Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information
For

Synthesis of Tetrahydrothiopyrano[2,3-*b*]indoles via [3+3] Annulation of Nitroallylic Acetates with Indoline-2-thiones

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FIDRES        0.151522 Hz
AQ            3.2998593 sec
RG                  161
DW               60.800 usec
DE                6.50 usec
TE               296.6 K
D1           1.00000000 sec
TD0                   1

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PL1               -1.00 dB
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SFO1        400.1324710 MHz

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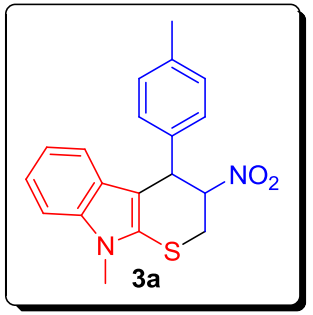


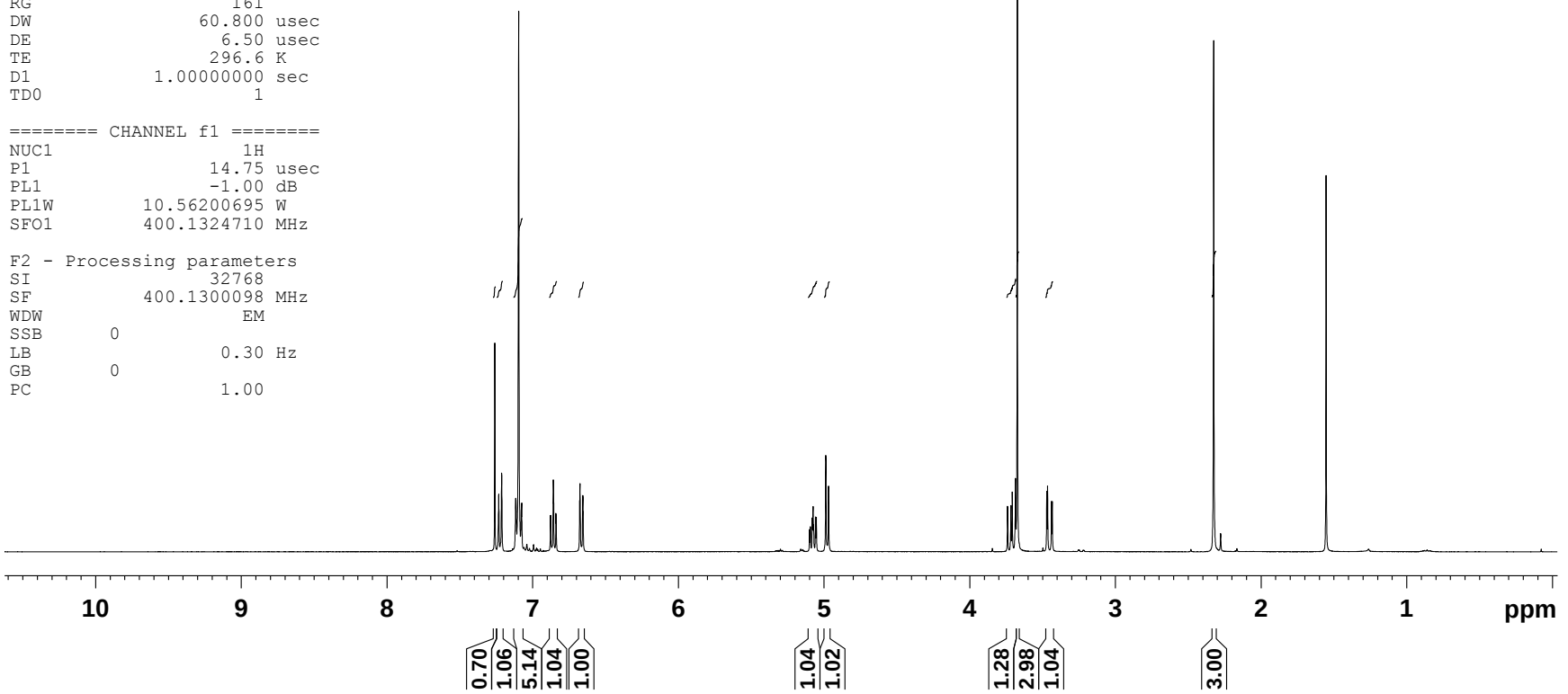
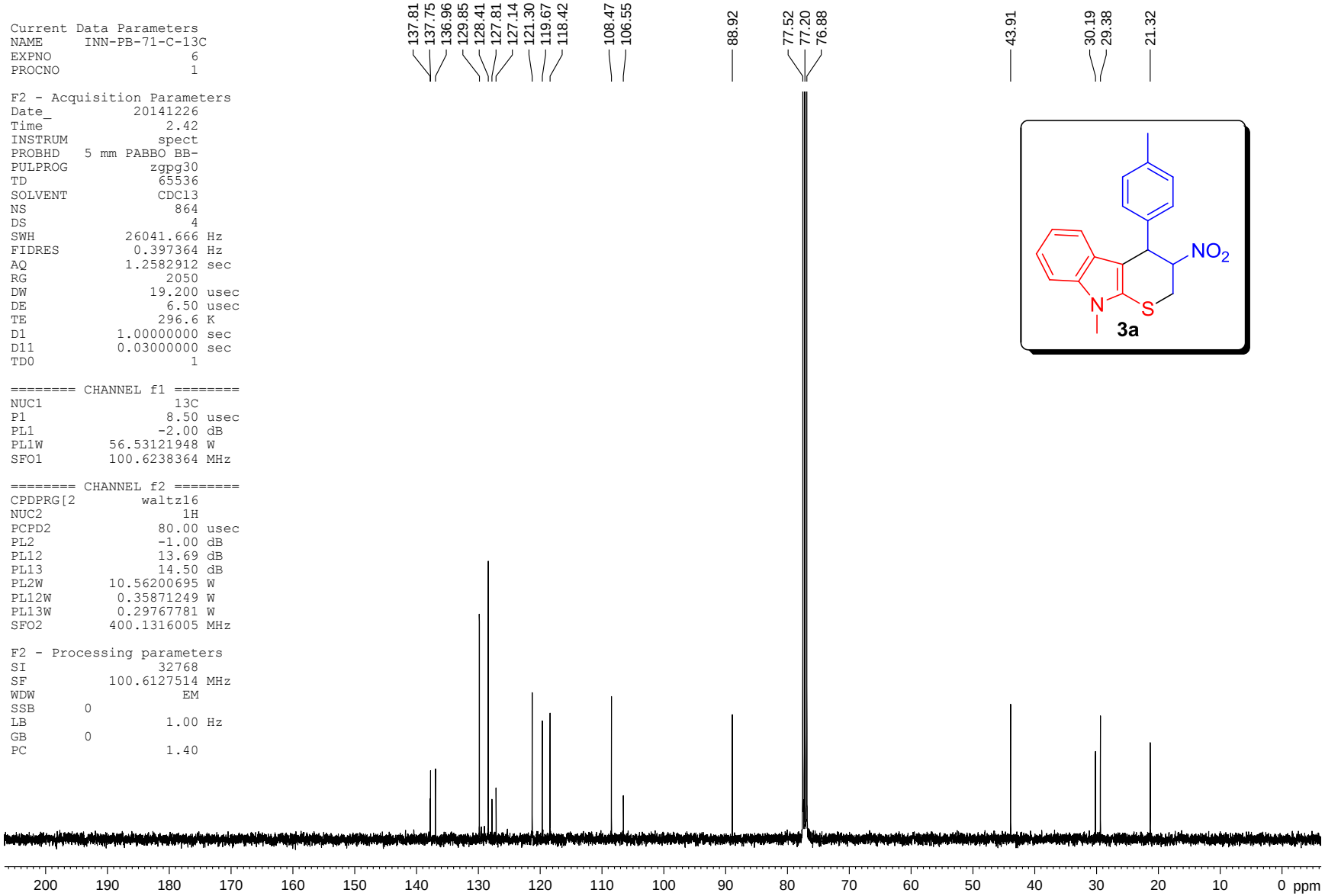


