %

ESI Mass Spectrum of monomeric ring



MW 1067.165

388.2 [M-2(PF6)]2+

514.4 [Ligand 1+]

912.4 [M-(PF6)]+

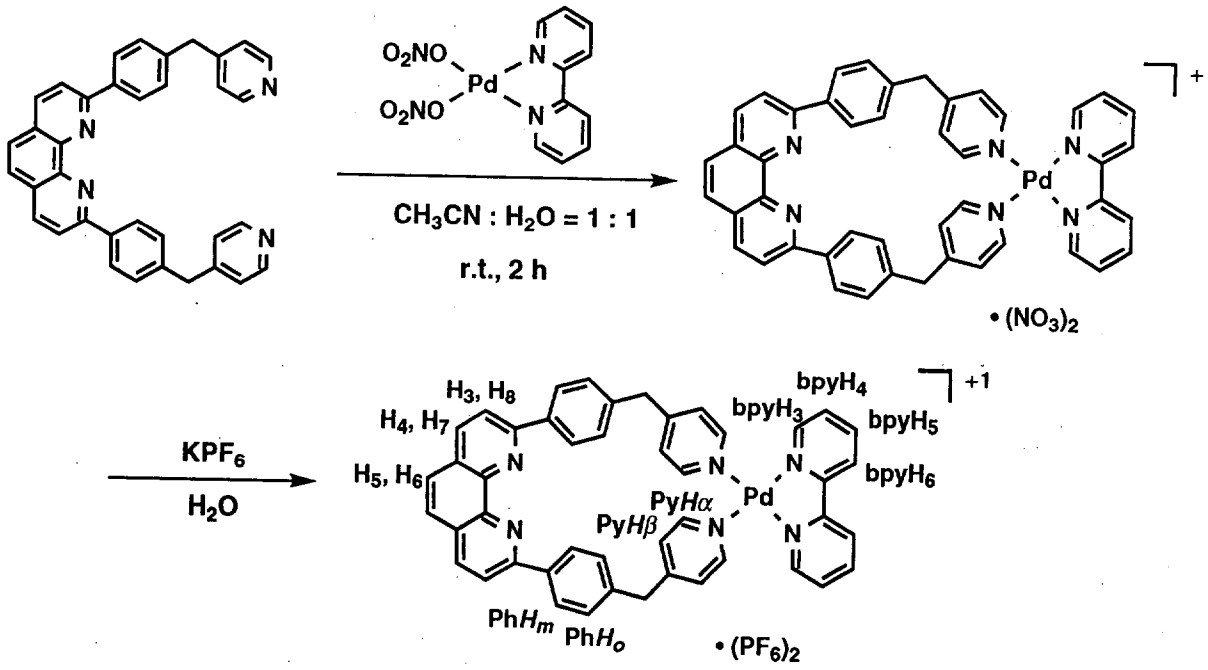
0 10 20 30 40 50 60 70 80 90

0 500 1000 1500 2000

m / z

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 35

Synthesis of bpy-protected palladium monomeric ring

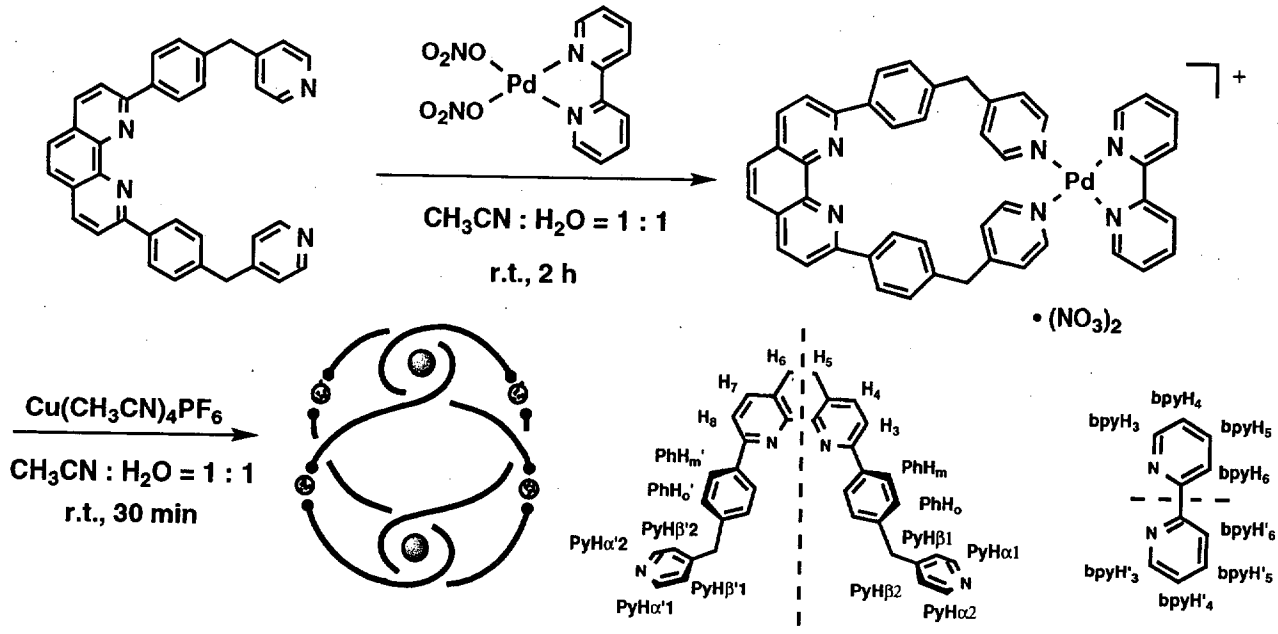


To an acetnitrile solution (1.5 mL) of ligand **1** (30.8 mg, 0.06 mmol), an aqueous solution (1.5 mL) of bpy-protected palladium complex (byp(Pd)$(ONO_2)_2$) (23.1 mg, 0.06 mmol) was added under nitrogen atmoshere. This solution was stirred at 25 °C for 2 h. To the pale yellow solution, an aqueous KPF_6 (2 mL, 213 mg) was added to form white precipitate. This reaction mixture was stirred for 12 h. The precipitate was filtered and dried to give the titled compounds as pale yellow solids (46.4 mg, 0.044 mmol, 73% yield).

