Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information
For

Regio- and stereoselective synthesis of functionalized and fused heterocycles from Morita-Baylis-Hillman adducts of dicyclopentadienone

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```
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NAME      INN-AS-DCPDMBHA-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20211129
Time              22.24
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                30.72
DW               50.000 usec
DE                 6.50 usec
TE                295.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                1H
P1                13.35 usec
PLW1        16.00000000 W

F2 - Processing parameters
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SF          500.1300133 MHz
WDW                 EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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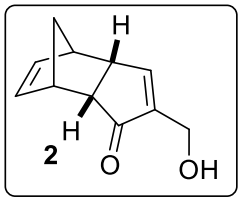

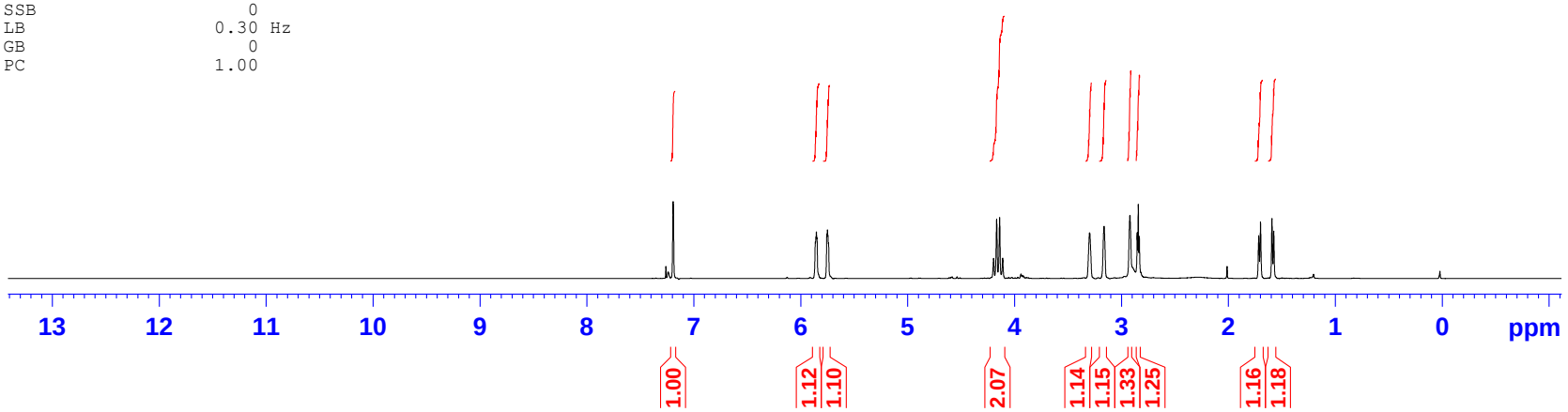

Figure S01. ^{1}H NMR Spectrum of 2

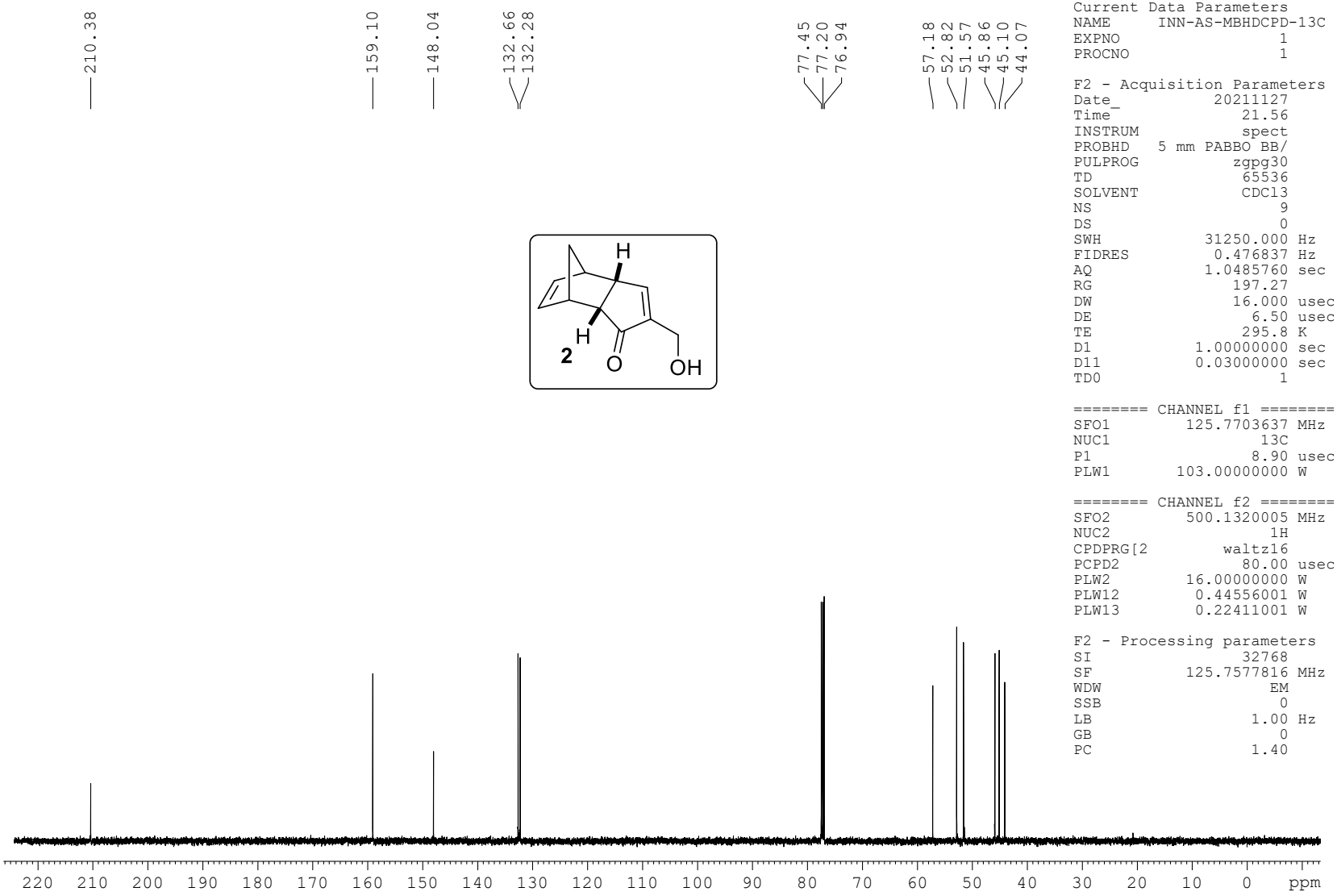

Figure S02. ^{13}C NMR Spectrum of 2

```
Current Data Parameters
NAME      INN-AS-I-11-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170721
Time              16.04
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES        0.151522 Hz
AQ            3.2998593 sec
RG                 11.3
DW               60.800 usec
DE                6.50 usec
TE               296.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
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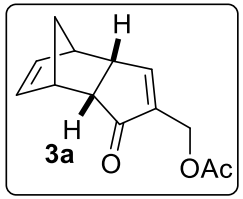


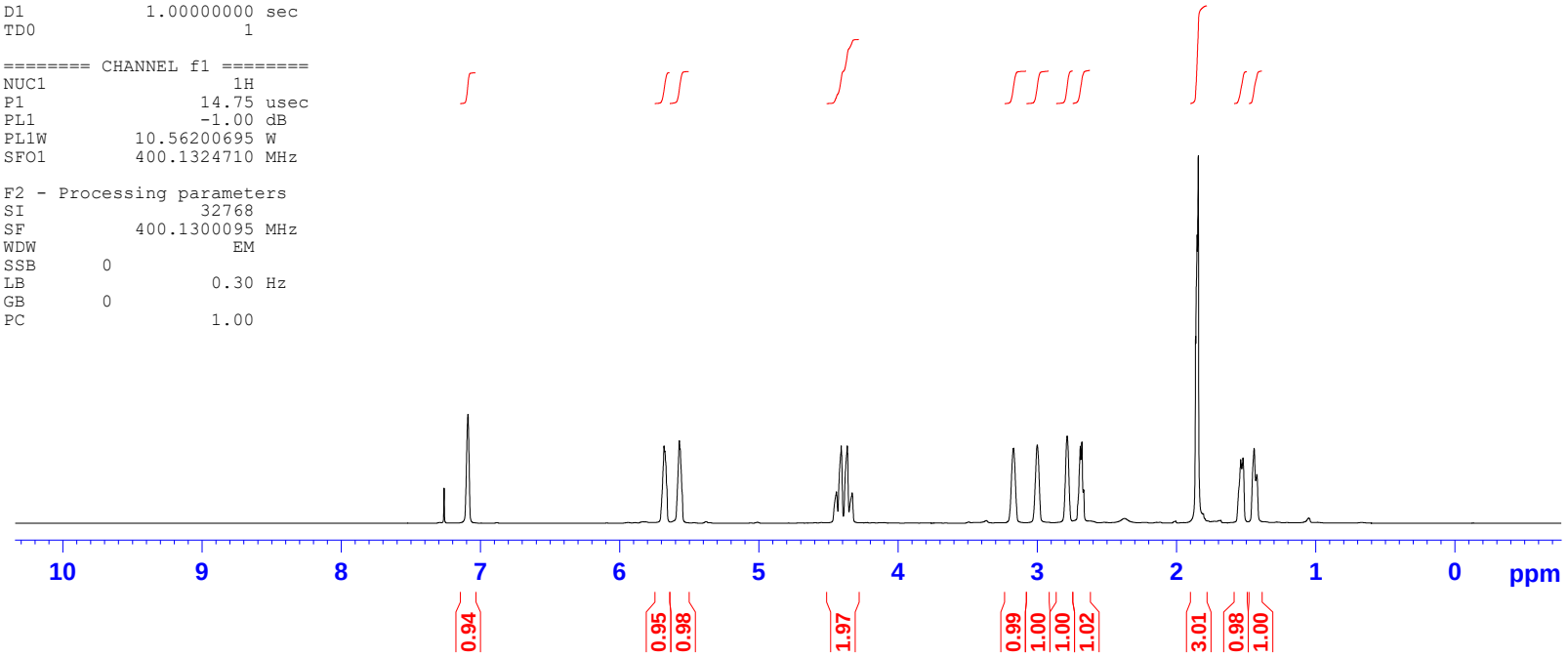
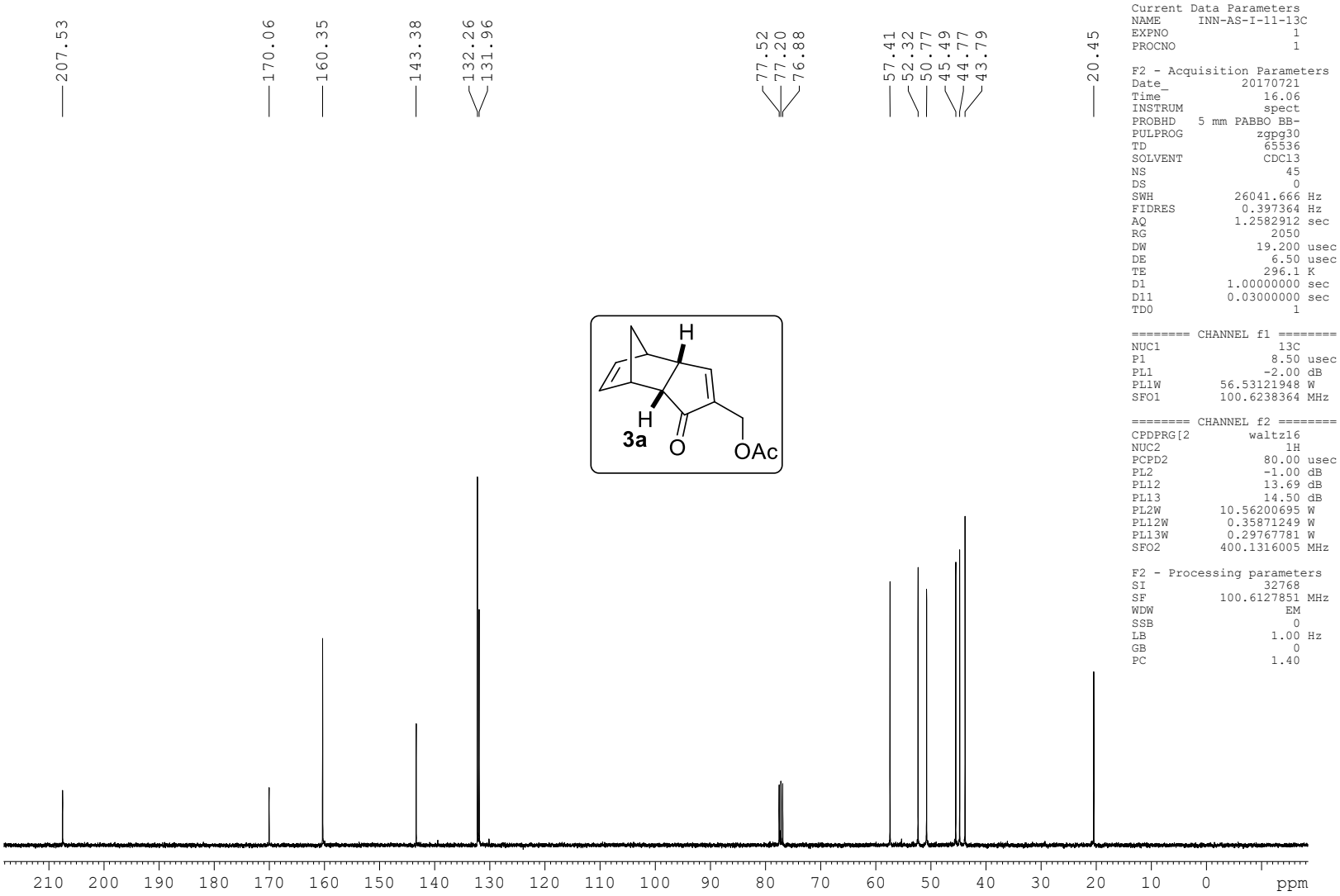


Figure S03. ^{1}H NMR Spectrum of 3a

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Current Data Parameters
NAME      INN-AS-I-11-13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170721
Time                16.06
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    45
DS                     0
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                  2050
DW                19.200 usec
DE                 6.50 usec
TE                296.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.50 usec
PL1                 -2.00 dB
PL1W         56.53121948 W
SFO1        100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W         10.56200695 W
PL12W         0.35871249 W
PL13W         0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127851 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Figure S04. ^{13}C NMR Spectrum of 3a

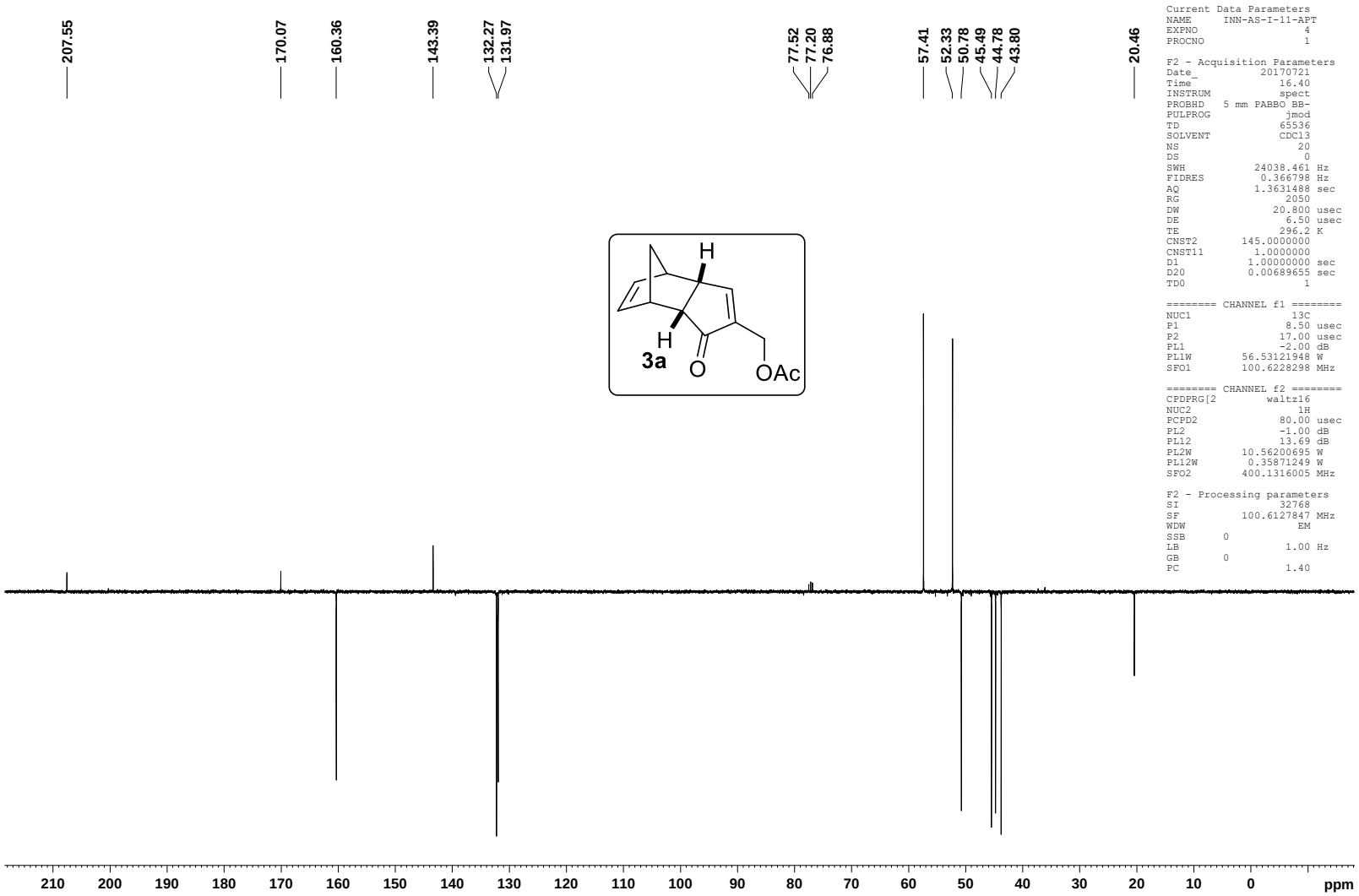


Figure S05. ^{13}C-APT NMR Spectrum of 3a

```
Current Data Parameters
NAME      INN-AS-81A2-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170808
Time              16.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                  181
DW                60.800 usec
DE                 6.50 usec
TE                297.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300102 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

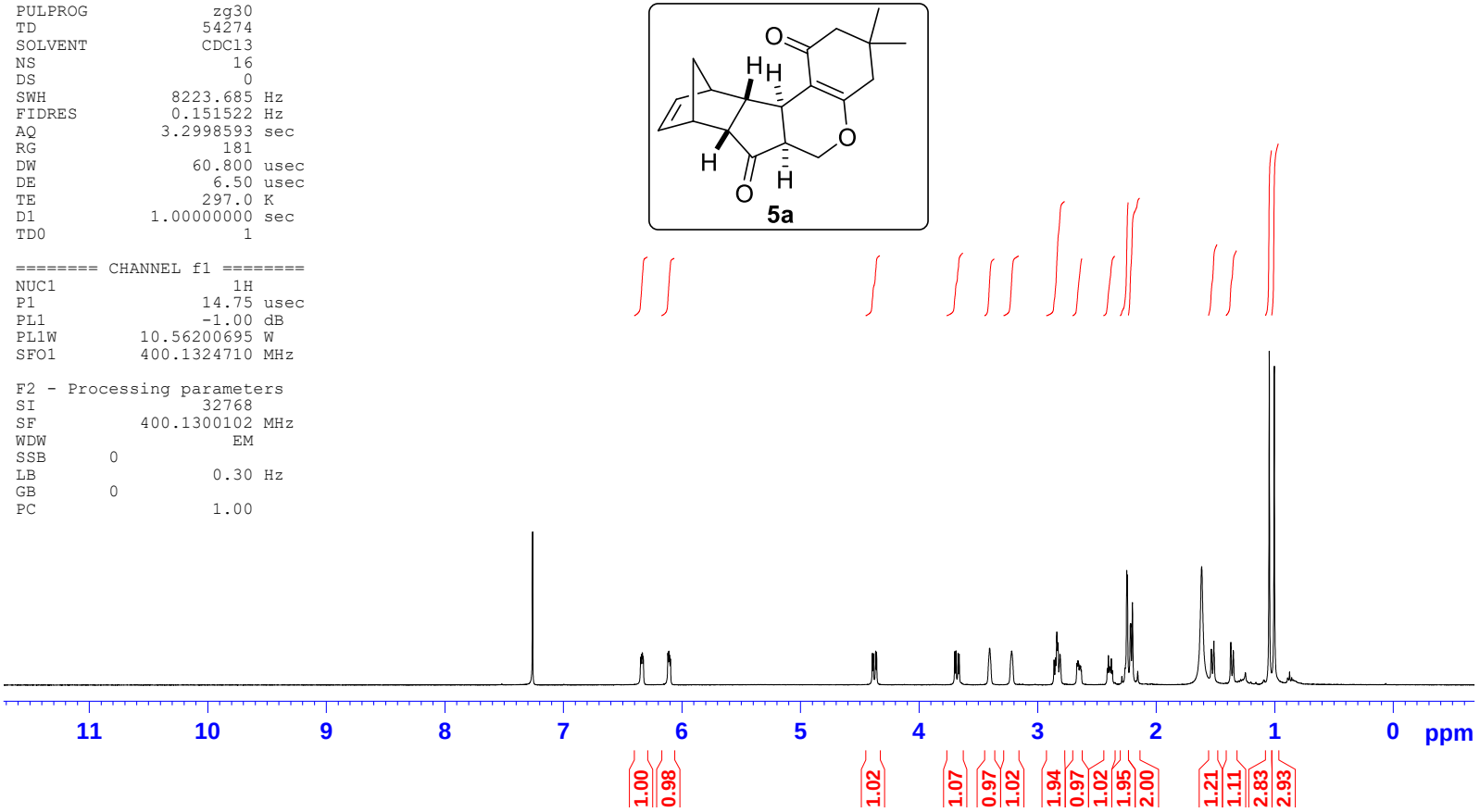


Figure S06. ^{1}H NMR Spectrum of 5a

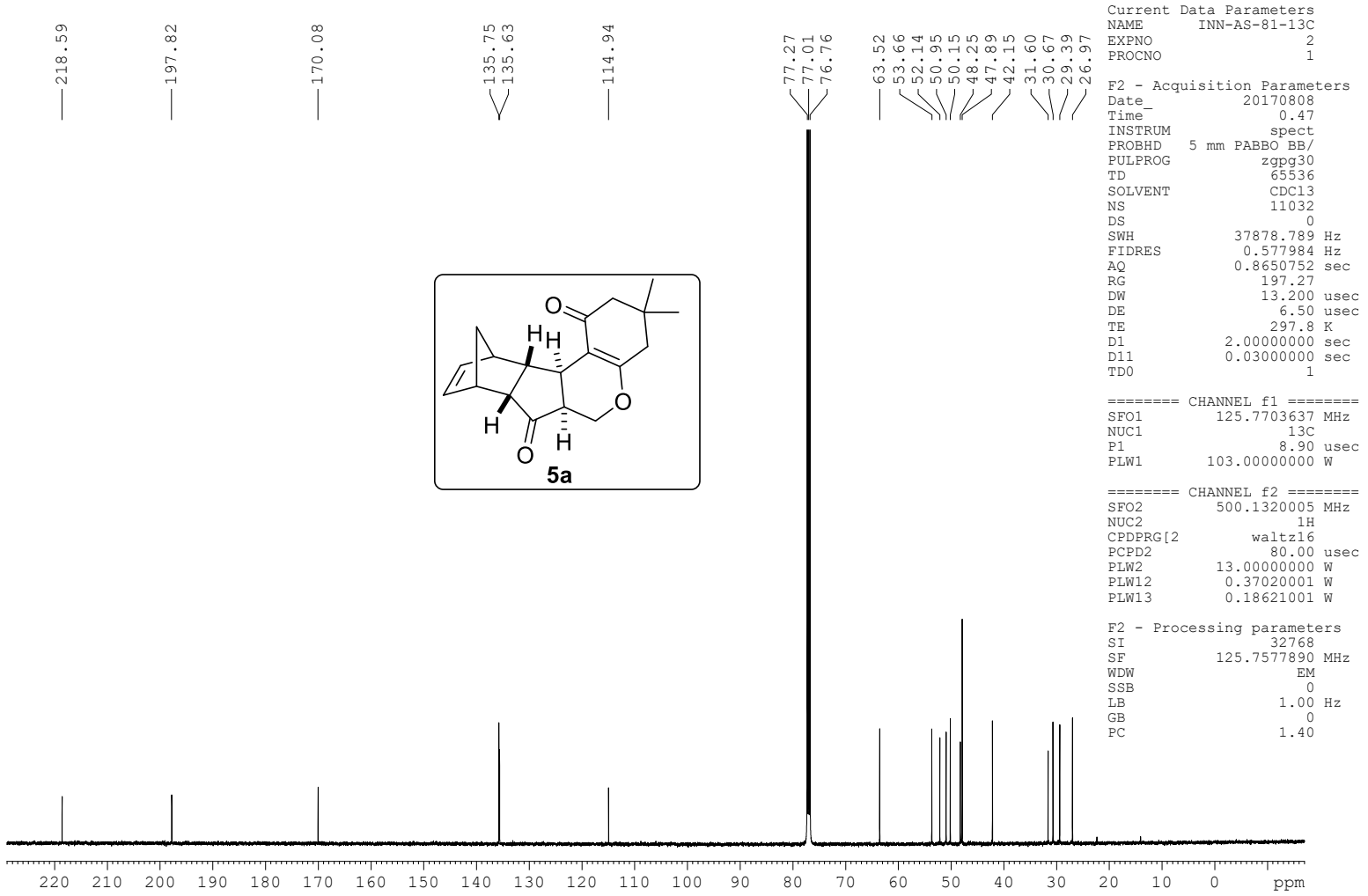


Figure S07. ^{13}C NMR Spectrum of 5a

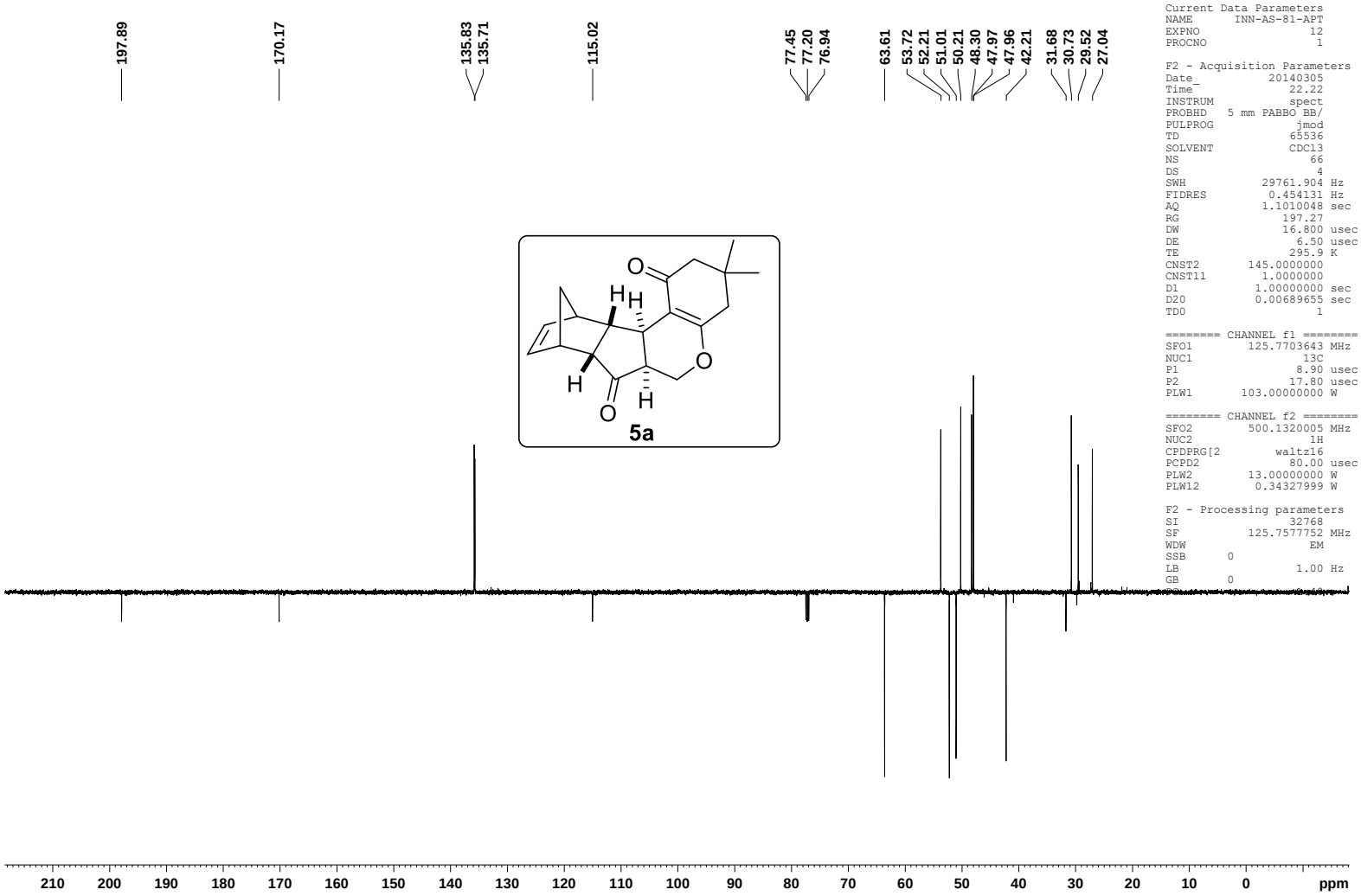
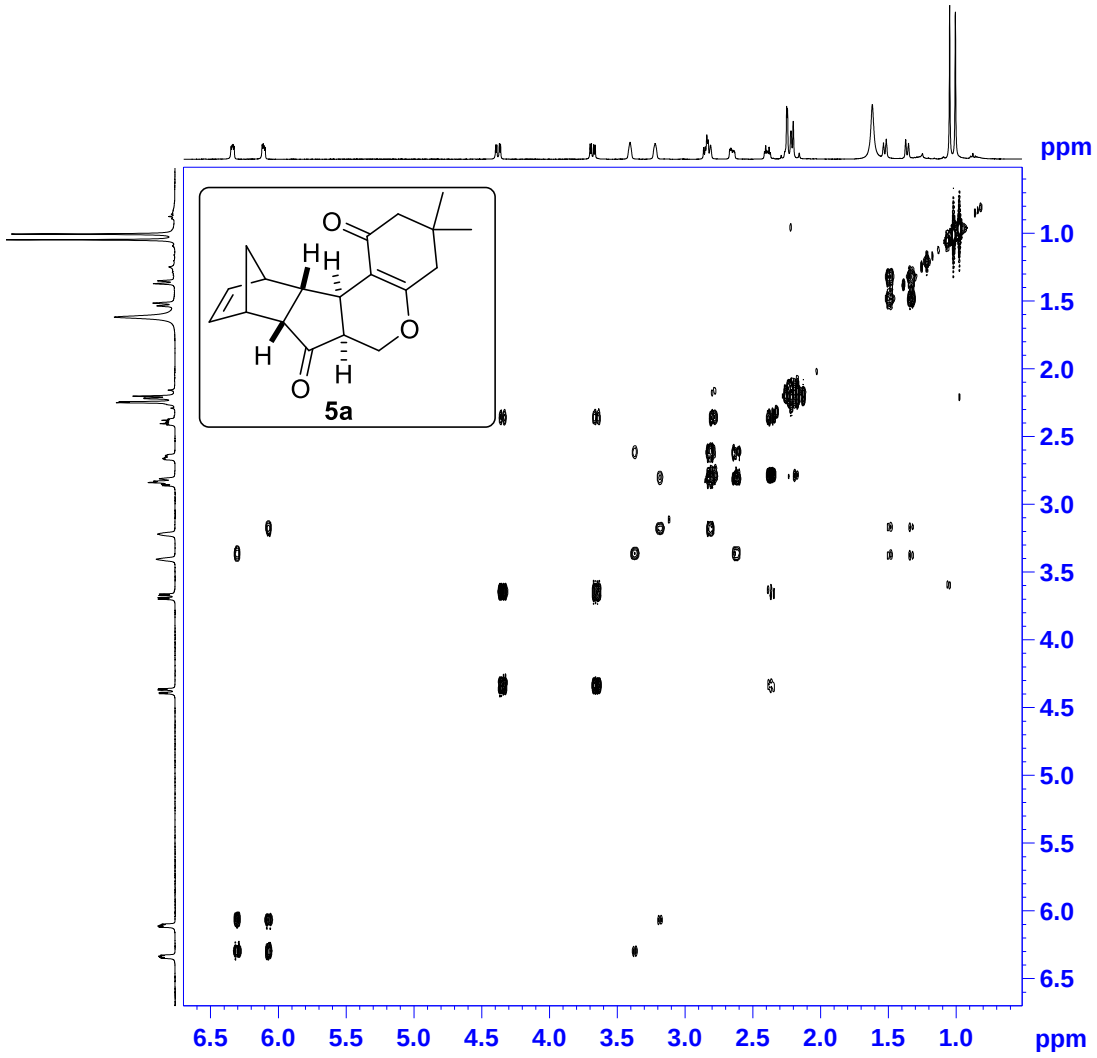