Figure S01. ^{1}H NMR Spectrum of 3a (Major isomer)

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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   864
DS                     4
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                  2050
DW                19.200 usec
DE                 6.50 usec
TE                296.6 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            100.6127514 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S02. ^{13}C NMR Spectrum of 3a (Major isomer)

```
Current Data Parameters
NAME      INN-PB-CH-37-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170210
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INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   18
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               296.6 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          500.1300136 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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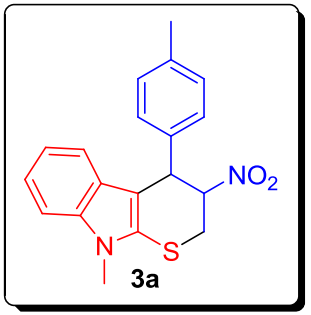


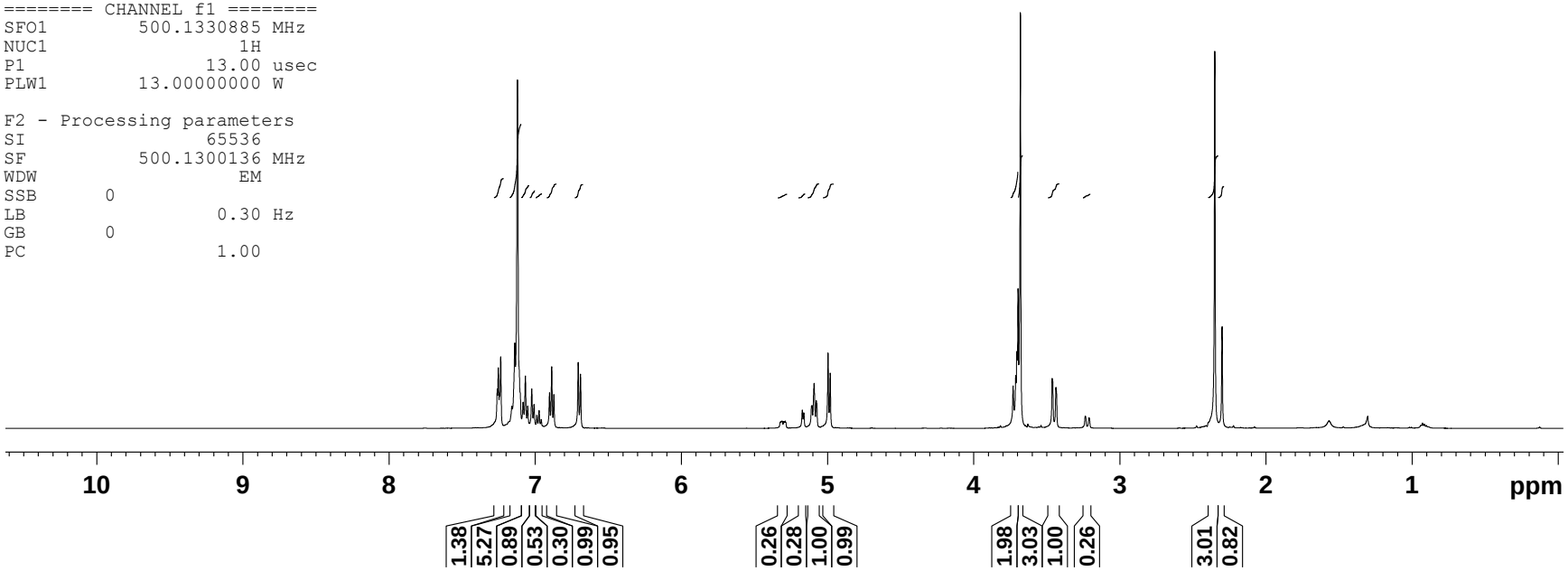


Figure S03. ^{1}H NMR Spectrum of 3a (major + minor, dr 80:20)

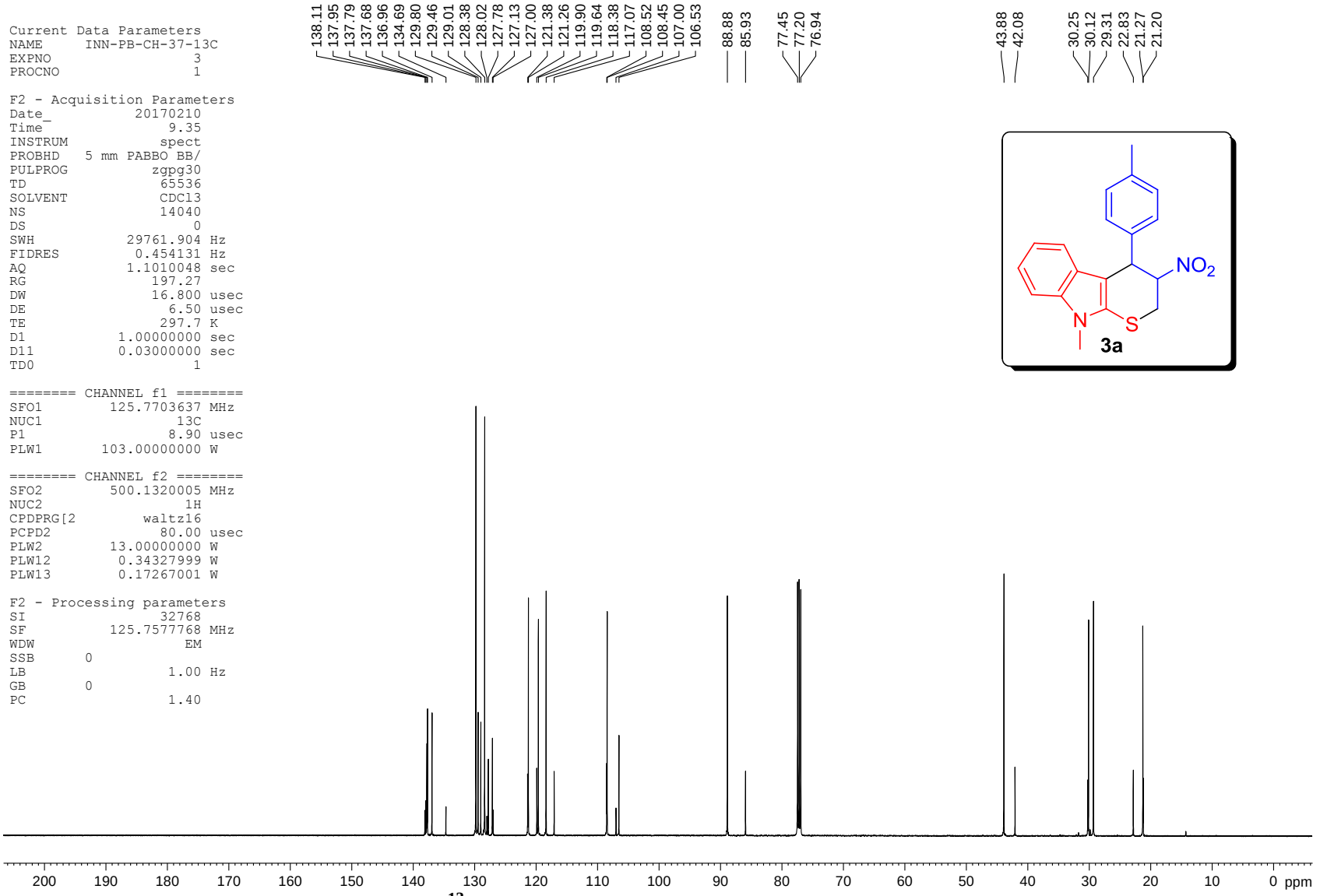
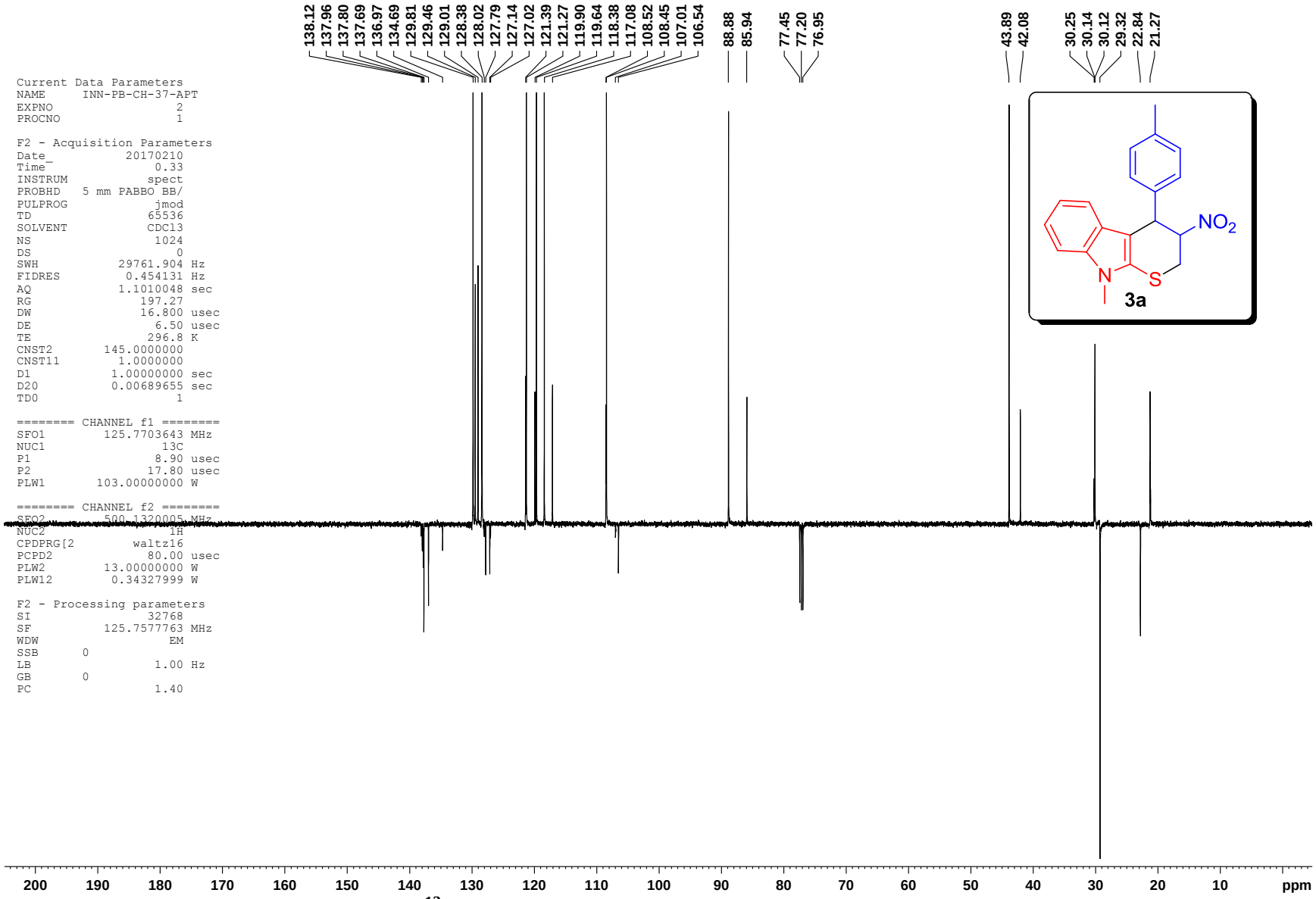


Figure S04. ^{13}C NMR Spectrum of 3a (major + minor, dr 80:20)

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PROCNO                  1

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INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE                296.8 K
CNST2        145.0000000
CNST11         1.0000000
D1             1.00000000 sec
D20            0.00689655 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703643 MHz
NUC1                13C
P1                 8.90 usec
P2                17.80 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         13.00000000 W
PLW12         0.34327999 W

F2 - Processing parameters
SI                 32768
SF           125.7577763 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S05. ^{13}C-APT NMR Spectrum of 3a (major + minor, dr 80:20)

