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SUPPORTING INFORMATION

Regioselective "hydroamination" of alk-3-ynones with non-symmetrical *o*-phenylenediamines. Synthesis of diversely substituted 3*H*-1,5-benzodiazepines via (*Z*)-3-amino-2-alkenones

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Experimental Section

Corrections. The manuscript states that ^{13}C NMR chemical shifts were reported in δ (ppm) values relative to C_6D_6 at 128.06 ppm. However, ^{13}C NMR tabulated data and spectra were referenced to 128.39 ppm.

Page 107086, left column, third paragraph, line 6: "vinamidine form **H9**" should read "vinamidine form **9**"

Page 107093, reference 30, line 2: "allenoue" should read "allenone"

Materials. Triethylamine was distilled over CaH_2. *o*-Phenylenediamine (Mallickrodt), 3,4-diaminotoluene, 3,4-diaminobenzophenone, 4,5-dimethyl-1,2-phenylenediamine (Aldrich), 4-methoxy-*o*-phenylenediamine (Ark Pharm or Alfa Aesar), 4-nitro-*o*-phenylenediamine (Alfa Aesar), 2,3-diaminobenzamide (Synthonix), ethanol (reagent grade 200 proof anhydrous, Pharmco Aaper), anhydrous ethanol (packaged under argon, Alfa Aesar), silica gel (Dynamic Adsorbents, 32-63 μ), and TLC plates (Whatman, hexanes/ethyl acetate 80:20) were used as received. Other materials not listed were used as received.

Fluorescence Quantum Yield. Fluorescence quantum yield (Φ_f) was determined in ethanol by the relative method,[1] using 9,10-dimethylanthracene as a standard,[2] 275 nm excitation, and analysis with Eq. (1) where *r* and *x* denote the reference and unknown, respectively, *A* is the absorption at excitation wavelength, *F* is the integrated fluorescence intensity. Consideration of refractive index was not necessary as both reference and unknown samples were measured in the same solvent. To avoid re-absorption and self-quenching, all working solutions absorbed less than 0.1 AU.

$$\Phi_x = \Phi_r \cdot \frac{A_r \cdot F_x}{A_x \cdot F_r} \qquad (1)$$

2-(4-Methylbenzyl)-4-phenyl-3*H*-benzo[*b*][1,5]diazepine (8aa). **Large Scale Procedure**. A 25 mL round bottom microwave vial equipped with a stir bar was charged with alkynone **1** (0.858 g, 3.66 mmol), *o*-phenylenediamine **4a** (0.398 g, 3.68 mmol), and ethanol (8 mL). The vial was sealed and the reaction was irradiated in a microwave reactor at 80 °C for 70 min. The post-reaction mixture rapidly crystalized after scratching the vial with glass pipette. Filtration gave **8aa** as pale yellow crystals (0.610 g, 1.88 mmol, 51%). An additional crystallization (ethanol/hexanes, layering, 4 °C) increased the overall amount of crystalline solid to 0.760 g, 2.34 mmol, 64%. The yield could potentially be increased via column chromatography of the mother liquor. We are grateful to Mr. Wojciech Gołębiewski for this observation.

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1) (a) C. A. Parker, W. T. Rees, *Analyst*, 1960, **85**, 587. (b) A. T. R. Williams, S. A. Winfield, J. N. Miller, *Analyst*, 1983, **108**, 1067.

2) R. L. Barnes, J. B. Birks, *Proc. Royal Soc. London A. Mat. Phys. Sci.*, 1966, **291**, 570.

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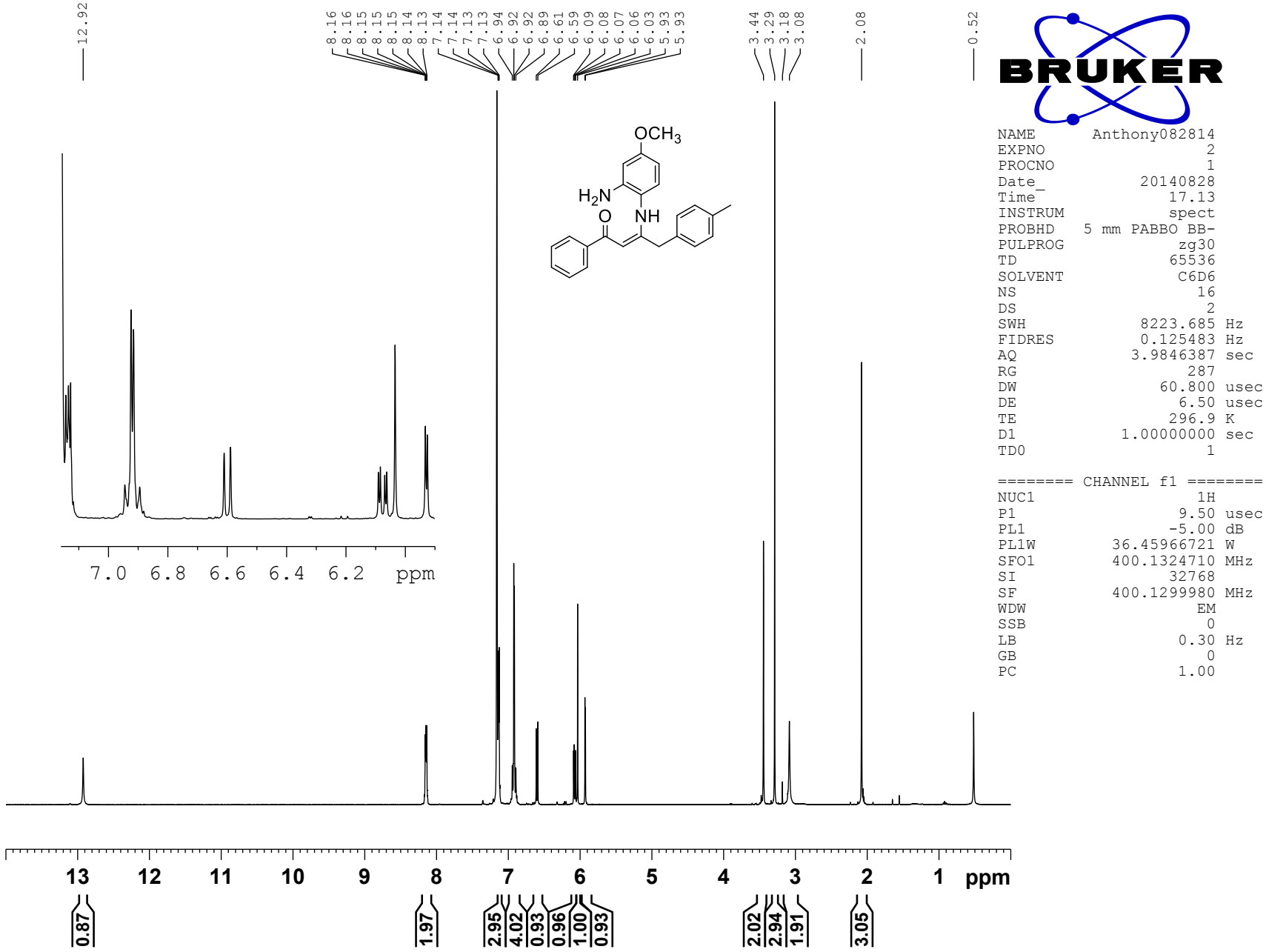
^{1}H NMR spectrum for **5ac** (C_6D_6)



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TD0	1
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SI	32768
SF	400.1299980 MHz
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SSB	0
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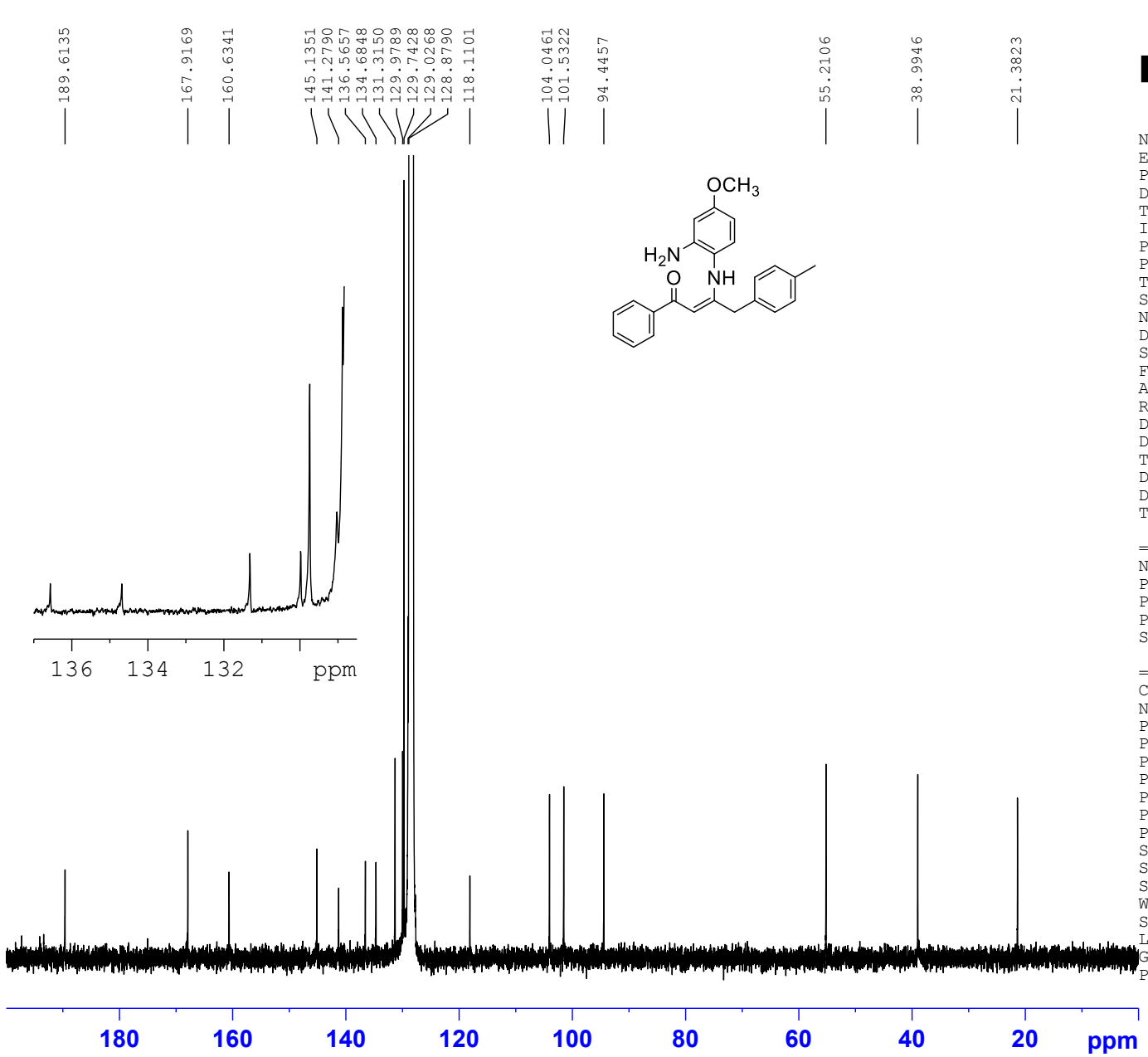
GB	0
PC	1.00

^{13}C NMR spectrum for **5ac** (C_6D_6)



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PROCNO	1
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FIDRES	0.366798 Hz
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DE	6.50 usec
TE	300.8 K
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D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126963 MHz
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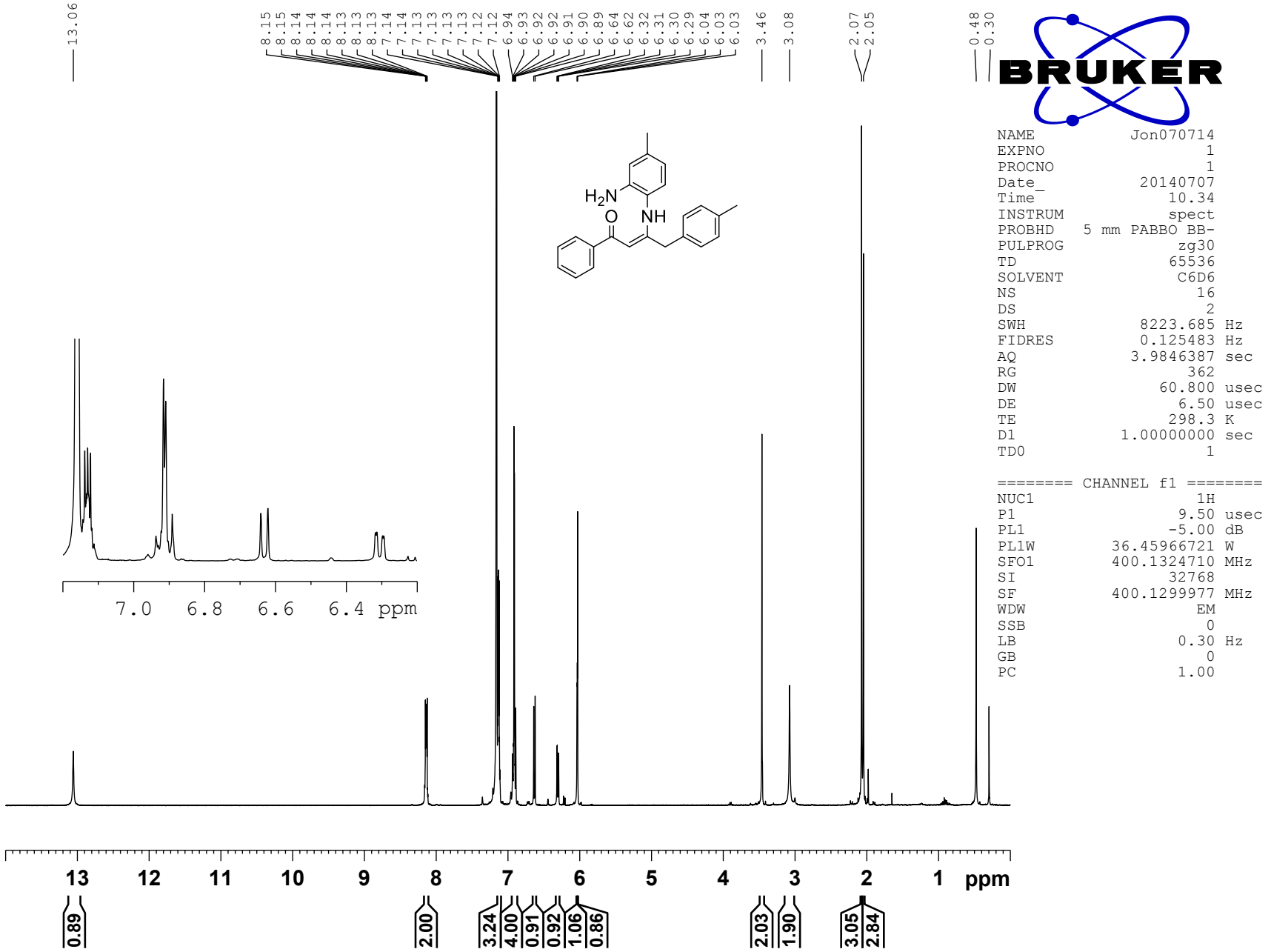
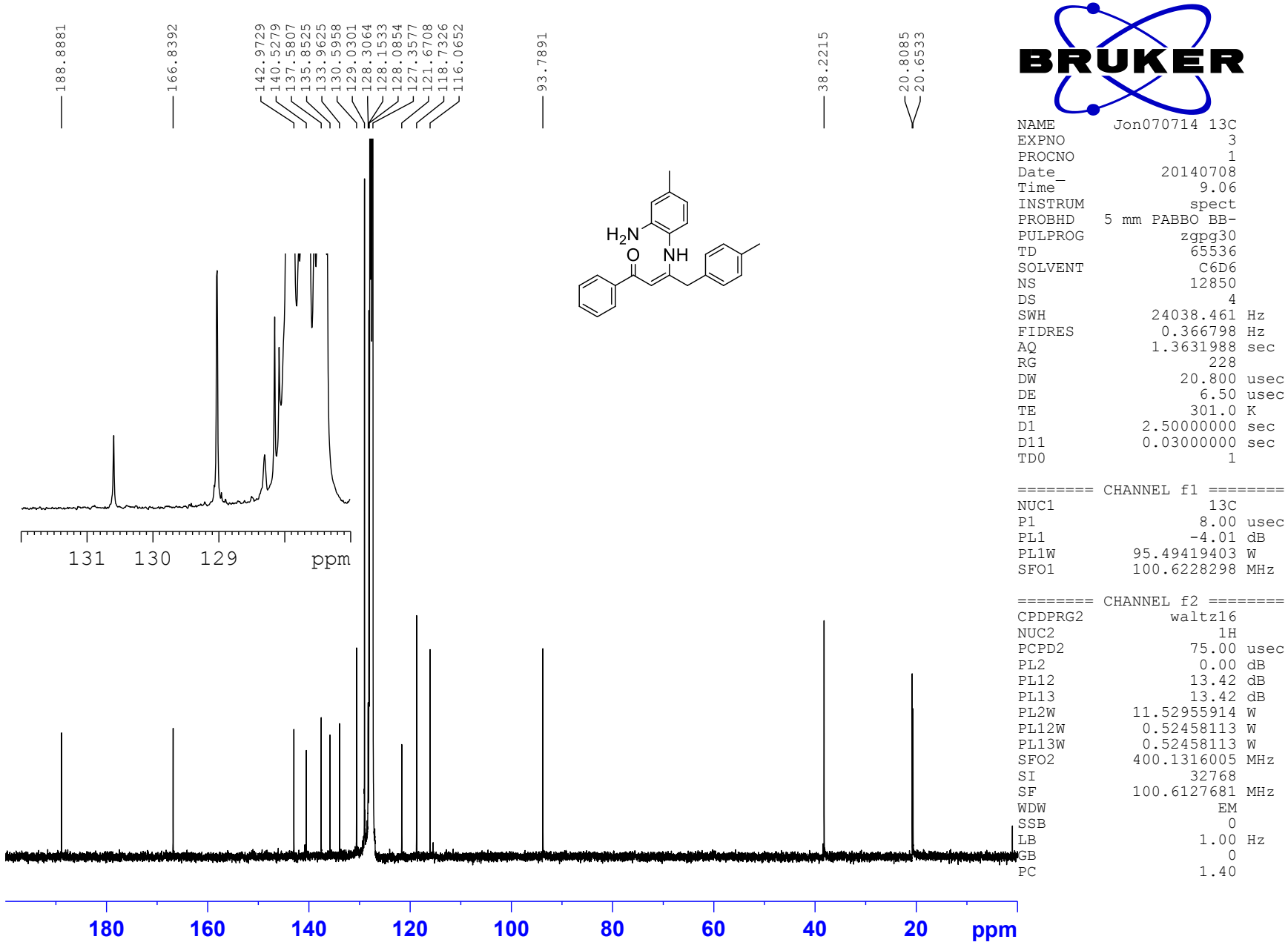
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H NMR spectrum for **5ad** (C_6D_6)