Figure S08. ^{13}C-APT NMR Spectrum of 5a

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Current Data Parameters
NAME      INN-AS-81-COSY
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140306
Time              15.50
INSTRUM           spect
PROBHD   5 mm SEI 1H/D-
PULPROG        cosygpqf
TD                2048
SOLVENT           CDCl3
NS                   8
DS                  16
SWH            2475.248 Hz
FIDRES         1.208617 Hz
AQ             0.4136960 sec
RG                40.3
DW               202.000 usec
DE                 6.50 usec
TE                294.0 K
D0           0.00000300 sec
D1           1.00000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00040400 sec

======== CHANNEL f1 ========
NUC1                1H
P0                6.75 usec
P1                6.75 usec
PL1              -3.00 dB
PL1W        16.73965454 W
SFO1       400.1314532 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPZ1              10.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  90
SFO1          400.1315 MHz
FIDRES        55.005627 Hz
SW                6.186 ppm
FnMODE               QF

F2 - Processing parameters
SI                2048
SF          400.1300101 MHz
WDW               SINE
SSB       0
LB        0 Hz
GB        0
PC                1.40

F1 - Processing parameters
SI                 512
MC2                 QF
SF          400.1300101 MHz
WDW               SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S09. ^{1}H-^{1}H COSY NMR Spectrum of 5a

```
Current Data Parameters
NAME      INN-AS-86I-1H
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           20140608
Time              12.26
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG                98.91
DW               50.000 usec
DE                6.50 usec
TE                297.4 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                1H
P1                13.00 usec
PLW1        13.00000000 W

F2 - Processing parameters
SI                65536
SF          500.1300120 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
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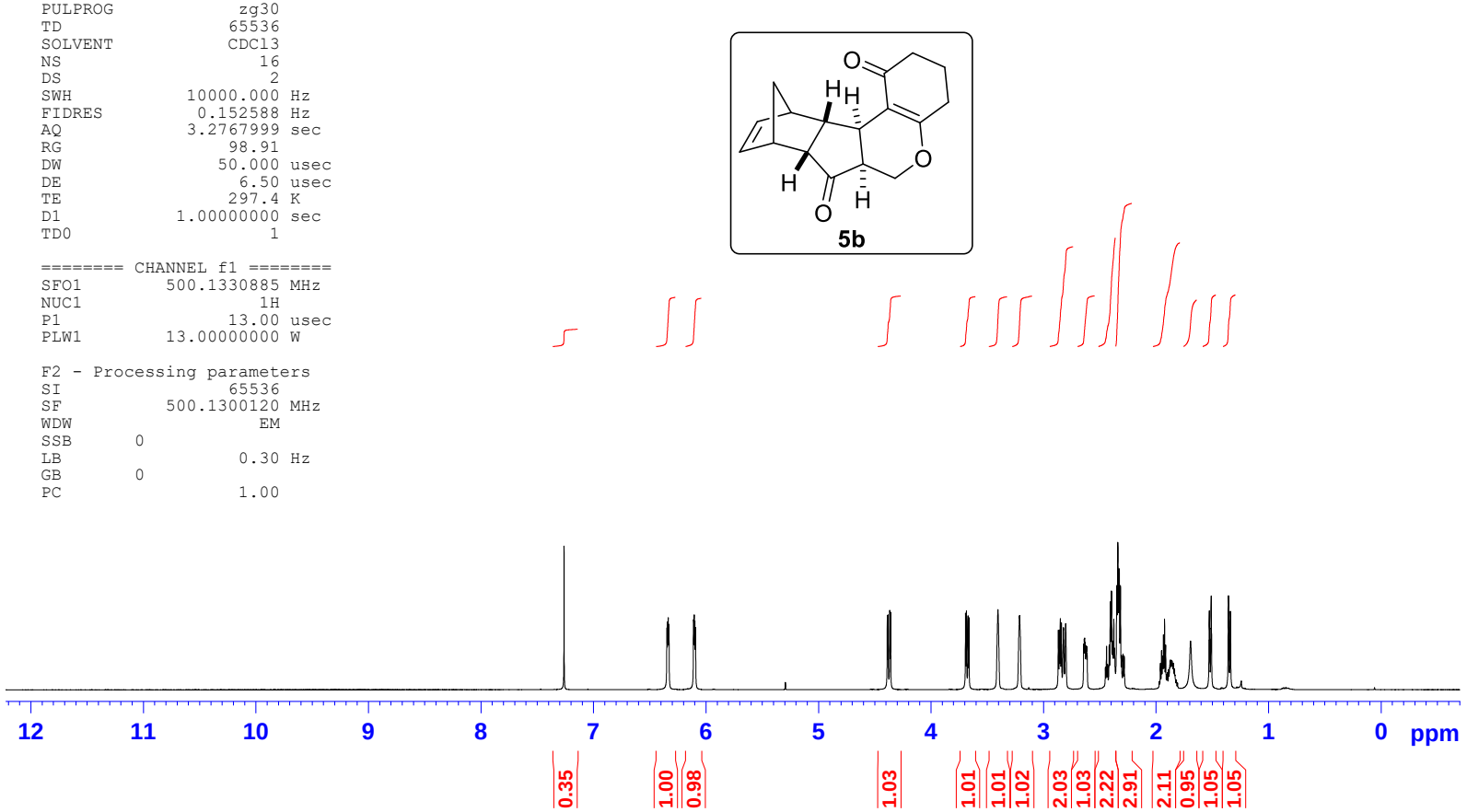


Figure S10. ^{1}H NMR Spectrum of 5b

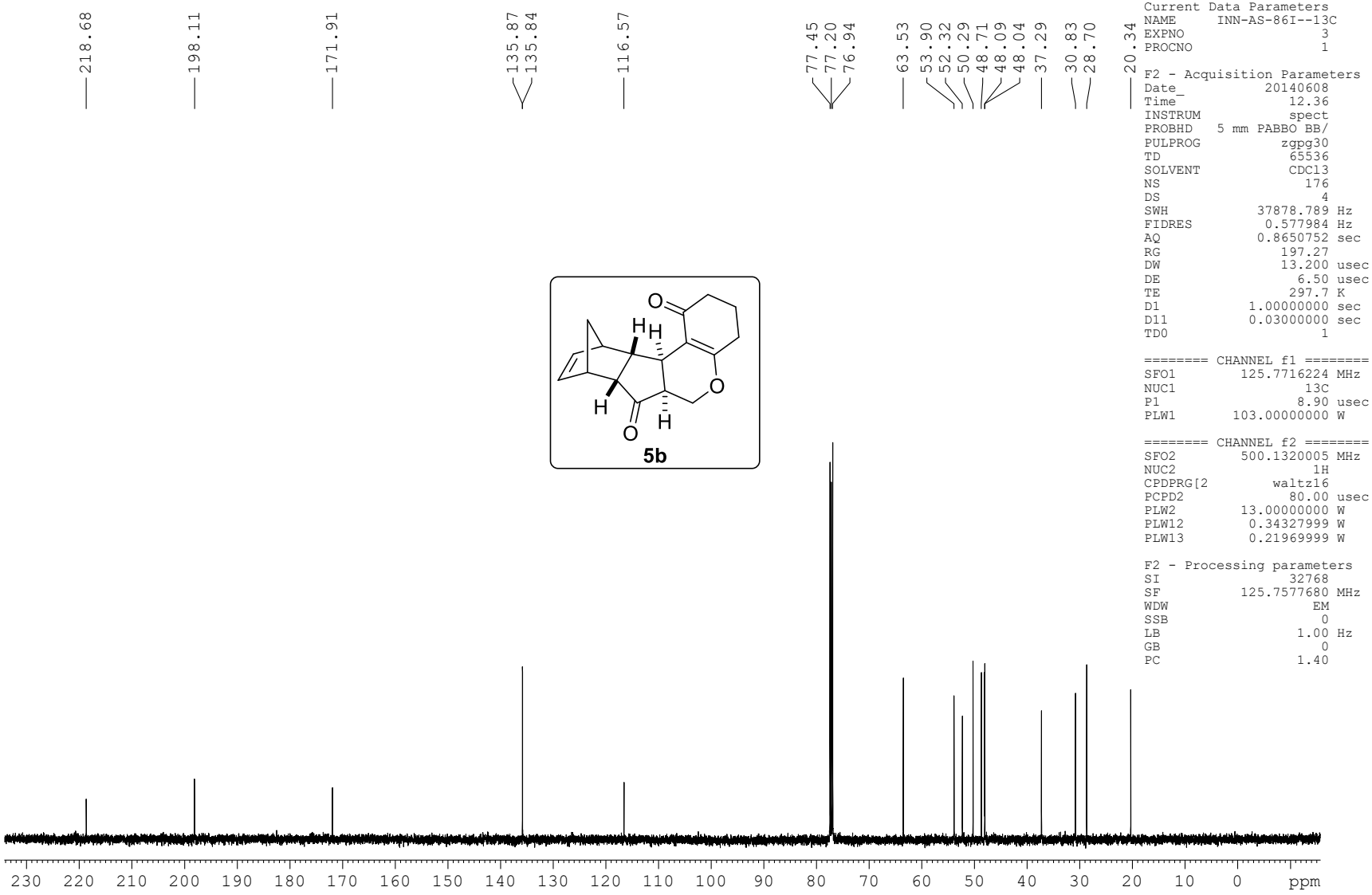


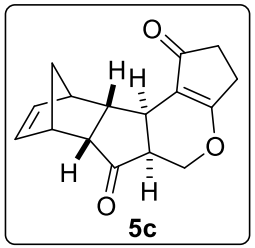
Figure S11. ^{13}C NMR Spectrum of 5b

```
Current Data Parameters
NAME      inn-as-186c-1h
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150527
Time              17.02
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                   32
DW               60.800 usec
DE                6.50 usec
TE               300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



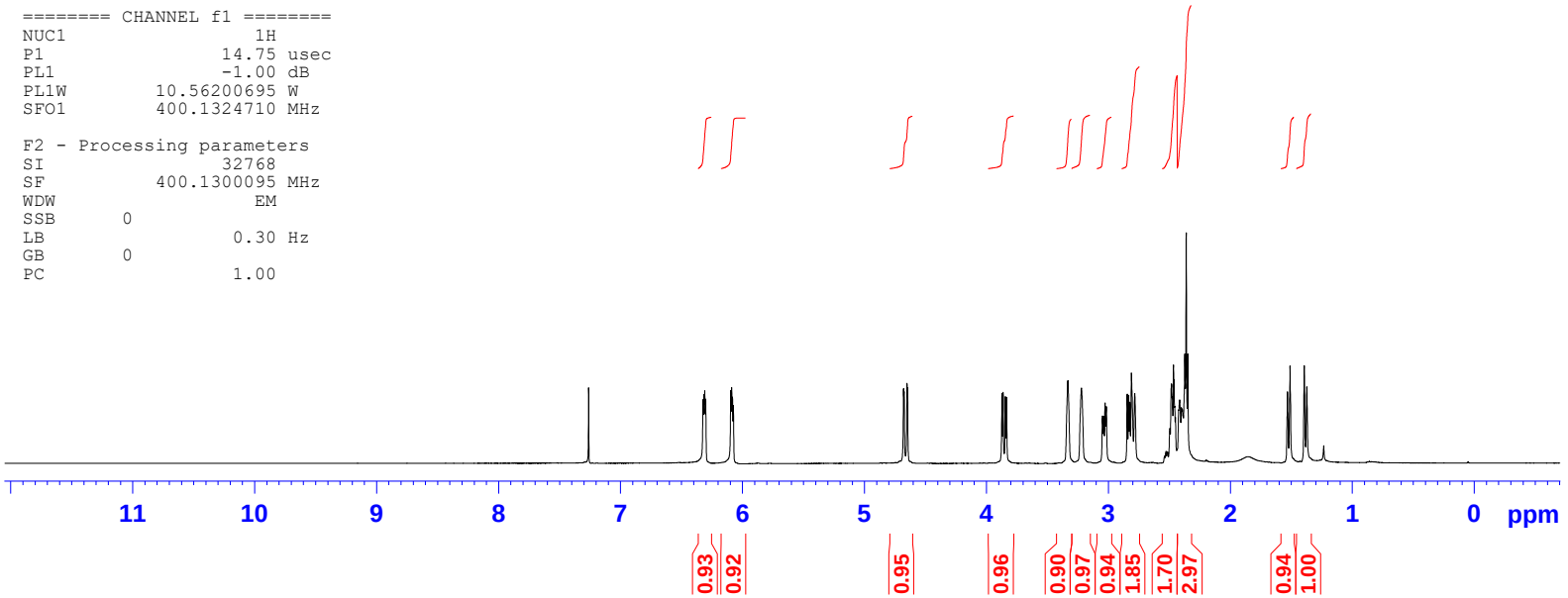


Figure S12. ^{1}H NMR Spectrum of 5c

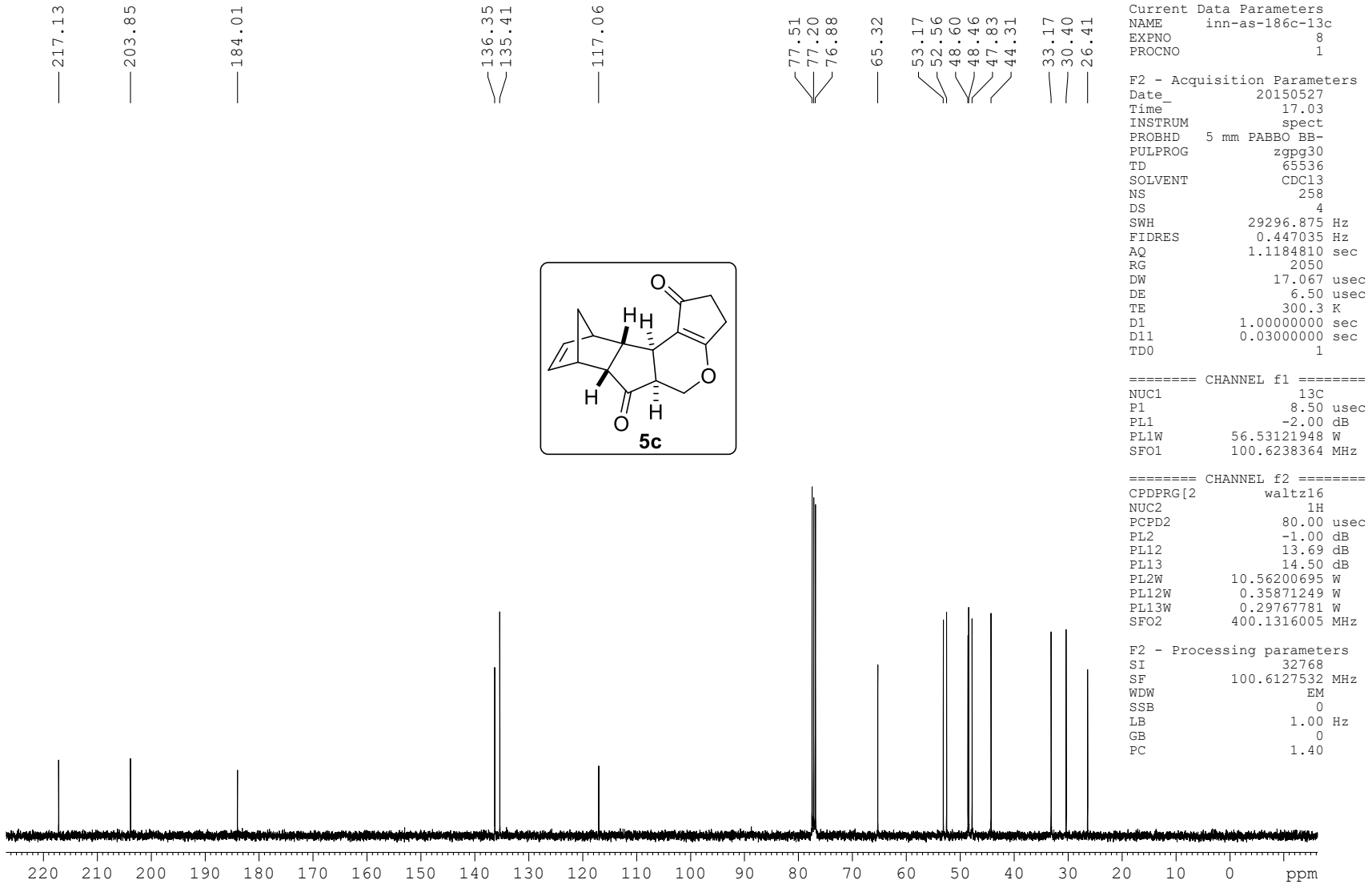


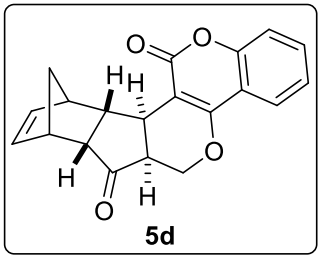
Figure S13. ^{13}C NMR Spectrum of 5c

```
Current Data Parameters
NAME       INN-AS-86A-1H
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_           20150522
Time              17.57
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                30.72
DW               50.000 usec
DE                6.50 usec
TE                301.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                 1H
P1                13.00 usec
PLW1        13.00000000 W

F2 - Processing parameters
SI                65536
SF           500.1300120 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



5d

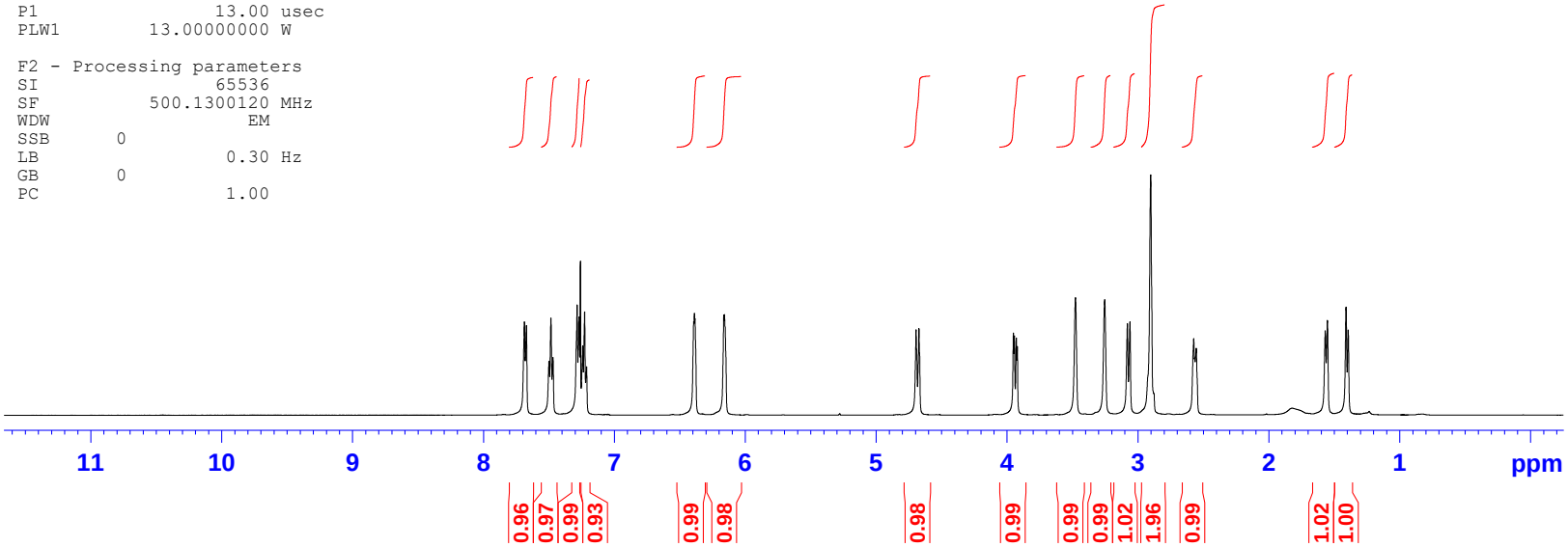


Figure S14. ^{1}H NMR Spectrum of 5d

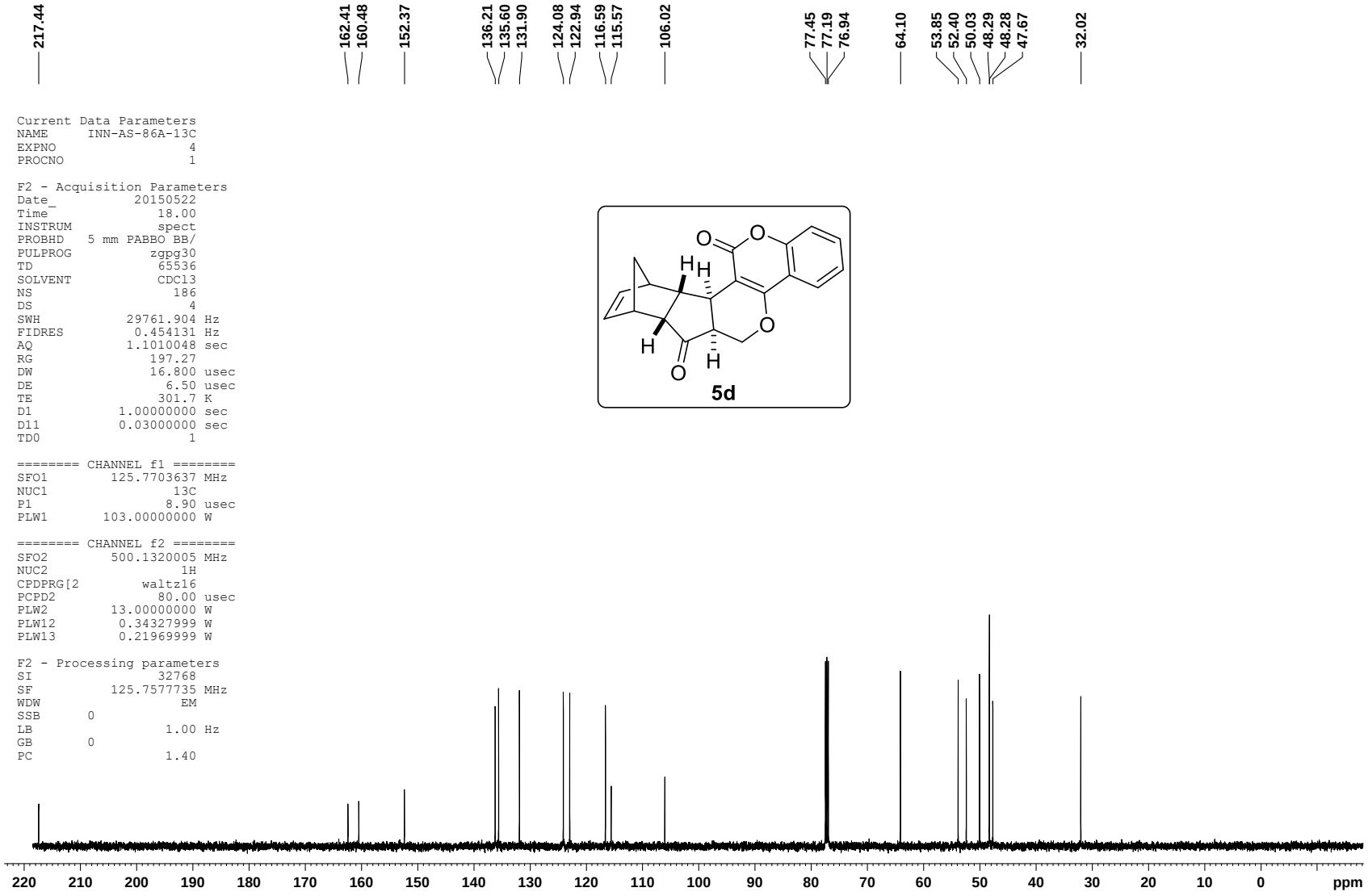


Figure S15. ^{13}C NMR Spectrum of 5d

```
Current Data Parameters
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EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140409
Time              23.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   14
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                30.72
DW               50.000 usec
DE                6.50 usec
TE                295.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                 1H
P1                13.00 usec
PLW1         13.00000000 W

F2 - Processing parameters
SI                65536
SF           500.1300132 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