```
Current Data Parameters
NAME       INN-CH-67-1H
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_           20140414
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INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   13
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                294.3 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          500.1300122 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
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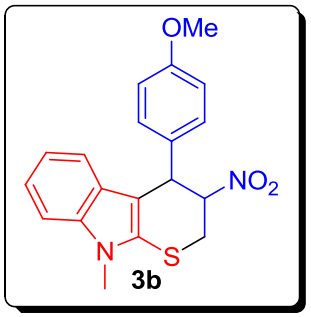


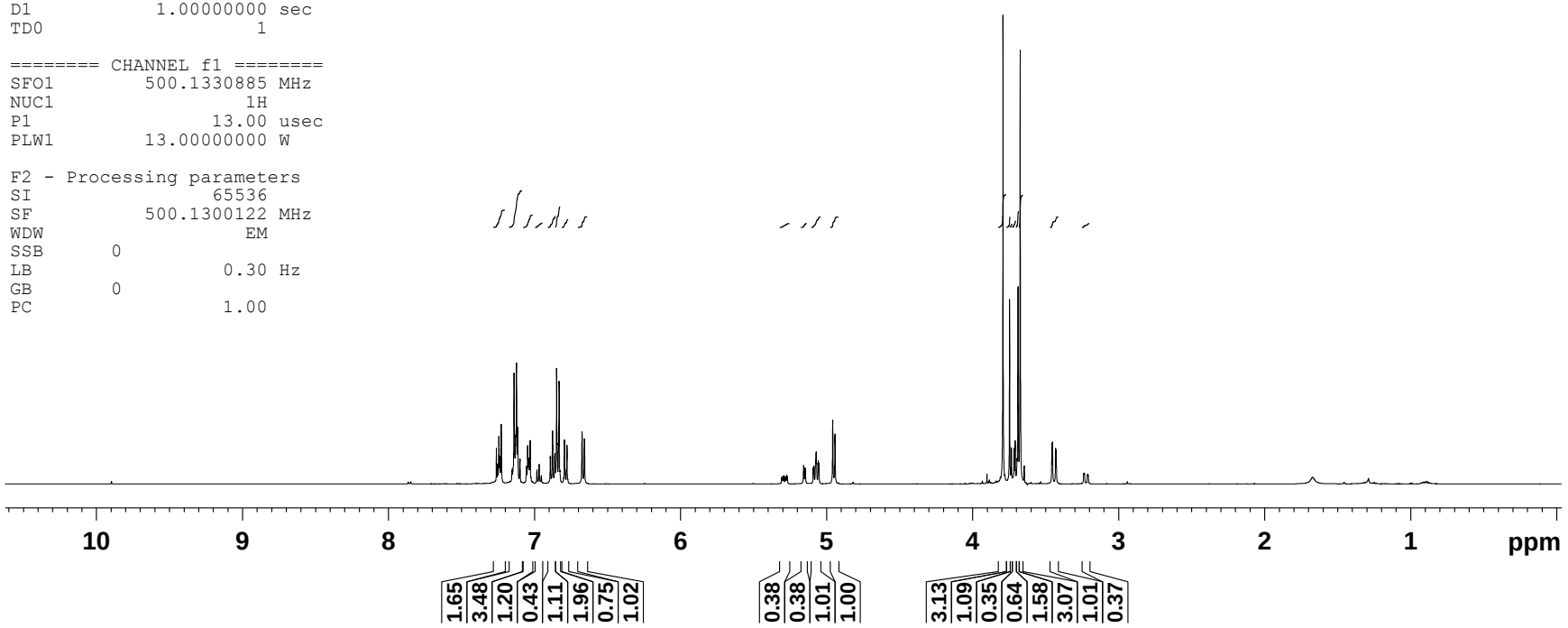
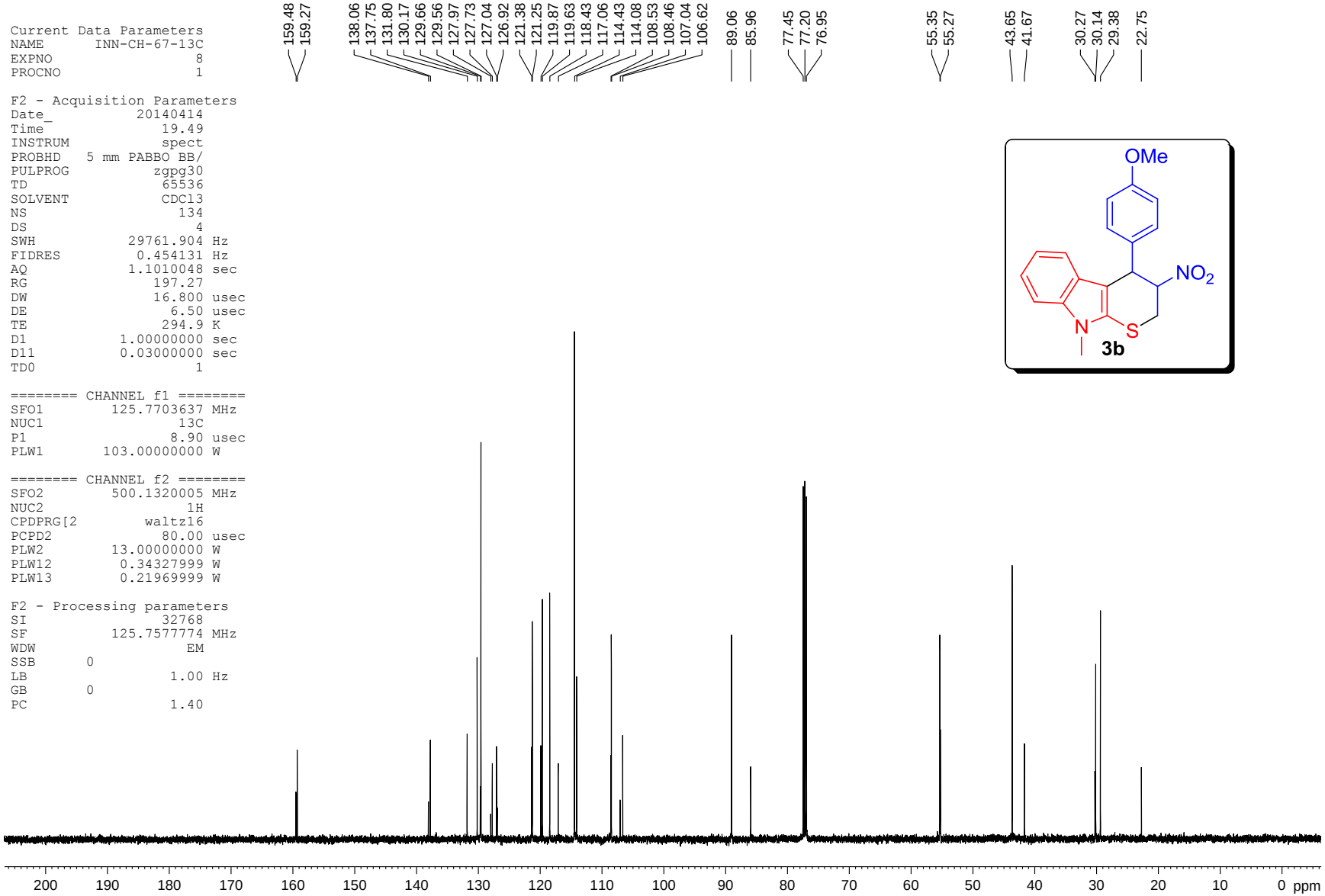