^{13}C NMR spectrum for **5ad** (C_6D_6)

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Time                  9.06
INSTRUM              spect
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TD                   65536
SOLVENT                C6D6
NS                   12850
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     228
DW                  20.800 usec
DE                   6.50 usec
TE                  301.0 K
D1               2.50000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -4.01 dB
PL1W           95.49419403 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                75.00 usec
PL2                   0.00 dB
PL12                 13.42 dB
PL13                 13.42 dB
PL2W           11.52955914 W
PL12W           0.52458113 W
PL13W           0.52458113 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127681 MHz
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SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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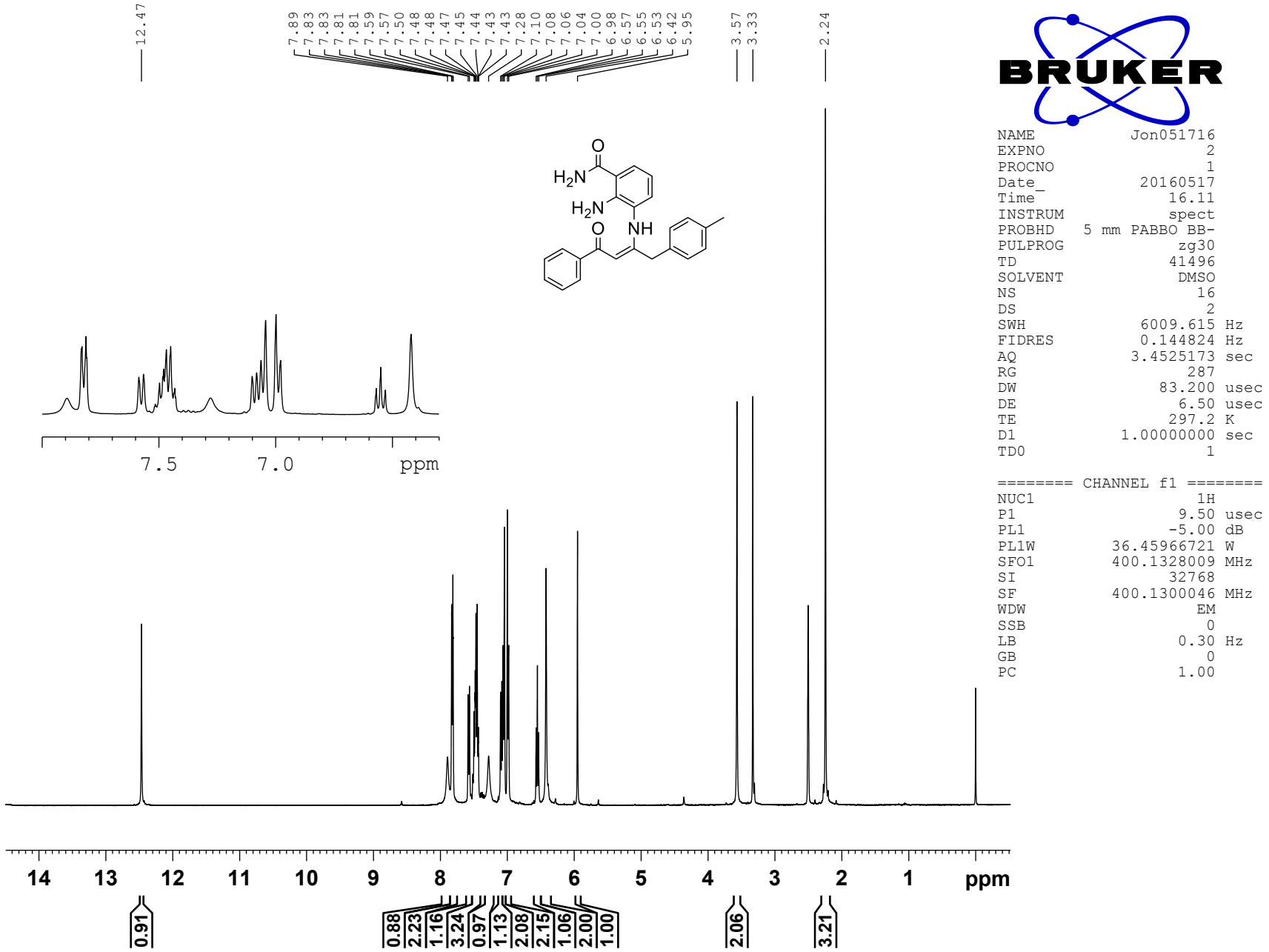
^{1}H NMR spectrum for **5af** (DMSO-d_6)



BRUKER

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EXPNO	2
PROCNO	1
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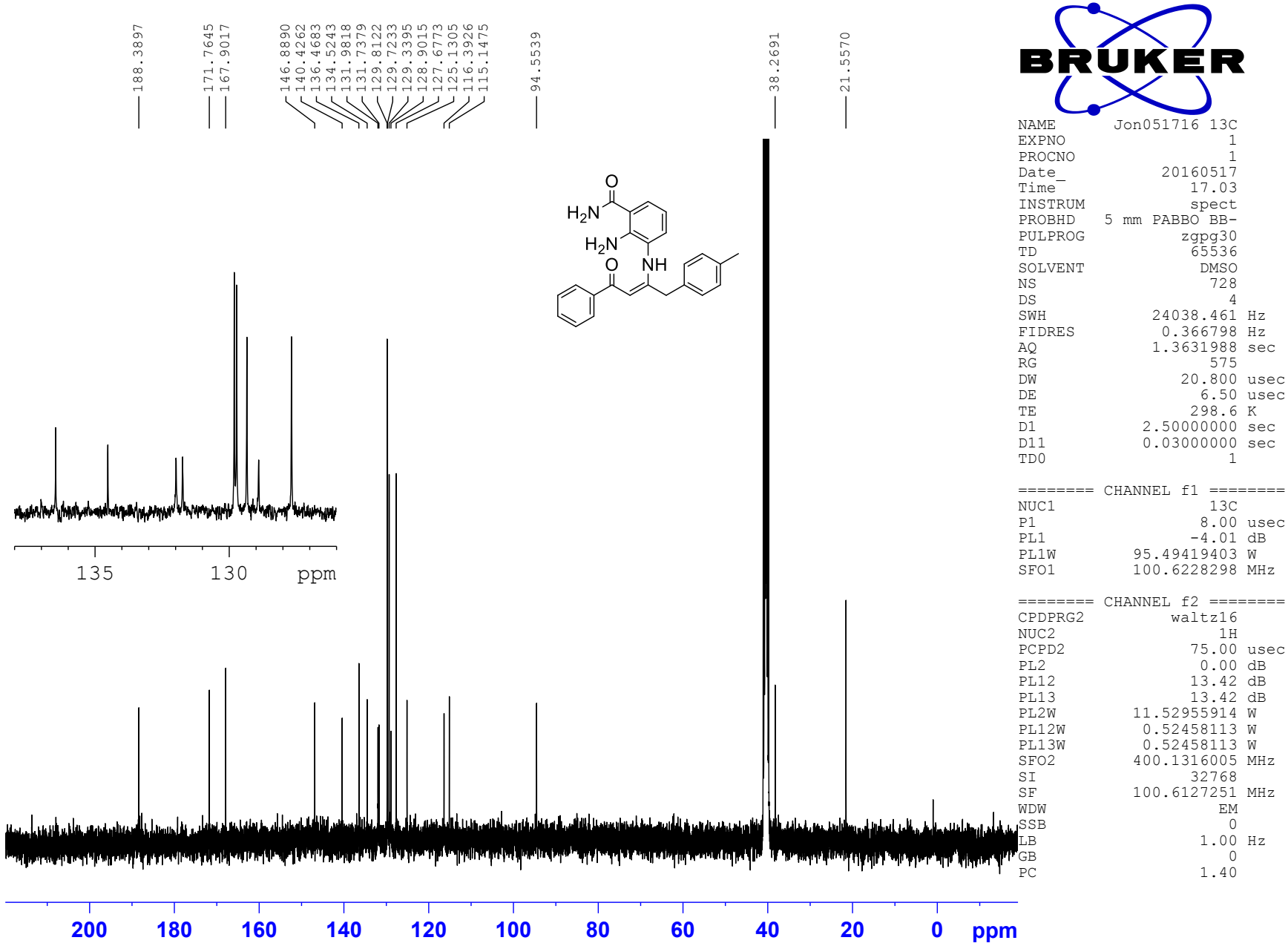
PULPROG	zg30
TD	41496
SOLVENT	DMSO
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	287
DW	83.200 usec
DE	6.50 usec
TE	297.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300046 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum for **5af** (DMSO-d_6)

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PULPROG             zgpg30
TD                   65536
SOLVENT                DMSO
NS                     728
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                     575
DW                  20.800 usec
DE                   6.50 usec
TE                  298.6 K
D1               2.50000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -4.01 dB
PL1W           95.49419403 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                75.00 usec
PL2                   0.00 dB
PL12                 13.42 dB
PL13                 13.42 dB
PL2W           11.52955914 W
PL12W           0.52458113 W
PL13W           0.52458113 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127251 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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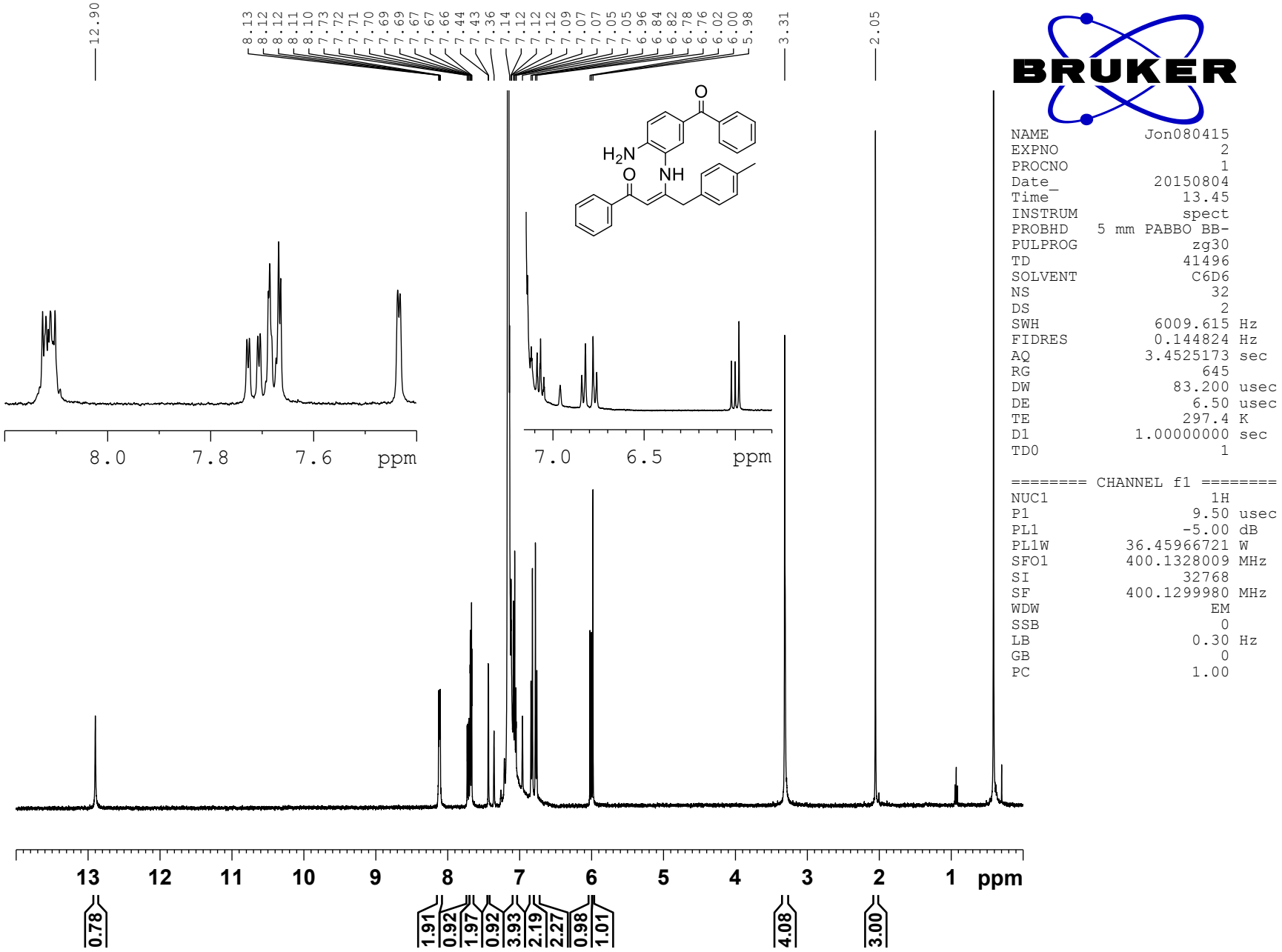
^{1}H NMR spectrum for **5ag** (C_6D_6)



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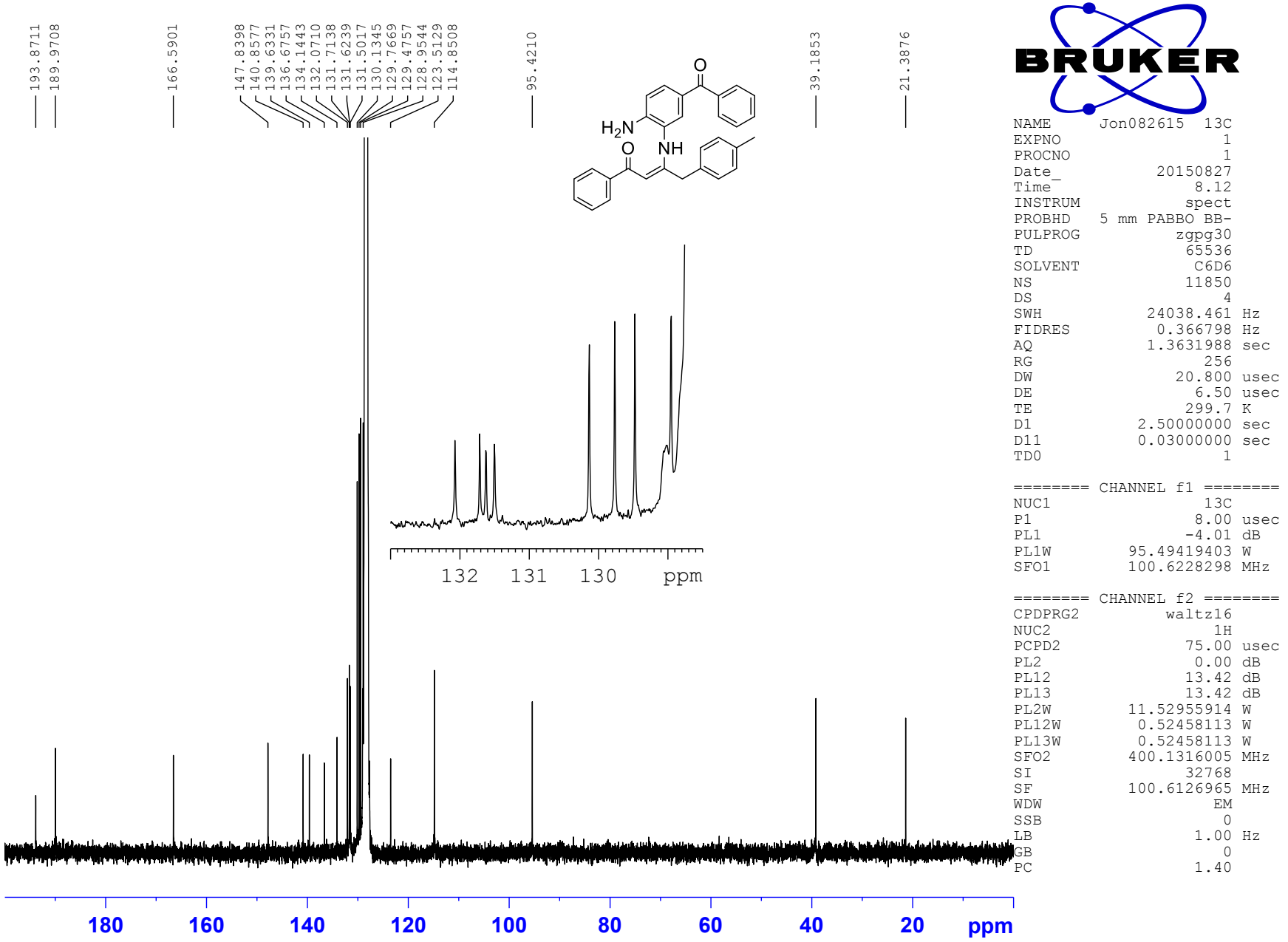
EXPNO	2
PROCNO	1
Date_	20150804
Time	13.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	C6D6
NS	32
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	645
DW	83.200 usec
DE	6.50 usec
TE	297.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299980 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