Physical data of monomeric ring (as PF_6 salt): ^{1}H NMR (500 MHz, DMSO-d_6, TMS as external standard) δ 8.76 (d-like, J = 6.1 Hz, 4 H, Py$H\alpha$), 8.33 (d, J = 8.1 Hz, 2 H, bpyH_3), 8.12 (d, J = 8.3 Hz, 2 H, H_4 and H_7), 8.06 (t-like, J = 8.1 Hz, J = 5.4 Hz, 2 H, bpyH_4), 7.82 (d, J = 8.3 Hz, 2 H, H_3 and H_8), 7.72 (d, J = 8.1 Hz, 4 H, PhH_m), 7.34 (d-like, J = 6.1 Hz, 4 H, Py$H\beta$), 7.29 (t-like, J = 8.1 Hz, J = 5.4 Hz, 2 H, bpyH_5), 6.84 (d, J = 8.1 Hz, 4 H, PhH_0), 6.70 (d, J = 5.4 Hz, 2 H, bpyH_6), 3.87 (s, 4 H, -CH_2-); ^{13}C NMR (DMSO-d_6, 126 MHz, TMS as external standard) 156.16, 155.88, 155.77, 151.44, 149.44, 144.95, 142.68, 140.00, 138.60, 137.06, 129.10, 128.99, 128.69, 128.35, 127.00, 125.89, 124.67, 119.92. mp 220 °C dec. Anal. Calcd for $C_{46}H_{34}F_{12}N_6P_2Pd$•0.5($CHCl_3$): C, 49.56; H, 3.09; N, 7.46. Found: C, 49.22; H, 3.02; N, 7.59.: ESI-MS (CH_3CN) *m/z* (relative intensity) 921.4 {[M - (PF_6^-)]$^+$, 100%}, 388.2 {[M - (PF_6^-)$_2$]$^{2+}$, 44%}.