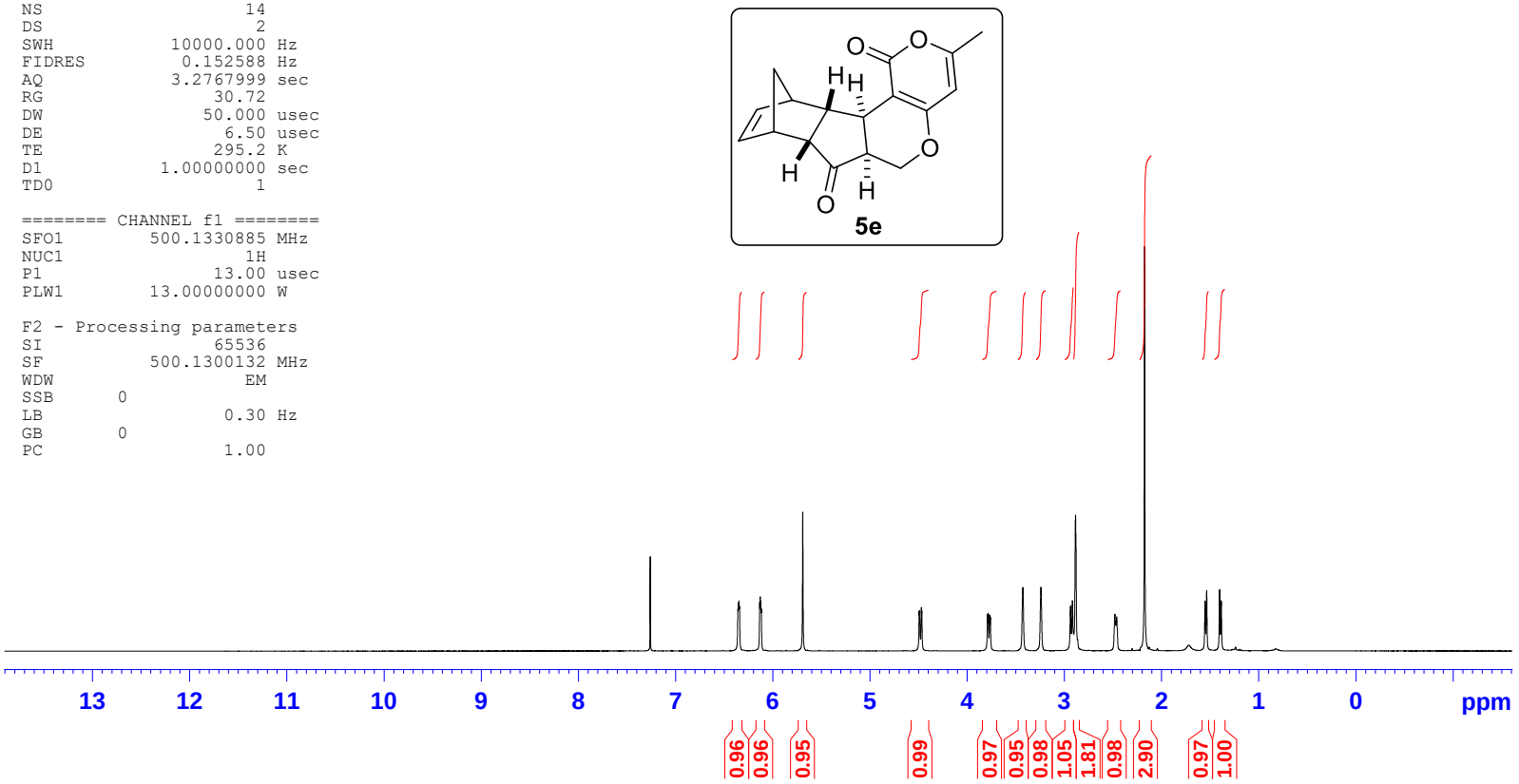

Figure S16. ^{1}H NMR Spectrum of 5e

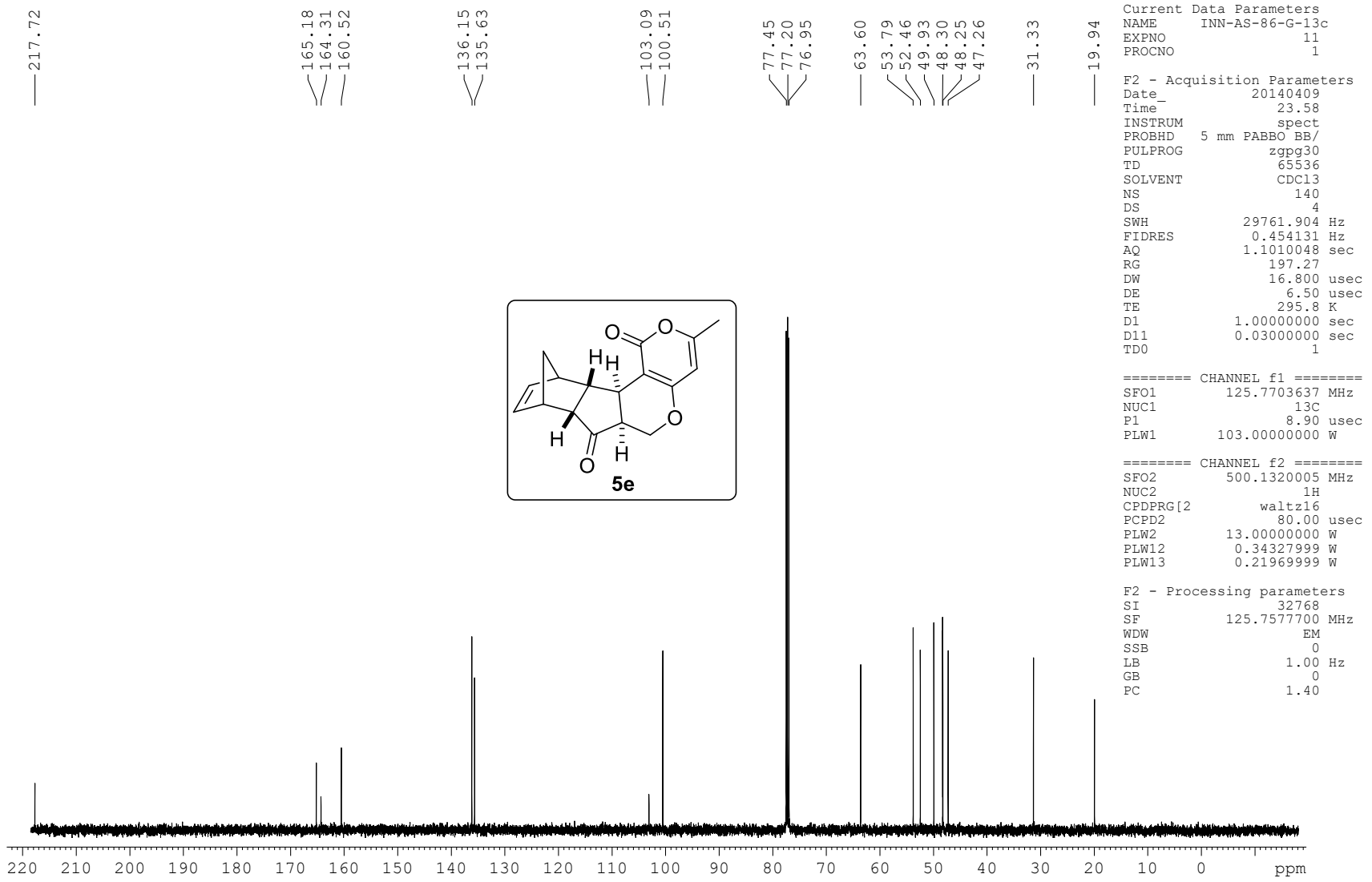

Figure S17. ^{13}C NMR Spectrum of 5e

```
Current Data Parameters
NAME      INN-AS-86D-1H
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           20150523
Time              11.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               54274
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           8223.685 Hz
FIDRES        0.151522 Hz
AQ           3.2998593 sec
RG                  32
DW              60.800 usec
DE               6.50 usec
TE              300.3 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1              14.75 usec
PL1             -1.00 dB
PL1W       10.56200695 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI               32768
SF          400.1300095 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
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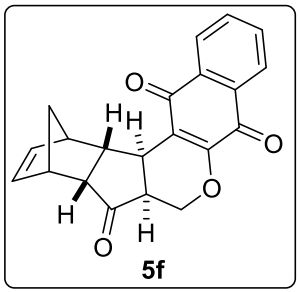

5f

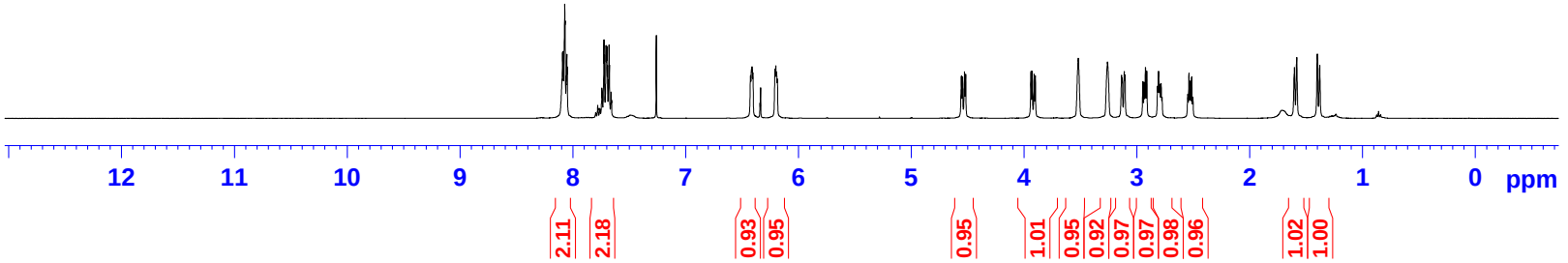

Figure S18. ^{1}H NMR Spectrum of 5f

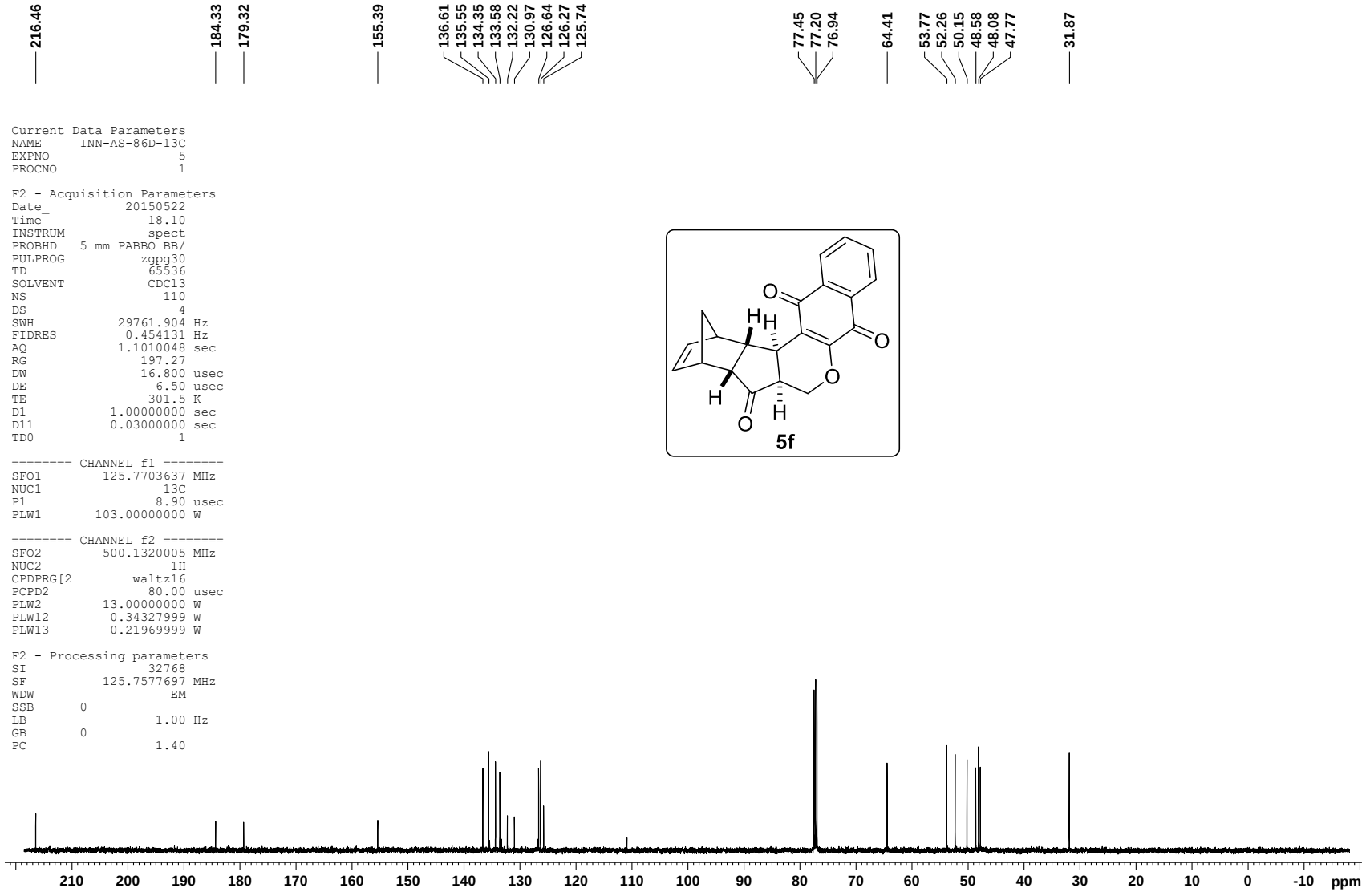

Figure S19. ^{13}C NMR Spectrum of 5f

```
Current Data Parameters
NAME       INN-AS-65-1H
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20140716
Time              18.19
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   20
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                30.72
DW               50.000 usec
DE                6.50 usec
TE                297.5 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                1H
P1                13.00 usec
PLW1        13.00000000 W

F2 - Processing parameters
SI                65536
SF           500.1300123 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
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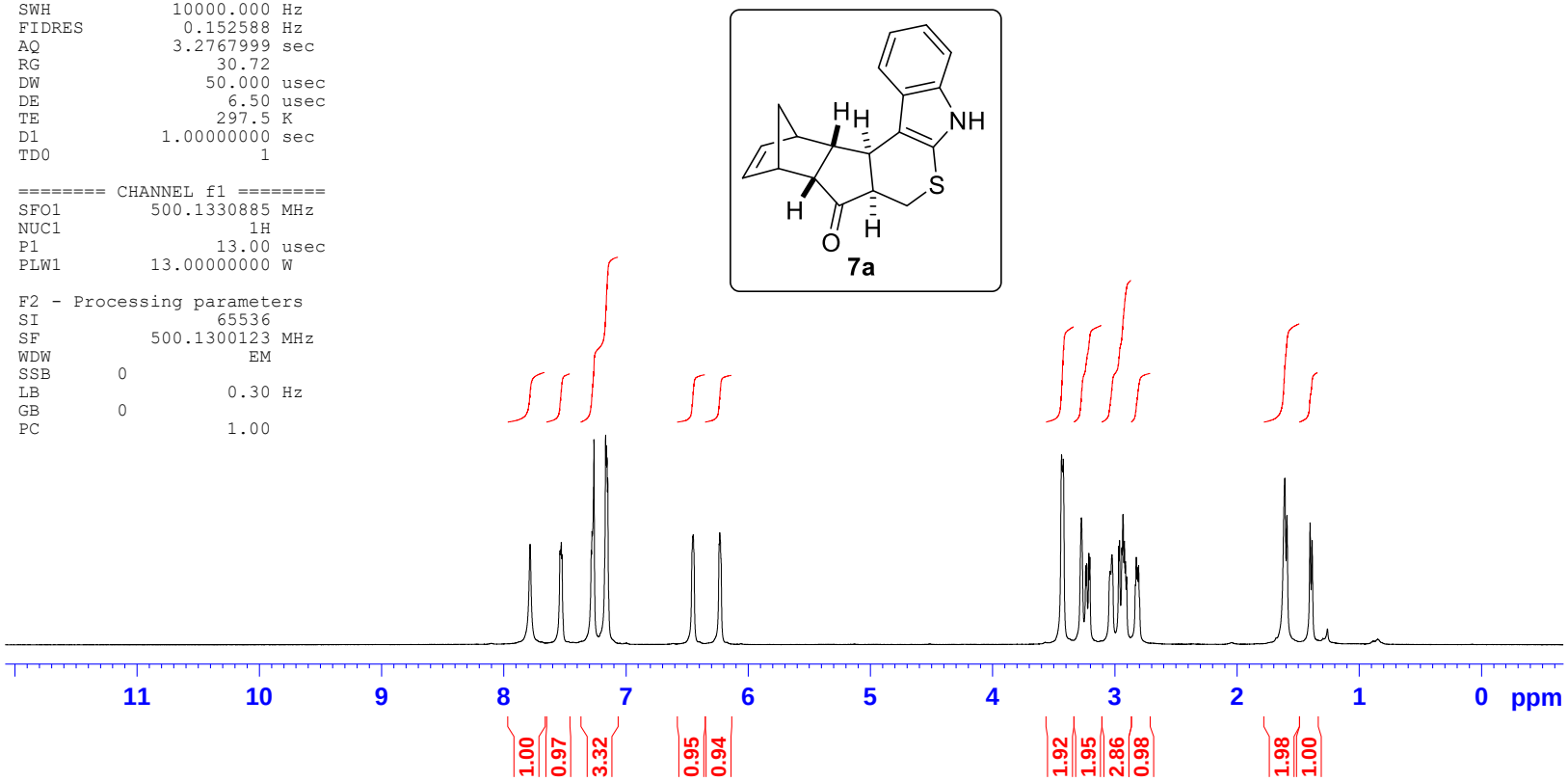


Figure S20. ^{1}H NMR Spectrum of 7a

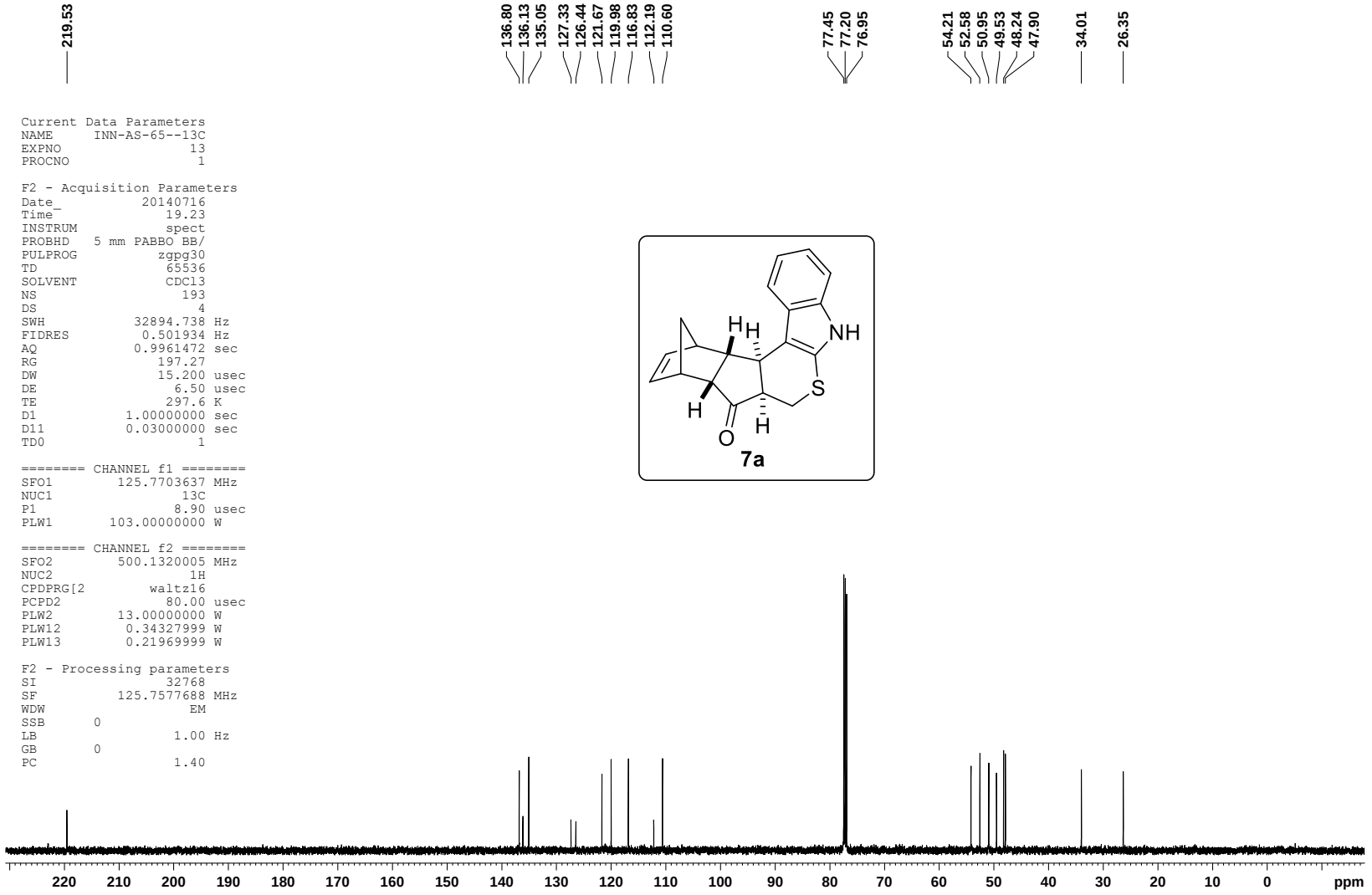


Figure S21. ^{13}C NMR Spectrum of 7a

```
Current Data Parameters
NAME      INN-AS-I-56-A-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170803
Time               11.42
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             8223.685 Hz
FIDRES          0.151522 Hz
AQ             3.2998593 sec
RG                  71.8
DW                60.800 usec
DE                 6.50 usec
TE                297.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300095 MHz
WDW                   EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

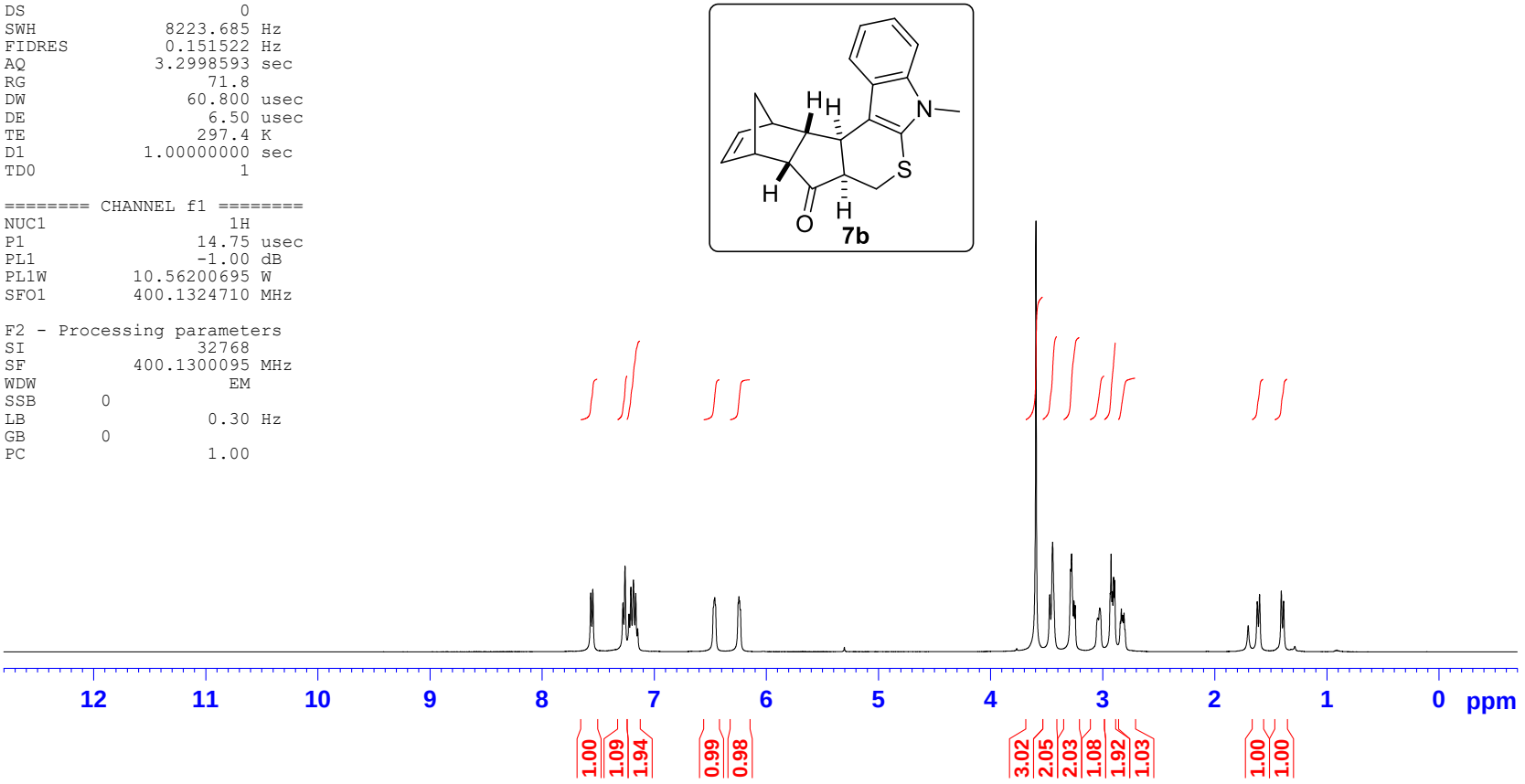


Figure S22. ^{1}H NMR Spectrum of 7b

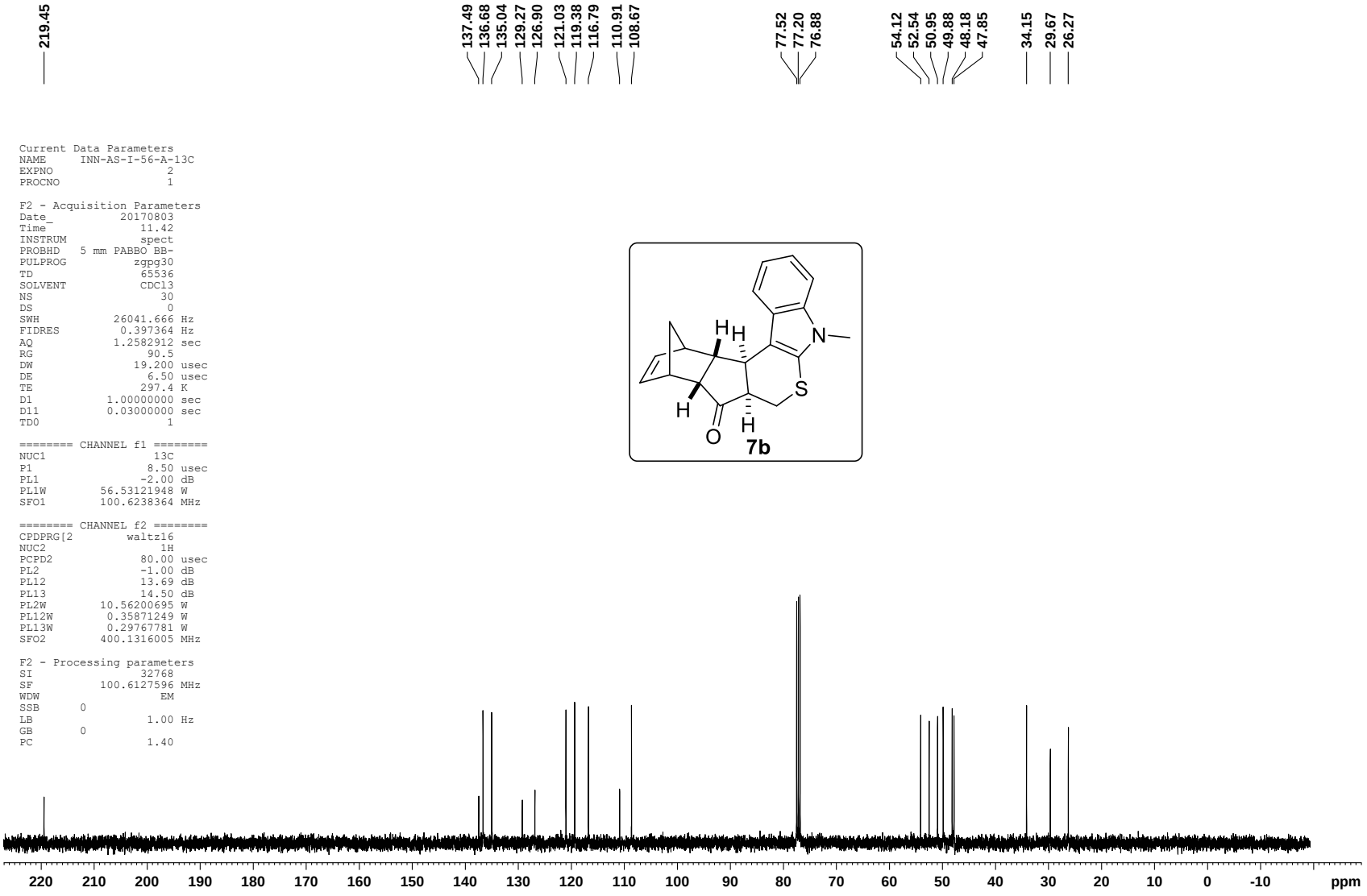


Figure S23. ^{13}C NMR Spectrum of 7b

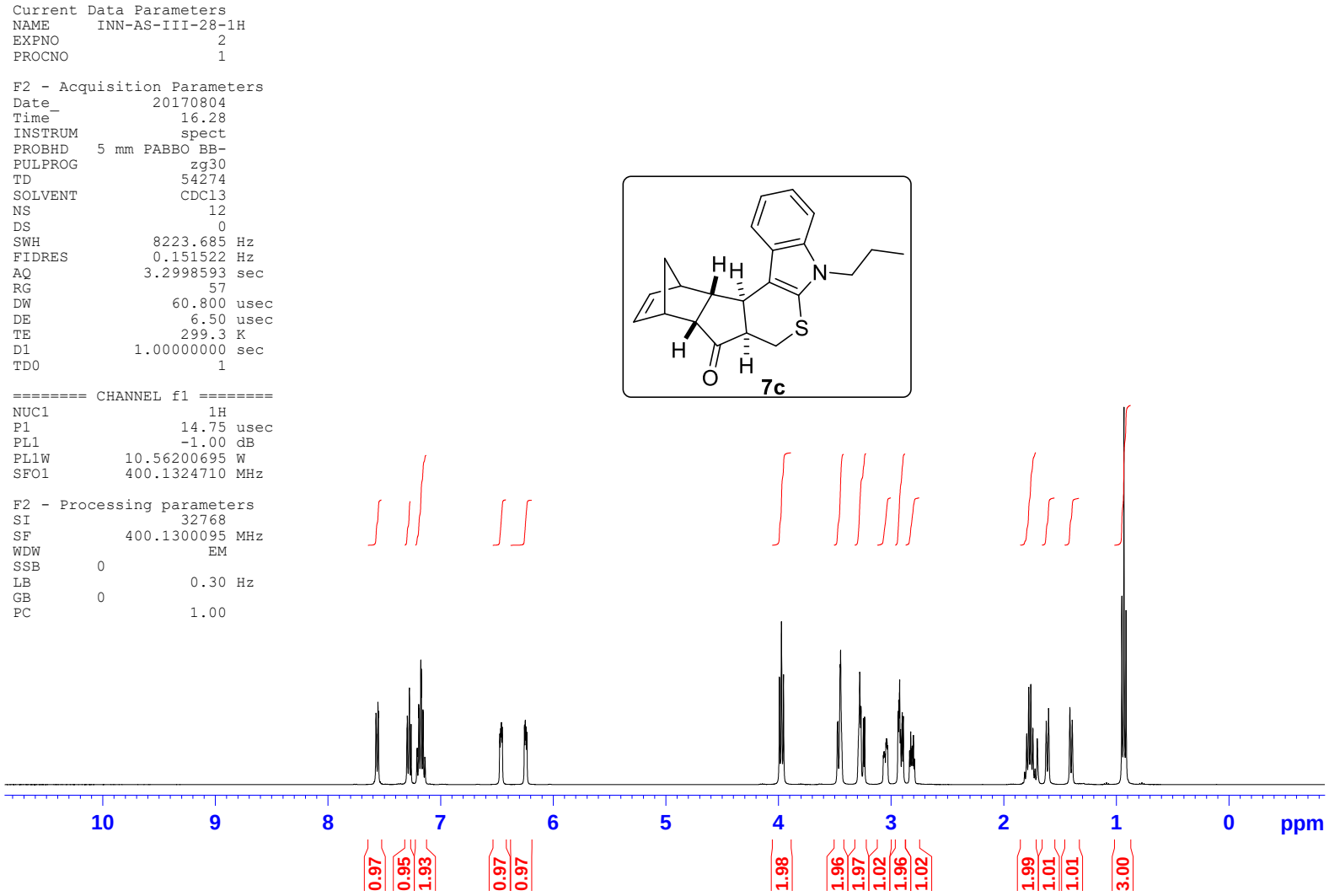


Figure S24. ^{1}H NMR Spectrum of 7c

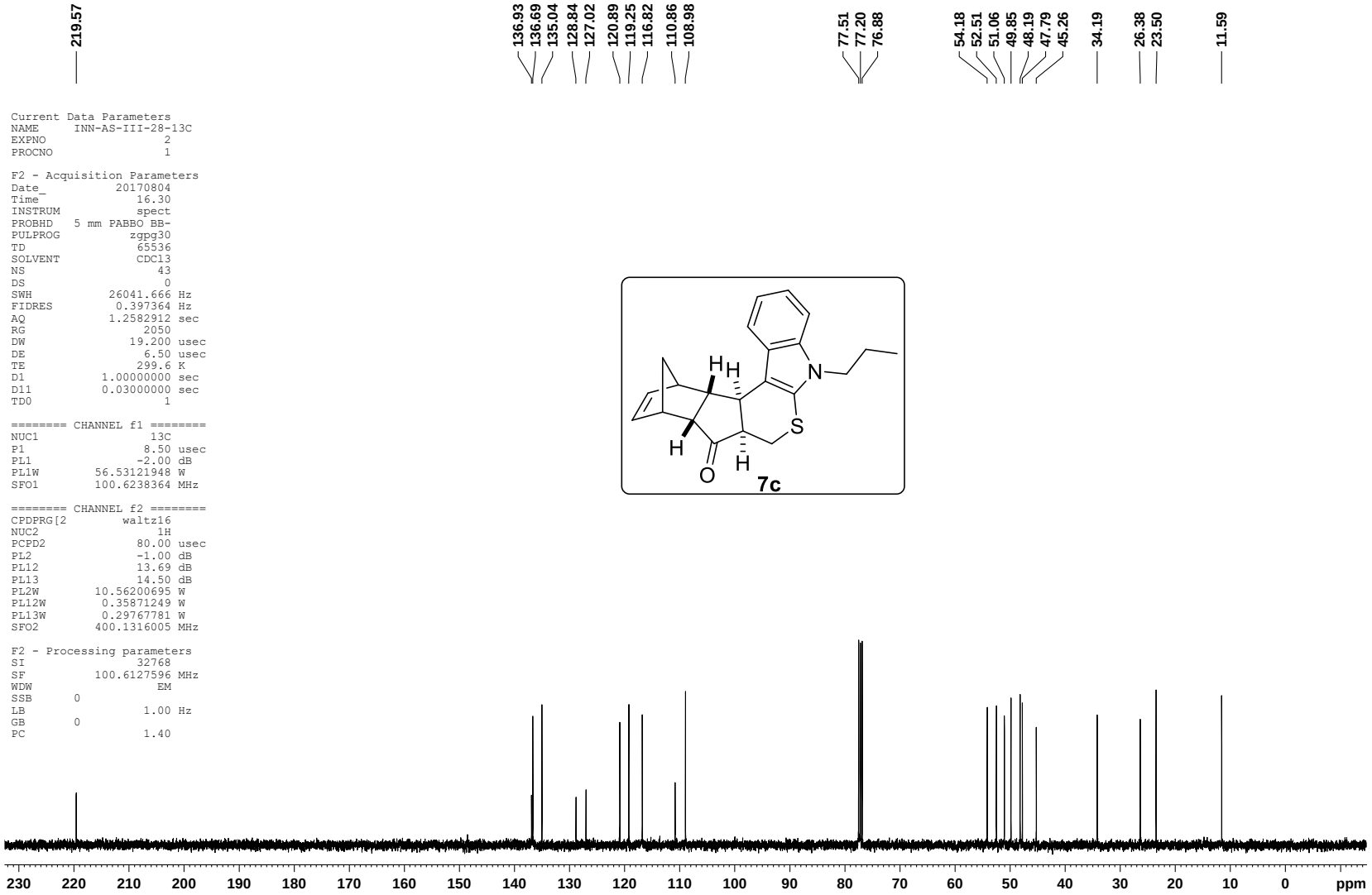


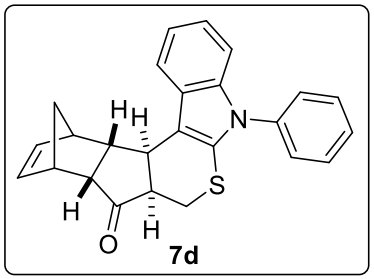
Figure S25. ^{13}C NMR Spectrum of 7c