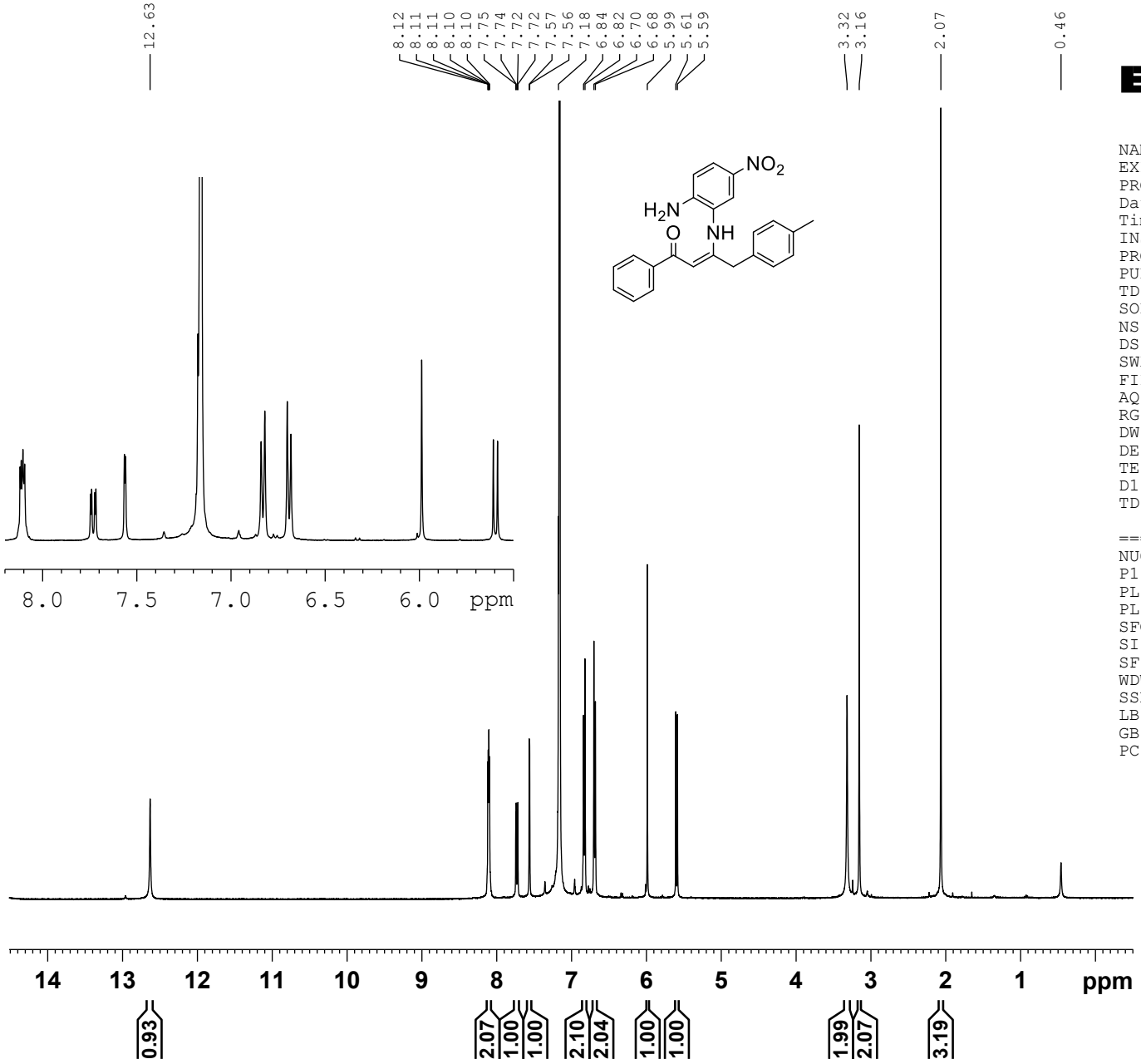
^{13}C NMR spectrum for **5ag** (C_6D_6)



BRUKER

NAME	Jon082615 13C
EXPNO	1
PROCNO	1
Date_	20150827
Time	8.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	11850
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	256
DW	20.800 usec
DE	6.50 usec
TE	299.7 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126965 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H NMR spectrum for **5ah** (C_6D_6)

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PROCNO                    1
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INSTRUM               spect
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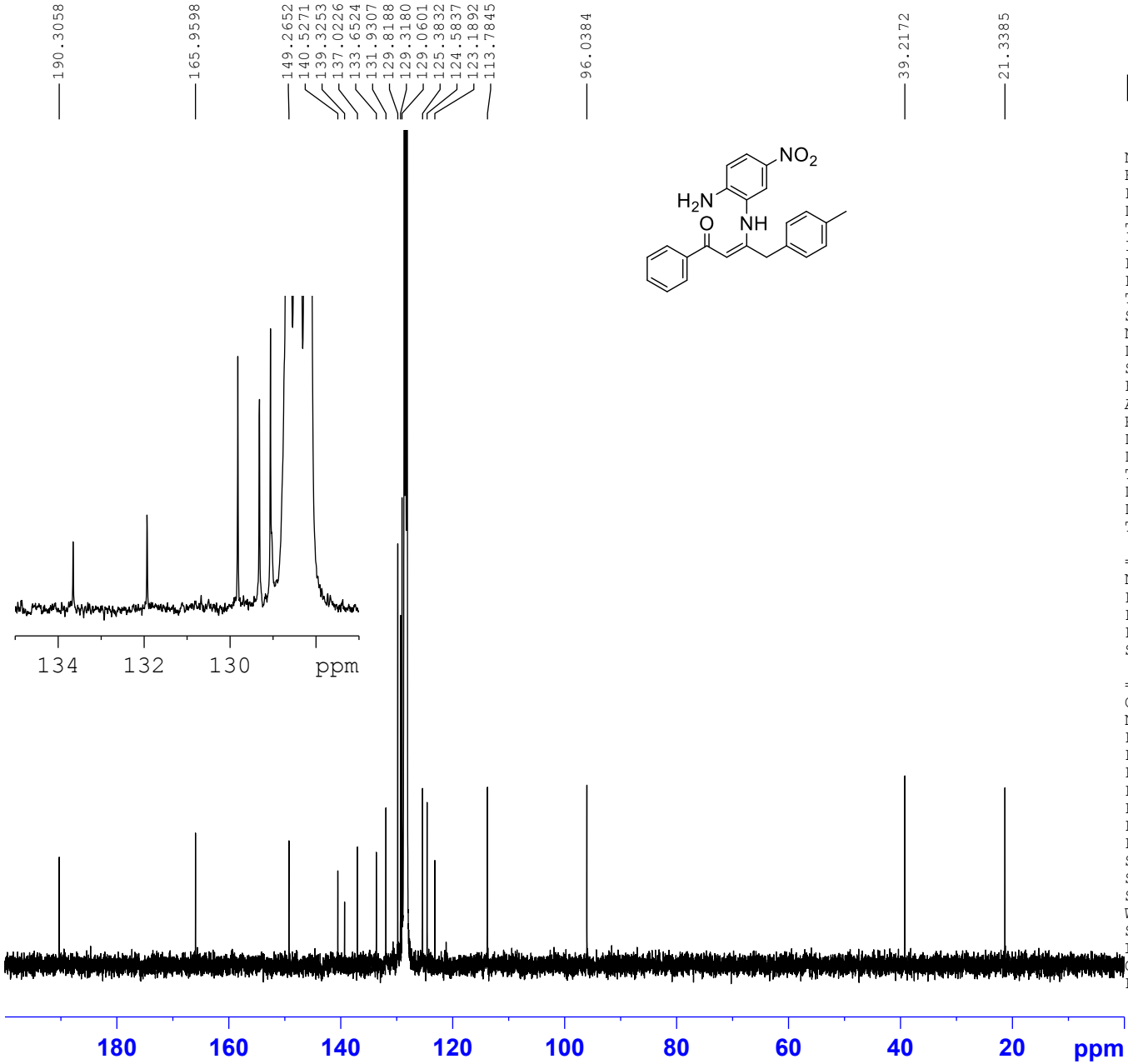
PULPROG                zg30
TD                    41496
SOLVENT                C6D6
NS                       16
DS                        2
SWH                6009.615 Hz
FIDRES             0.144824 Hz
AQ                 3.4525173 sec
RG                       406
DW                    83.200 usec
DE                     6.50 usec
TE                    299.7 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    9.50 usec
PL1                  -5.00 dB
PL1W           36.45966721 W
SFO1           400.1328009 MHz
SI                    32768
SF             400.1299977 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

^{13}C NMR spectrum for **5ah** (C_6D_6)

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PROCNO               1
Date_         20130814
Time_            14.01
INSTRUM          spect
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PULPROG       zgpg30
TD               65536
SOLVENT          C6D6
NS               1300
DS                  4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                228
DW               20.800 usec
DE                6.50 usec
TE               300.0 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                8.00 usec
PL1              -4.01 dB
PL1W        95.49419403 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           75.00 usec
PL2              0.00 dB
PL12            13.42 dB
PL13            13.42 dB
PL2W        11.52955914 W
PL12W        0.52458113 W
PL13W        0.52458113 W
SFO2       400.1316005 MHz
SI               32768
SF         100.6126973 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```
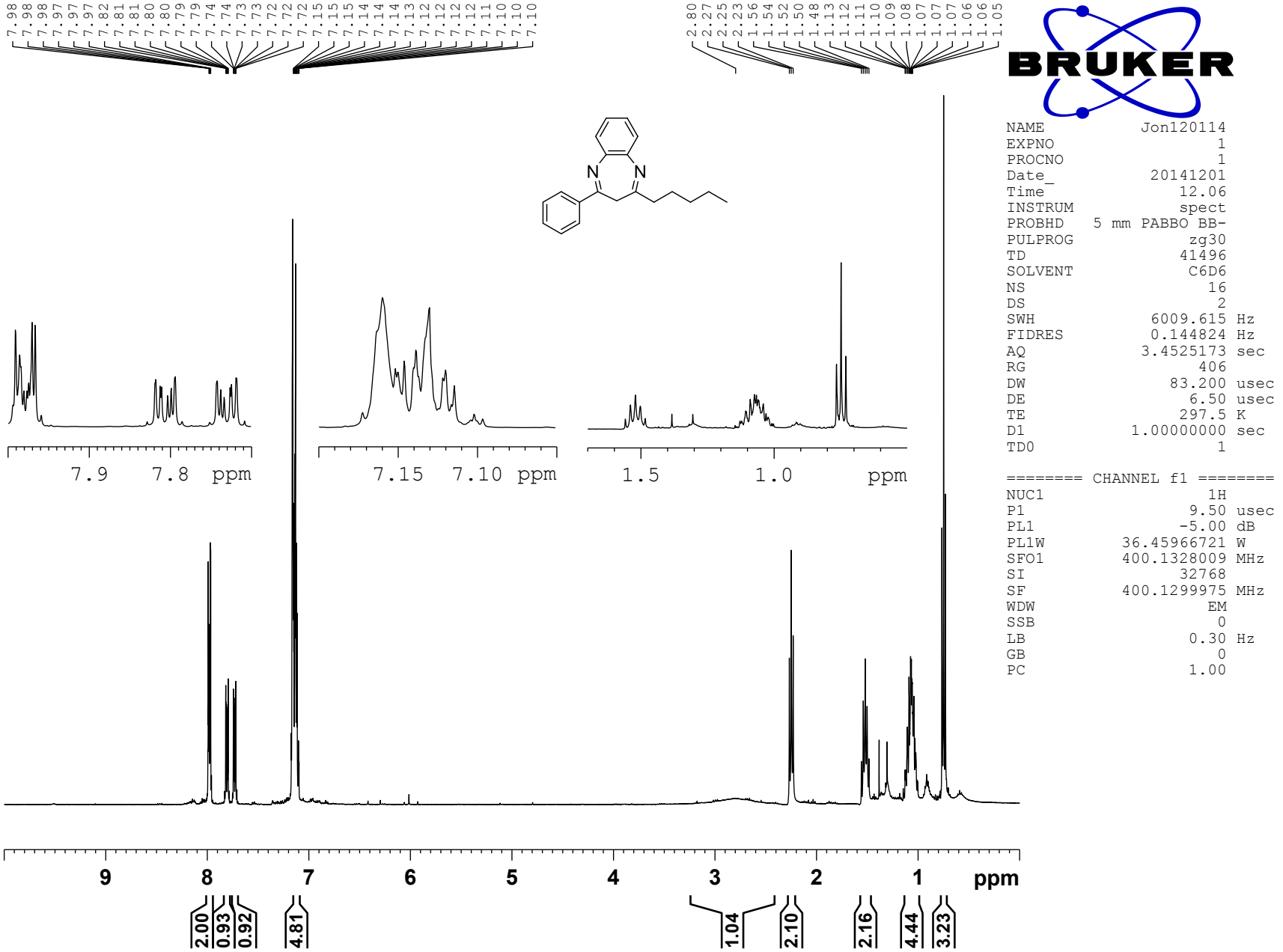

^{1}H NMR spectrum for **8da** (C_6D_6)



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PROCNO	1
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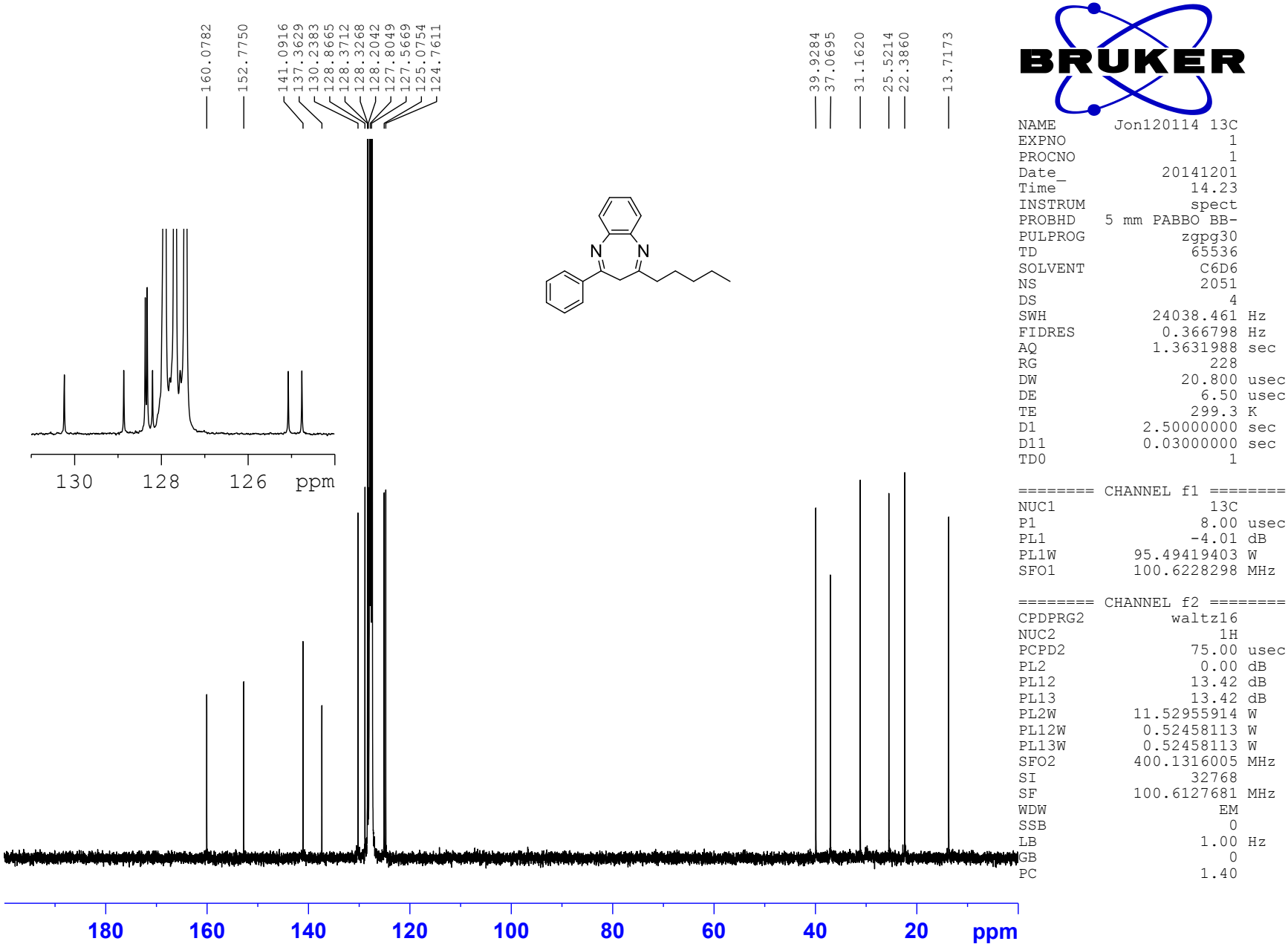
TD	41496
SOLVENT	C6D6
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	406
DW	83.200 usec
DE	6.50 usec
TE	297.5 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299975 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum for **8da** (C_6D_6)