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 36

The synthesis of Doubly Locking [2]Catenane analogue (bpy-protected analogue)



Under nitrogen atmosphere, was reacted the mixture of an acetonitrile (2 mL) solution of ligand **1** (20.6 mg, 0.04 mmol) and an aqueous solution (1 mL) of bpy-protected palladium complex (byp(Pd)(ONO_2)$_2$) (15.4 mg, 0.04 mmol). After stirred for 15 min, tetrakis(acetonitrile)copper(I) hexafluorophasphate (7.4 mg, 0.02 mmol) was added. The reaction mixture was stirred for 30 min at 25 °C. This solution was poured into an aqueous KPF_6 (148 mg, H_2O 1.5 mL). Immediately, red brown precipitate was formed. This reaction mixture was stirred for 1 h. Then, the precipitate was filtered and dried to give the titled compounds as brown solids (38.7 mg, 0.0083 mmol, 83% yield). ^1H NMR (500 MHz, D_2O, TMS as an external standard) δ 9.46 (d, J = 5.9 Hz, 2 H, Py$H\alpha$1), 9.27 (d, J = 5.9 Hz, 2 H, Ph$H\alpha$2), 9.20 (d, J = 6.1 Hz, 2 H, Py$H\alpha$' 1), 9.03 (d, J = 5.6 Hz, 2 H, Ph$H\alpha$'2), 8.56 (d, J = 9.1 Hz, 2 H, bpyH_3), 8.54 (d, J = 10.7 Hz, 2 H, bpyH_3'), 8.47 (t, J = 8.7 Hz, J = 5.4 Hz, 2 H, bpyH_5), 8.40 (t, J = 8.7 Hz, J = 5.4 Hz, 2 H, bpyH_5'), 8.32 (d, J = 8.6 Hz, 2 H, H_4), 7.92 (d, J = 5.4 Hz, 2 H, Py$H\beta$1), 7.85 (d, J = 8.6 Hz, 2 H, H_3), 7.84 (broad signal, 2 H, Py$H\beta$'2), 7.74 (broad signal, 2 H, bpyH_4), 7.71 (d, J = 8.3 Hz, 2 H, H_7), 7.58 (t, J = 7.4 Hz, J = 5.4 Hz, 2 H, bpyH_4'), 7.50 (d, J = 4.9 Hz, 2 H, bpyH_6), 7.43 (d, J = 5.9 Hz, 2 H, Py$H\beta$'1), 7.26 (d, J = 8.3 Hz, 4 H, PhH_m), 7.21 (d, J = 5.2 Hz, 2 H, Py$H\beta$'2),

7.11 (d, J = 4.9 Hz, 2 H, bpyH_6'), 6.58 (d, J = 9.0 Hz, 2 H, H_5), 6.55 (d, J = 8.8 Hz, 2 H, H_6), 6.52 (d, J = 8.3 Hz, 4 H, PhH_o), 6.40 (d, J = 8.1 Hz, 2 H, H_8), 5.85 (broad singlets, 8 H, PhH_o', PhH_m'), 3.92 (d, J = 15.6 Hz, 2 H, CH_b), 3.74 (d, J = 13.0 Hz, 2 H,CH_a), 3.46 (d, J = 13.1 Hz, 2 H,CH_a'), 3.32 (d, J = 15.4 Hz, 2 H, CH_b'). High Resolution ESI MS Calcd for [M-6(PF_6^-)] 635.9127, Found 635.9147. +2.0mmu, 3.1 ppm. Anal. Calcd for $C_{188}H_{148}Cl_{12}Cu_2F_{60}N_{24}O_4P_{10}Pd_4$: C, 43.13; H, 2.85; N, 6.42. Found: C, 43.14; H, 2.78; N, 6.65.

© 1999 American Chemical Society, J. Am. Chem. Soc., Fujita ja992391r Supporting Info Page 38

The molecular coordinates of compound 3^{10+}

The structure of compound 3^{10+} was optimized by MM2 force field calculation with Cerius^2 Ver 3.5 package software. The molecular coordinates are indicated below.