```
Current Data Parameters
NAME        INN-AS-76-1H
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140724
Time               23.01
INSTRUM            spect
PROBHD   5 mm SEI 1H/D-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    12
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9845889 sec
RG                  80.6
DW                60.800 usec
DE                 6.50 usec
TE                296.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 6.75 usec
PL1               -3.00 dB
PL1W        16.73965454 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300104 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



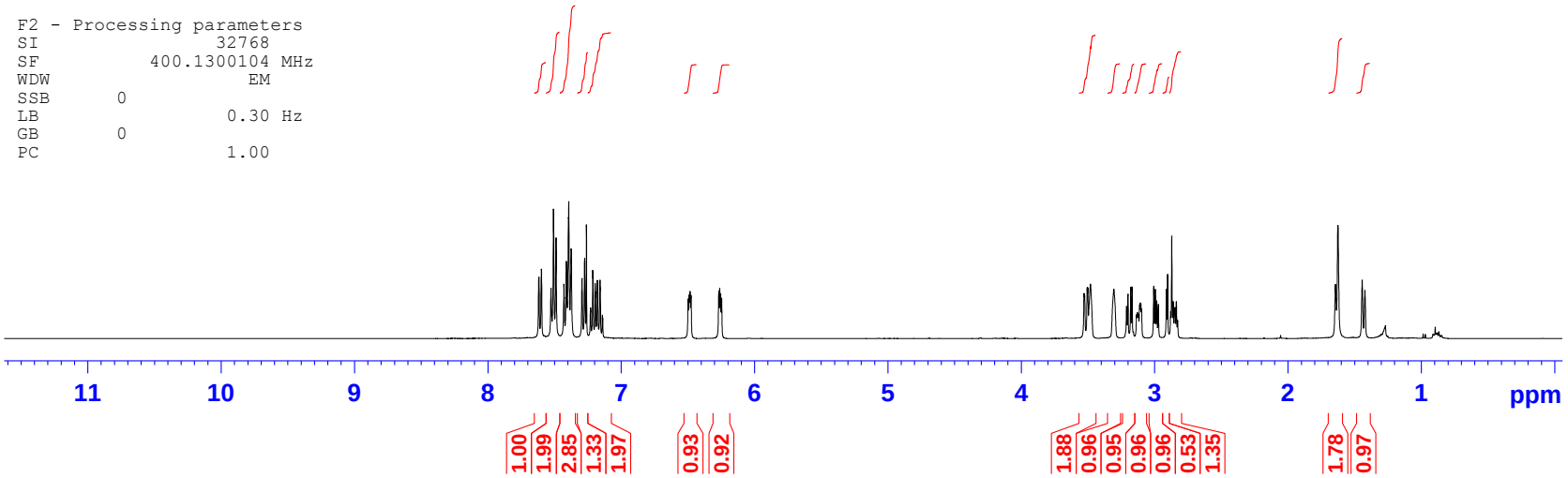


Figure S26. ^{1}H NMR Spectrum of 7d

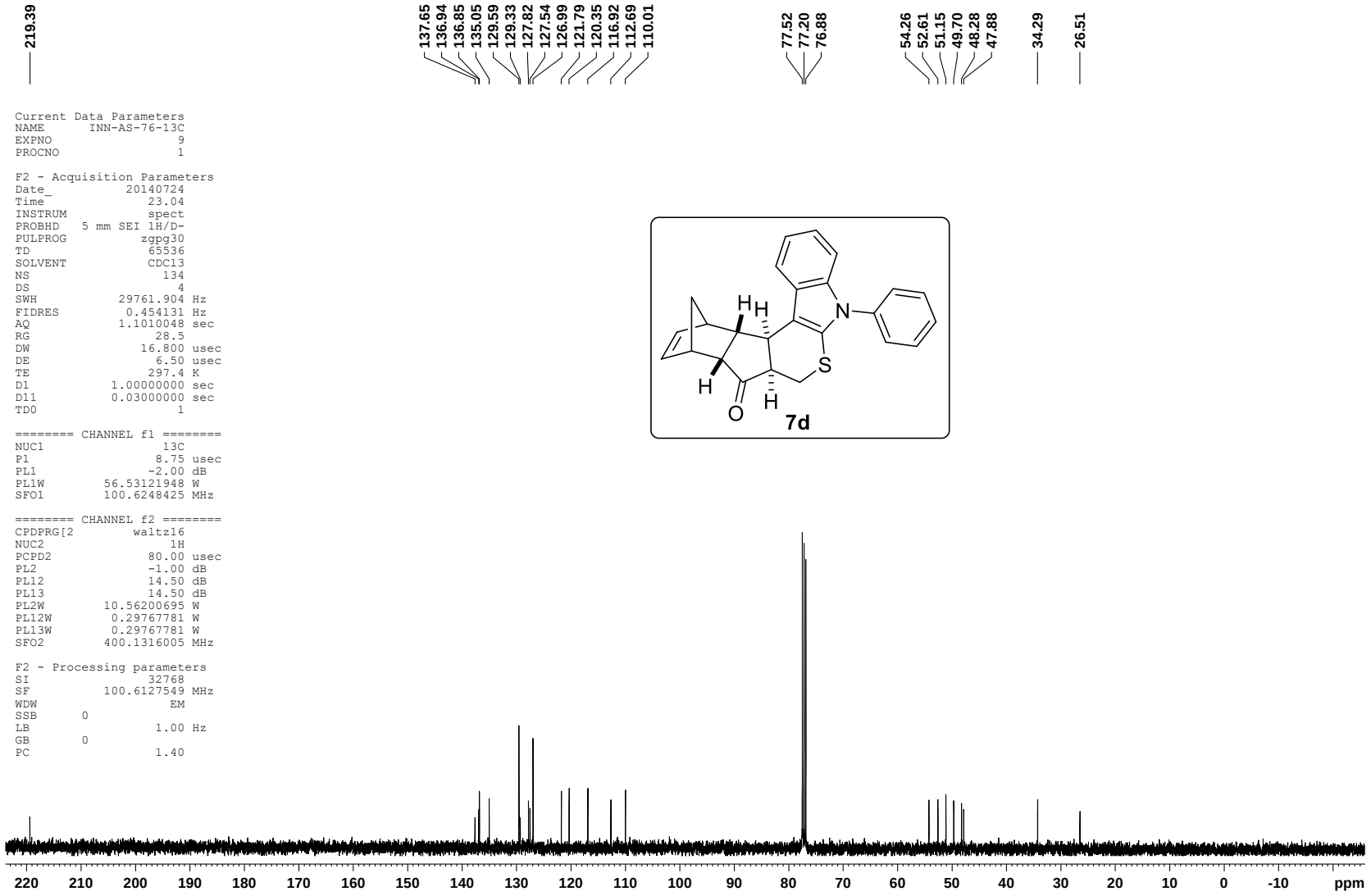


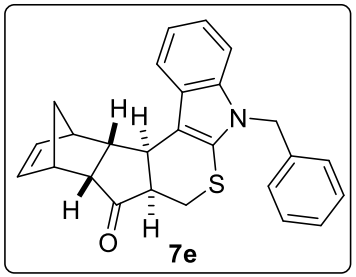
Figure S27. ^{13}C NMR Spectrum of 7d

```
Current Data Parameters
NAME      INN-AS-III-107-1H
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180123
Time                11.50
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                    10
DS                     0
SWH             8223.685 Hz
FIDRES          0.151522 Hz
AQ             3.2998593 sec
RG                    32
DW                60.800 usec
DE                 6.50 usec
TE                298.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.75 usec
PL1                -1.00 dB
PL1W         10.56200695 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300095 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



7e

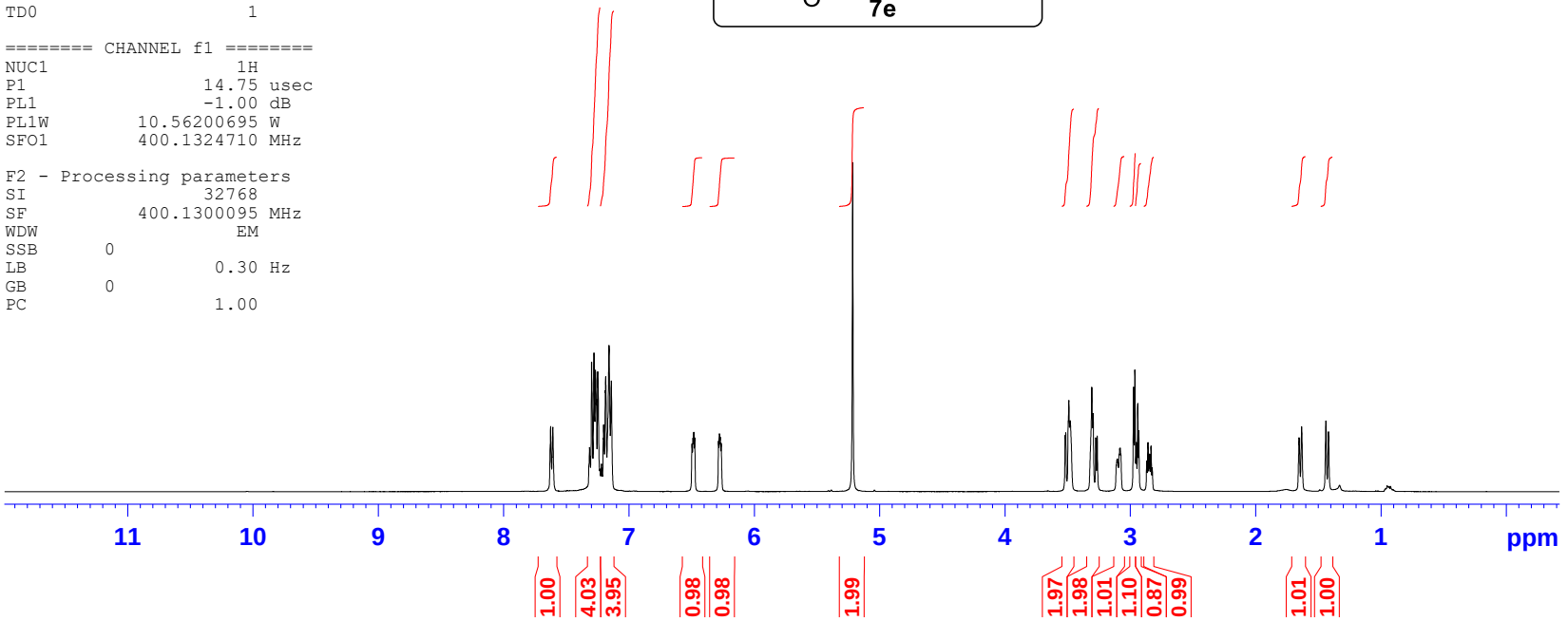


Figure S28. ^{1}H NMR Spectrum of 7e

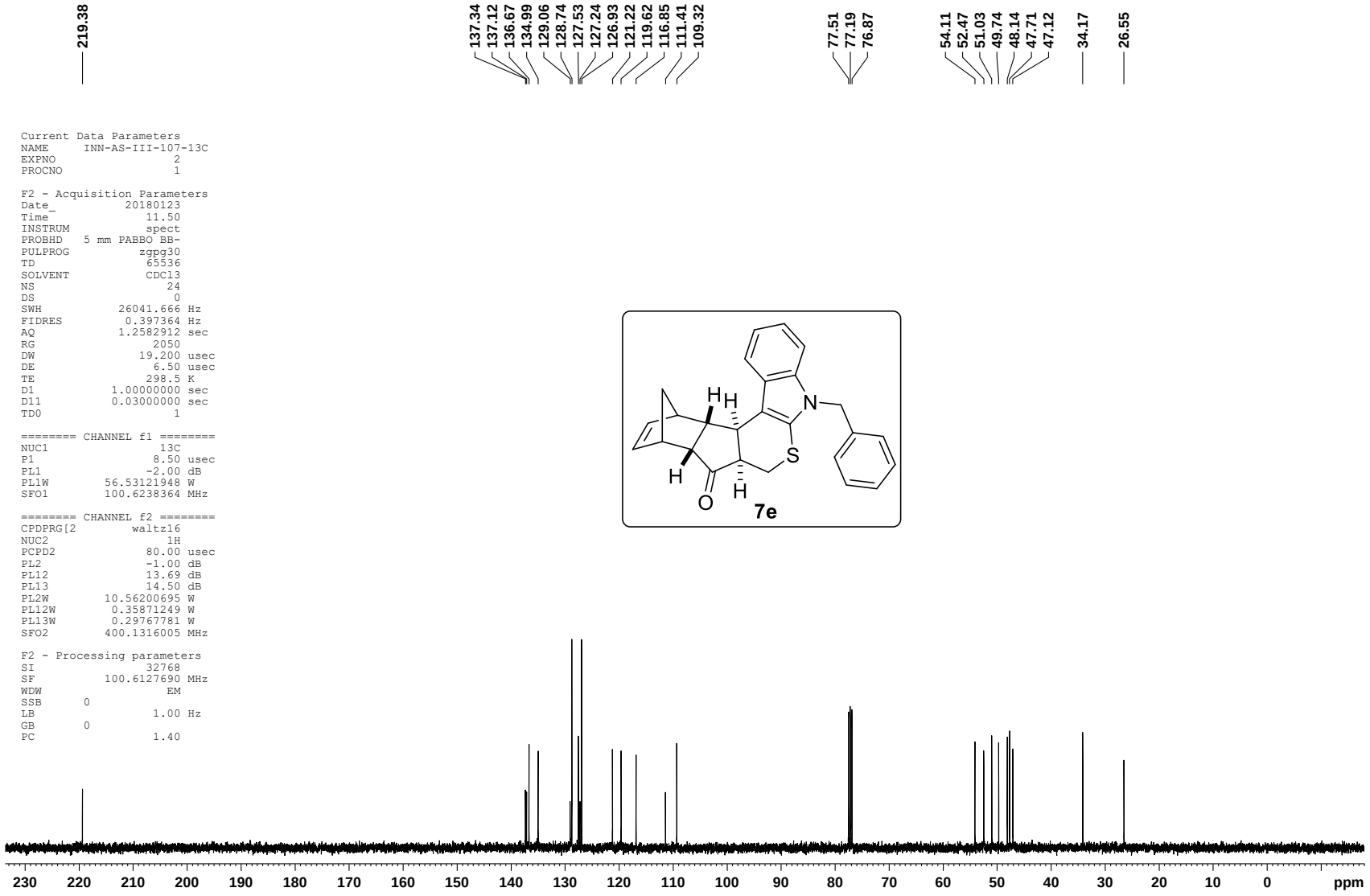


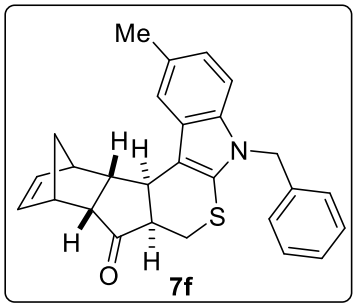
Figure S29. ^{13}C NMR Spectrum of 7e

```
Current Data Parameters
NAME      INN-AS-IV-48-1H
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20210125
Time              16.02
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                    5
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ             3.2998593 sec
RG                  161
DW                60.800 usec
DE                 6.50 usec
TE                297.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



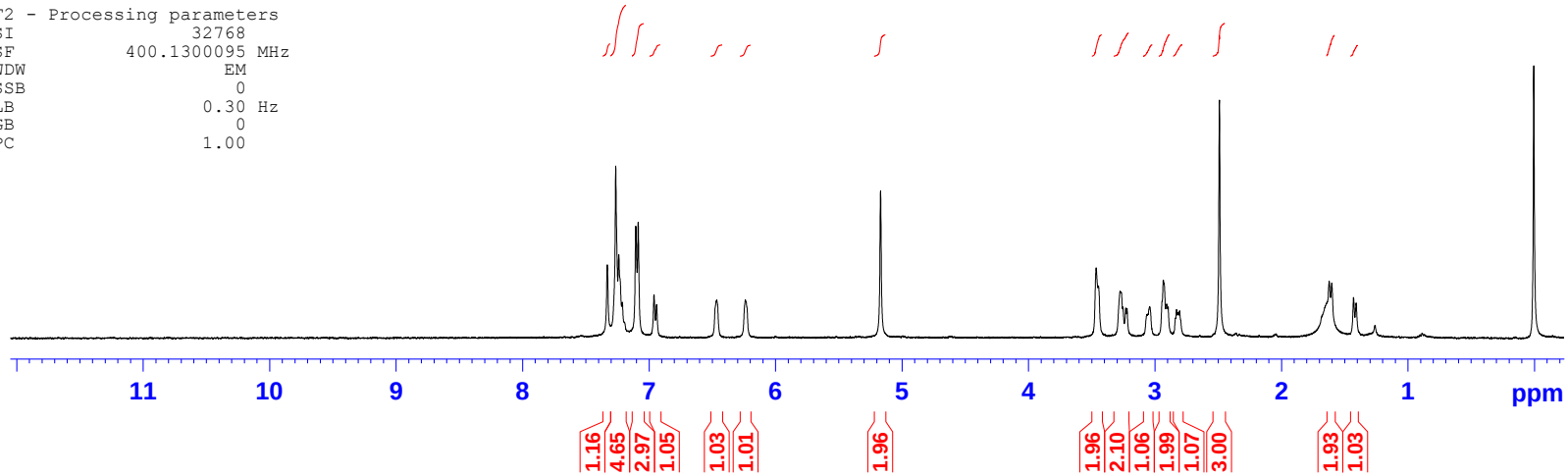


Figure S30. ^{1}H NMR Spectrum of 7f

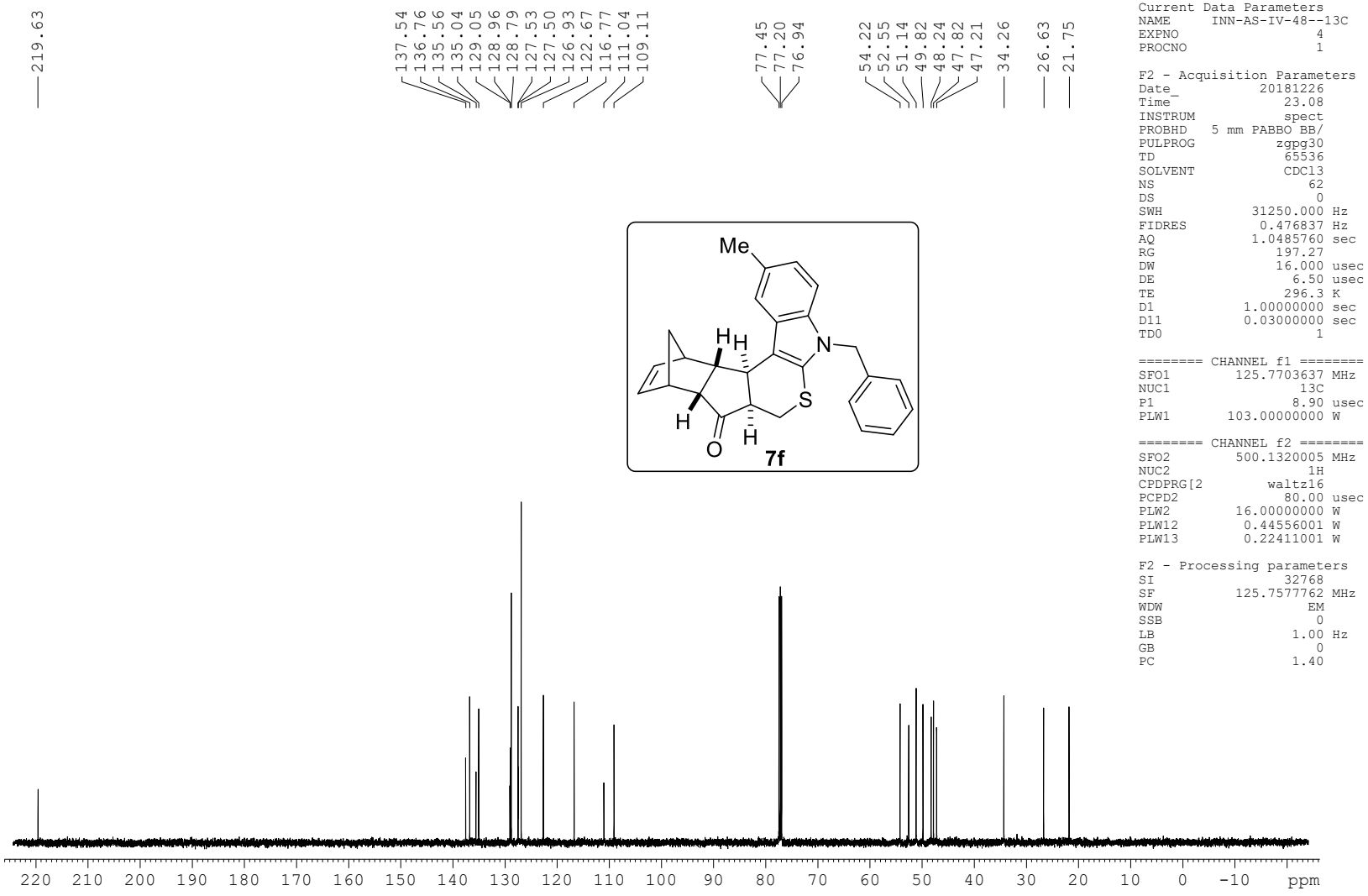


Figure S31. ^{13}C NMR Spectrum of 7f

```
Current Data Parameters
NAME      INN-AS--IV-49-1H
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20181229
Time                2.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                    25
DS                     0
SWH             8223.685 Hz
FIDRES          0.151522 Hz
AQ             3.2998593 sec
RG                   256
DW                60.800 usec
DE                 6.50 usec
TE                295.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300101 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

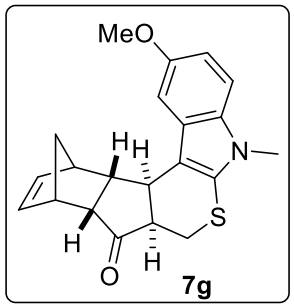


Figure S32. ^{1}H NMR Spectrum of 7g

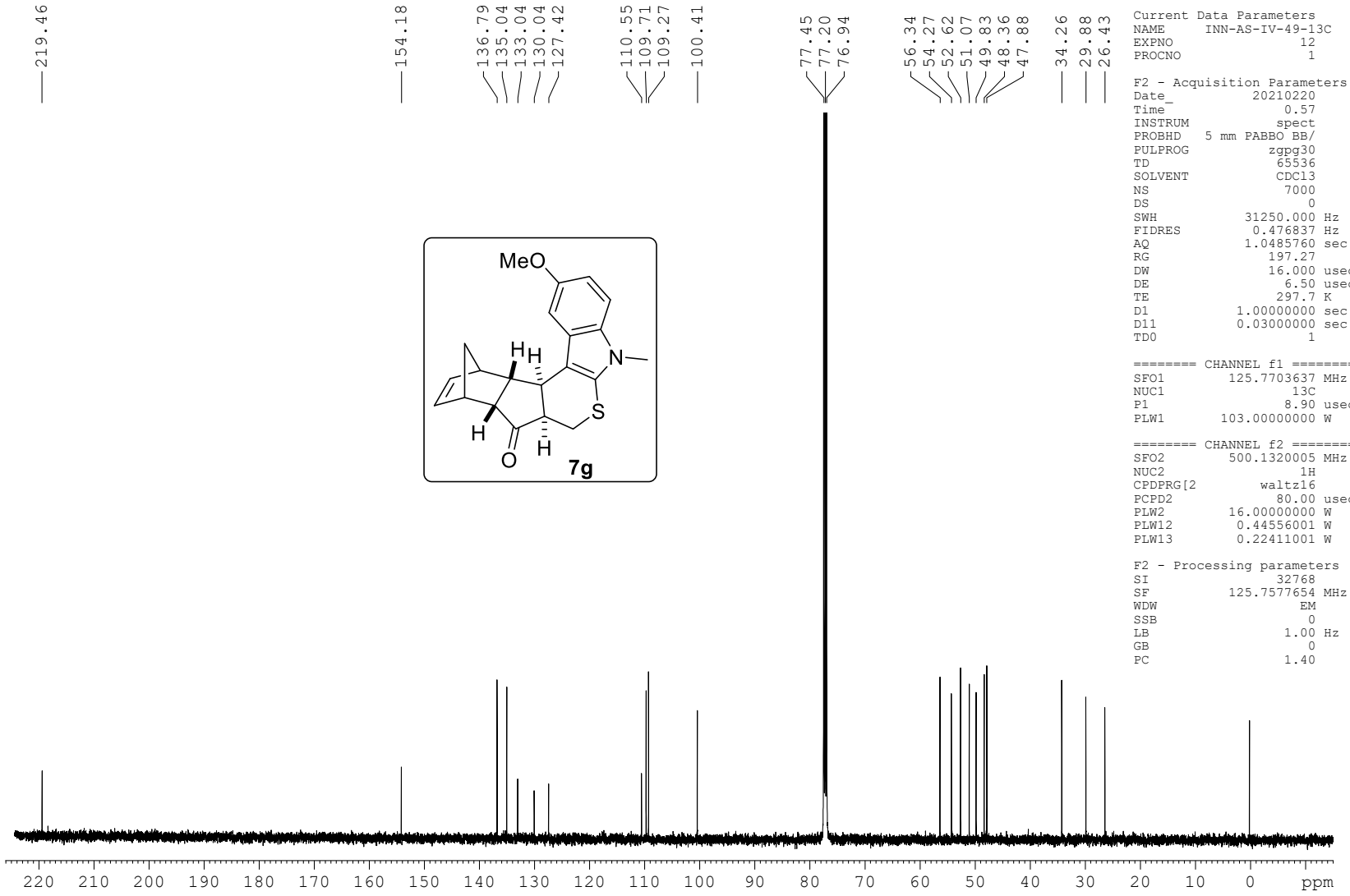


Figure S33. ^{13}C NMR Spectrum of 7g

```
Current Data Parameters
NAME      INN-AS-IV-65-1H
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190313
Time               13.13
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ             3.2767999 sec
RG                 98.91
DW                50.000 usec
DE                 6.50 usec
TE                 296.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                 13.35 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300146 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