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PROCNO                   1
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Time                 14.23
INSTRUM              spect
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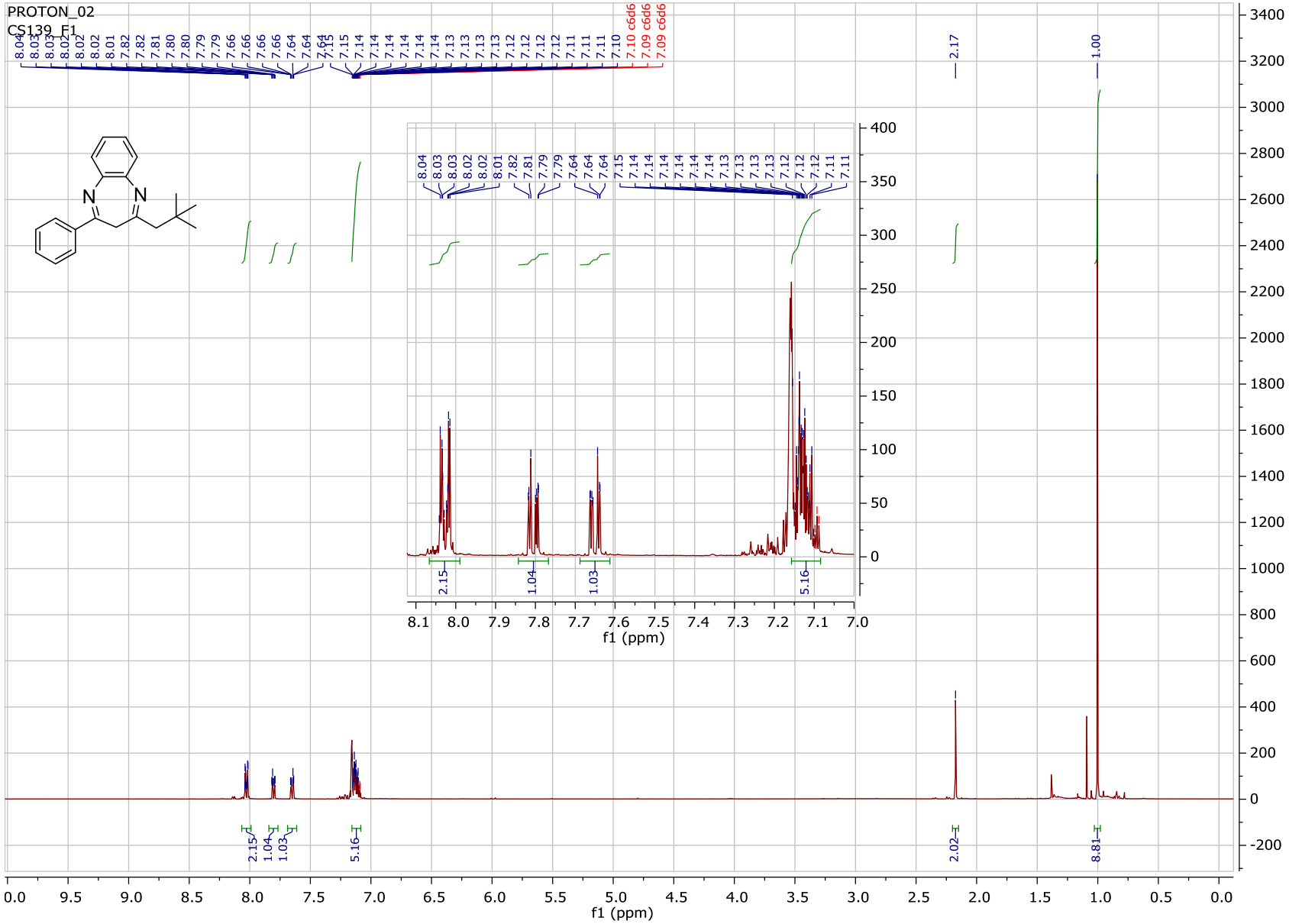
PULPROG             zgpg30
TD                   65536
SOLVENT                C6D6
NS                     2051
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      228
DW                   20.800 usec
DE                    6.50 usec
TE                   299.3 K
D1             2.50000000 sec
D11            0.03000000 sec
TD0                      1

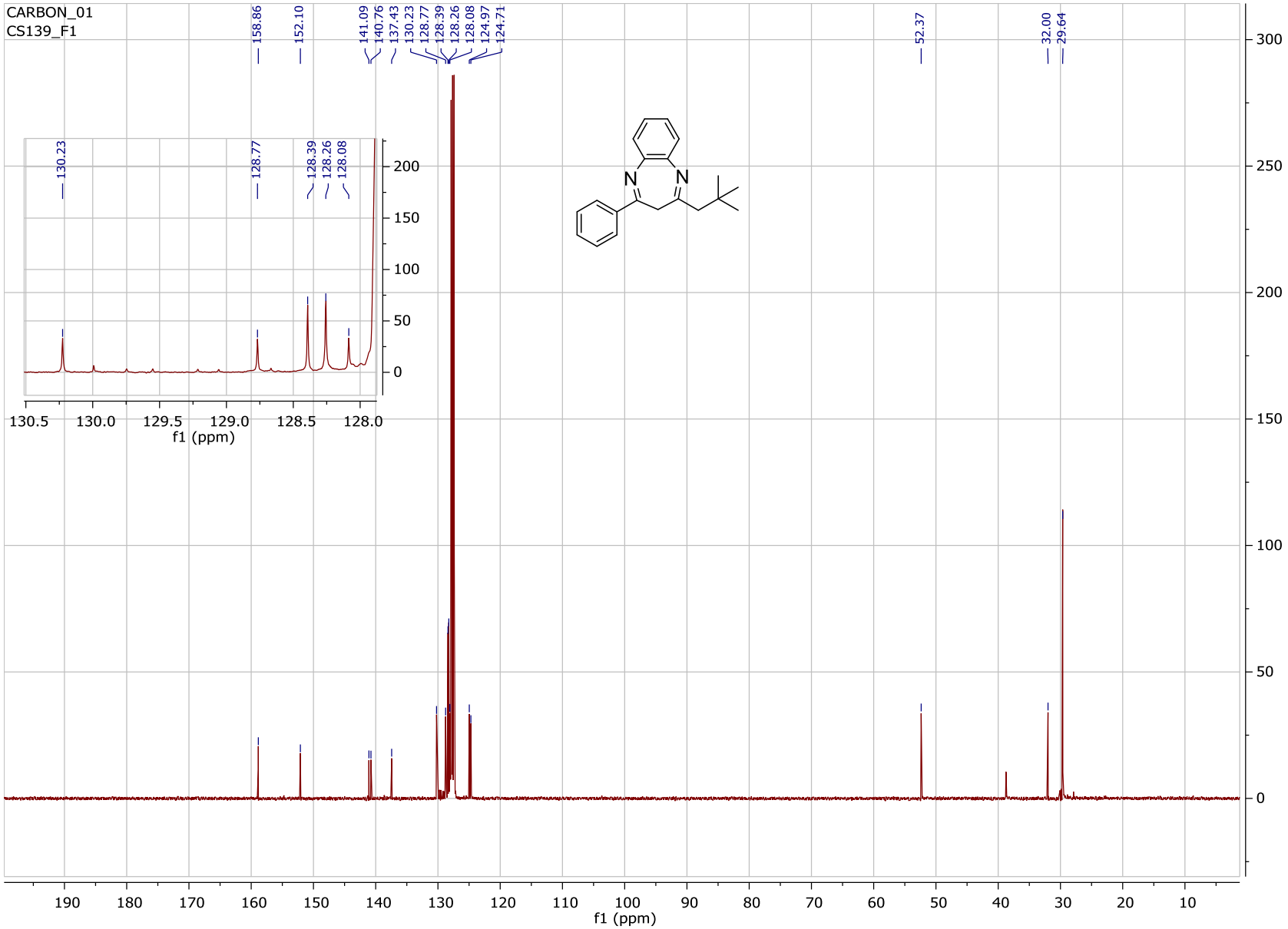
======== CHANNEL f1 ========
NUC1                    13C
P1                   8.00 usec
PL1                 -4.01 dB
PL1W          95.49419403 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                75.00 usec
PL2                   0.00 dB
PL12                 13.42 dB
PL13                 13.42 dB
PL2W          11.52955914 W
PL12W          0.52458113 W
PL13W          0.52458113 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127681 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

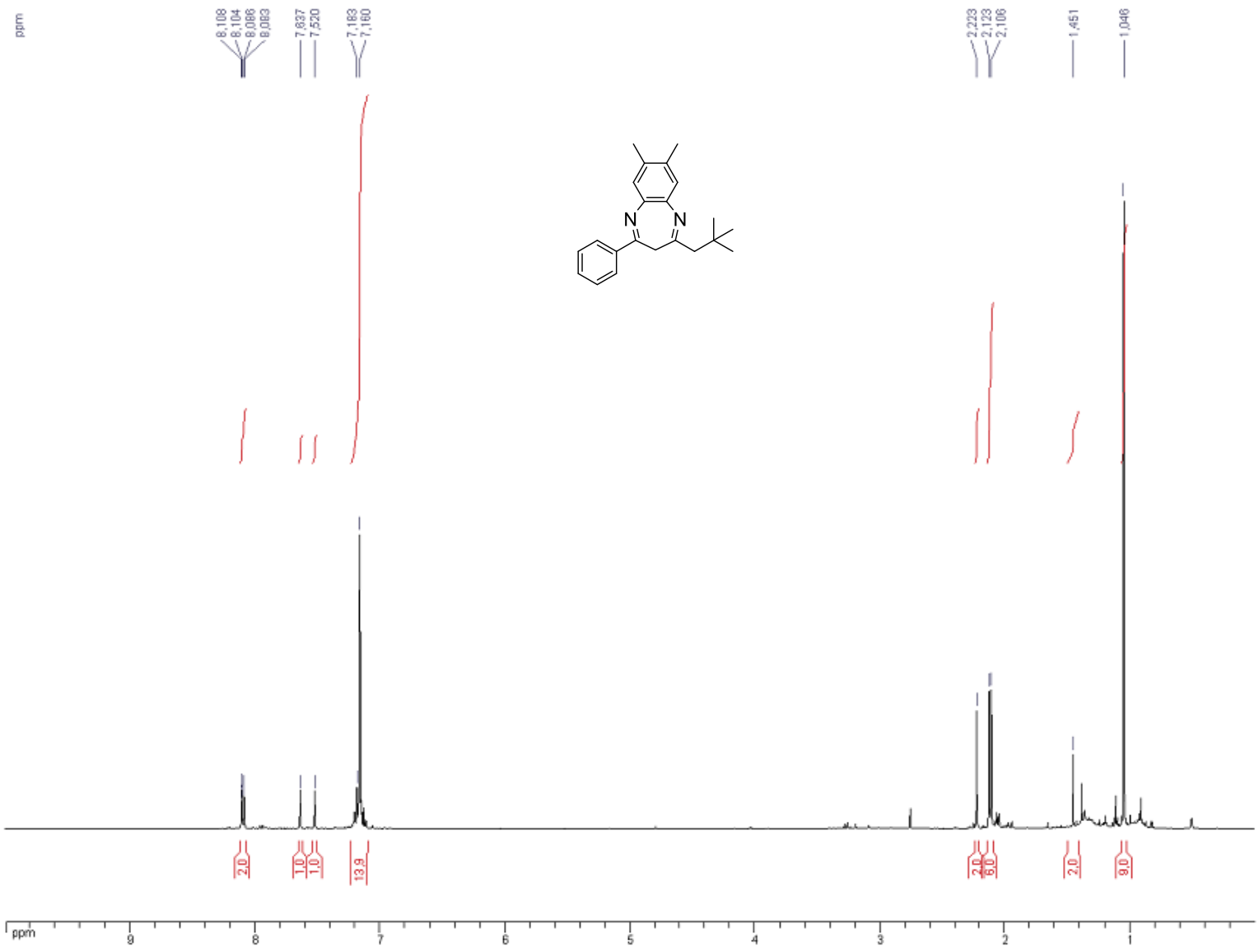
^{1}H NMR spectrum for **8ea** (C_6D_6)



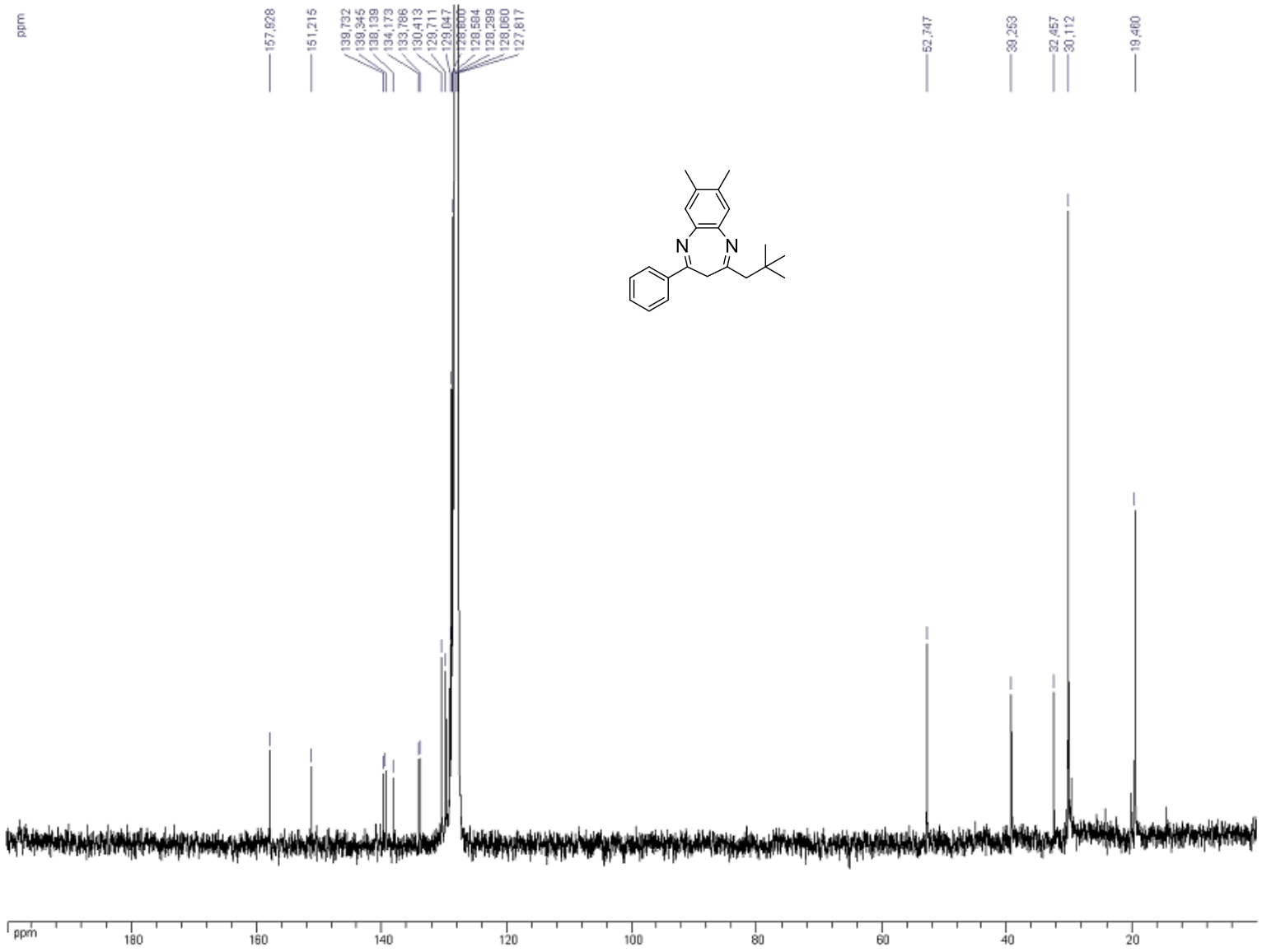
^{13}C NMR spectrum for **8ea** (C_6D_6)



^{1}H NMR spectrum for **8eb** (C_6D_6)



^{13}C NMR spectrum for **8eb** (C_6D_6)