Coordinates of compound 3^{10+}

1	H	-10.293	8.567	-3.579
2	Pd	-13.369	14.456	-2.635
3	H	-16.351	-1.250	-8.194
4	H	-11.476	8.000	-2.395
5	H	-9.643	-1.342	-1.147
6	H	-11.123	-2.253	-0.849
7	Pd	-23.023	-1.091	-7.982
8	C	-14.355	4.543	-9.713
9	C	-14.064	5.464	-8.692
10	C	-13.489	5.022	-7.489
11	N	-13.253	3.694	-7.338
12	C	-13.474	2.782	-8.330
13	C	-14.034	3.188	-9.548
14	H	-14.809	4.888	-10.635
15	H	-16.524	0.330	-8.990
16	H	-14.289	6.514	-8.839
17	C	-12.277	7.090	-6.796
18	H	-14.660	2.544	-11.510
19	C	-13.350	0.472	-9.133
20	C	-13.129	1.425	-8.127
21	N	-12.581	1.045	-6.946
22	C	-12.292	-0.237	-6.635
23	C	-12.497	-1.227	-7.609
24	H	-9.455	2.626	-12.113
25	C	-13.010	-0.867	-8.869
26	H	-9.309	4.381	-12.141
27	H	-14.079	0.167	-11.147
28	C	-11.777	7.944	-5.806
29	H	-12.253	-2.264	-7.400
30	H	-13.152	-1.633	-9.623
31	C	-14.245	2.236	-10.560
32	C	-12.058	7.707	-4.451
33	C	-12.867	6.610	-4.107
34	C	-13.365	5.756	-5.099
35	C	-13.057	5.976	-6.448
36	C	-13.517	2.799	-1.435
37	H	-12.019	7.274	-7.833
38	H	-11.134	8.761	-6.099
39	C	-14.565	2.380	-2.282
40	H	-13.100	6.405	-3.068
41	H	-14.013	4.947	-4.810
42	C	-11.854	-0.555	-5.271
43	C	-12.595	-1.446	-4.485
44	C	-12.261	-1.646	-3.143
45	C	-11.183	-0.954	-2.572
46	C	-14.347	2.317	-3.665
47	N	-13.141	2.668	-4.147
48	C	-10.426	-0.082	-3.368
49	C	-10.758	0.111	-4.712
50	H	-13.453	-1.959	-4.902
51	H	-12.839	-2.346	-2.551
52	H	-9.549	0.407	-2.957
53	H	-10.125	0.735	-5.324
54	C	-11.924	9.927	-3.242
55	C	-11.506	10.939	-4.118

56	C	-12.098	3.029	-3.361
57	C	-11.930	12.254	-3.913
58	N	-12.724	12.566	-2.853
59	C	-12.252	3.101	-1.974
60	C	-13.140	11.606	-1.984
61	C	-12.751	10.273	-2.162
62	H	-10.842	10.719	-4.940
63	H	-11.629	13.028	-4.604
64	H	-13.784	11.871	-1.157
65	H	-13.087	9.520	-1.462
66	C	-10.288	0.535	0.541
67	C	-10.706	1.291	1.637
68	N	-12.013	1.288	2.014
69	C	-12.953	0.616	1.292
70	H	-13.686	2.860	-0.367
71	C	-12.574	-0.151	0.185
72	C	-11.221	-0.230	-0.170
73	H	-15.525	2.099	-1.864
74	H	-9.235	0.496	0.294
75	H	-9.979	1.839	2.221
76	C	-15.475	0.344	-4.594
77	H	-11.245	3.511	-0.108
78	C	-9.748	3.651	-3.185
79	C	-10.858	3.301	-3.964
80	N	-10.746	3.197	-5.313
81	C	-9.623	3.510	-5.989
82	C	-8.483	3.883	-5.259
83	C	-8.540	3.931	-3.850
84	H	-9.036	3.961	-1.161
85	C	-15.993	-0.301	-5.718
86	H	-7.554	4.119	-5.769
87	H	-7.651	4.201	-3.289
88	C	-11.138	3.444	-1.182
89	C	-9.886	3.705	-1.784
90	C	-16.357	0.438	-6.853
91	C	-16.246	1.833	-6.833
92	C	-15.695	2.474	-5.723
93	C	-15.288	1.730	-4.608
94	H	-15.134	-0.245	-3.750
95	H	-16.072	-1.380	-5.720
96	H	-16.537	2.412	-7.699
97	H	-15.557	3.544	-5.753
98	C	-9.663	3.512	-7.455
99	C	-9.534	4.716	-8.157
100	C	-9.678	4.741	-9.548
101	C	-9.961	3.561	-10.253
102	C	-10.101	2.357	-9.546
103	C	-9.957	2.334	-8.155
104	H	-9.352	5.643	-7.624
105	H	-9.570	5.680	-10.075
106	H	-10.277	1.429	-10.081
107	H	-10.031	1.389	-7.634
108	C	-18.321	-0.414	-8.052
109	C	-18.896	-1.343	-7.177
110	C	-20.279	-1.487	-7.145
111	N	-21.062	-0.742	-7.966
112	C	-20.532	0.168	-8.825
113	C	-19.150	0.355	-8.878
114	H	-18.282	-1.955	-6.533
115	H	-20.731	-2.208	-6.478
116	H	-21.183	0.738	-9.473
117	H	-18.732	1.089	-9.555
118	C	-11.842	2.666	-13.168
119	C	-13.007	2.885	-13.909
120	N	-13.637	4.090	-13.854
121	C	-13.191	5.079	-13.032