Figure S06. ^{1}H NMR Spectrum of 3b (major + minor, dr 73:27)

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Current Data Parameters
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EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20140414
Time              19.49
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 134
DS                   4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE                294.9 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        13.00000000 W
PLW12        0.34327999 W
PLW13        0.21969999 W

F2 - Processing parameters
SI                32768
SF          125.7577774 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S07. ^{13}C NMR Spectrum of 3b (major + minor, dr 73:27)

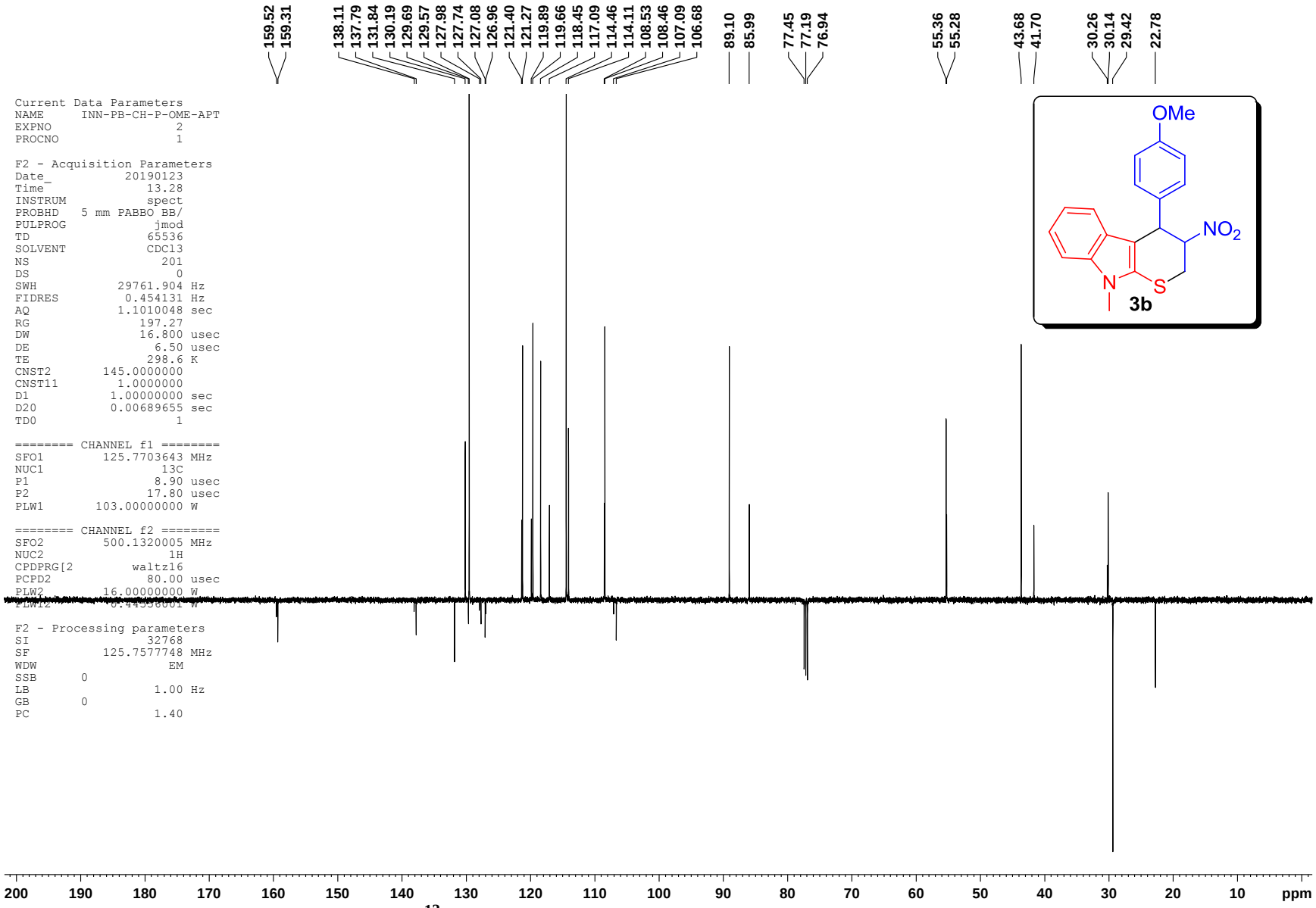


Figure S08. ^{13}C-APT NMR Spectrum of 3b (major + minor, dr 73:27)