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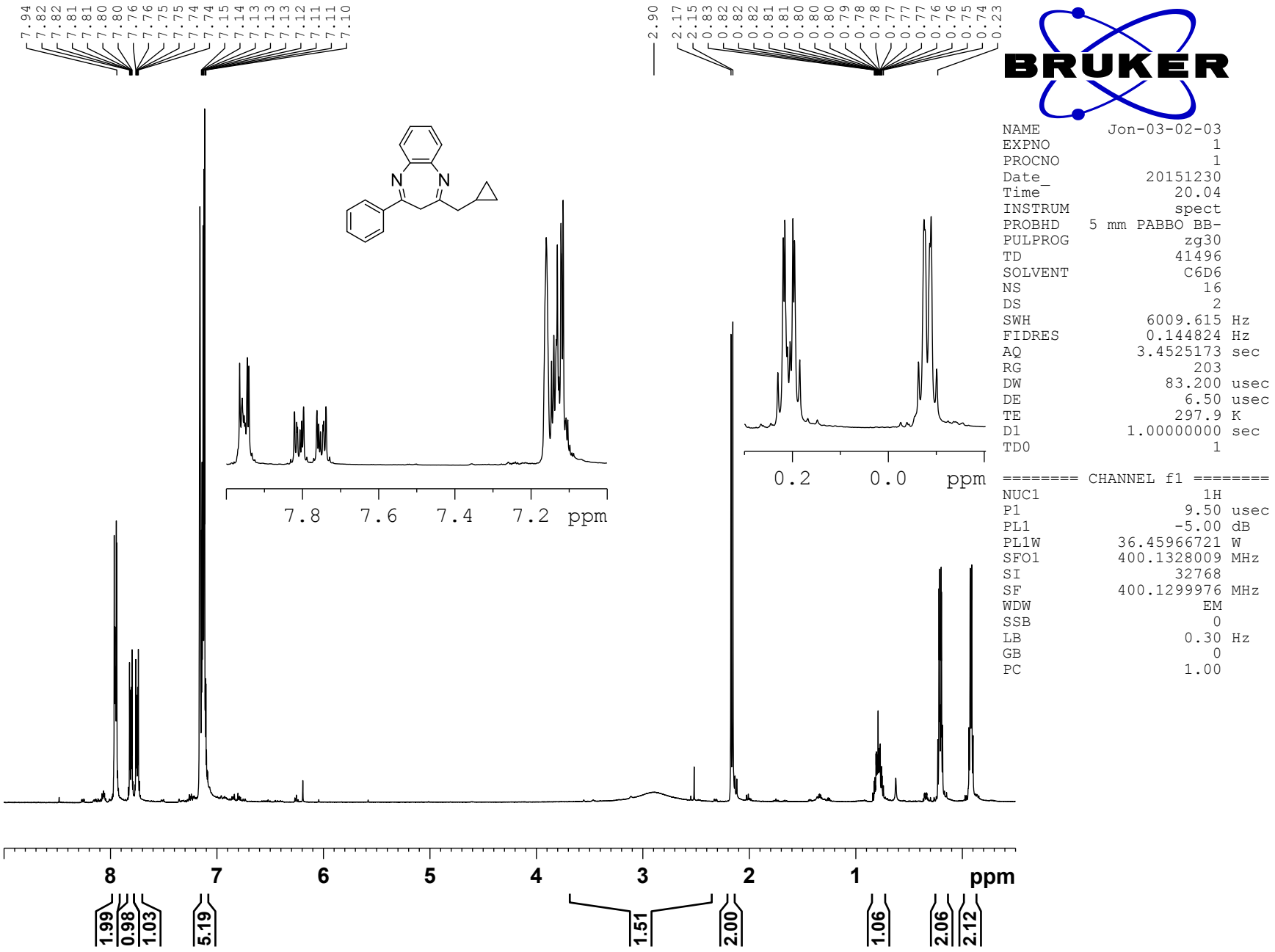
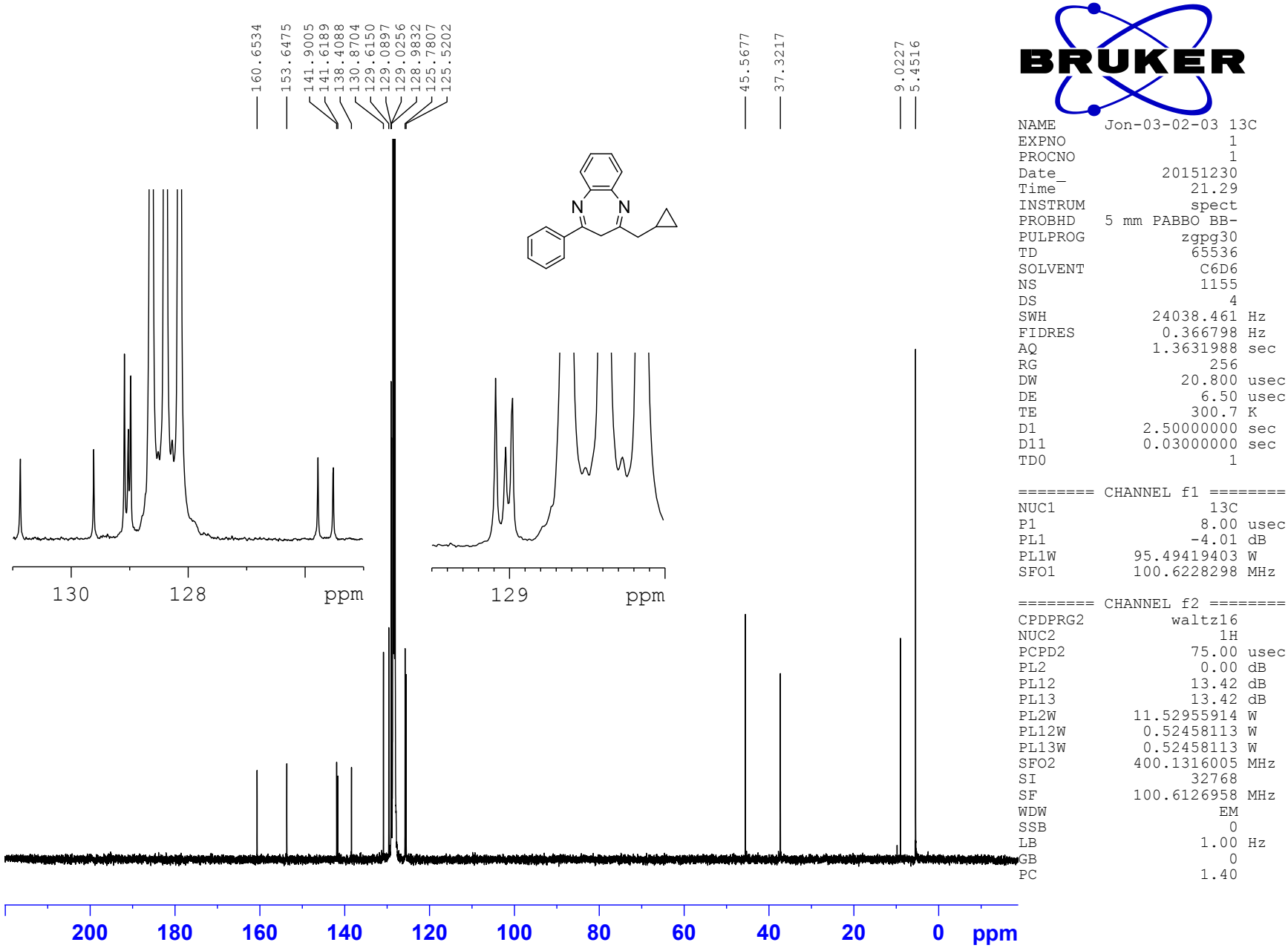
^{1}H NMR spectrum for **8fa** (C_6D_6)



^{13}C NMR spectrum for **8fa** (C_6D_6)

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PROCNO                      1
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Time                    21.29
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                   C6D6
NS                        1155
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         256
DW                      20.800 usec
DE                       6.50 usec
TE                      300.7 K
D1                  2.50000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       8.00 usec
PL1                     -4.01 dB
PL1W               95.49419403 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   75.00 usec
PL2                      0.00 dB
PL12                    13.42 dB
PL13                    13.42 dB
PL2W               11.52955914 W
PL12W               0.52458113 W
PL13W               0.52458113 W
SFO2              400.1316005 MHz
SI                       32768
SF                100.6126958 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```
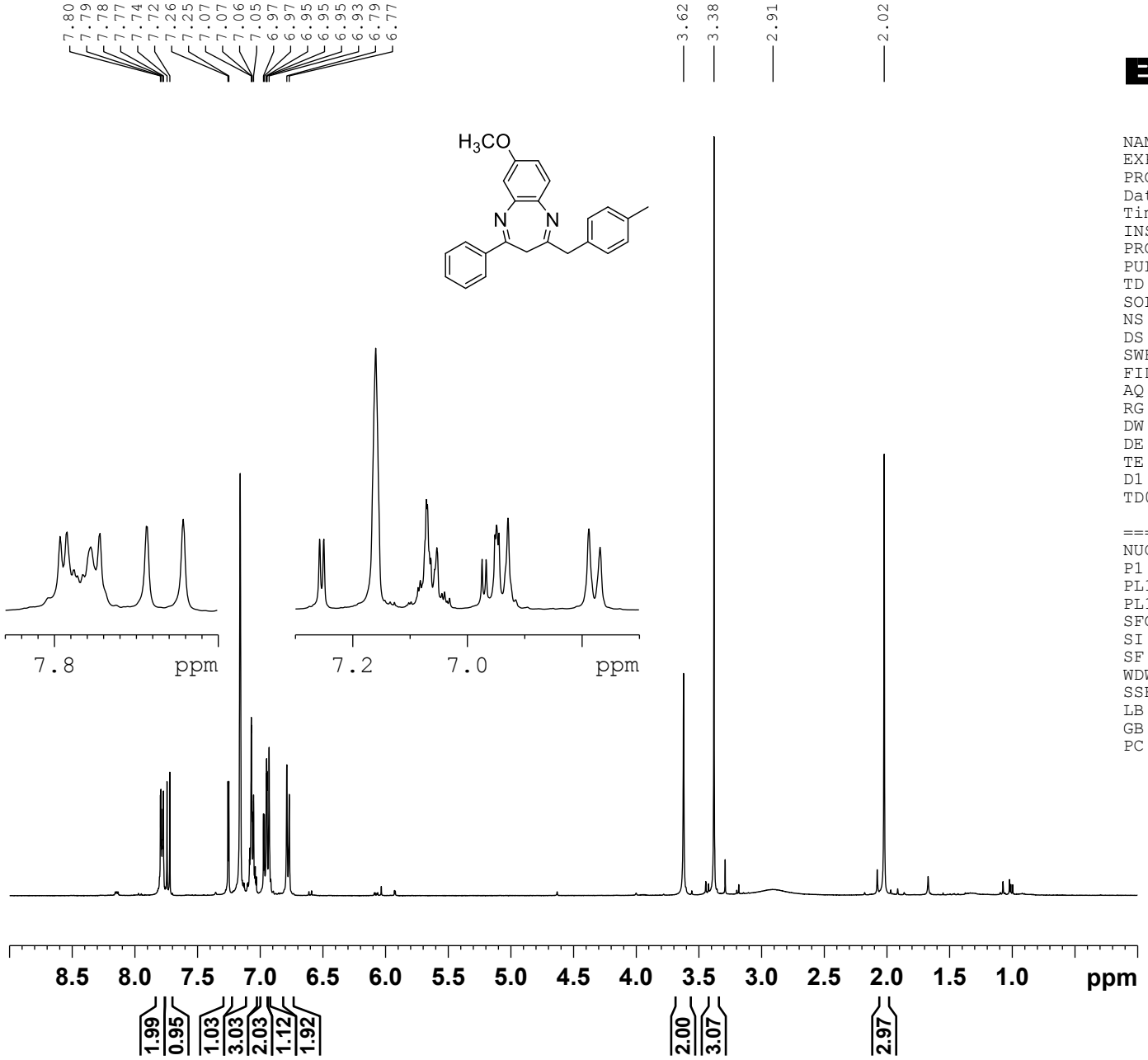
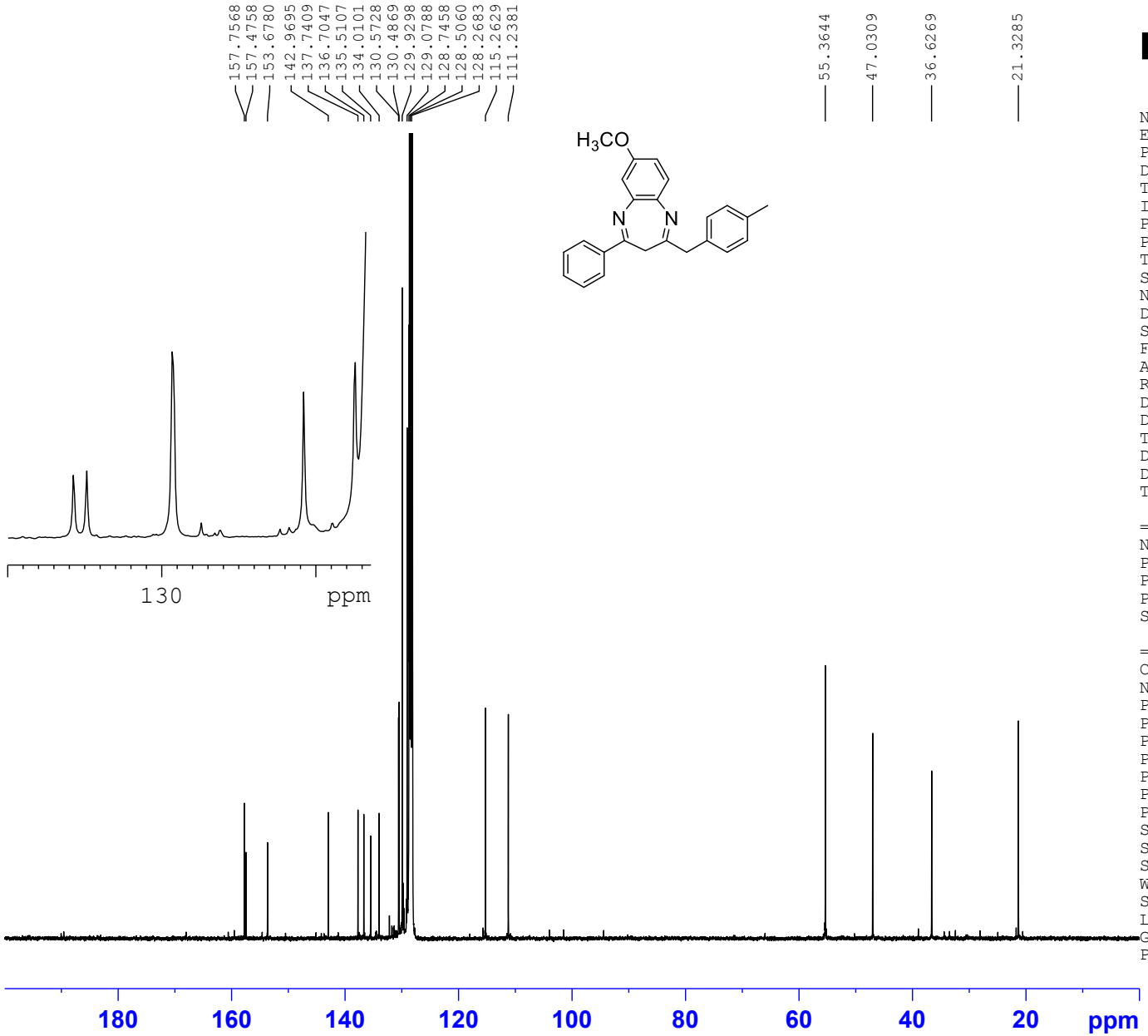

^{1}H NMR spectrum for **8ac** (C_6D_6)