122	C	-12.026	4.900	-12.278
123	C	-11.323	3.691	-12.367
124	H	-11.317	1.725	-13.272
125	H	-13.382	2.108	-14.563
126	H	-13.723	6.021	-12.985
127	H	-11.659	5.710	-11.661
128	C	-16.832	-0.254	-8.095
129	C	-9.952	3.557	-11.757
130	H	-13.990	0.646	1.597
131	H	-13.321	-0.719	-0.355
132	C	-11.383	8.521	-3.371
133	C	-10.751	-1.254	-1.167
134	H	-19.679	14.206	-4.786
135	Pd	-12.528	2.174	3.742
136	H	-18.770	14.363	-6.290
137	H	-17.233	6.280	1.315
138	H	-15.869	7.010	0.457
139	C	-22.337	7.144	-8.543
140	C	-22.000	8.446	-8.131
141	C	-21.129	8.627	-7.044
142	N	-20.654	7.534	-6.406
143	C	-20.909	6.263	-6.811
144	C	-21.773	6.033	-7.892
145	H	-23.020	7.010	-9.375
146	H	-22.418	9.302	-8.650
147	C	-20.025	10.789	-7.585
148	H	-22.698	4.512	-9.123
149	C	-20.547	3.865	-6.547
150	C	-20.293	5.181	-6.138
151	N	-19.460	5.423	-5.086
152	C	-18.896	4.435	-4.346
153	C	-19.111	3.103	-4.738
154	C	-19.920	2.820	-5.851
155	H	-21.632	2.621	-7.936
156	C	-19.432	11.988	-7.180
157	H	-18.657	2.289	-4.184
158	H	-20.078	1.792	-6.155
159	C	-22.034	4.711	-8.292
160	H	-25.481	4.082	-4.495
161	C	-21.420	3.634	-7.624
162	C	-19.452	12.364	-5.829
163	C	-20.105	11.547	-4.896
164	C	-20.705	10.353	-5.305
165	C	-20.644	9.954	-6.645
166	Pd	-15.203	4.456	-15.061
167	H	-19.969	10.493	-8.626
168	H	-18.964	12.624	-7.921
169	H	-20.190	11.865	-3.862
170	H	-21.262	9.773	-4.587
171	C	-18.178	4.766	-3.103
172	C	-18.560	4.167	-1.894
173	C	-17.959	4.553	-0.691
174	C	-16.950	5.530	-0.679
175	C	-16.551	6.110	-1.895
176	H	-24.898	3.034	-3.206
177	C	-17.161	5.730	-3.095
178	H	-19.356	3.430	-1.877
179	H	-18.313	4.116	0.231
180	H	-15.775	6.867	-1.912
181	H	-16.816	6.170	-4.014
182	C	-17.605	13.603	-4.670
183	C	-17.526	14.011	-3.333
184	C	-16.276	14.180	-2.735
185	H	-19.897	5.991	-10.540
186	N	-15.139	13.945	-3.443
187	H	-19.390	4.473	-9.765