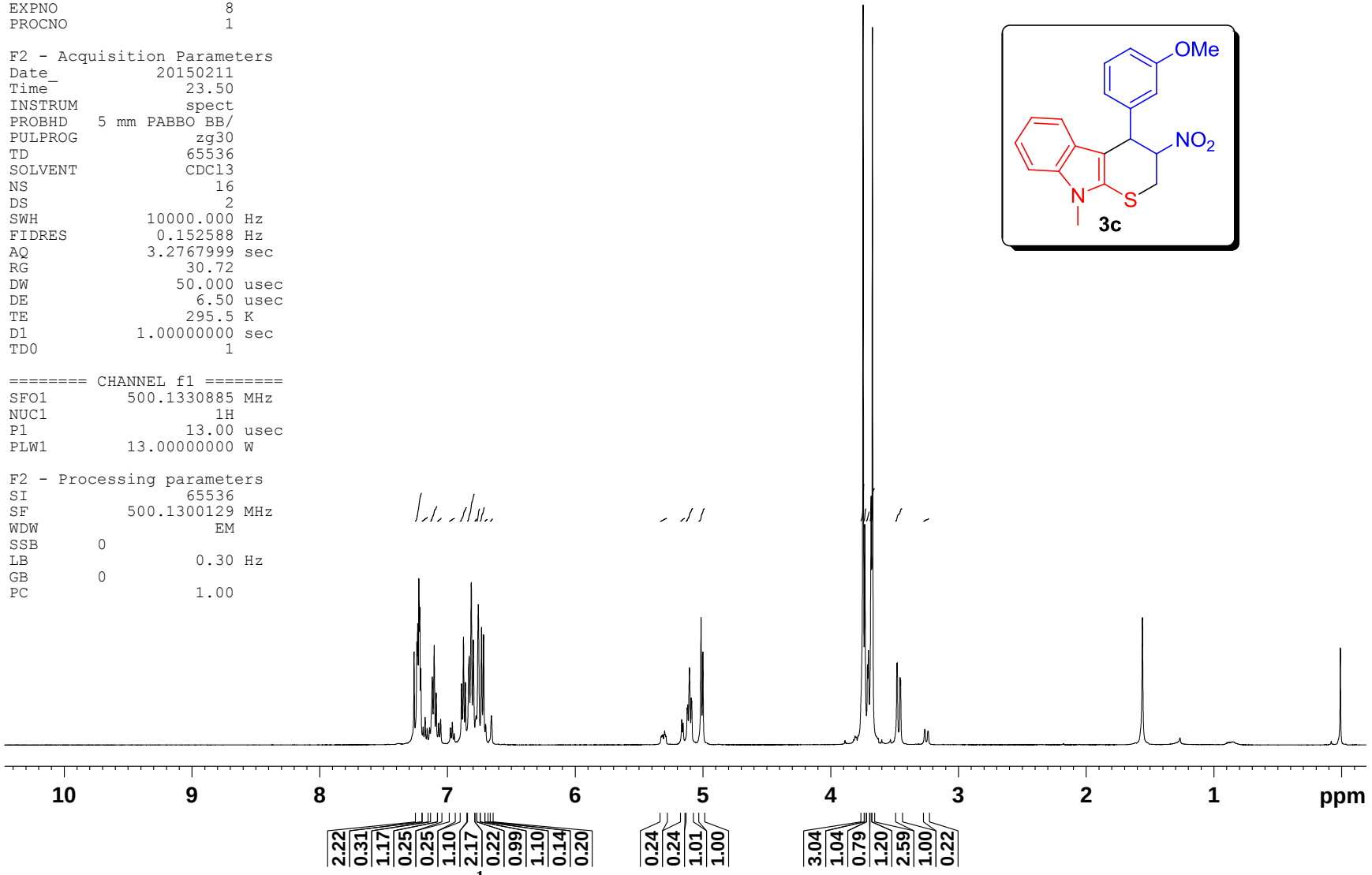


Figure S09. ^{1}H NMR Spectrum of 3c (major + minor, dr 80:20)