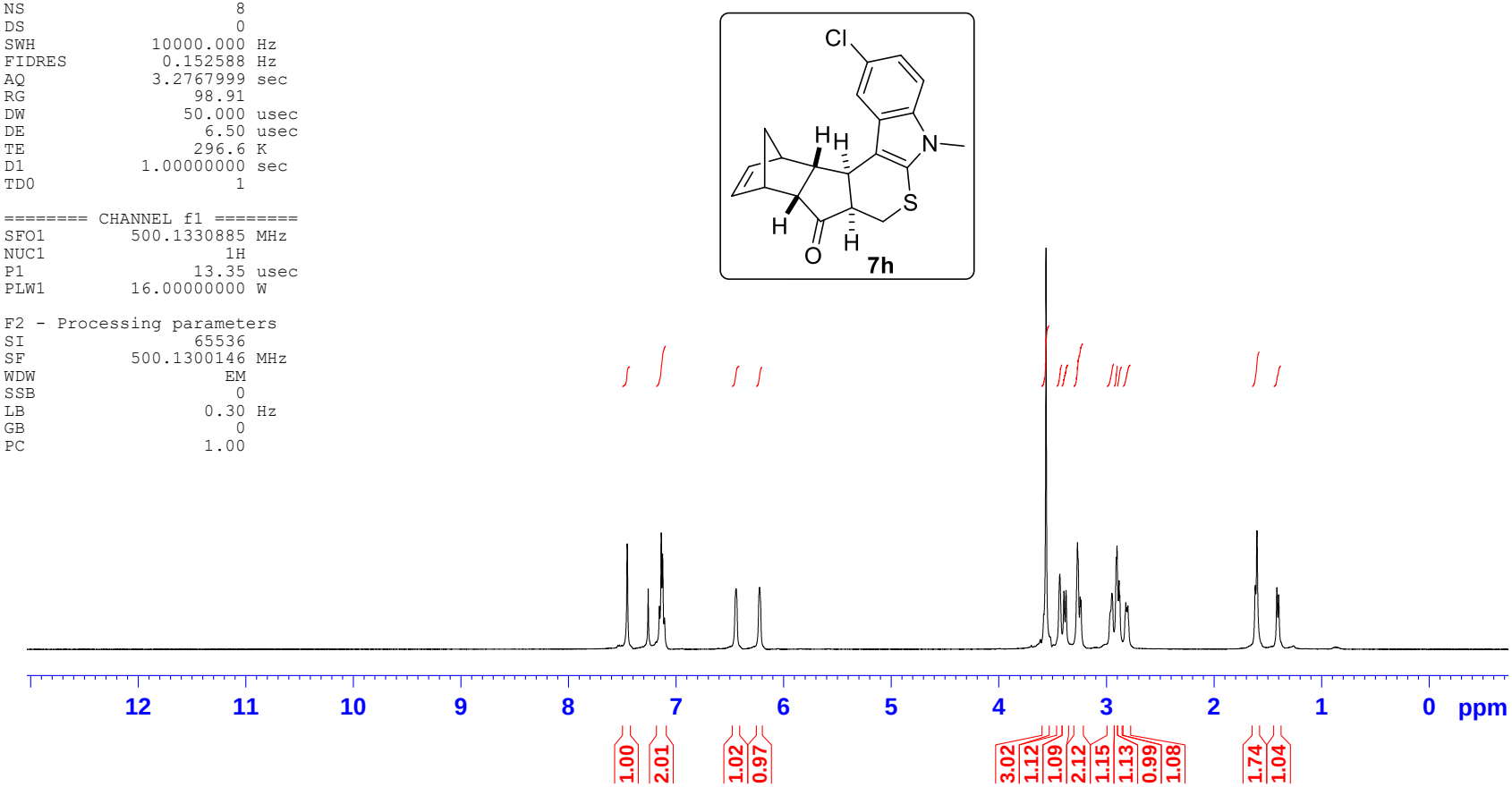


Figure S34. ^{1}H NMR Spectrum of 7h

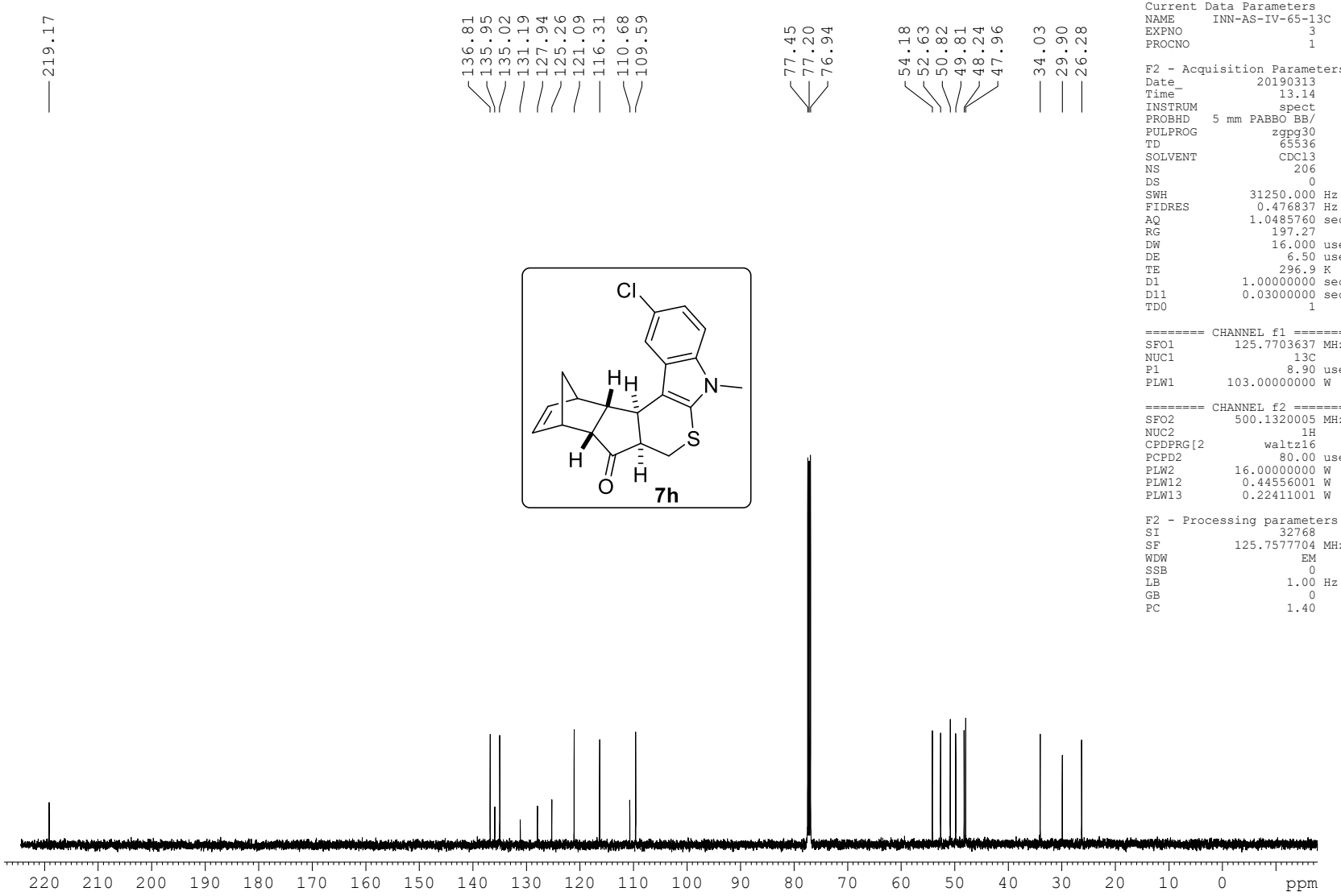


Figure S35. ^{13}C NMR Spectrum of 7h

```
Current Data Parameters
NAME      INN-AS-IV-64-1H
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190724
Time              18.05
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    3
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                98.91
DW               50.000 usec
DE                6.50 usec
TE                297.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                1H
P1                13.35 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                65536
SF           500.1300144 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

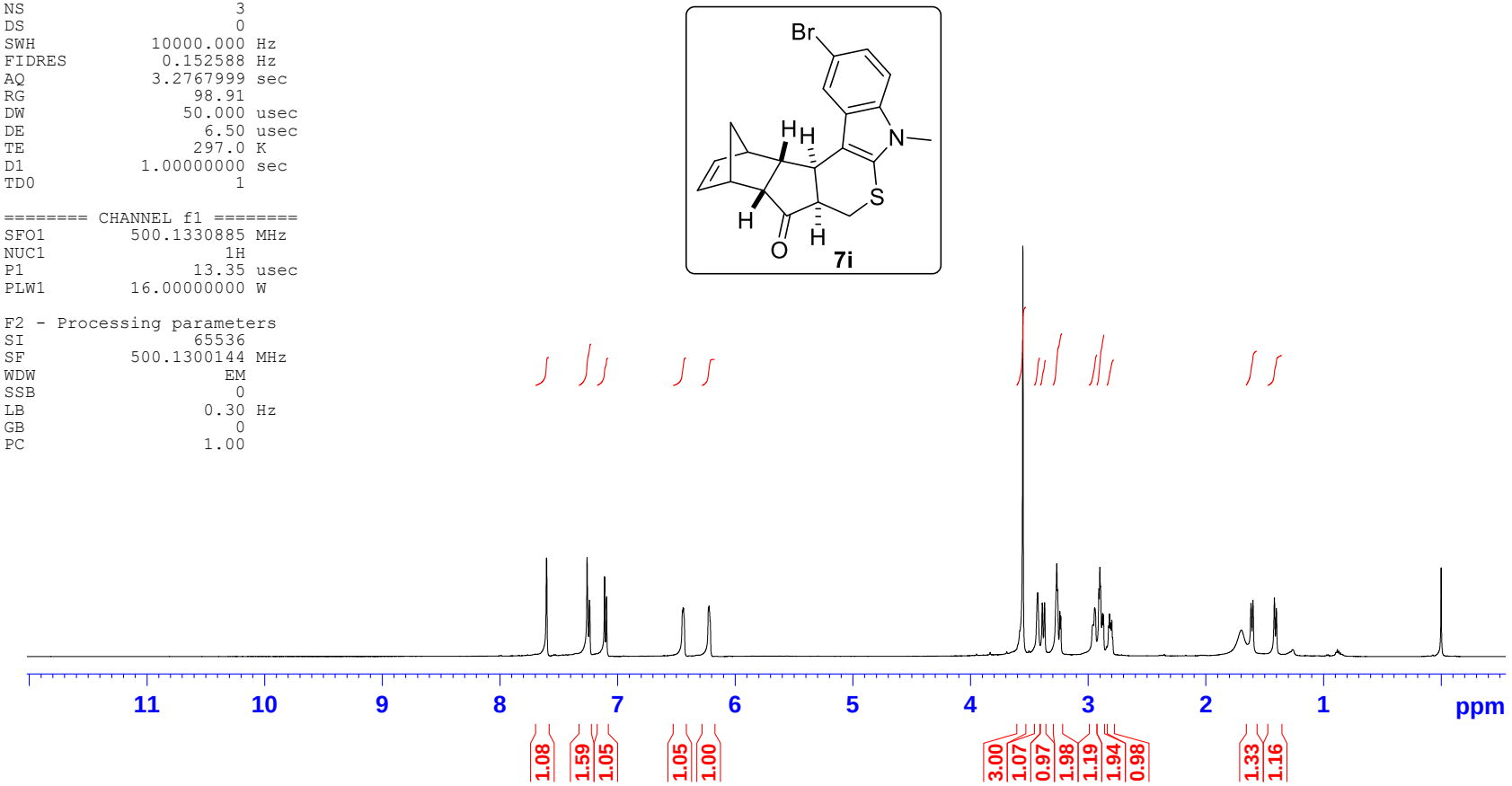
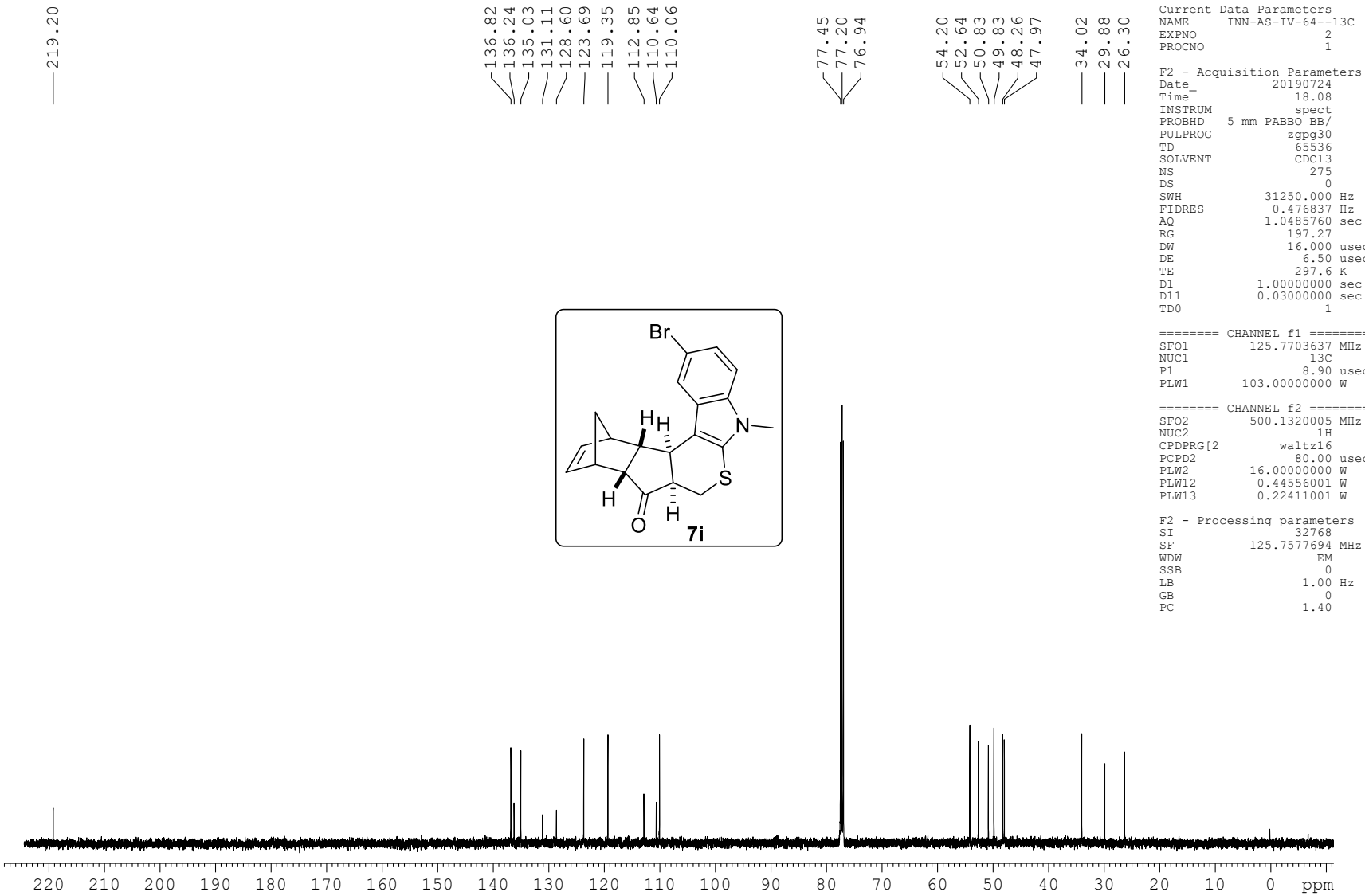


Figure S36. ^{1}H NMR Spectrum of 7i




```
Current Data Parameters
NAME      INN-AS-IV-64--13C
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190724
Time               18.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  275
DS                    0
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0485760 sec
RG               197.27
DW               16.000 usec
DE                6.50 usec
TE                297.6 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                13C
P1                 8.90 usec
PLW1       103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W
PLW13        0.22411001 W

F2 - Processing parameters
SI                 32768
SF           125.7577694 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

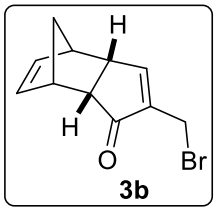
Figure S37. ^{13}C NMR Spectrum of 7i

```
Current Data Parameters
NAME      INN-AS-444-1H
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_           20170505
Time              20.00
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   13
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                80.35
DW               50.000 usec
DE                6.50 usec
TE                299.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                1H
P1                14.25 usec
PLW1        15.00000000 W

F2 - Processing parameters
SI                65536
SF          500.1300140 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



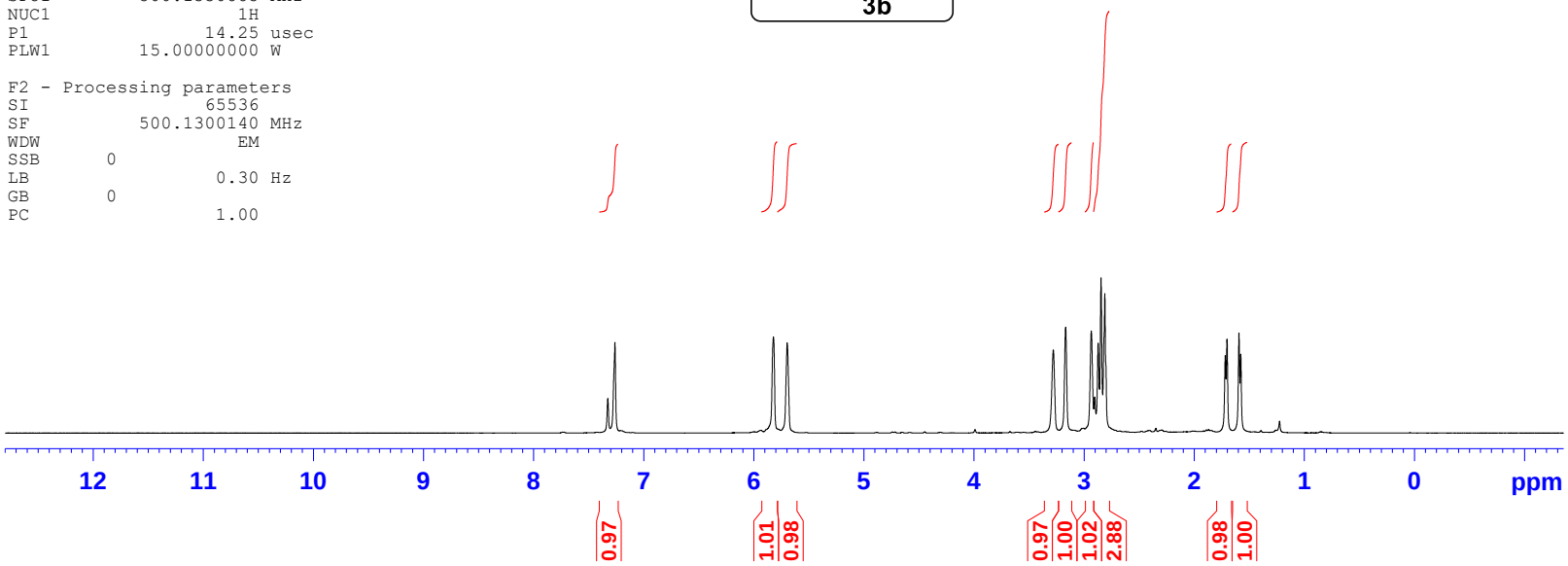


Figure S38. ^{1}H NMR Spectrum of 3b

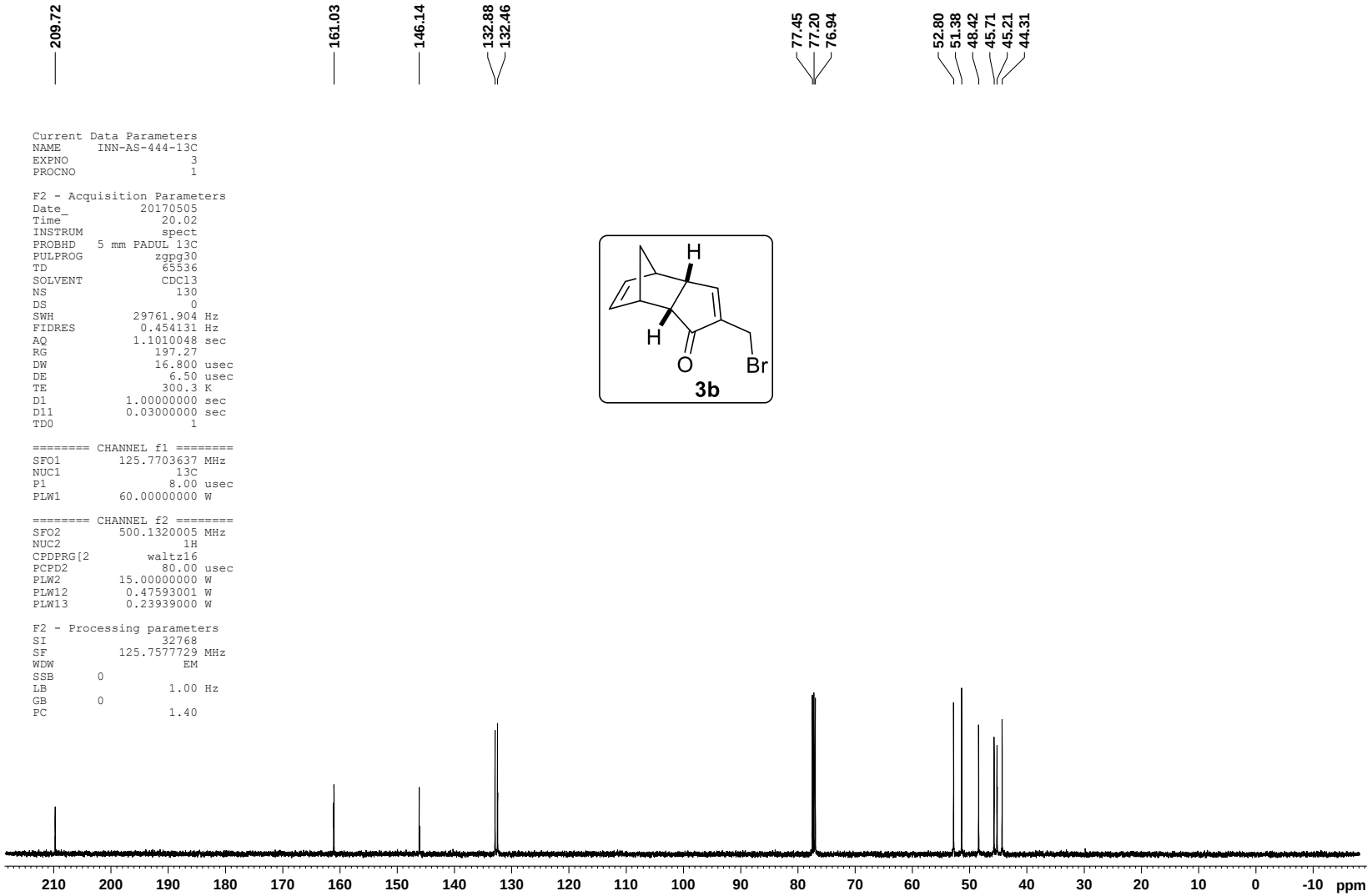


Figure S39. ^{13}C NMR Spectrum of 3b

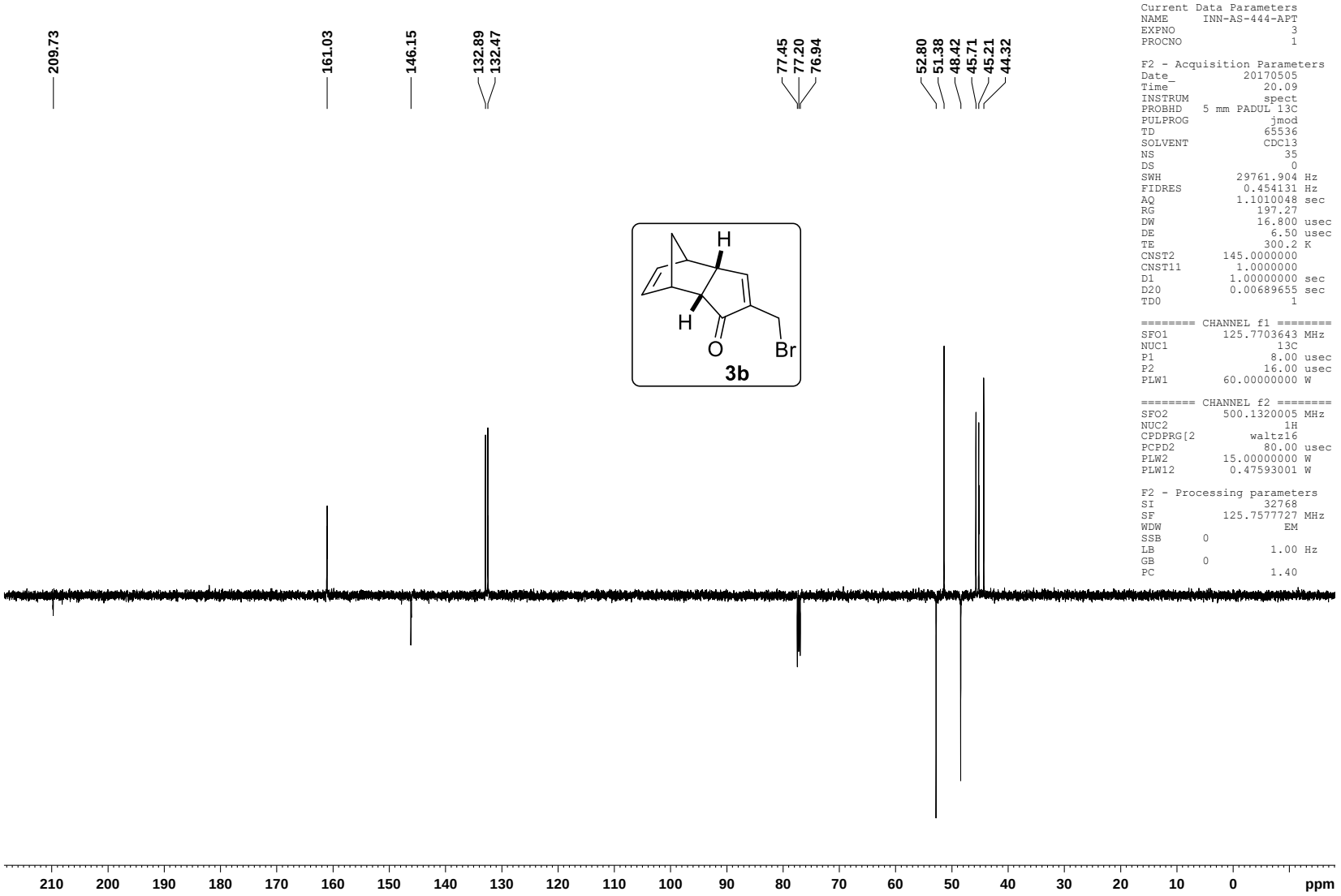


Figure S40. ^{13}C-APT NMR Spectrum of 3b

```
Current Data Parameters
NAME      INN-AS-186-1H
EXPNO                7
PROCNO               1

F2 - Acquisition Parameters
Date_           20150526
Time              14.18
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ             3.2998593 sec
RG                71.8
DW               60.800 usec
DE                 6.50 usec
TE                300.9 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300100 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