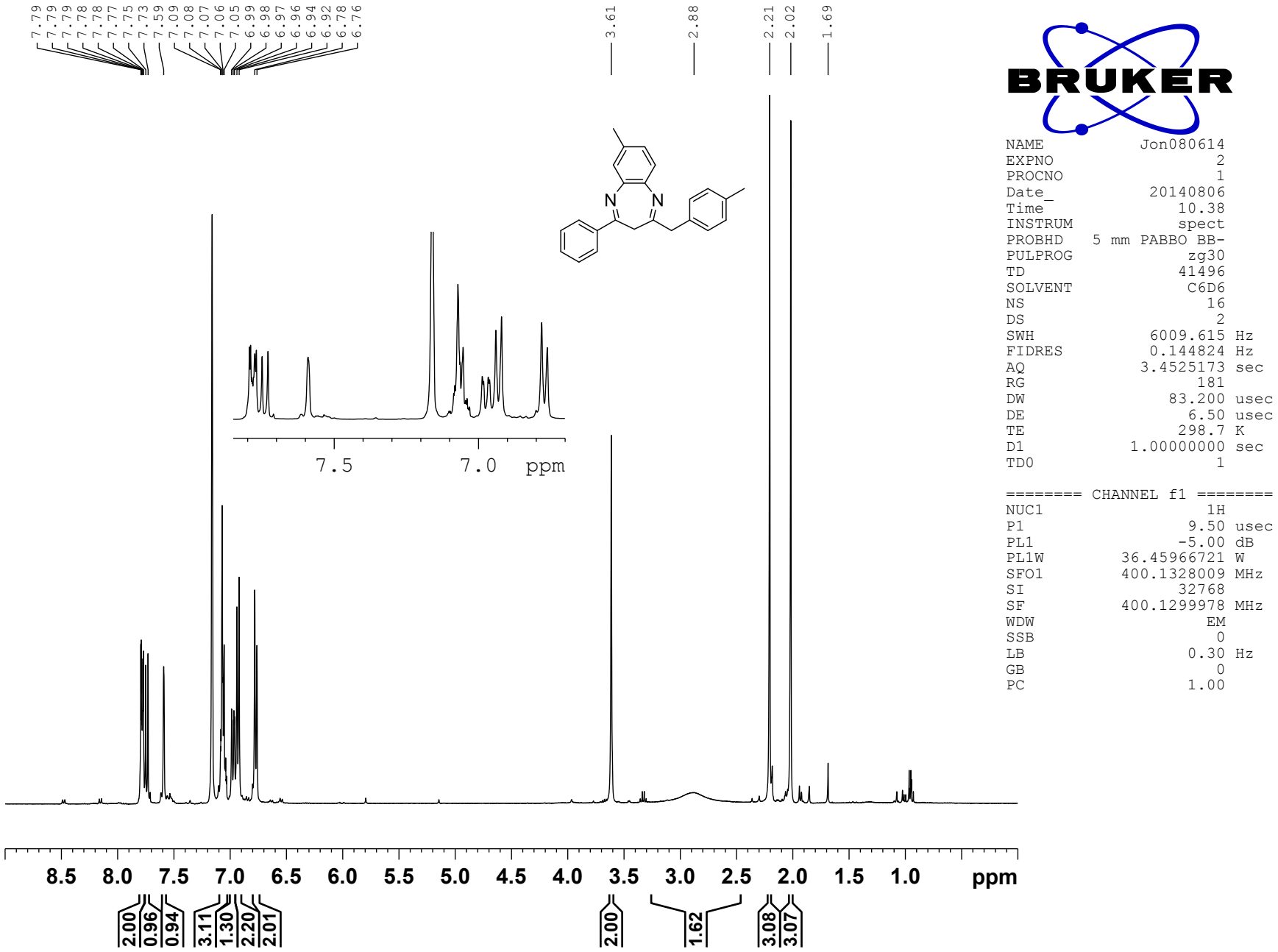
NAME	Anthony103014
EXPNO	1
PROCNO	1
Date_	20141030
Time	15.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	C6D6
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	296.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299977 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum for **8ac** (C_6D_6)




```
NAME        Anthony 103014 C13
EXPNO                       1
PROCNO                      1
Date_                20141031
Time                     9.06
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                  C6D6
NS                      14290
DS                          4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        203
DW                     20.800 usec
DE                      6.50 usec
TE                     298.2 K
D1                 2.50000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      8.00 usec
PL1                    -4.01 dB
PL1W              95.49419403 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  75.00 usec
PL2                     0.00 dB
PL12                   13.42 dB
PL13                   13.42 dB
PL2W              11.52955914 W
PL12W              0.52458113 W
PL13W              0.52458113 W
SFO2             400.1316005 MHz
SI                      32768
SF               100.6126976 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```

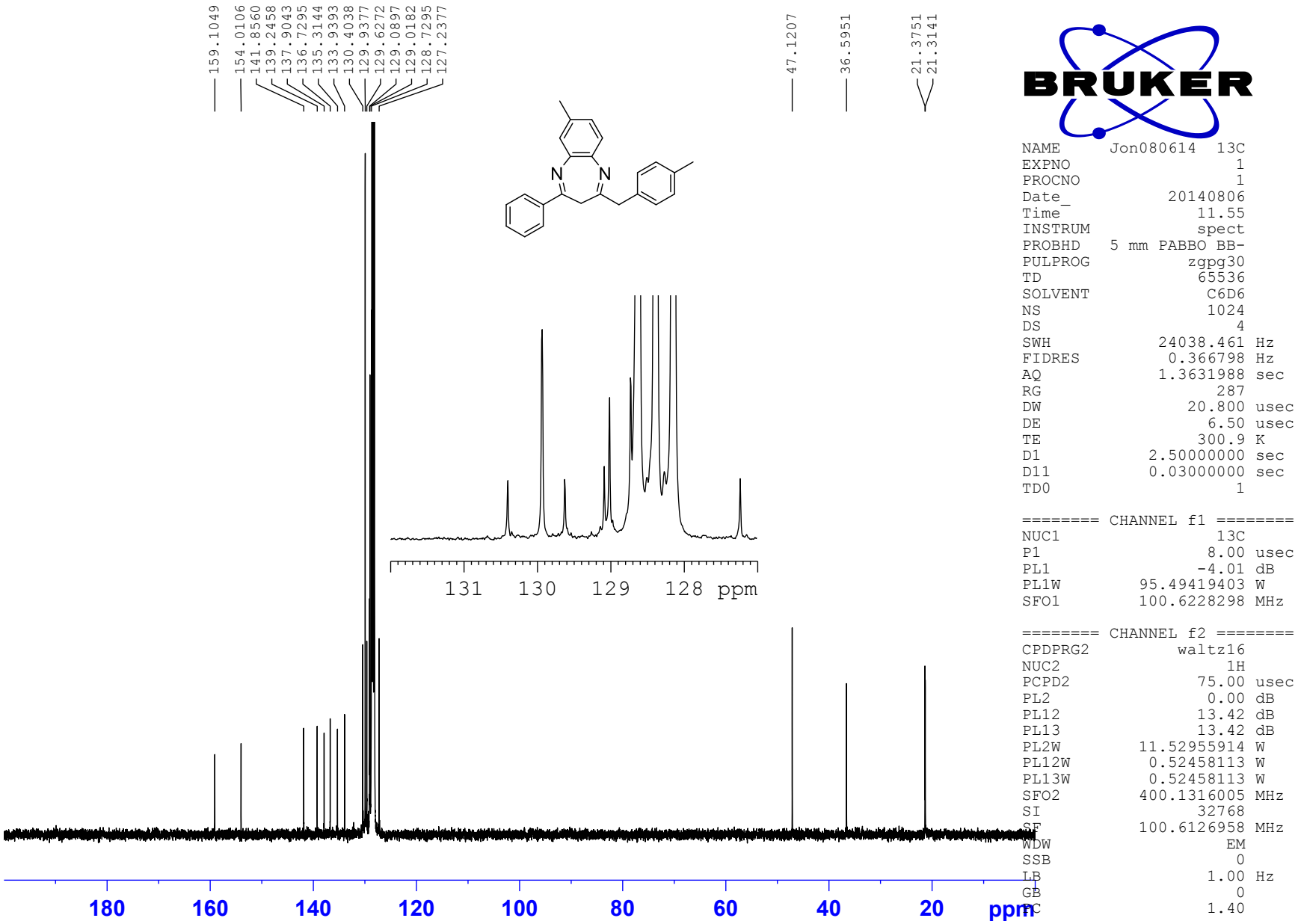
^{1}H NMR spectrum for **8ad** (C_6D_6)



BRUKER

NAME	Jon080614
EXPNO	2
PROCNO	1
Date_	20140806
Time	10.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	C6D6
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	181
DW	83.200 usec
DE	6.50 usec
TE	298.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299978 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

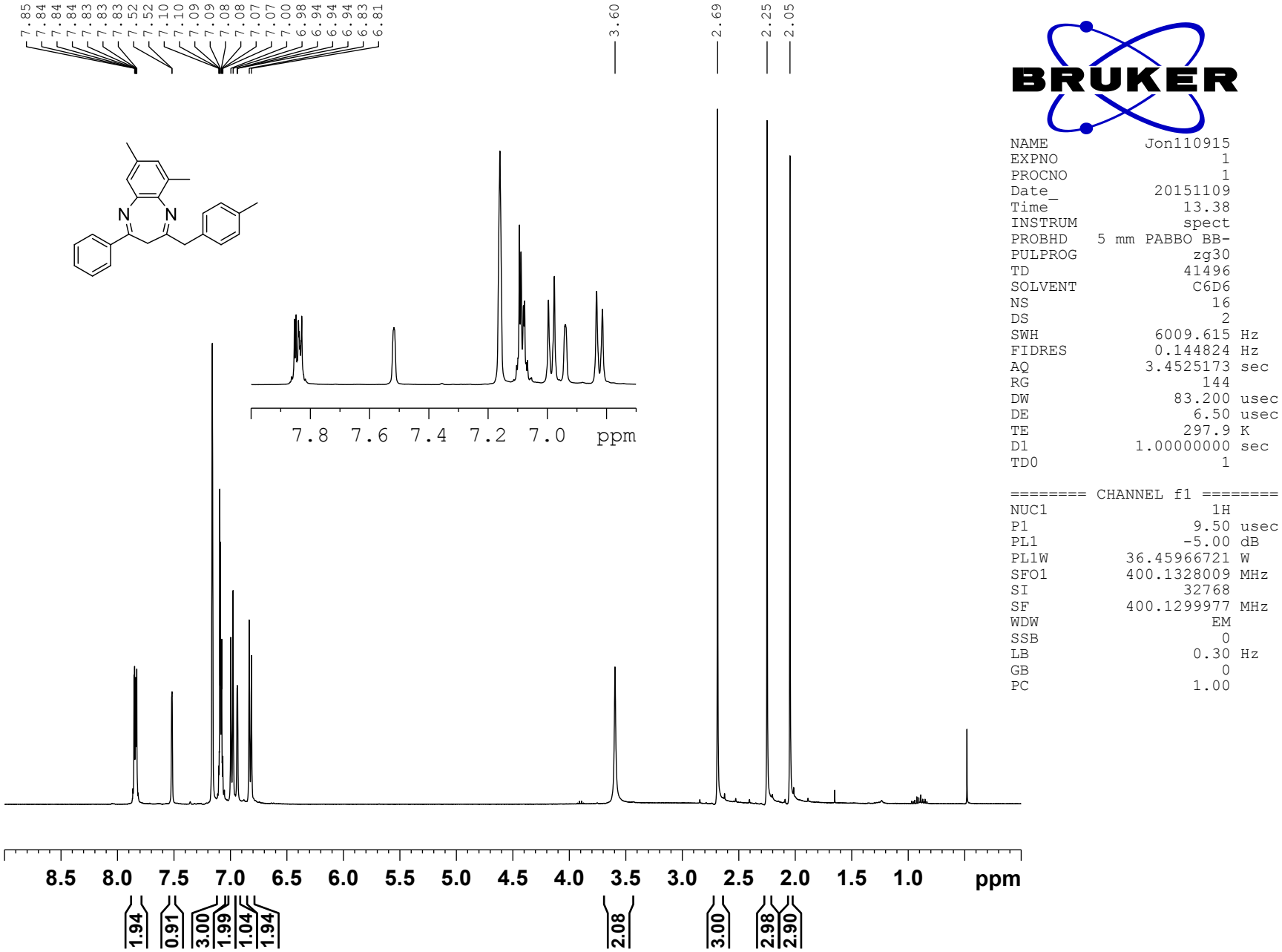
^{13}C NMR spectrum for **8ad** (C_6D_6)



BRUKER

NAME	Jon080614 13C
EXPNO	1
PROCNO	1
Date_	20140806
Time	11.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	287
DW	20.800 usec
DE	6.50 usec
TE	300.9 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126958 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

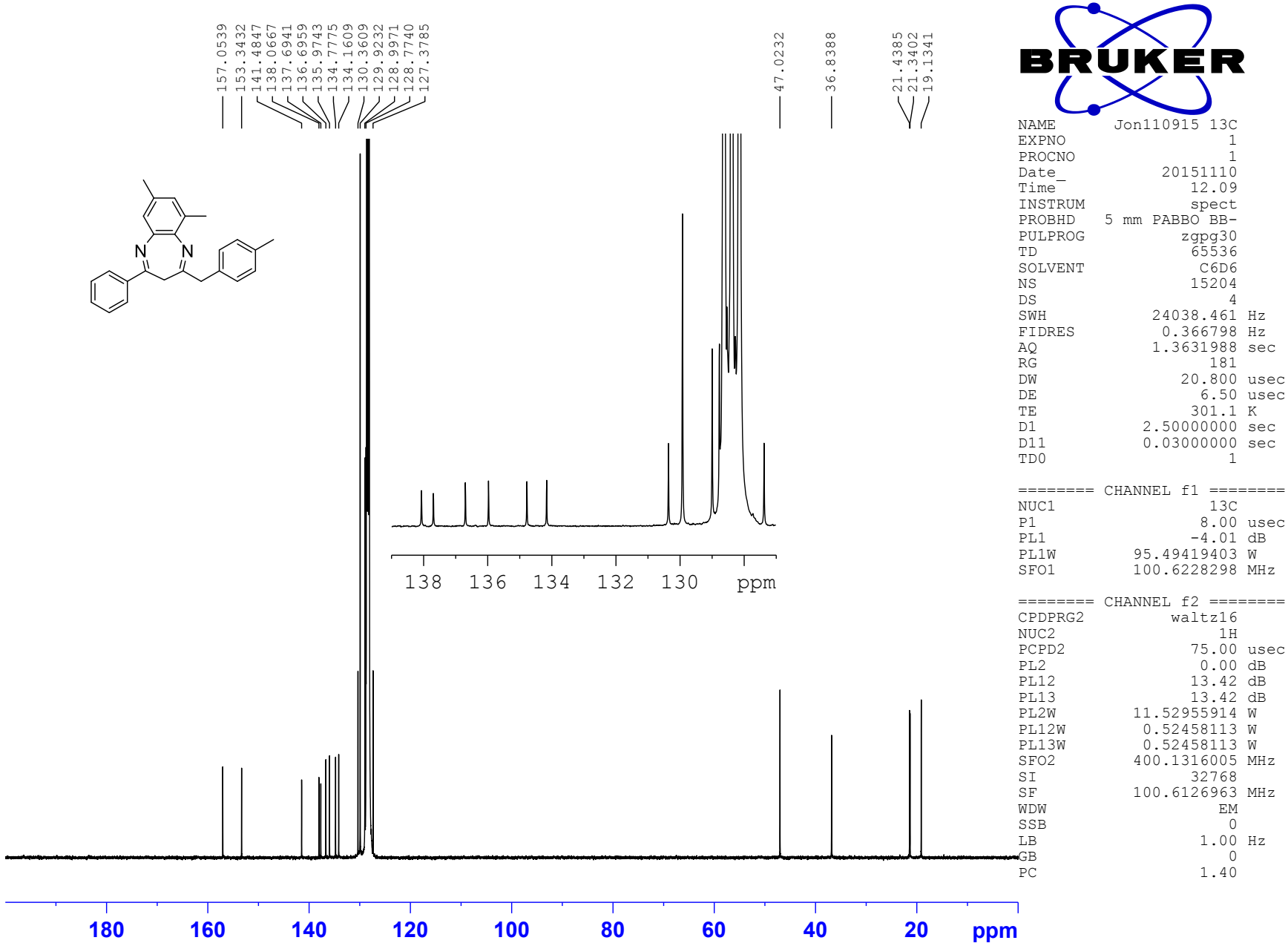
^{1}H NMR spectrum for **8ae** (C_6D_6)



BRUKER

NAME	Jon110915
EXPNO	1
PROCNO	1
Date_	20151109
Time	13.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	C6D6
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	144
DW	83.200 usec
DE	6.50 usec
TE	297.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299977 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

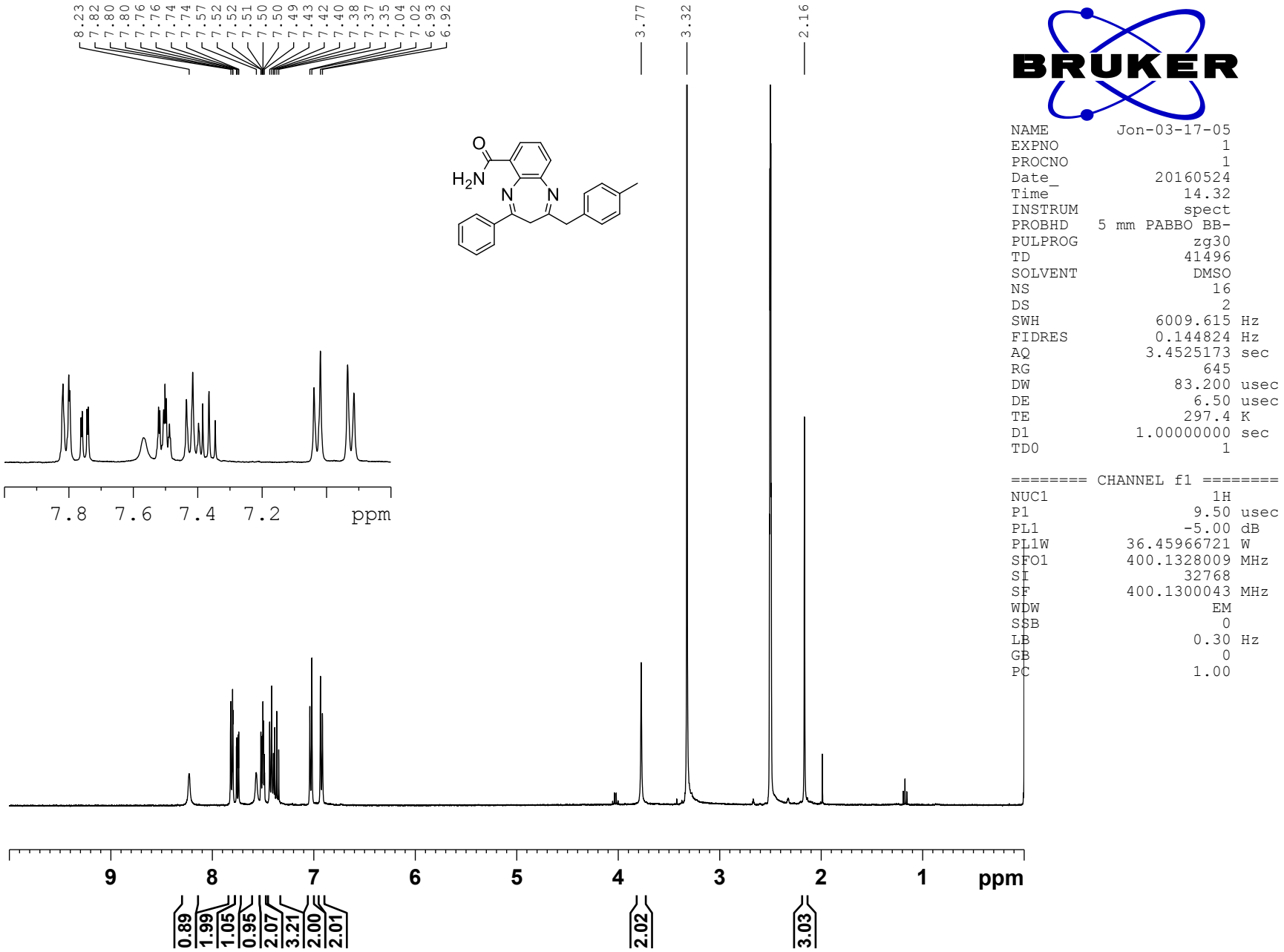
^{13}C NMR spectrum for **8ae** (C_6D_6)



BRUKER

NAME	Jon110915 13C
EXPNO	1
PROCNO	1
Date_	20151110
Time	12.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	15204
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	181
DW	20.800 usec
DE	6.50 usec
TE	301.1 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126963 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

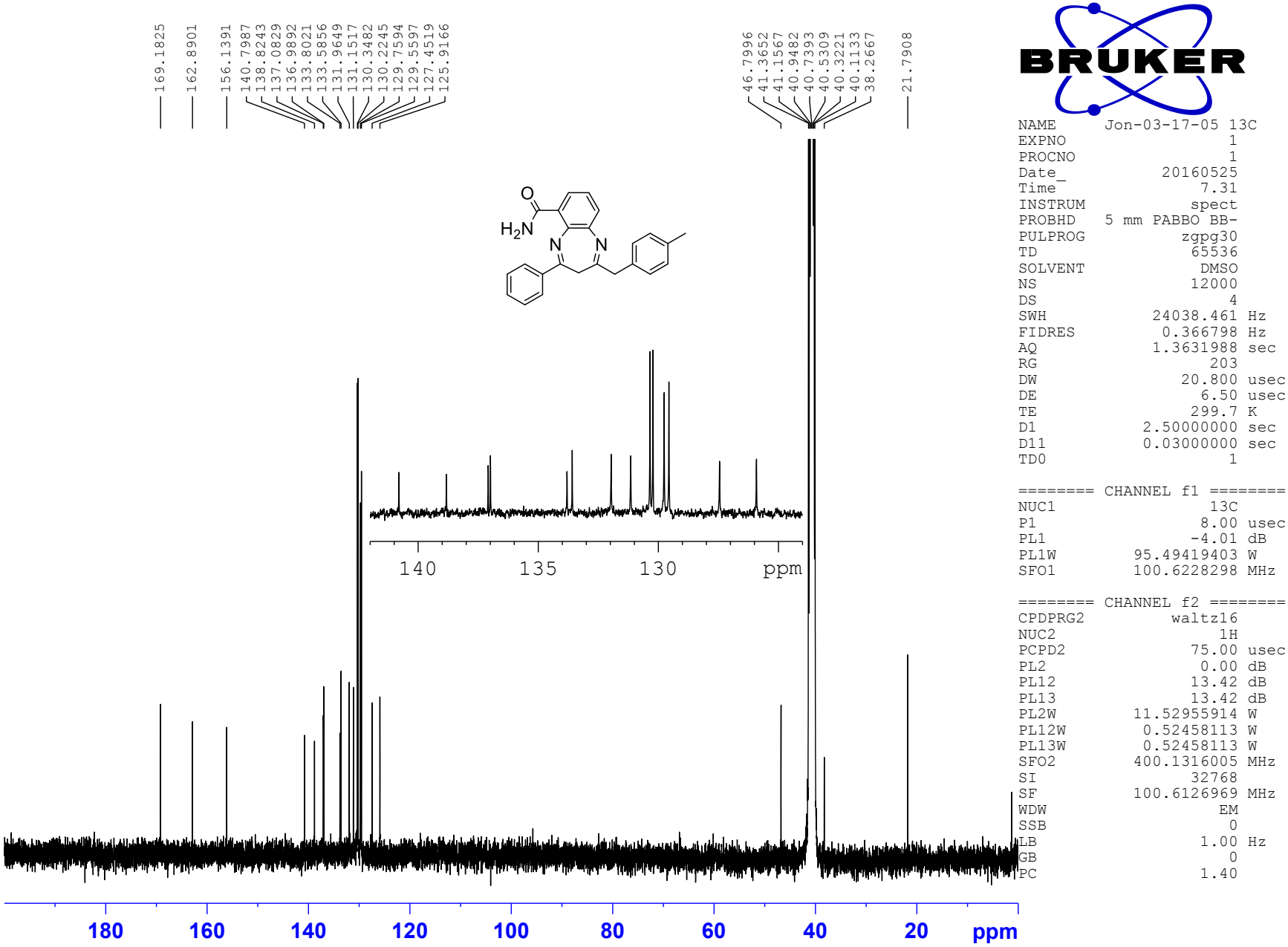
^{1}H NMR spectrum for **8af** (DMSO-d_6)



BRUKER

NAME	Jon-03-17-05
EXPNO	1
PROCNO	1
Date_	20160524
Time	14.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	DMSO
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	645
DW	83.200 usec
DE	6.50 usec
TE	297.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1300043 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum for **8af** (DMSO-d_6)

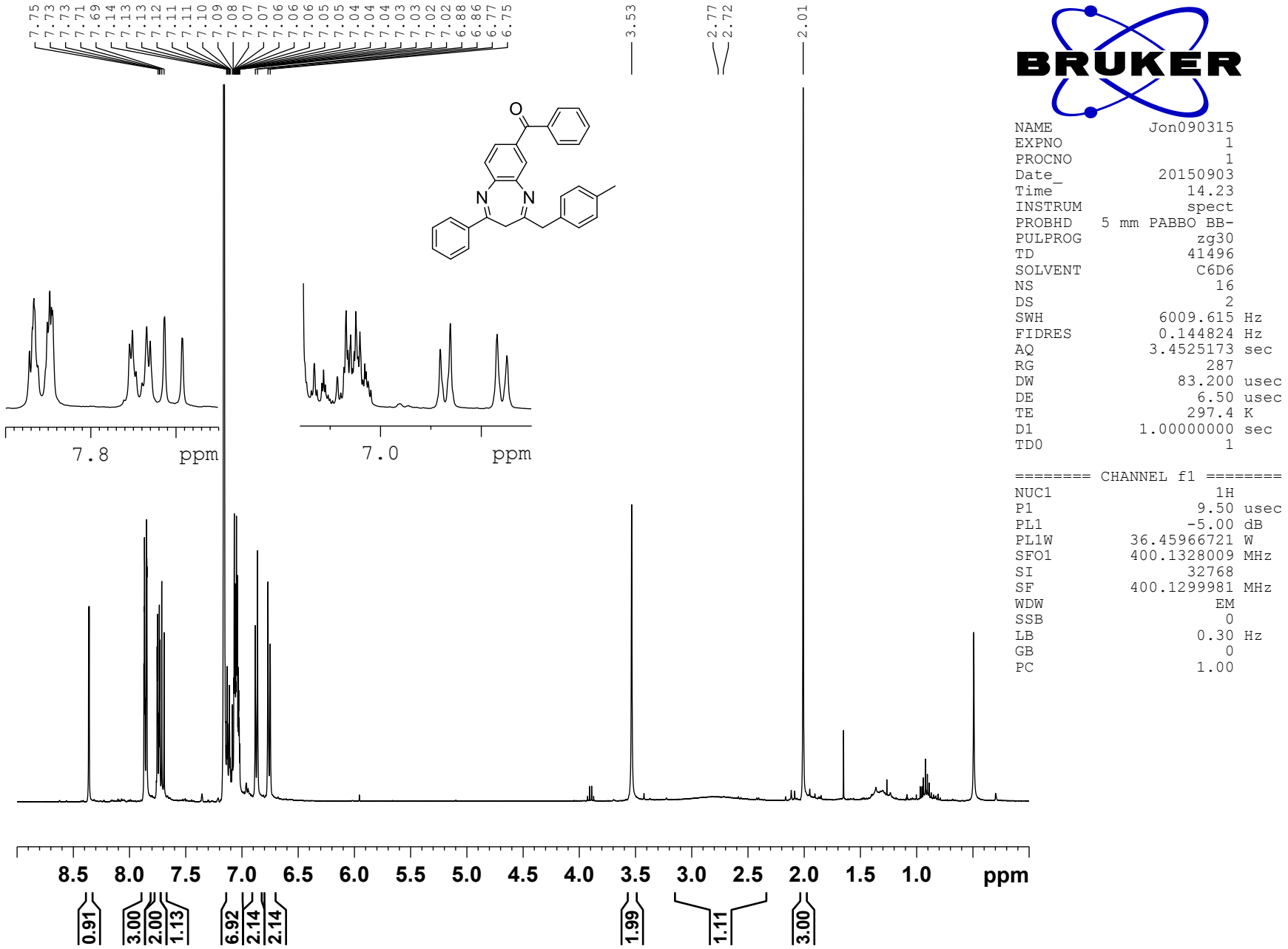


BRUKER

NAME	Jon-03-17-05 13C
EXPNO	1
PROCNO	1
Date_	20160525
Time	7.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	12000
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	299.7 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126969 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

RSC Advances 2016, 6, 107081. doi: 10.1039/c6ra24291j

^{1}H NMR spectrum for **8ag** (C_6D_6)

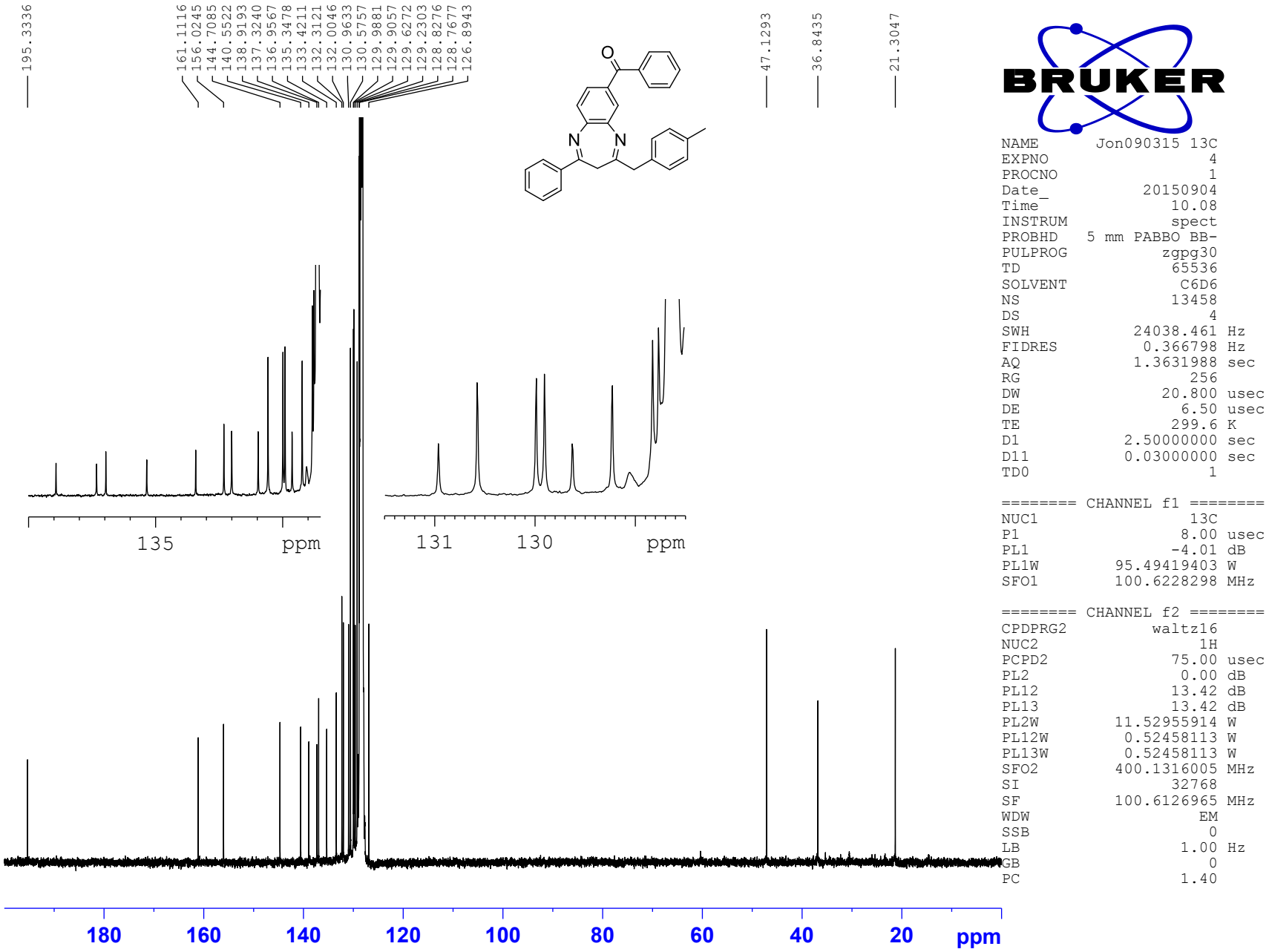


BRUKER

NAME	Jon090315
EXPNO	1
PROCNO	1
Date_	20150903
Time	14.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	C6D6
NS	16
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	287
DW	83.200 usec
DE	6.50 usec
TE	297.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299981 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

RSC Advances 2016, 6, 107081. doi: 10.1039/c6ra24291j

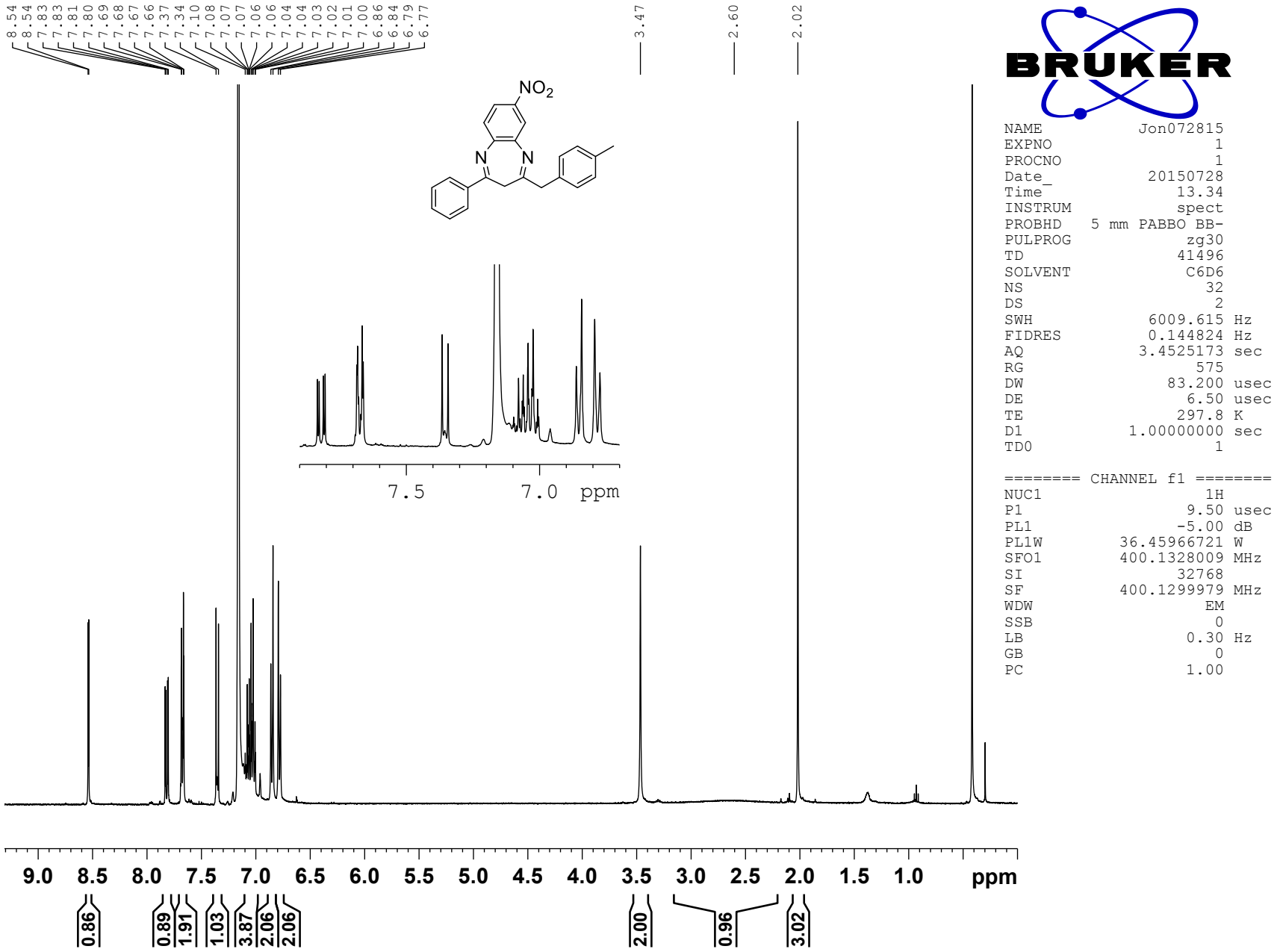
^{13}C NMR spectrum for **8ag** (C_6D_6)



BRUKER

NAME	Jon090315 13C
EXPNO	4
PROCNO	1
Date_	20150904
Time	10.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	13458
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	256
DW	20.800 usec
DE	6.50 usec
TE	299.6 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126965 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

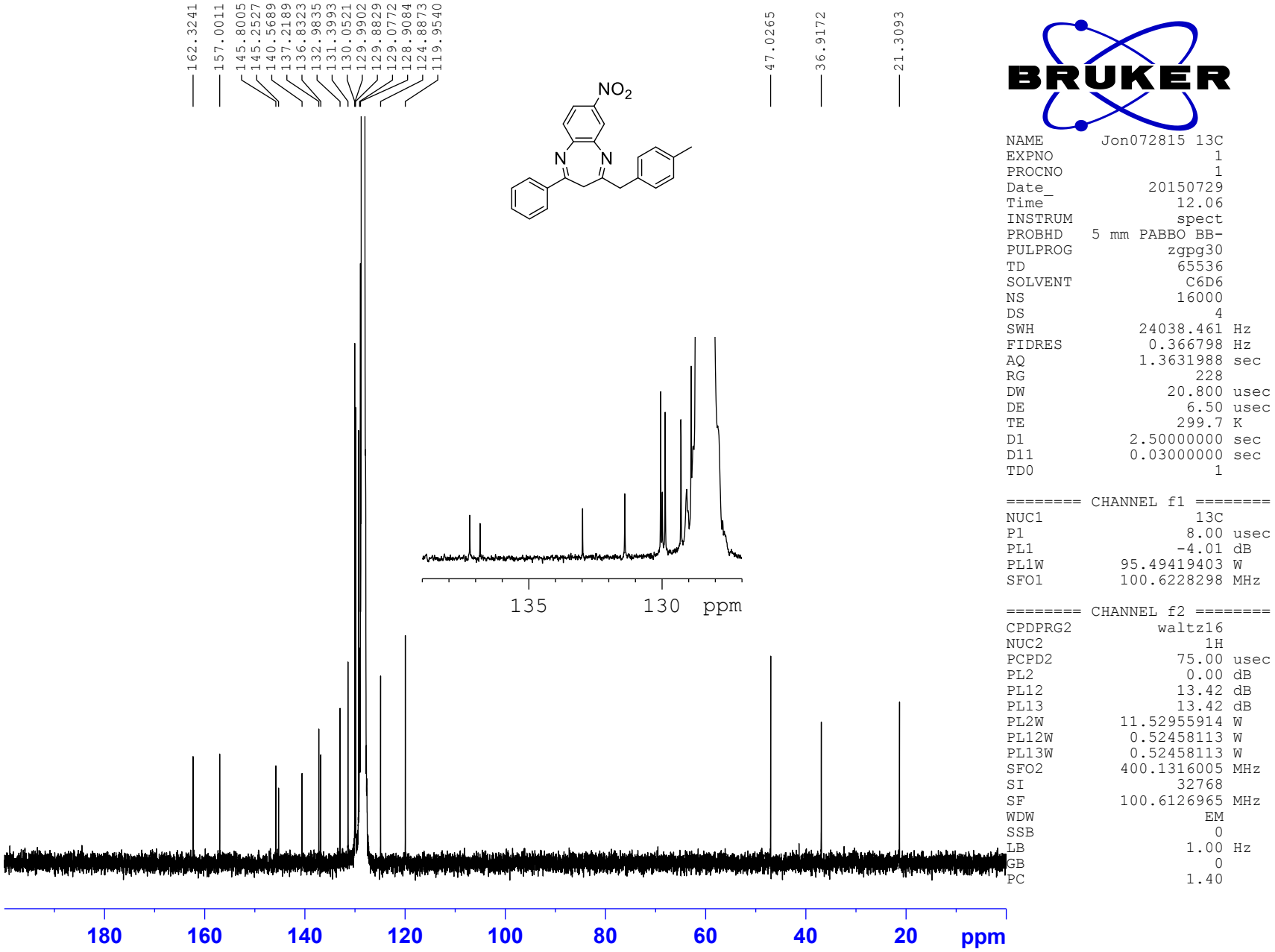
^{1}H NMR spectrum for **8ah** (C_6D_6)



BRUKER

NAME	Jon072815
EXPNO	1
PROCNO	1
Date_	20150728
Time	13.34
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	41496
SOLVENT	C6D6
NS	32
DS	2
SWH	6009.615 Hz
FIDRES	0.144824 Hz
AQ	3.4525173 sec
RG	575
DW	83.200 usec
DE	6.50 usec
TE	297.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.50 usec
PL1	-5.00 dB
PL1W	36.45966721 W
SFO1	400.1328009 MHz
SI	32768
SF	400.1299979 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum for **8ah** (C_6D_6)



BRUKER

NAME	Jon072815 13C
EXPNO	1
PROCNO	1
Date_	20150729
Time	12.06
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	C6D6
NS	16000
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	228
DW	20.800 usec
DE	6.50 usec
TE	299.7 K
D1	2.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-4.01 dB
PL1W	95.49419403 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	0.00 dB
PL12	13.42 dB
PL13	13.42 dB
PL2W	11.52955914 W
PL12W	0.52458113 W
PL13W	0.52458113 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6126965 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

DSC traces for enaminone **5ab**.

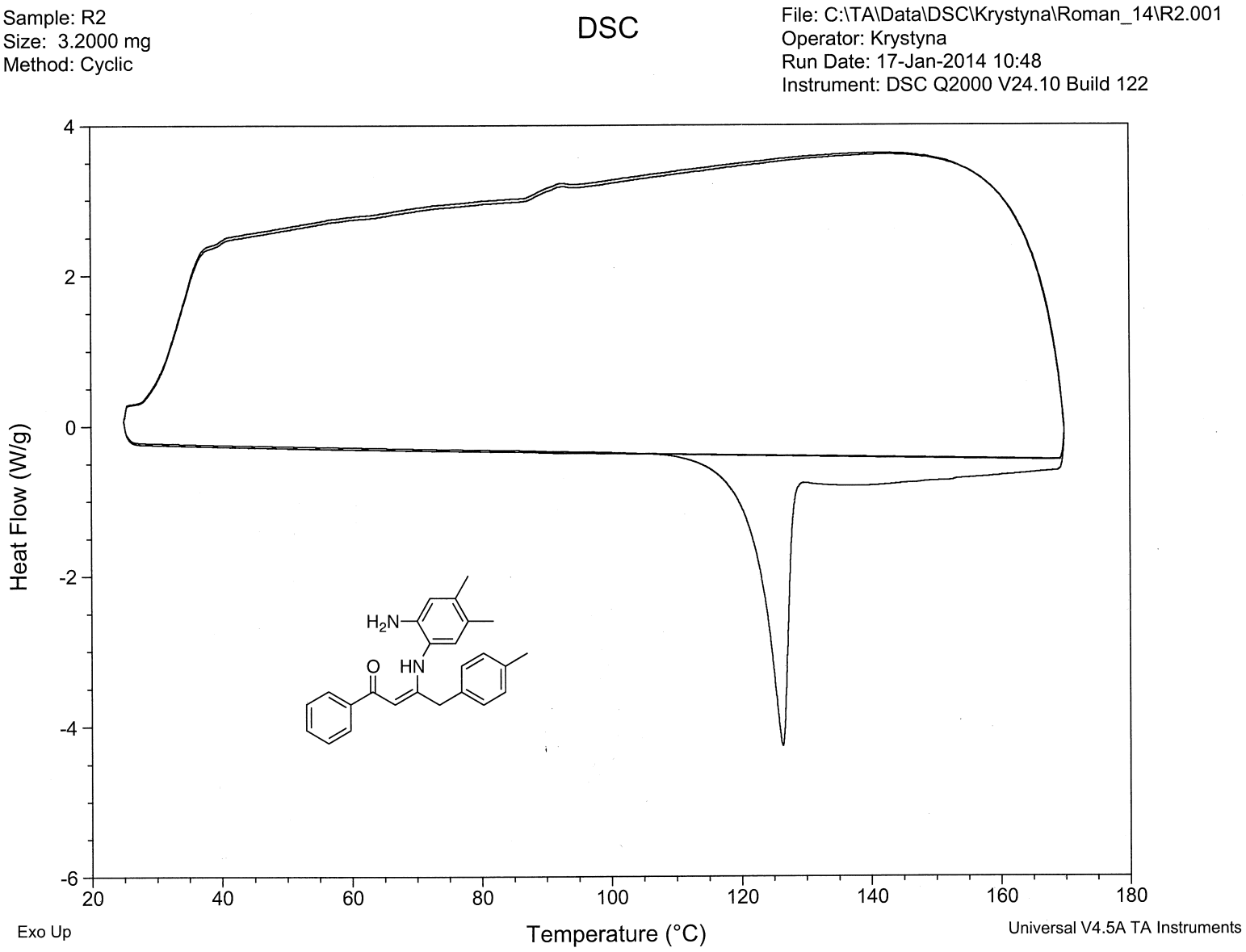


Table S1. Crystal data and structure refinement for enaminones **2, 3**, **5ad**, and **5cb**.

	2	**3**	**5ad**	**5cb** [ref.25]
CCDC number	929589	929587	1477556	950049
Empirical formula	$C_{18}H_{18}ClNO$	$C_{23}H_{21}NO$	$C_{24}H_{24}N_2O$	$C_{28}H_{31}ClN_2O$
Formula weight	299.78	327.41	356.45	447.00
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/n$
Unit cell dimensions	a = 5.8282(2) Å	a = 11.9333(3) Å	a = 12.2036(7) Å	a = 5.7713(9) Å
	b = 10.3586(3) Å	b = 6.7797(2) Å	b = 10.1274(5) Å	b = 16.573(2) Å
	c = 13.2061(4) Å	c = 12.1298(3) Å	c = 15.5213(8) Å	c = 25.145(4) Å
	α = 77.465(2)°	α = 90.00°	α = 90.00°	α = 90.00°
	β = 86.009(2)°	β = 116.667(1)°	β = 93.535(3)°	β = 92.354(8)°
	γ = 76.595(1)°	γ = 90.00°	γ = 90.00°	γ = 90.00°
Volume	756.91(4) Å^3	876.97(4) Å^3	1914.64(18) Å^3	2403.0(6) Å^3
Z	2	2	4	4
Density (calculated)	1.315 Mg/m^3	1.240 Mg/m^3	1.237 Mg/m^3	1.236 Mg/m^3
Absorption coefficient	2.206 mm^{-1}	0.583 mm^{-1}	0.590 mm^{-1}	1.569 mm^{-1}
F(000)	316	348	760	952
Crystal size	0.46 × 0.19 × 0.14 mm^3	0.30 × 0.23 × 0.11 mm^3	0.266 × 0.241 × 0.192 mm^3	0.34 × 0.14 × 0.06 mm^3
Theta range for data collection	3.43 to 67.62°	4.08 to 68.02°	3.674 to 66.301°	3.152 to 67.739°
Index ranges	h = -6 → 6	h = -14 → 14	h = -14 → 14	h = -6 → 6
	k = -12 → 12	k = -8 → 7	k = -12 → 12	k = -18 → 19
	l = -14 → 15	l = -14 → 14	l = -18 → 18	l = -28 → 30
Reflections collected	8132	4927	6626	6787