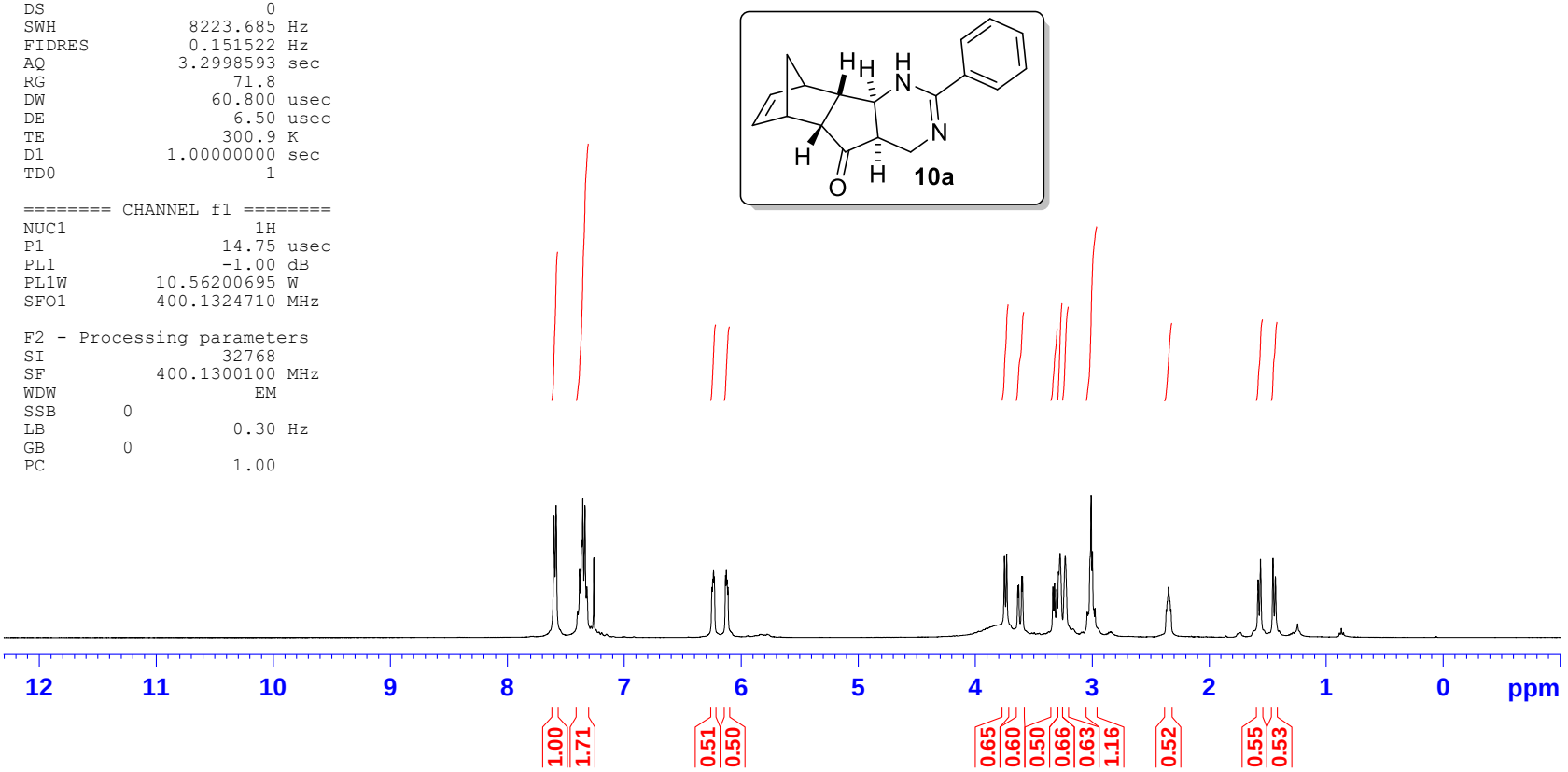


Figure S41. ^{1}H NMR Spectrum of 10a

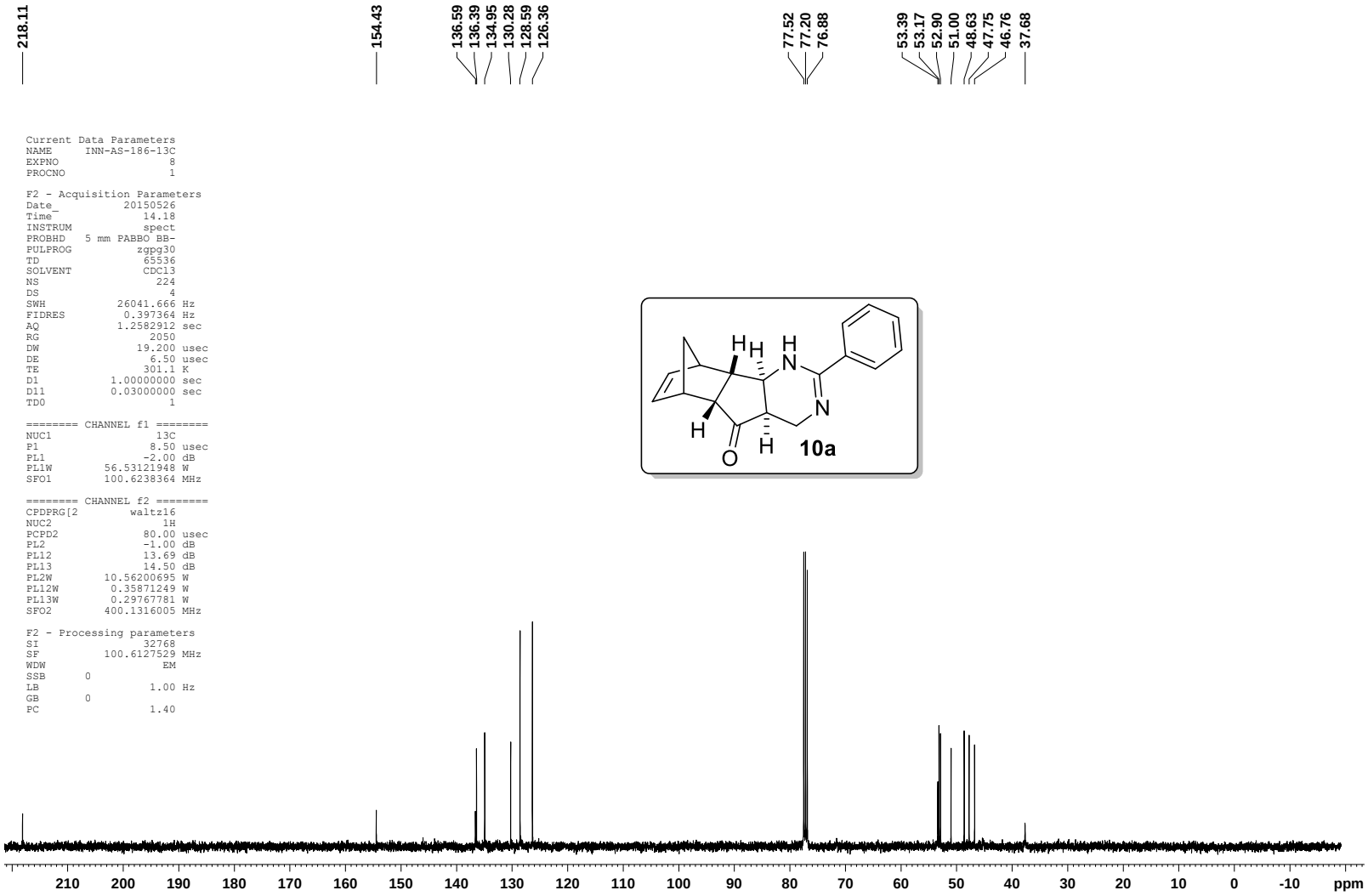


Figure S42. ^{13}C NMR Spectrum of 10a

```
Current Data Parameters
NAME      INN-AS-III-76-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20171122
Time              14.31
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   21
DS                    0
SWH            8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                 71.8
DW               60.800 usec
DE                6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300096 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

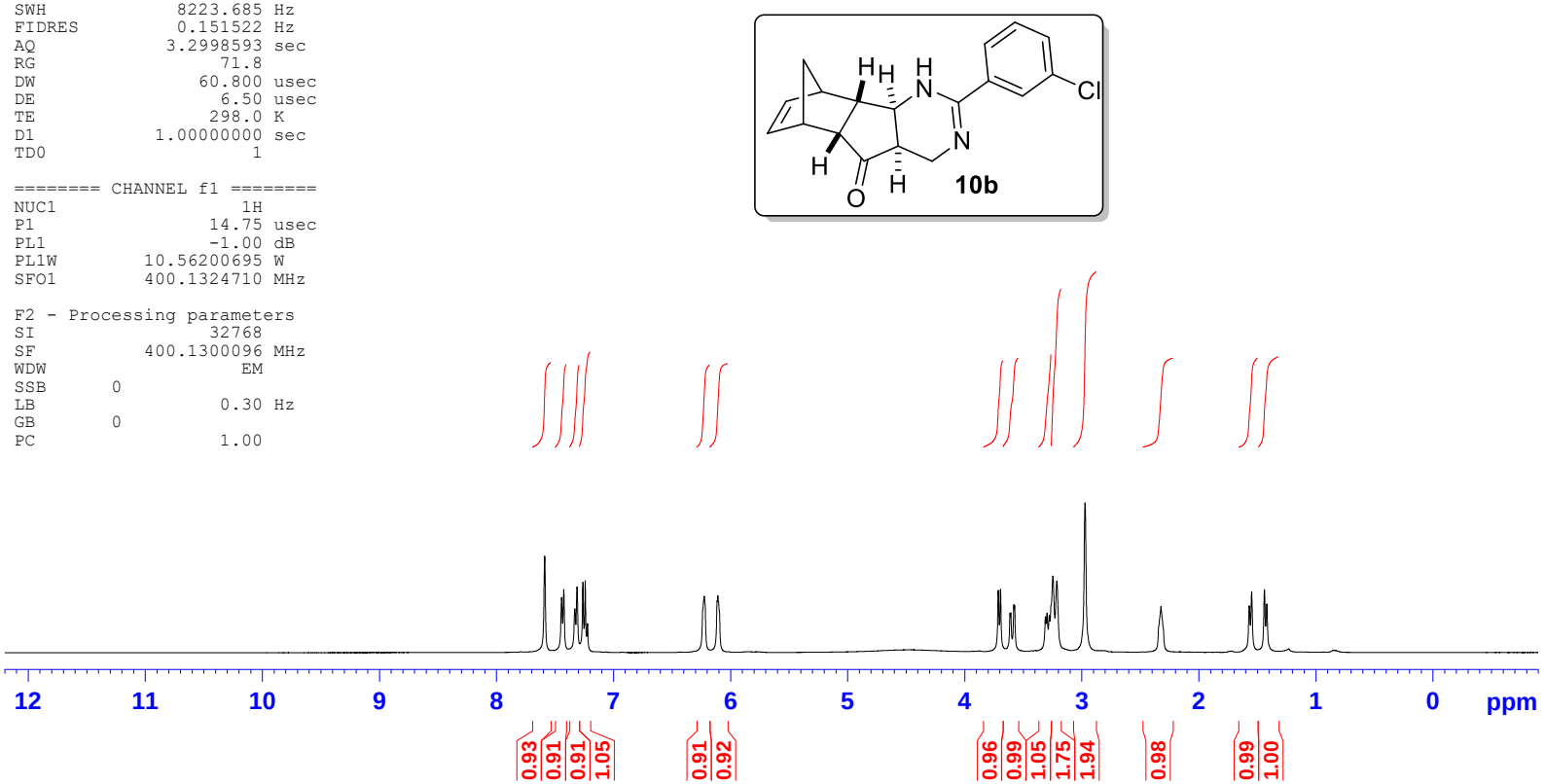


Figure S43. ^{1}H NMR Spectrum of 10b

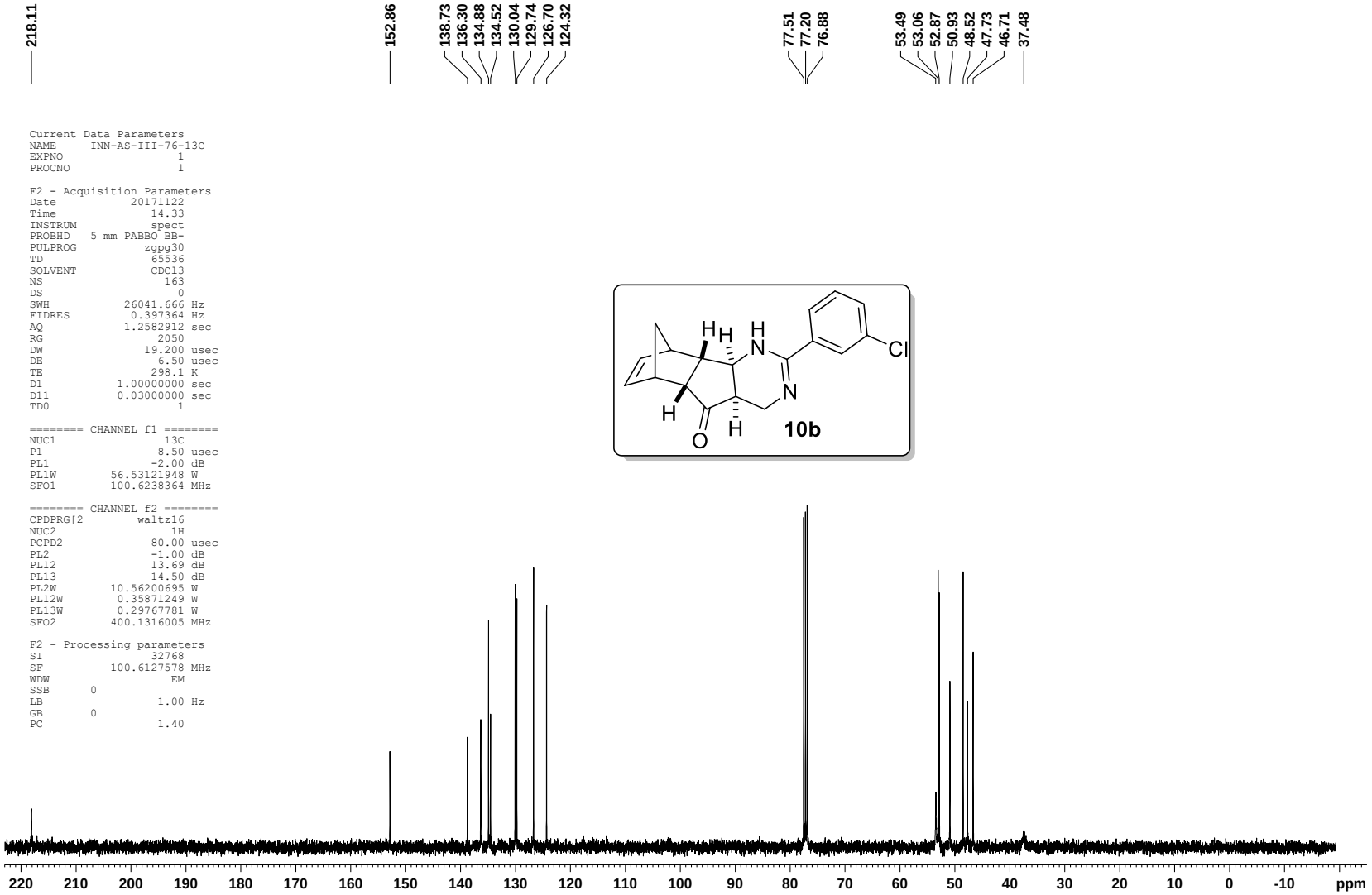


Figure S44. ^{13}C NMR Spectrum of 10b

```
Current Data Parameters
NAME      INN-AS-III-72-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171112
Time                13.11
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 61.42
DW                50.000 usec
DE                 6.50 usec
TE                294.8 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                 13.35 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300151 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

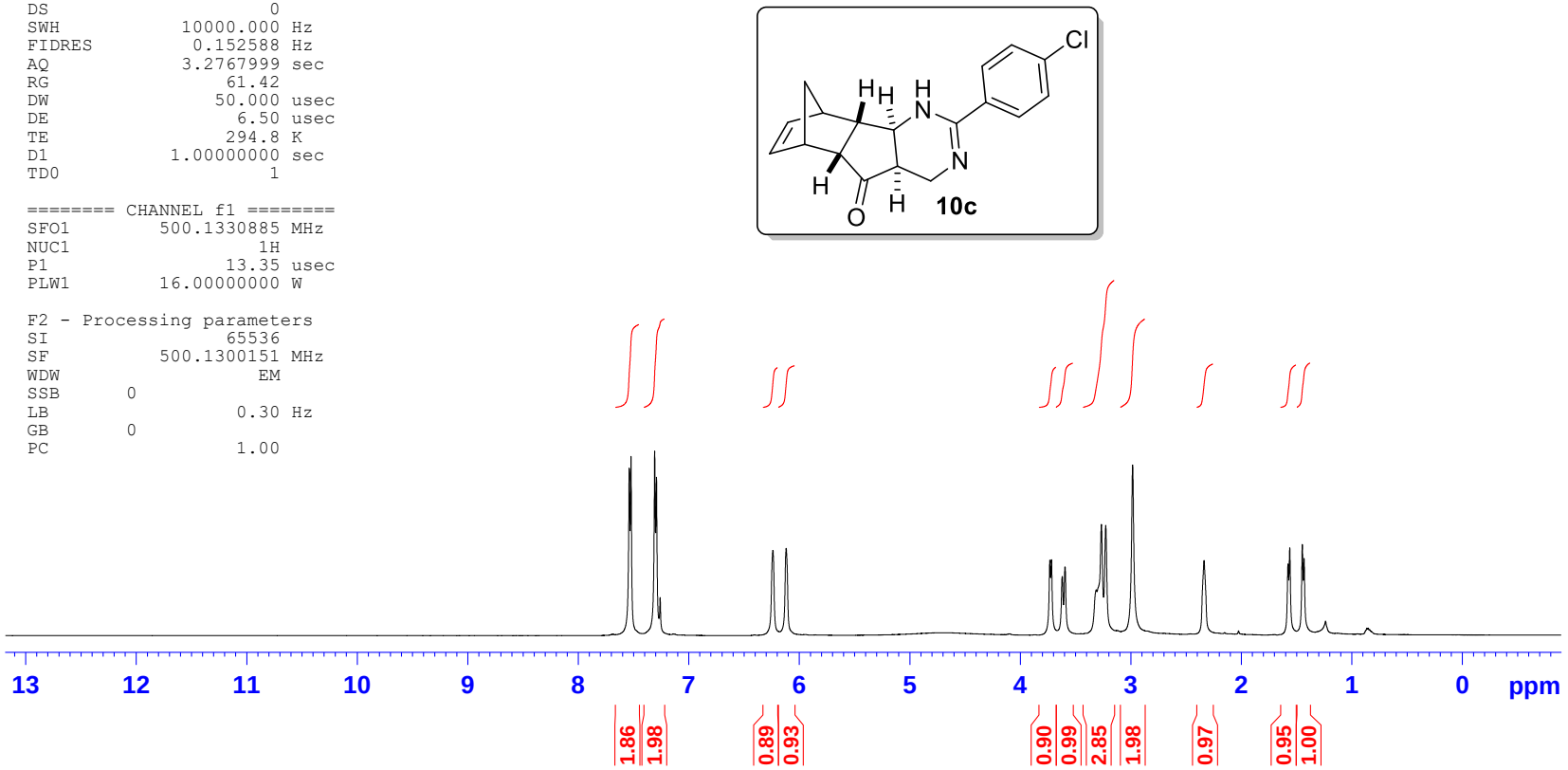


Figure S45. ^{1}H NMR Spectrum of 10c

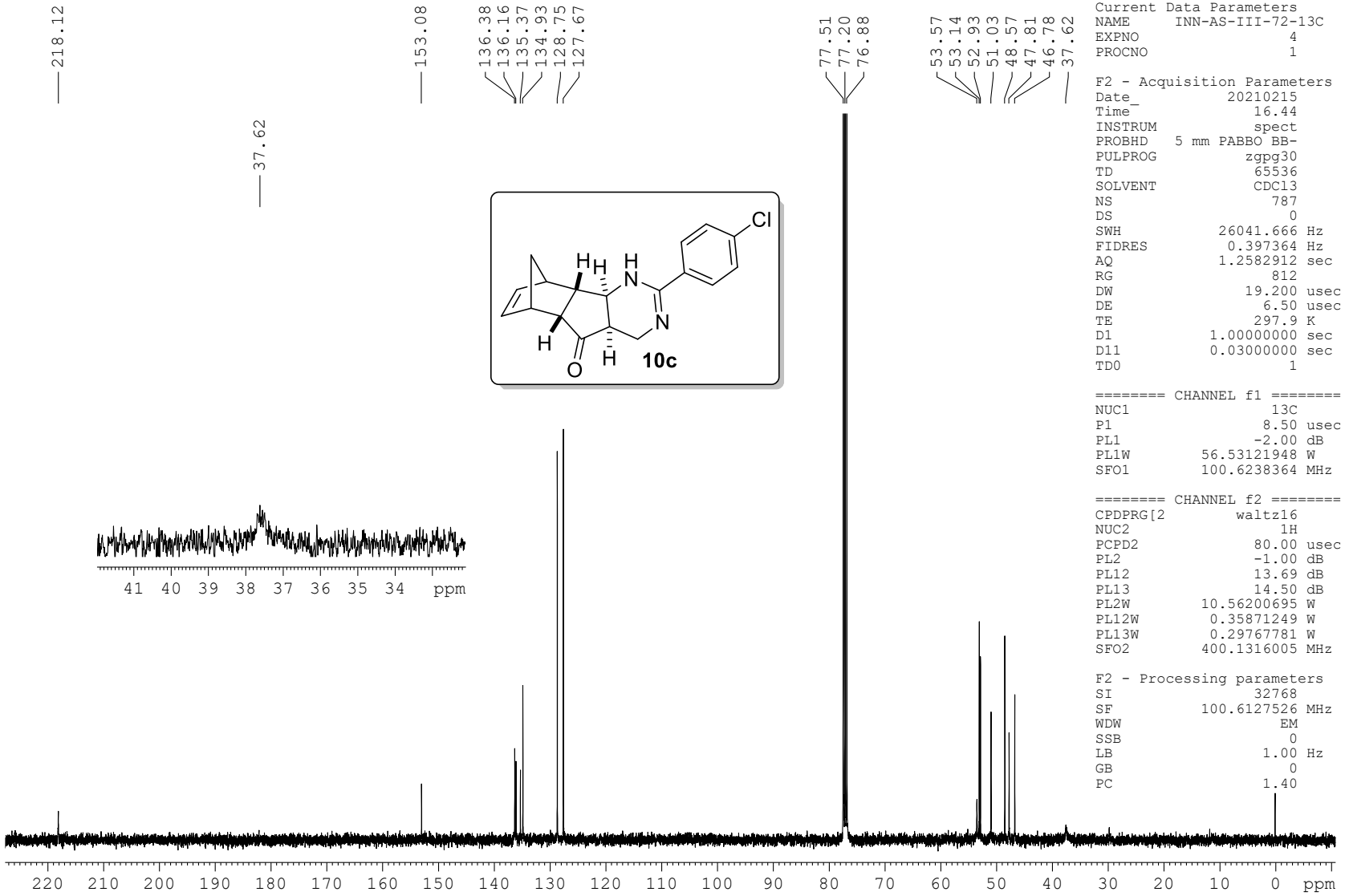


Figure S46. ^{13}C NMR Spectrum of 10c

```
Current Data Parameters
NAME      INN-SOHAN-II-355-R-1H
EXPNO                   46
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210727
Time                1.49 h
INSTRUM            spect
PROBHD    Z104450_0346 (
PULPROG             zg30
TD                 54274
SOLVENT            CDCl3
NS                    42
DS                     0
SWH              8223.685 Hz
FIDRES           0.303043 Hz
AQ               3.2998593 sec
RG                   161
DW                60.800 usec
DE                 6.50 usec
TE                 295.5 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324710 MHz
NUC1                  1H
P0                  5.00 usec
P1                 15.00 usec
PLW1          9.69999981 W

F2 - Processing parameters
SI                 32768
SF           400.1300103 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

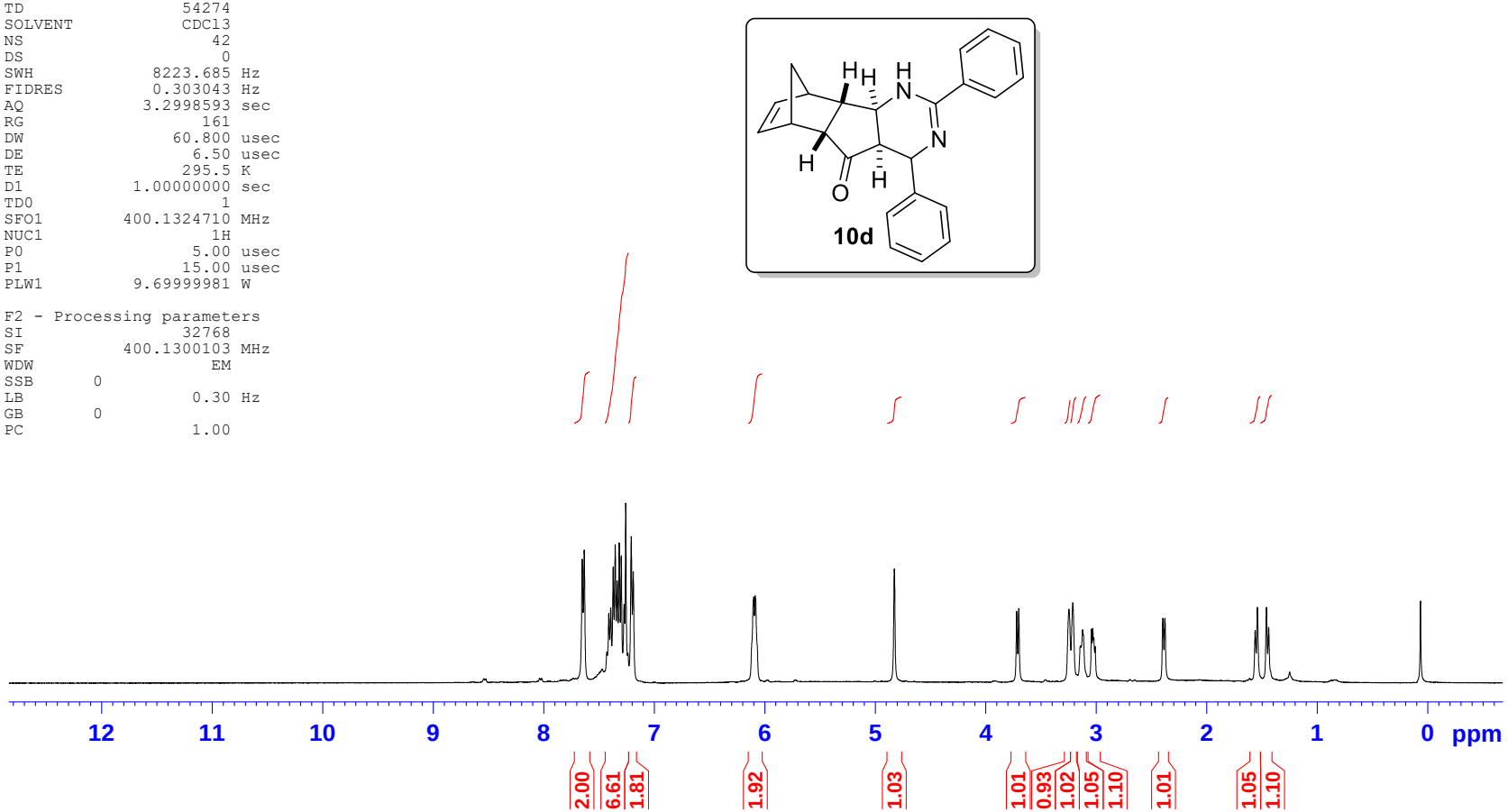


Figure S47. ^{1}H NMR Spectrum of 10d

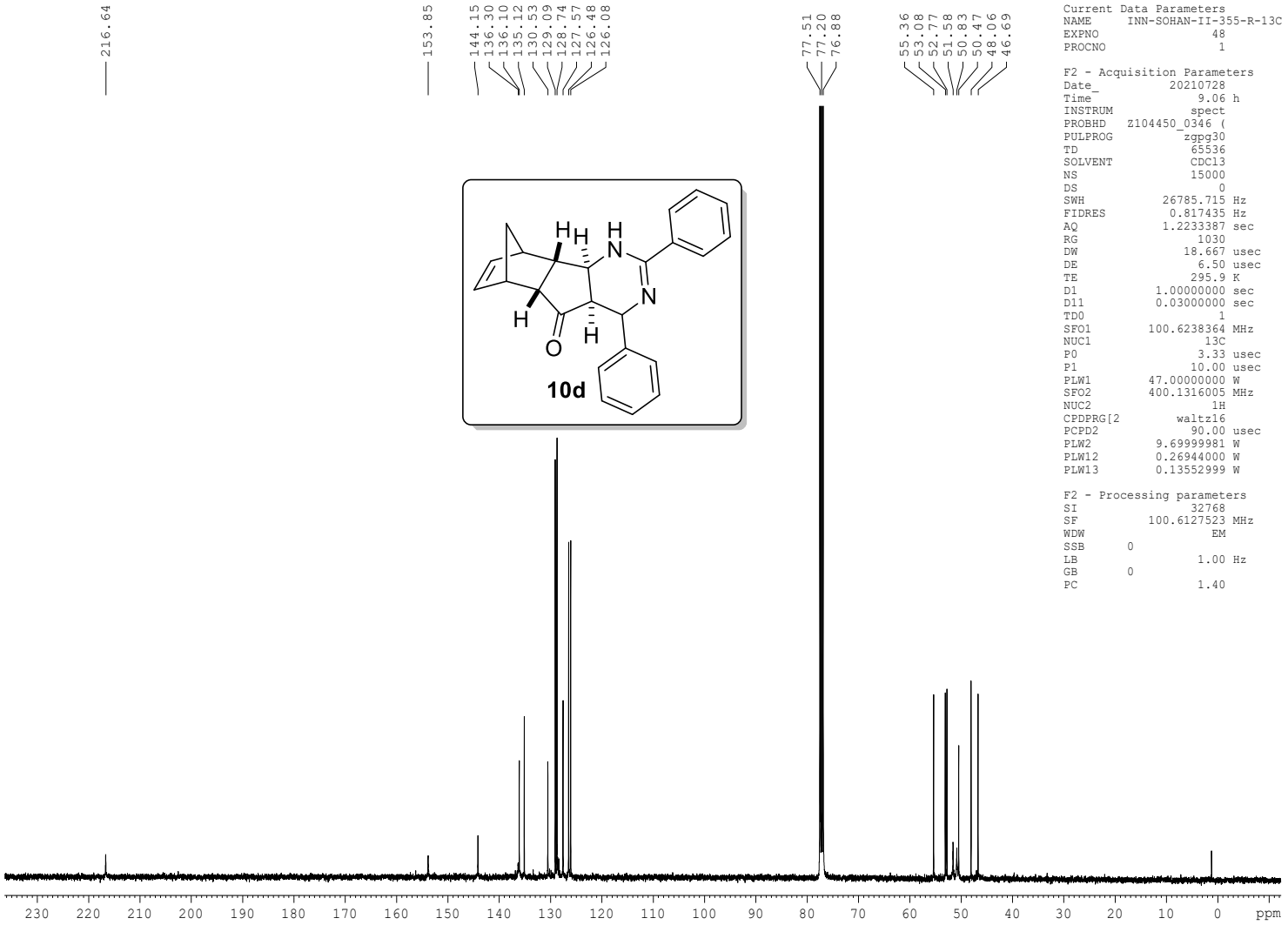


Figure S48. ^{13}C NMR Spectrum of 10d

```
Current Data Parameters
NAME      INN-SOHAN-II-361P-R-1H
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210712
Time              14.23 h
INSTRUM           spect
PROBHD   Z104450_0346 (
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.303043 Hz
AQ             3.2998593 sec
RG                  101
DW                60.800 usec
DE                 6.50 usec
TE               -1465.8 K
D1            1.00000000 sec
TD0                   1
SFO1         400.1324710 MHz
NUC1                 1H
P0                 5.00 usec
P1                15.00 usec
PLW1          9.69999981 W

F2 - Processing parameters
SI                32768
SF           400.1300133 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

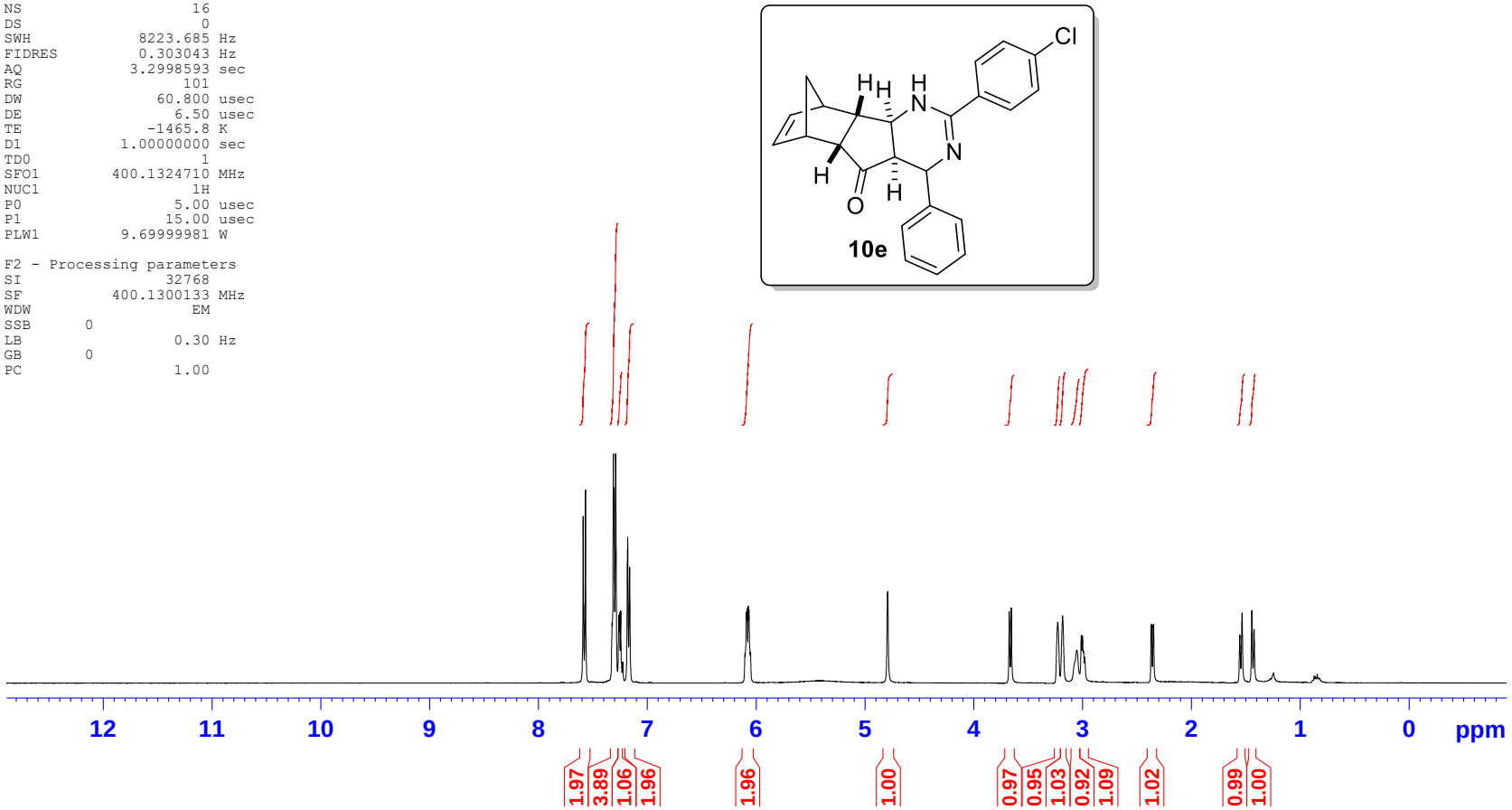


Figure S49. ^{1}H NMR Spectrum of 10e

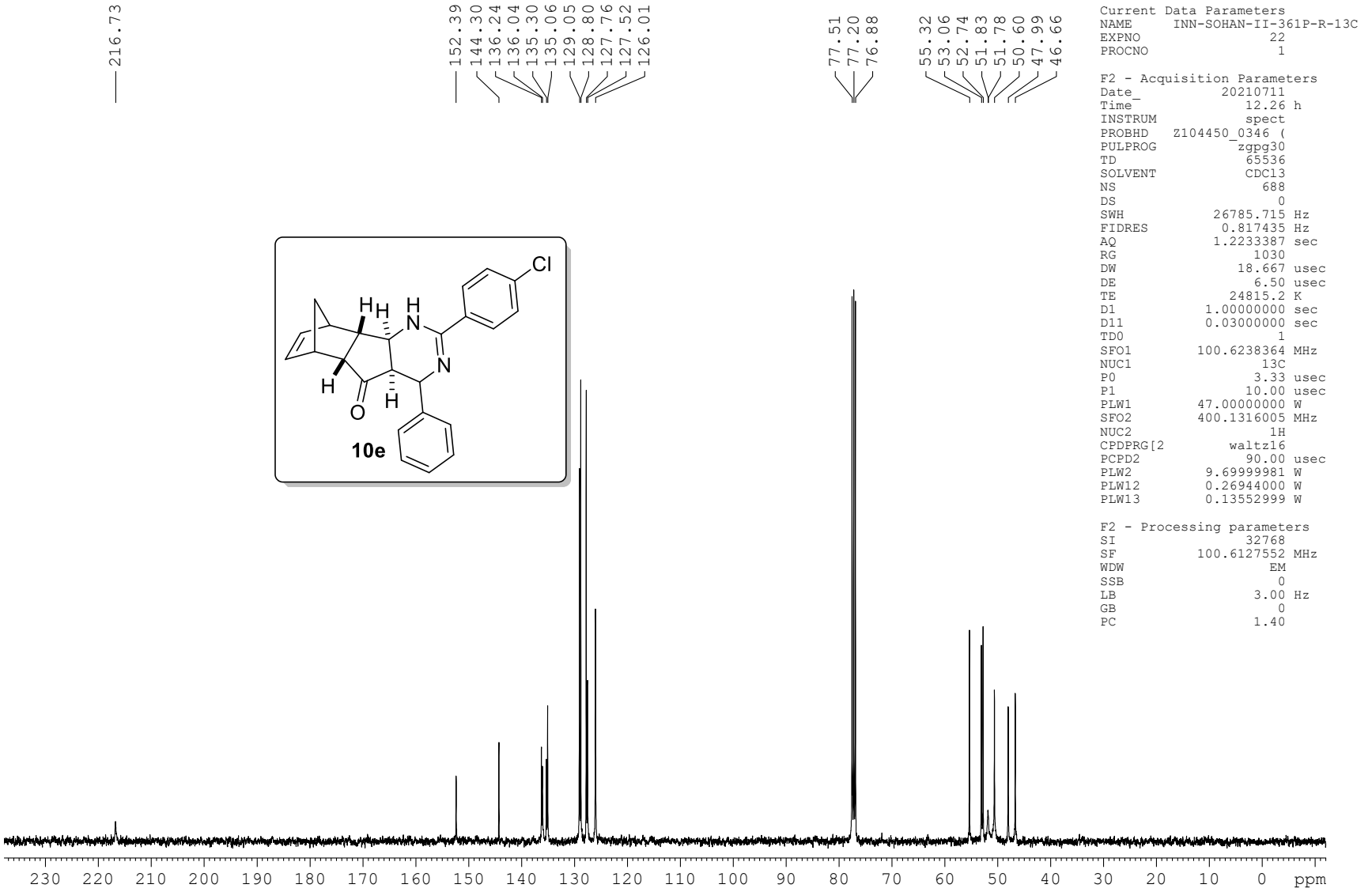
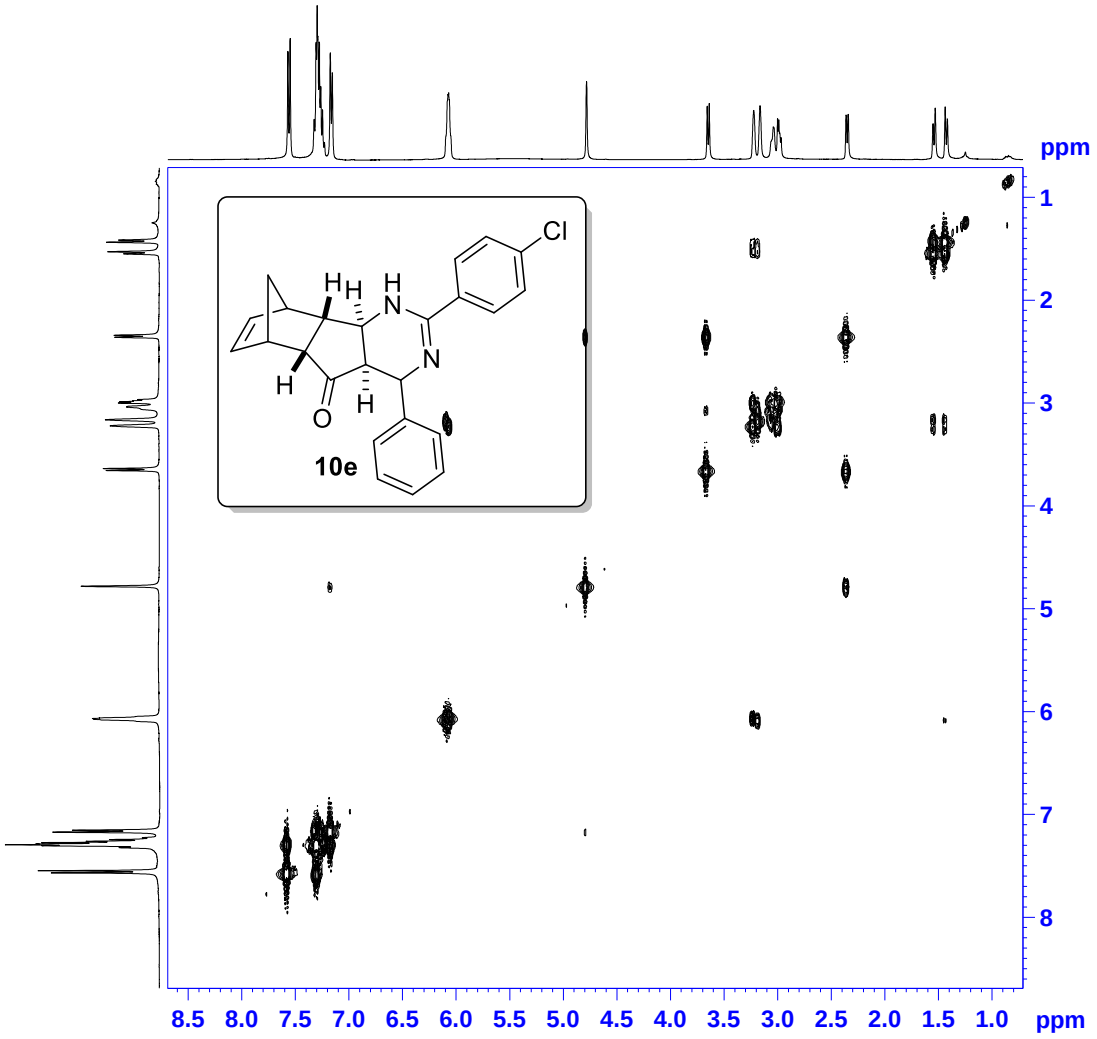


Figure S50. ^{13}C NMR Spectrum of 10e




```
Current Data Parameters
NAME      INN-SOHAN-II-361P-R-COSY
EXPNO                   41
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210712
Time                 15.28 h
INSTRUM              spect
PROBHD    Z104450_0346 (
PULPROG           cosygpqf
TD                   2048
SOLVENT              CDCl3
NS                     32
DS                      0
SWH               3192.848 Hz
FIDRES            3.118016 Hz
AQ               0.3207168 sec
RG                     322
DW                156.600 usec
DE                  6.50 usec
TE                -11662.8 K
D0              0.00000300 sec
D1              1.00000000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00031320 sec
TDav                    1
SFO1          400.1318913 MHz
NUC1                   1H
P0                  15.00 usec
P1                  15.00 usec
PLW1           9.69999981 W
GPNAM[1]          SINE.100
GPZ1                10.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                     85
SFO1              400.1319 MHz
FIDRES           75.125839 Hz
SW                  7.979 ppm
FnMODE                 QF

F2 - Processing parameters
SI                   1024
SF            400.1300102 MHz
WDW                  SINE
SSB                     0
LB                      0 Hz
GB                      0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2                    QF
SF            400.1300102 MHz
WDW                  SINE
SSB                     0
LB                      0 Hz
GB                      0
```

Figure S51. ^{1}H -^{1}H COSY NMR Spectrum of 10e

```
Current Data Parameters
NAME      INN-AS-2MBHAMDNNO2-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210928
Time              22.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT           DMSO
NS                   8
DS                   0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG               85.91
DW              50.000 usec
DE               6.50 usec
TE              297.2 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1               1H
P1              13.35 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI               65536
SF          500.1300094 MHz
WDW                EM
SSB      0
LB              0.30 Hz
GB       0
PC              1.00
```

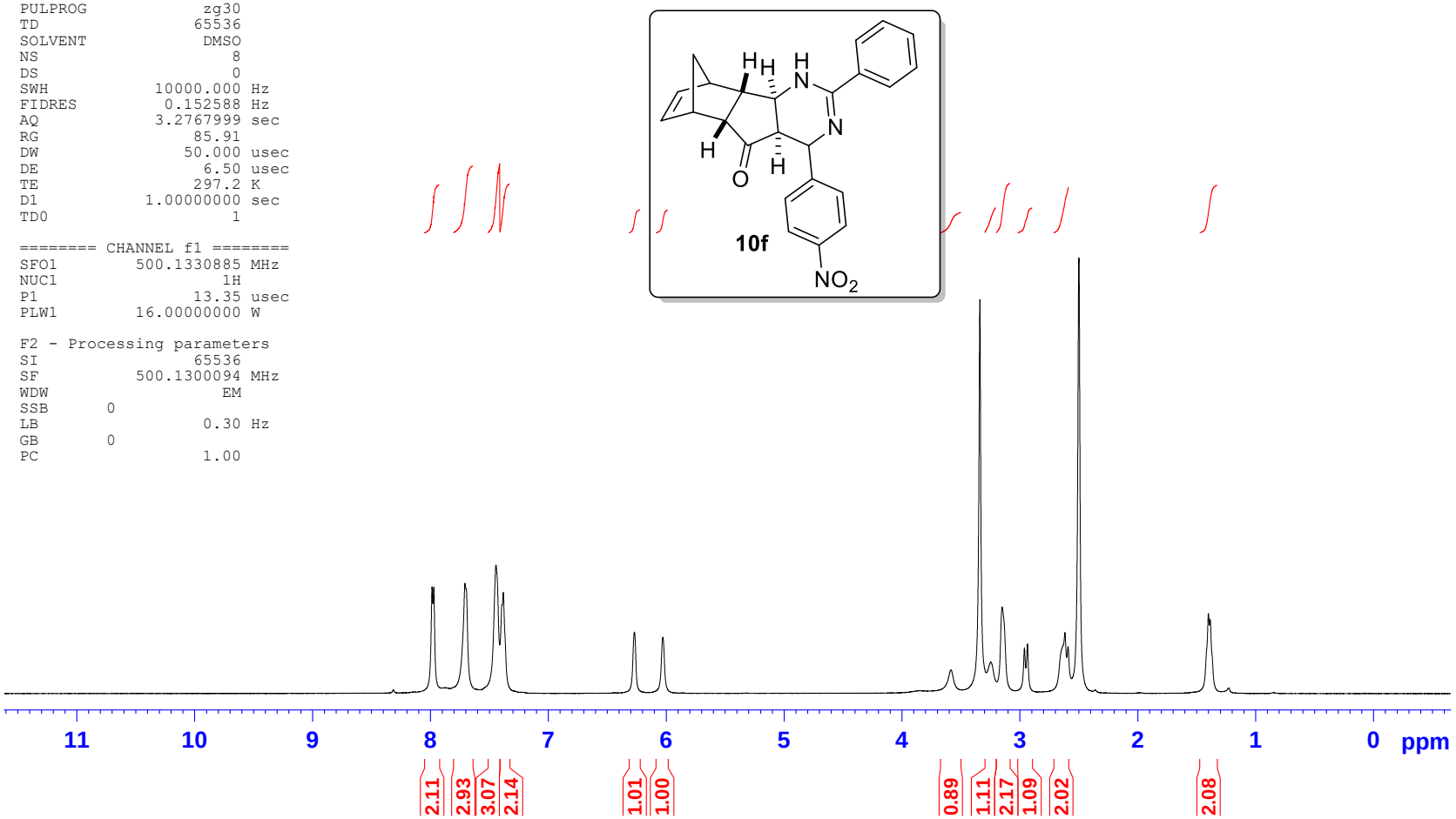


Figure S52. ^{1}H NMR Spectrum of 10f

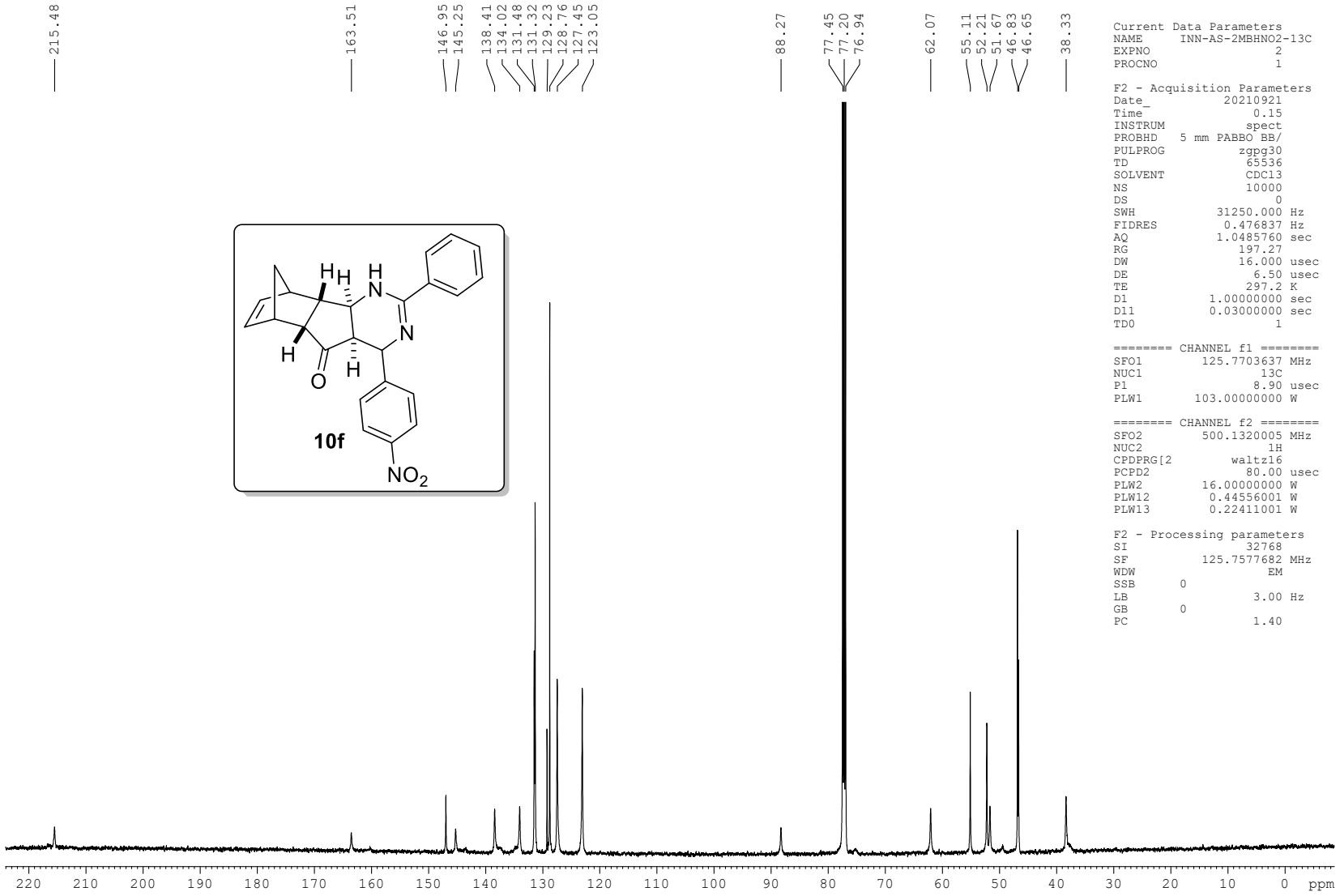


Figure S53. ^{13}C NMR Spectrum of 10f

```
Current Data Parameters
NAME      INN-AS-DIMEDONERETRO-1H
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210507
Time              23.47
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                30.72
DW               50.000 usec
DE                6.50 usec
TE               296.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                 1H
P1                13.35 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                65536
SF           500.1300136 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

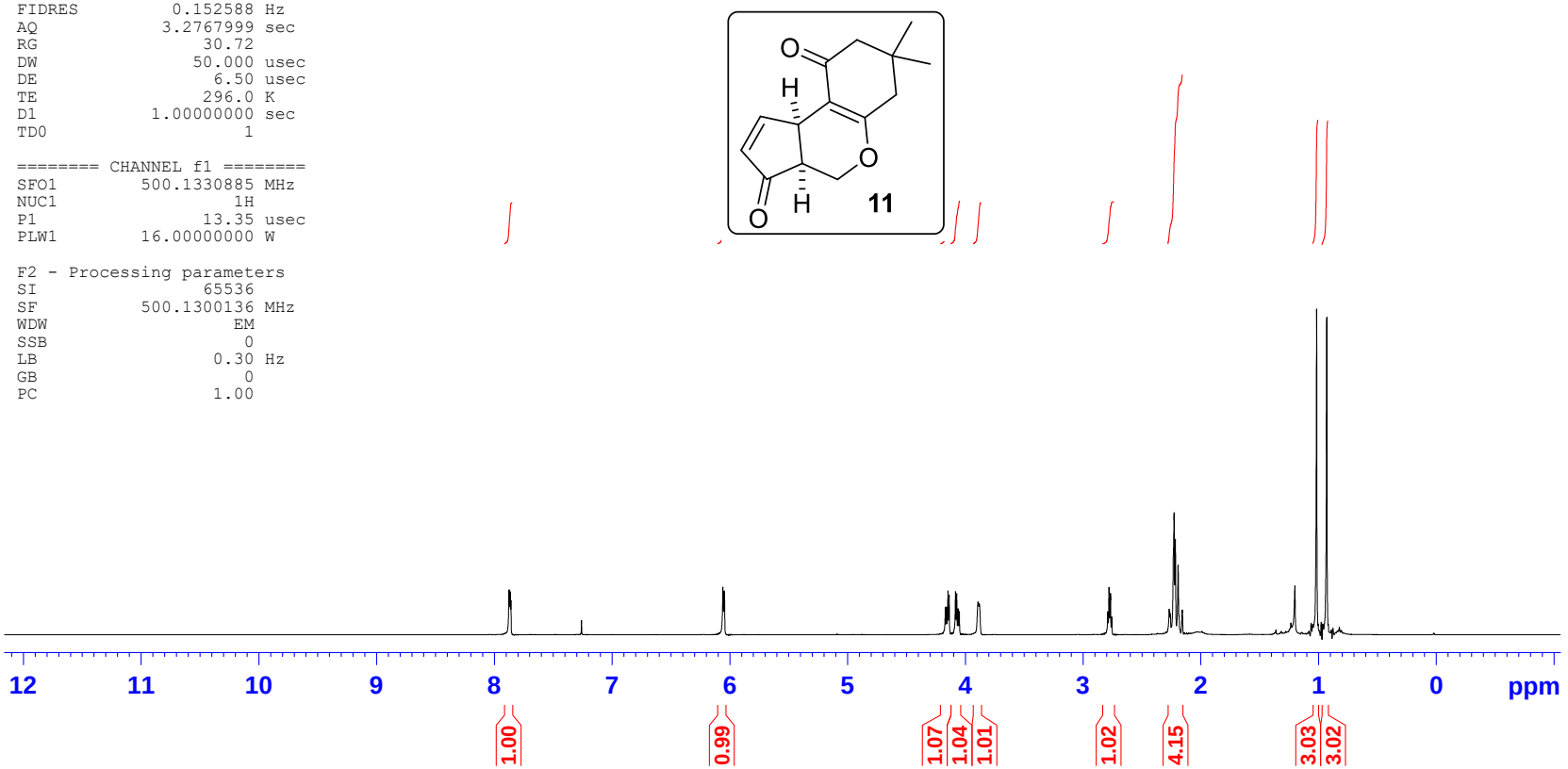


Figure S54. ^{1}H NMR Spectrum of 11

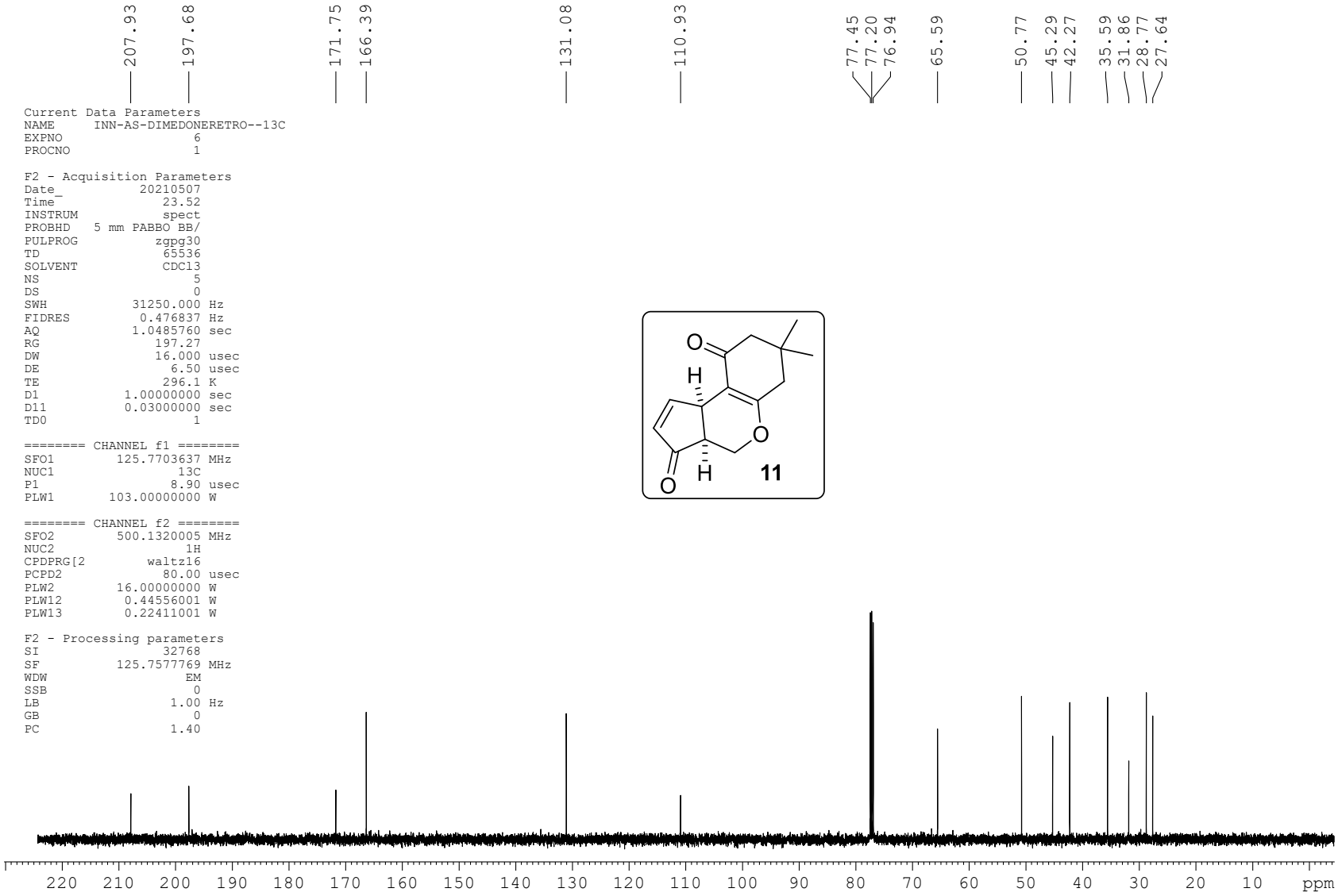


Figure S55. ^{13}C NMR Spectrum of 11

```
Current Data Parameters
NAME      INN-AS-ThioNMeRetro-1H
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210501
Time               13.10
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ             3.2767999 sec
RG                106.54
DW                50.000 usec
DE                 6.50 usec
TE                295.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                  1H
P1                13.35 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF            500.1300139 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