Independent reflections	2658 [R(int) = 0.0301]	3024 [R(int) = 0.0319]	3493 [R(int) = 0.0472]	4215 [R(int) = 0.0744]
Completeness Absorption	97.4%	99.8%	99.9%	97.5%
correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.7535 and 0.4289	0.9386 and 0.8426		0.9090 and 0.6159
Data / restraints / parameters	2658 / 1 / 194	3024 / 2 / 230	3493 / 3 / 255	4215 / 0 / 294
Goodness-of-fit on F^2	1.059	1.066	1.038	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0785	R1 = 0.0299, wR2 = 0.0722	R1 = 0.0387, wR2 = 0.0994	R1 = 0.0403, wR2 = 0.0874
R indices (all data)	R1 = 0.0316, wR2 = 0.0798	R1 = 0.0332, wR2 = 0.0745	R1 = 0.0466, wR2 = 0.1042	R1 = 0.0753, wR2 = 0.0997
Largest diff. peak and hole	0.321 and -0.194 e•Å^{-3}	0.124 and -0.177 e•Å^{-3}	0.221 and -0.207 e•Å^{-3}	0.195 and -0.261 e•Å^{-3}

Table S1. Crystal data and structure refinement for enaminones **2, 3**, **5ad**, and **5cb**.

	2	**3**	**5ad**	**5cb** [ref.25]
CCDC number	929589	929587	1477556	950049
Empirical formula	$C_{18}H_{18}ClNO$	$C_{23}H_{21}NO$	$C_{24}H_{24}N_2O$	$C_{28}H_{31}ClN_2O$
Formula weight	299.78	327.41	356.45	447.00
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_1/n$
Unit cell dimensions	a = 5.8282(2) Å	a = 11.9333(3) Å	a = 12.2036(7) Å	a = 5.7713(9) Å
	b = 10.3586(3) Å	b = 6.7797(2) Å	b = 10.1274(5) Å	b = 16.573(2) Å
	c = 13.2061(4) Å	c = 12.1298(3) Å	c = 15.5213(8) Å	c = 25.145(4) Å
	α = 77.465(2)°	α = 90.00°	α = 90.00°	α = 90.00°
	β = 86.009(2)°	β = 116.667(1)°	β = 93.535(3)°	β = 92.354(8)°
	γ = 76.595(1)°	γ = 90.00°	γ = 90.00°	γ = 90.00°
Volume	756.91(4) Å^3	876.97(4) Å^3	1914.64(18) Å^3	2403.0(6) Å^3
Z	2	2	4	4
Density (calculated)	1.315 Mg/m^3	1.240 Mg/m^3	1.237 Mg/m^3	1.236 Mg/m^3
Absorption coefficient	2.206 mm^{-1}	0.583 mm^{-1}	0.590 mm^{-1}	1.569 mm^{-1}
F(000)	316	348	760	952
Crystal size	0.46 × 0.19 × 0.14 mm^3	0.30 × 0.23 × 0.11 mm^3	0.266 × 0.241 × 0.192 mm^3	0.34 × 0.14 × 0.06 mm^3
Theta range for data collection	3.43 to 67.62°	4.08 to 68.02°	3.674 to 66.301°	3.152 to 67.739°
Index ranges	h = -6 → 6	h = -14 → 14	h = -14 → 14	h = -6 → 6
	k = -12 → 12	k = -8 → 7	k = -12 → 12	k = -18 → 19
	l = -14 → 15	l = -14 → 14	l = -18 → 18	l = -28 → 30
Reflections collected	8132	4927	6626	6787
Independent reflections	2658 [R(int) = 0.0301]	3024 [R(int) = 0.0319]	3493 [R(int) = 0.0472]	4215 [R(int) = 0.0744]
Completeness Absorption	97.4%	99.8%	99.9%	97.5%
correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.7535 and 0.4289	0.9386 and 0.8426		0.9090 and 0.6159
Data / restraints / parameters	2658 / 1 / 194	3024 / 2 / 230	3493 / 3 / 255	4215 / 0 / 294
Goodness-of-fit on F^2	1.059	1.066	1.038	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0785	R1 = 0.0299, wR2 = 0.0722	R1 = 0.0387, wR2 = 0.0994	R1 = 0.0403, wR2 = 0.0874
R indices (all data)	R1 = 0.0316, wR2 = 0.0798	R1 = 0.0332, wR2 = 0.0745	R1 = 0.0466, wR2 = 0.1042	R1 = 0.0753, wR2 = 0.0997
Largest diff. peak and hole	0.321 and -0.194 e•Å^{-3}	0.124 and -0.177 e•Å^{-3}	0.221 and -0.207 e•Å^{-3}	0.195 and -0.261 e•Å^{-3}

Deuterated Solvent (MeOD) Experimental Data and Product Ratios

Figure S1. Reaction of ketone **1a** and diamine **4a** to enaminone **5aa**

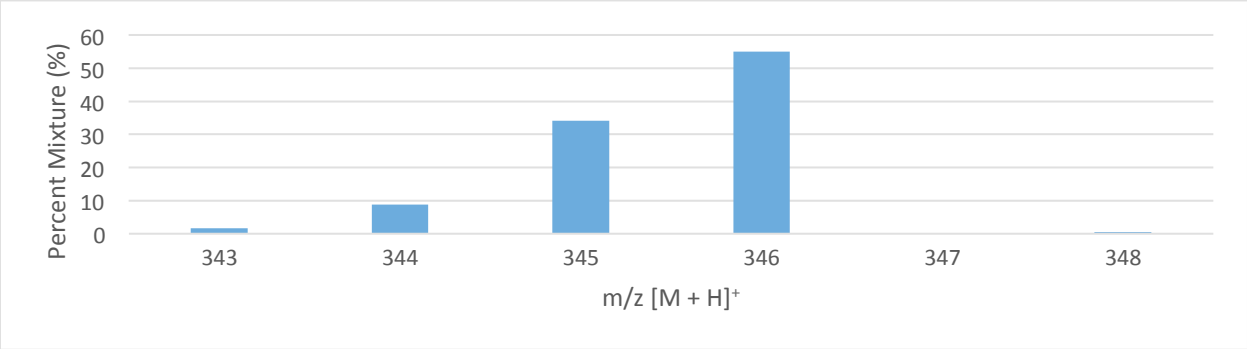


Figure S2. Reaction of ketone **1a** and diamine **4a** to diazepine **8aa**

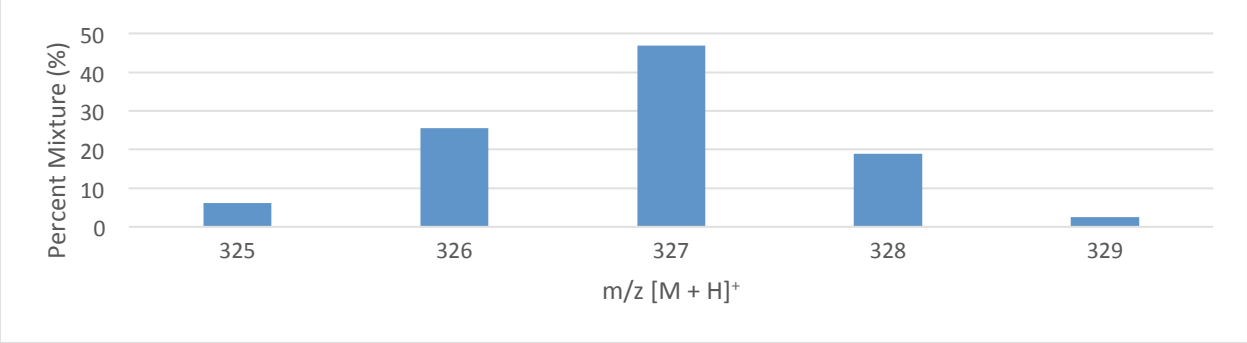
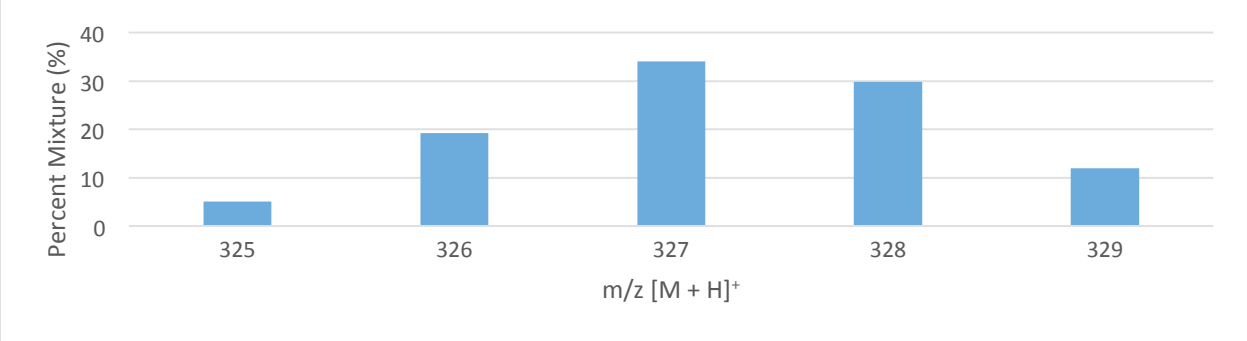


Figure S3. Cyclization of non-deuterated enaminone **5aa** to diazepine **8aa**



Post-reaction ratios of deuterated products

Reaction	d_0 (%)	d_1 (%)	d_2 (%)	d_3 (%)	d_4 (%)	d_5 (%)
1a + 4a → 5aa	1.6	8.8	34.1	**55.0**	0.2	0.5
1a + 4a → 8aa	6.2	25.6	**46.9**	18.8	2.4	0.0
5aa → 8aa	5.0	19.2	**34.0**	29.9	12.0	0.0