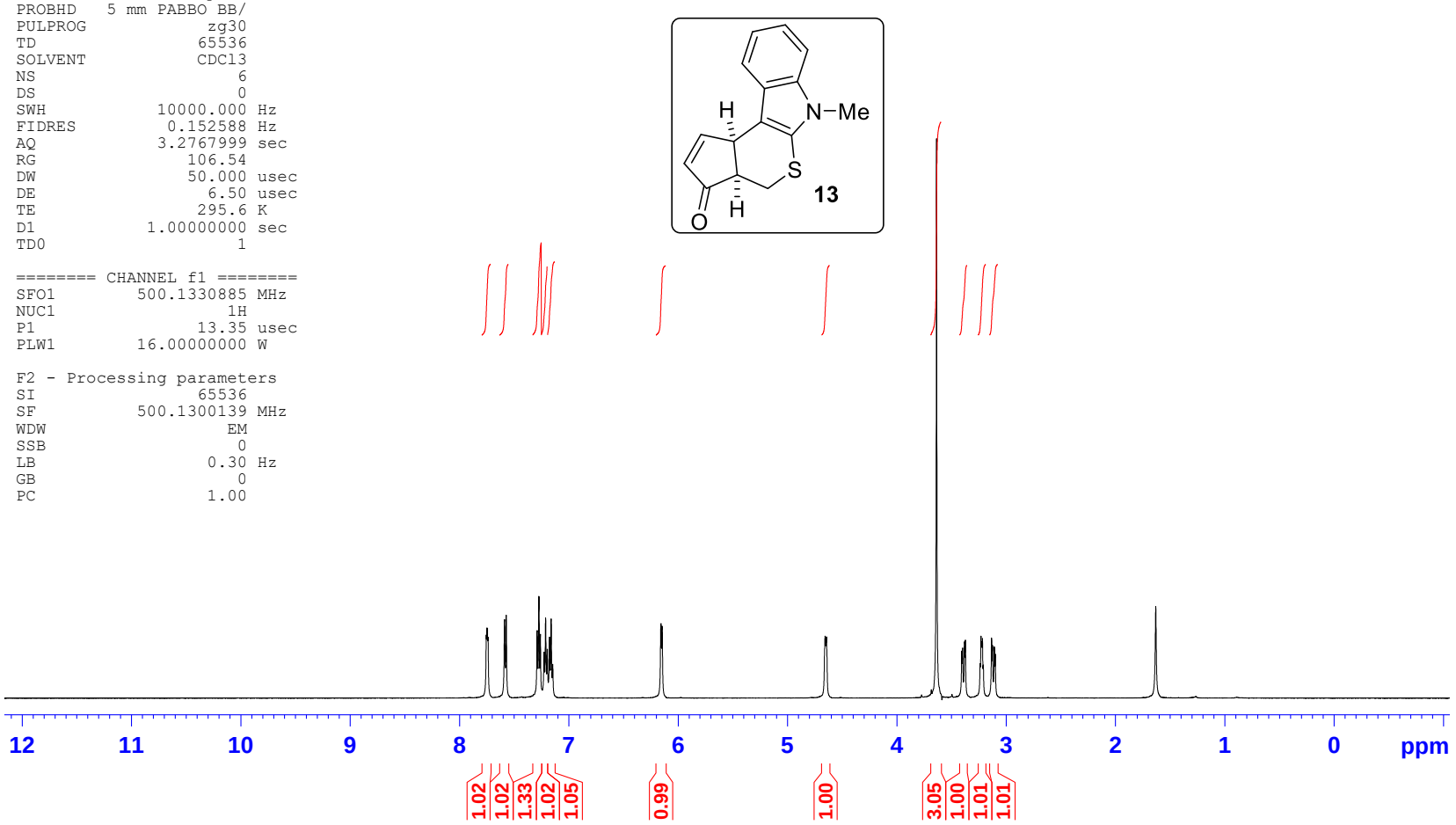


Figure S56. ^{1}H NMR Spectrum of 13

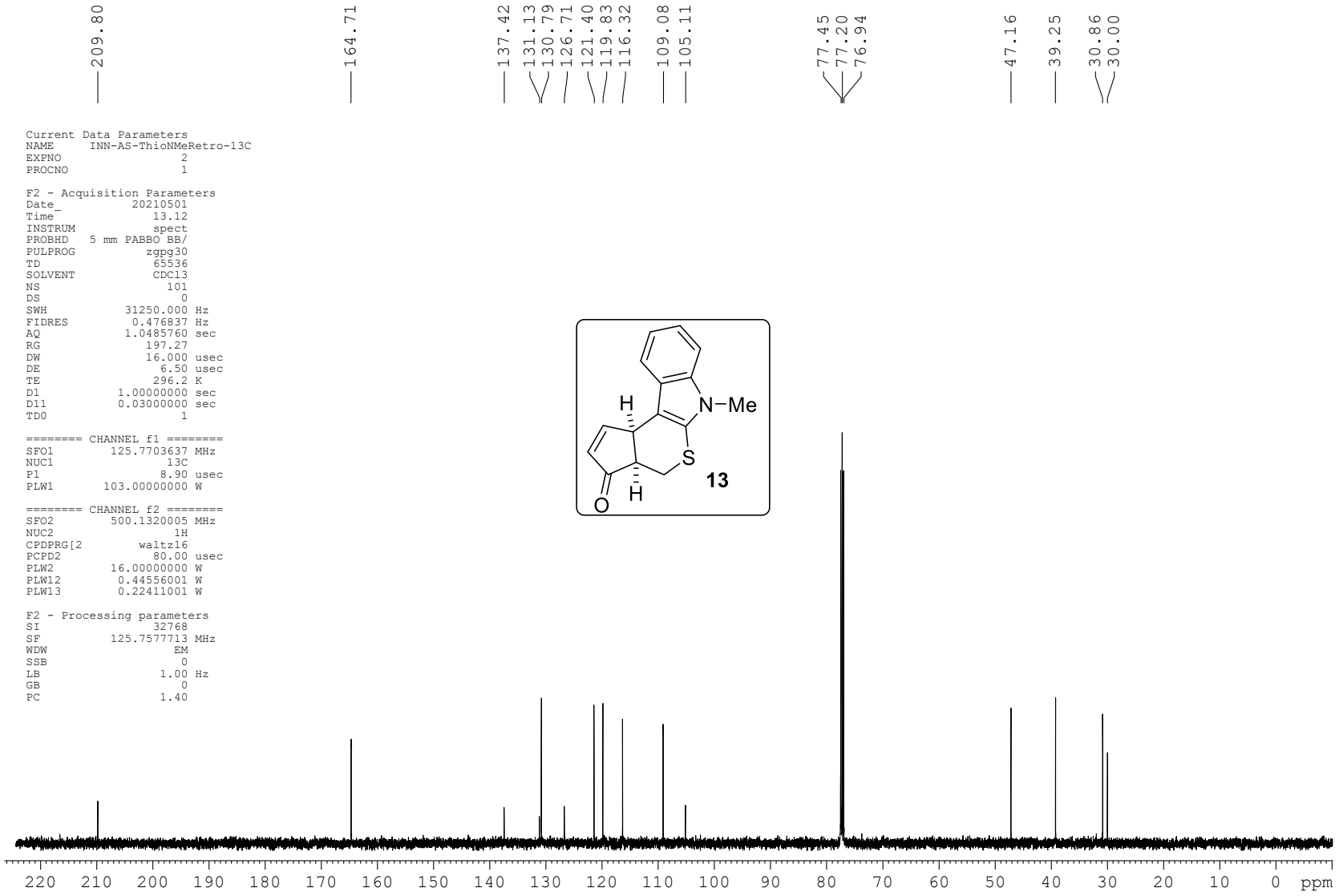


Figure S57. ^{13}C NMR Spectrum of 13

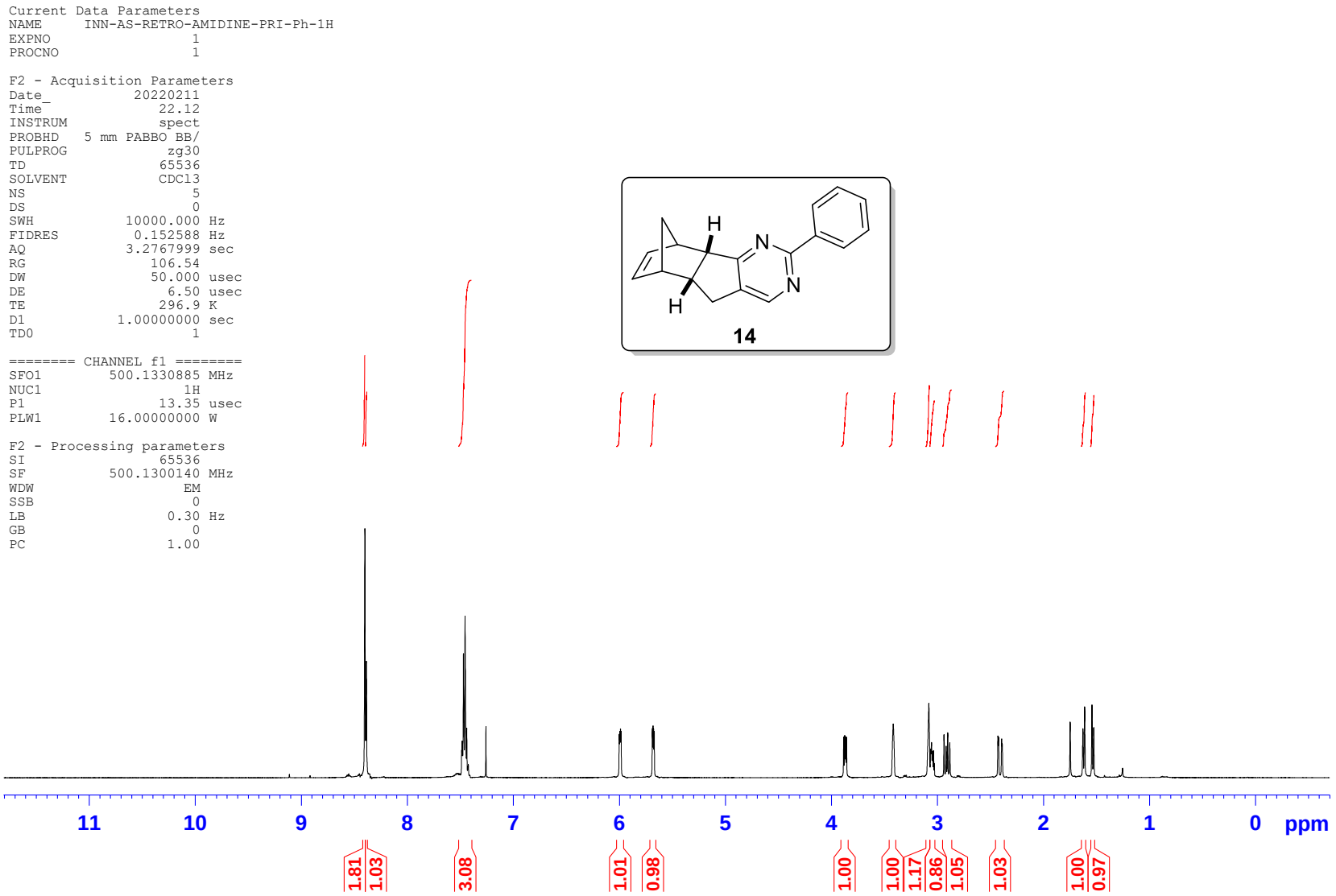


Figure S58. ^{1}H NMR Spectrum of 14

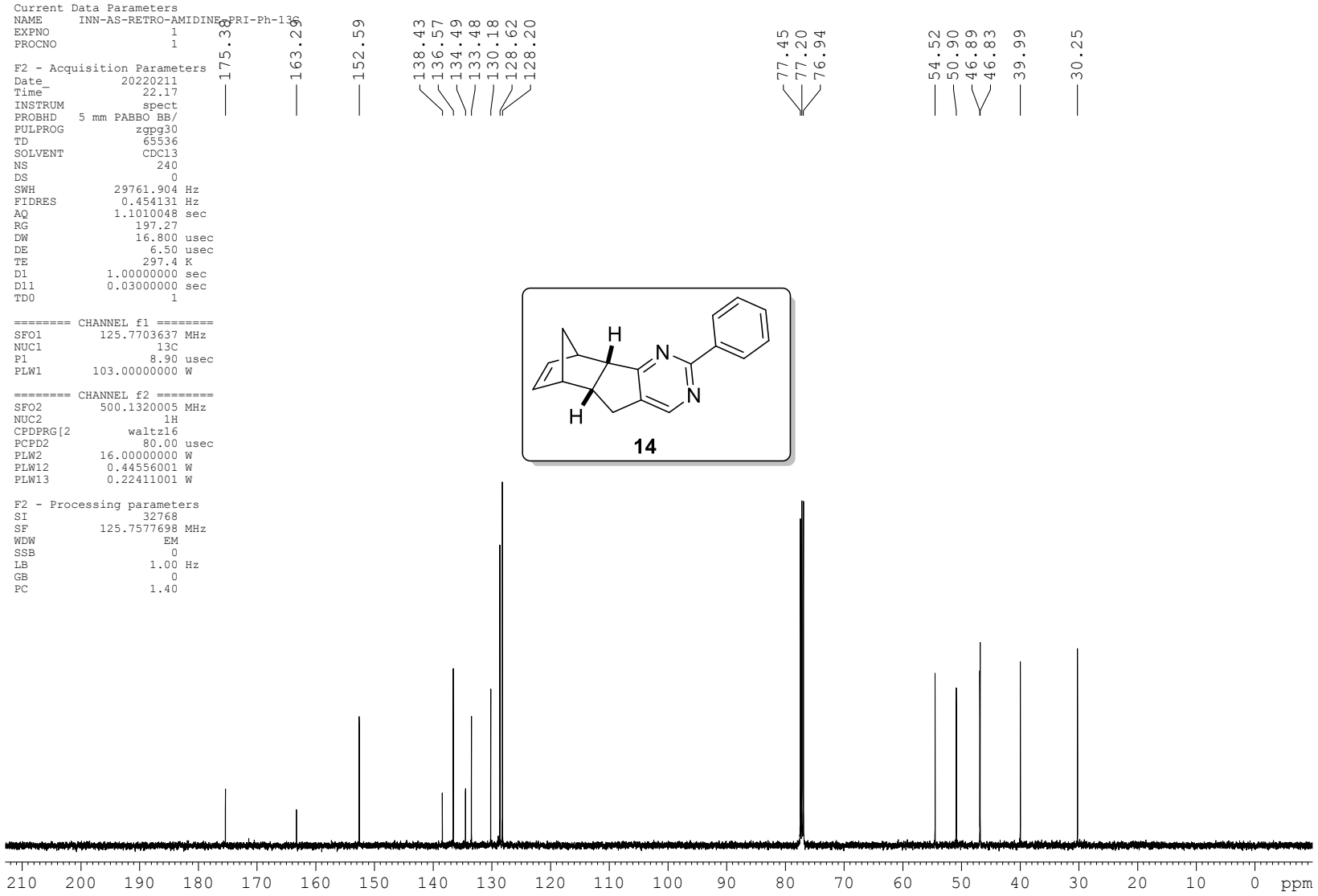


Figure S59. ^{13}C NMR Spectrum of 14

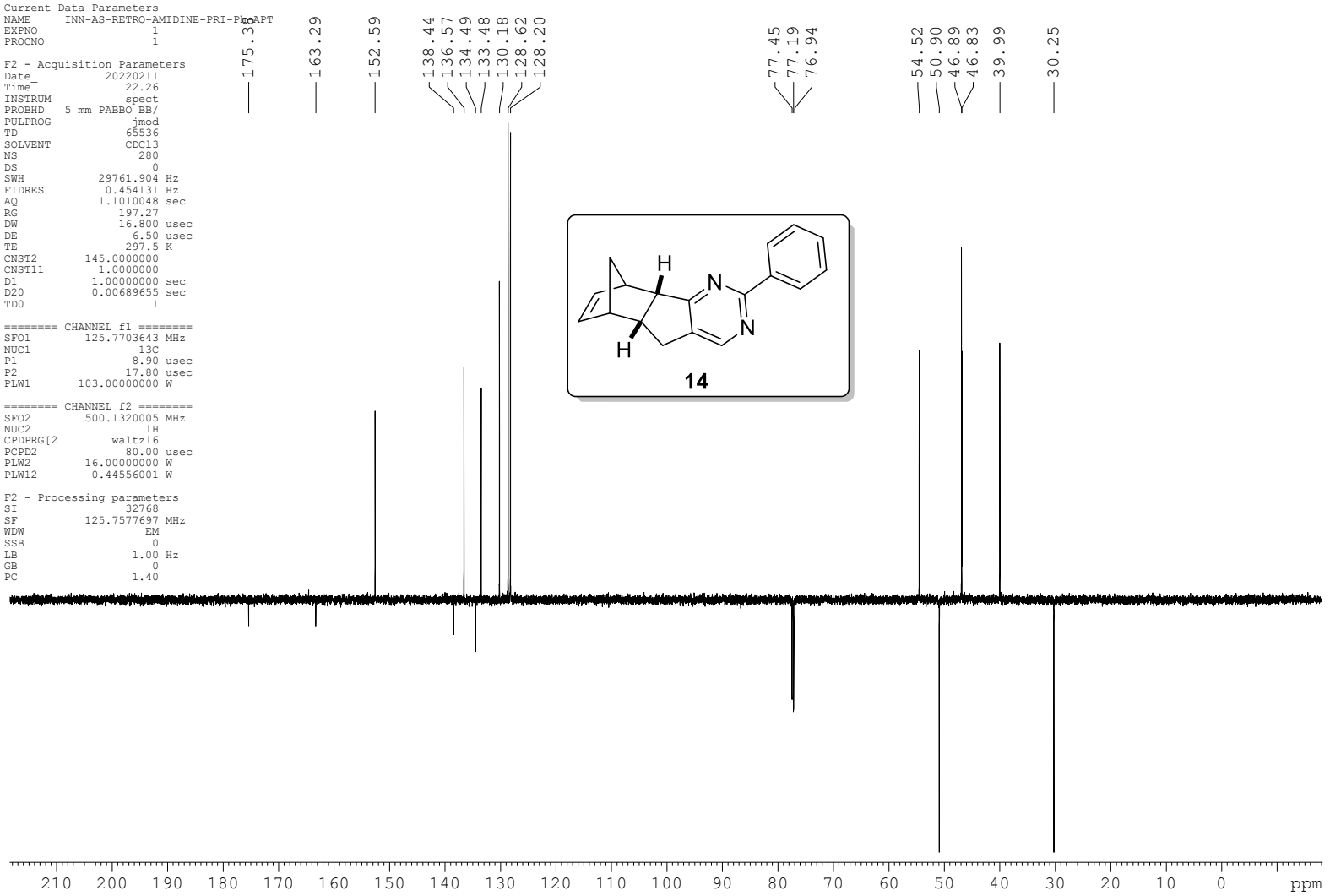
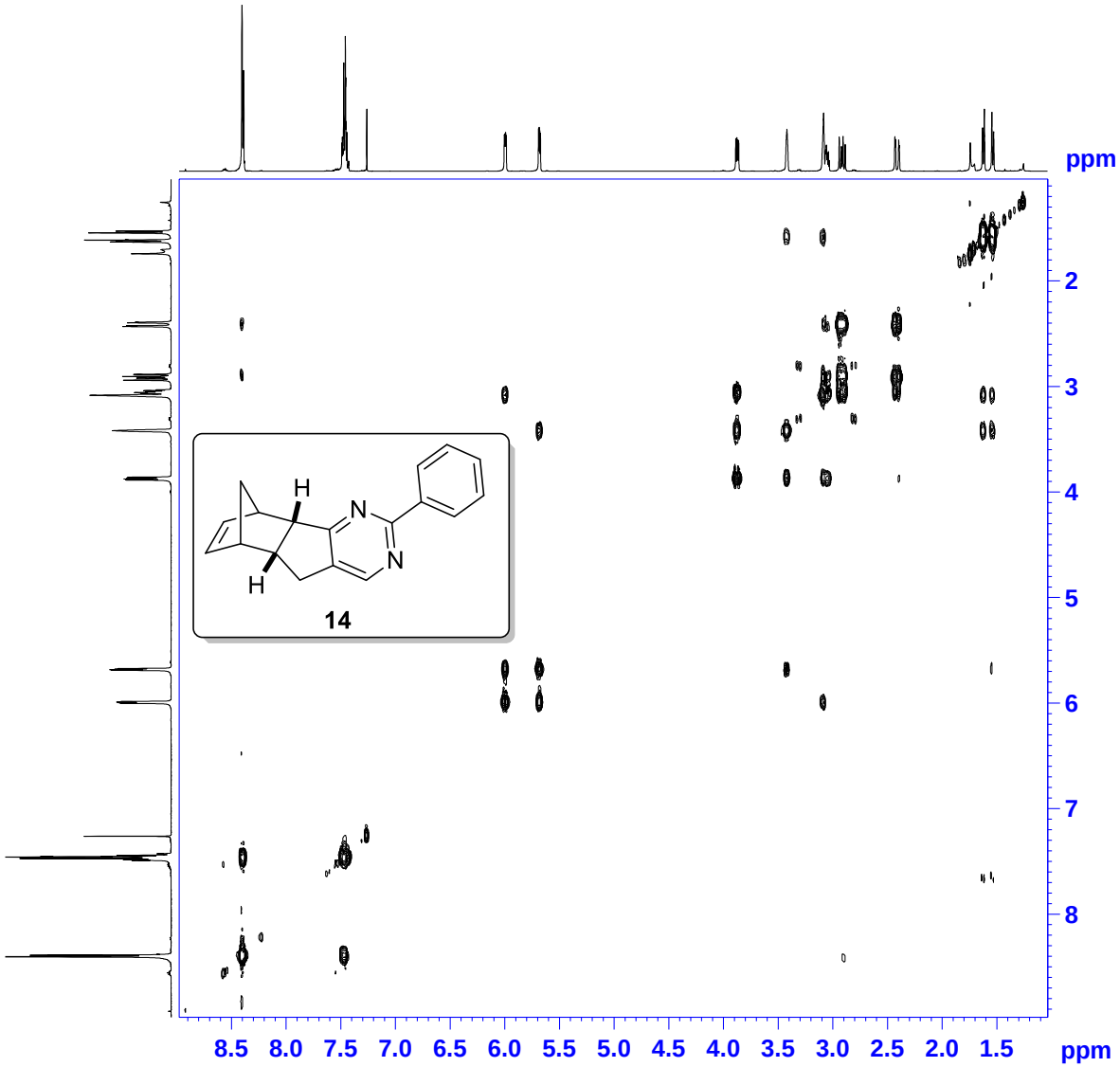


Figure S60. ^{13}C-APT NMR Spectrum of 14




```
Current Data Parameters
NAME      INN-AS-RETRO-AMIDINE-PRI-PH-COSY
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220214
Time              16.15
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      cosygpppqf
TD                2048
SOLVENT           CDCl3
NS                  32
DS                   0
SWH            3972.458 Hz
FIDRES         1.939677 Hz
AQ             0.2577749 sec
RG                197.27
DW              125.867 usec
DE                6.50 usec
TE                297.2 K
D0            0.00000300 sec
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00025180 sec

======== CHANNEL f1 ========
SFO1         500.1325169 MHz
NUC1                1H
P0                13.35 usec
P1                13.35 usec
P17             5000.00 usec
PLW1         16.00000000 W
PLW10         3.16840005 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1              10.00 %
P16             1000.00 usec

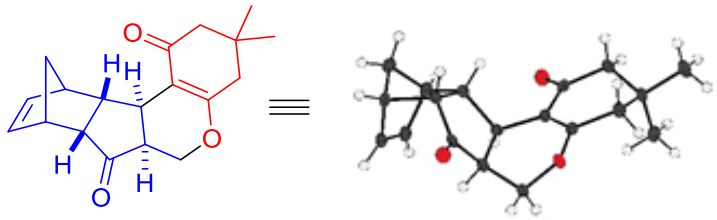
F1 - Acquisition parameters
TD                 110
SFO1            500.1325 MHz
FIDRES         72.207382 Hz
SW                7.941 ppm
FnMODE              QF

F2 - Processing parameters
SI                1024
SF           500.1300134 MHz
WDW               QSINE
SSB                  0
LB                   0 Hz
GB                   0
PC                1.40

F1 - Processing parameters
SI                1024
MC2                 QF
SF           500.1300134 MHz
WDW               QSINE
SSB                  0
LB                   0 Hz
GB                   0
```

Figure S61. ^{1}H-^{1}H COSY NMR Spectrum of 14

Table 1. Crystal data and structure refinement for 5a (CCDC 1879813)

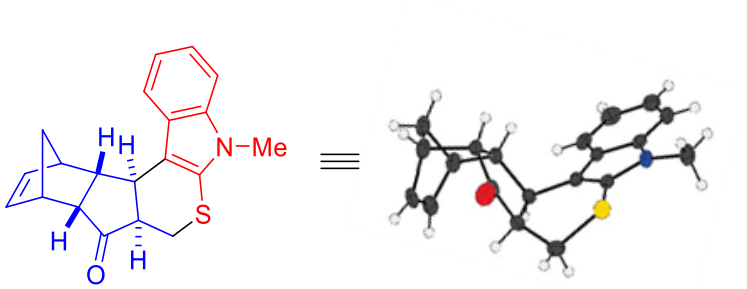


Identification code	INN-AS-81
Empirical Formula	$C_{19}H_{22}O_3$
Formula Weight	298.15
Crystal Color, Habit	colourless, prism
Crystal Dimensions	0.310 X 0.240 X 0.140 mm
Crystal System	monoclinic
Lattice Type	Primitive
Unit cell dimensions	a = 6.144(2) Å α = 90 deg.
b = 11.089(4) Å	β = 90.296(7) deg.
c = 22.162(7) Å	γ = 90 deg.
Volume	1509.8(9) $Å^3$
Space Group	$P2_1/c$ (#14)

Z value	1
D_{calc}	1.313 g/cm^3
F_{000}	640.00
m(MoKa)	0.872 cm^{-1}
Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Fnction Minimized	S w (Fo^2 - Fc2)2
Least Squares Weights	w = 1/ [s^2(Fo2) + (0.0938 .P)2
+ 0.1963 .P]	
Where P = (Max(Fo^2,0) + 2Fc2)/3	
$2q_{max}$cutoff	50.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2643
No. Variables	199
Reflection/Parameter Ratio	13.28
Residuals: R1 (I>2.00s(I))	0.0501
Residuals: R (All reflections)	0.0661
Residuals: wR2 (All reflections)	0.1735

Goodness of Fit Indicator	1.169
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.44 e/Å^3
Minimum peak in Final Diff. Map	-0.41 e/Å^3

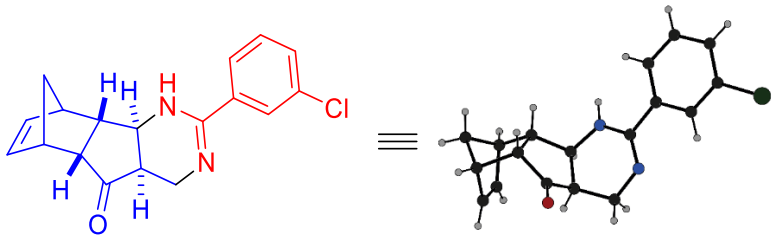
Table 2. Crystal data and structure refinement for 7b (CCDC 1879460)



Identification code	inn-as-56a_mo	
Empirical formula	C20 H19 N O S	
Formula weight	321.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.4480(5) Å	α= 90°.

b = 15.4161(5) Å	β= 101.362(4)°.
c = 17.7415(7) Å	γ = 90°.
Volume	3069.7(2) $Å^3$
Z	8
Density (calculated)	1.391 Mg/m^3
Absorption coefficient	0.215 mm^{-1}
F(000)	1360
Crystal size	0.090 x 0.178 x 0.275 mm^3
Theta range for data collection	1.77 to 25.00°.
Index ranges	-13<=h<=12, -17<=k<=18, -21<=l<=21
Reflections collected	19112
Independent reflections	5379 [R(int) = 0.0602]
Completeness to theta = 25.00°	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5379 / 0 / 567
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0952
R indices (all data)	R1 = 0.0591, wR2 = 0.1052
Largest diff. peak and hole	0.298 and -0.331 $e.Å^{-3}$

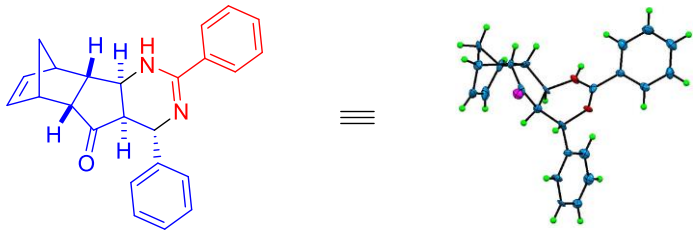
Table 3. Crystal data and structure refinement for 10b (CCDC 1879722)



Identification code	INN-AS-III-76-C_Mo
Empirical formula	$C_{18}H_{17}ClN_2O$
Formula weight	312.79
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.208(2)
b/Å	9.2277(12)
c/Å	12.4378(19)
α/°	90.00
β/°	98.905(15)
γ/°	90.00

Volume/Å^3	1497.6(4)
Z	4
ρ_{calc}g/cm^3	1.387
μ/mm^{-1}	0.258
F(000)	656.0
Crystal size/mm^3	0.095 × 0.08 × 0.043
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.4 to 50
Index ranges	-15 ≤ h ≤ 14, -10 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	11828
Independent reflections	2636 [R_{int} = 0.1352, R_{sigma} = 0.1377]
Data/restraints/parameters	2636/0/199
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0811, wR_2 = 0.1545
Final R indexes [all data]	R_1 = 0.1487, wR_2 = 0.1951
Largest diff. peak/hole / e Å^{-3}	0.34/-0.31

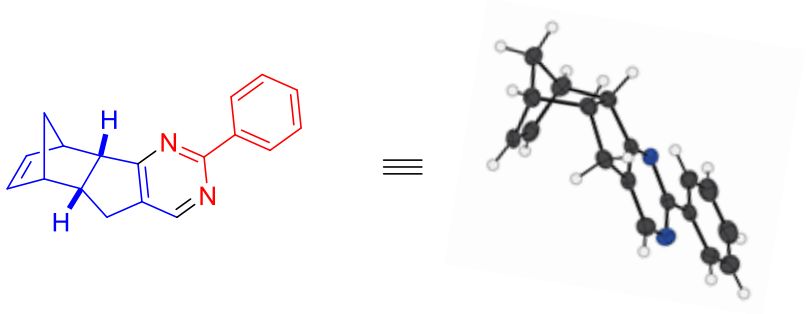
Table 4. Single crystal X-ray data and structure refinement for compounds 10d (CCDC 1974426)



Identification code	**10d**
CCDC	1974426
Empirical formula	$CHCl_3.C_{24}H_{23}N_2O$
Formula weight	473.80
Temperature/K	150
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.8183(14)
b/Å	17.594(3)
c/Å	25.274(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4366.0(11)
Z	8
ρ_{calc} g/cm^3	1.442
μ/ mm^{-1}	0.441
F(000)	1968.0
Crystal size/mm^3	0.231 × 0.06 × 0.031

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.63 to 49.984
Index ranges	-11 ≤ h ≤ 10, -20 ≤ k ≤ 20, -14 ≤ l ≤ 30
Reflections collected	14078
Independent reflections	3820 [R_{int} = 0.1606, R_{sigma} = 0.1808]
Data/restraints/parameters	3820/264/280
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0805, wR_2 = 0.1427
Final R indexes [all data]	R_1 = 0.1671, wR_2 = 0.1902
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.51

Table 5. Single crystal X-ray data and structure refinement for compounds 14 (CCDC 2151617)



Empirical formula	$C_{18}H_{15}N_2$
Formula weight	260.34
Temperature/K	150.00(10)
Crystal system	monoclinic

Space group	$P2_1/n$
a/Å	6.3943(2)
b/Å	18.0605(5)
c/Å	11.5544(4)
α/°	90
β/°	98.892(3)
γ/°	90
Volume/Å^3	1318.31(7)
Z	4
ρ_{calc}g/cm^3	1.3116
μ/mm^{-1}	0.078
F(000)	552.2
Crystal size/mm^3	0.25 × 0.21 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.22 to 49.96
Index ranges	$-9 \leq h \leq 7$, $-25 \leq k \leq 24$, $-16 \leq l \leq 14$
Reflections collected	28488
Independent reflections	2326 [R_{int} = 0.1382, R_{sigma} = 0.1307]
Data/restraints/parameters	2326/0/189
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1266
Largest diff. peak/hole / e Å^{-3}	0.29/-0.33