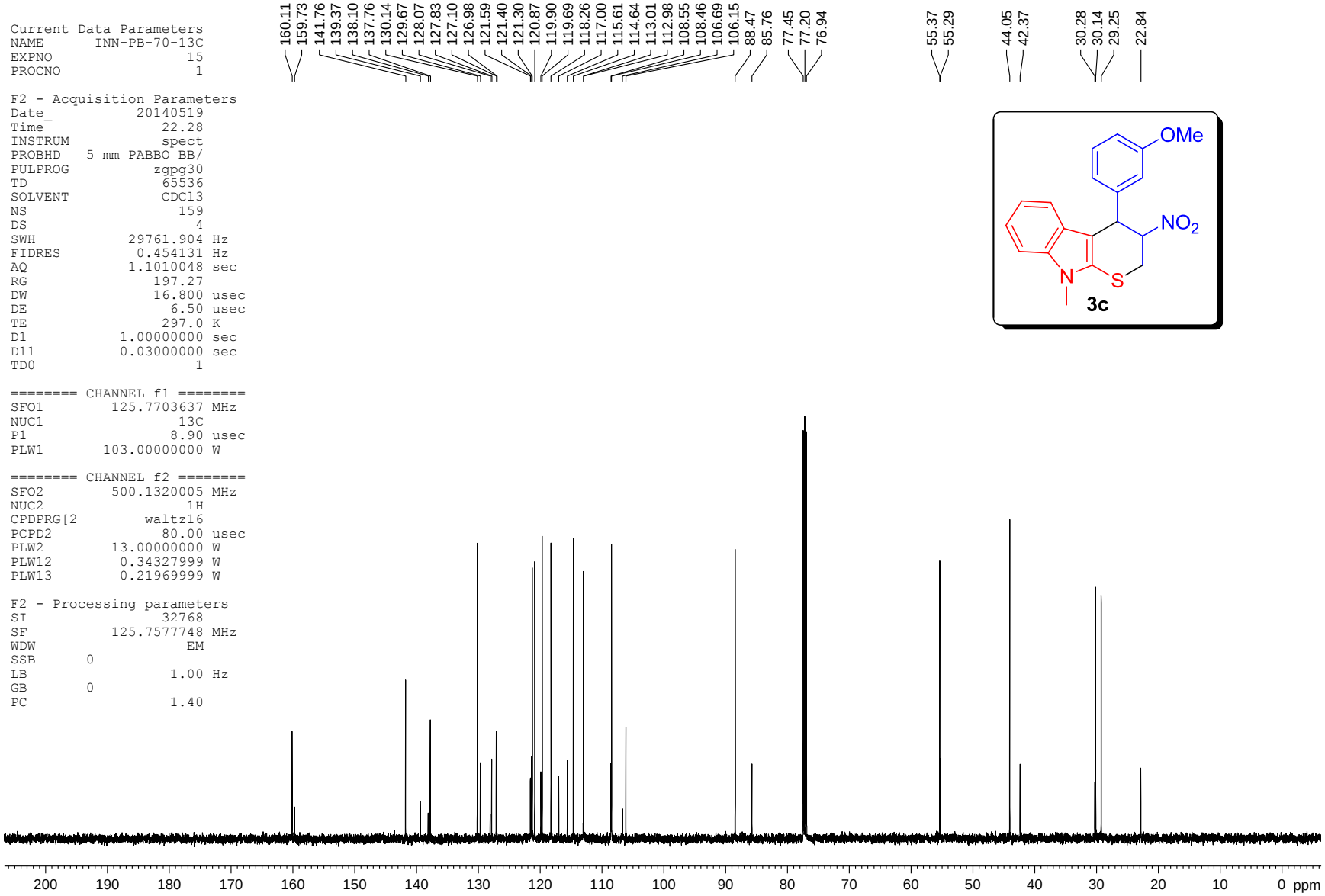
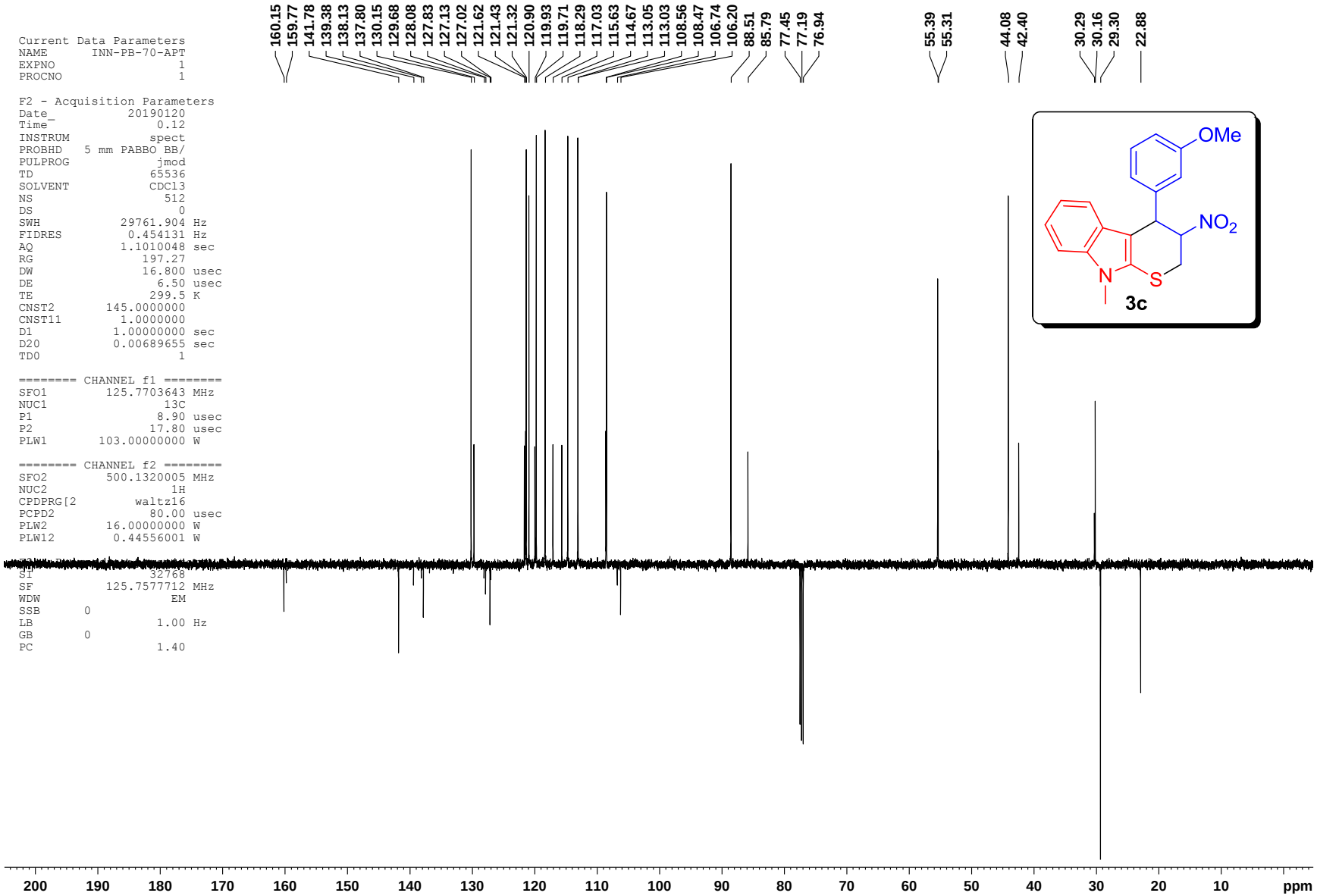


Figure S10. ^{13}C NMR Spectrum of 3c (major + minor, dr 80:20)

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PROBHD   5 mm PABBO BB/
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE               299.5 K
CNST2       145.0000000
CNST11        1.0000000
D1            1.00000000 sec
D20           0.00689655 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        125.7703643 MHz
NUC1               13C
P1                8.90 usec
P2               17.80 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

SI                32768
SF          125.7577712 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S11. ^{13}C-APT NMR Spectrum of 3c (major + minor, dr 80:20)

```
Current Data Parameters
NAME       INN-PB-69-1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20170217
Time              17.47
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                  181
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          400.1300100 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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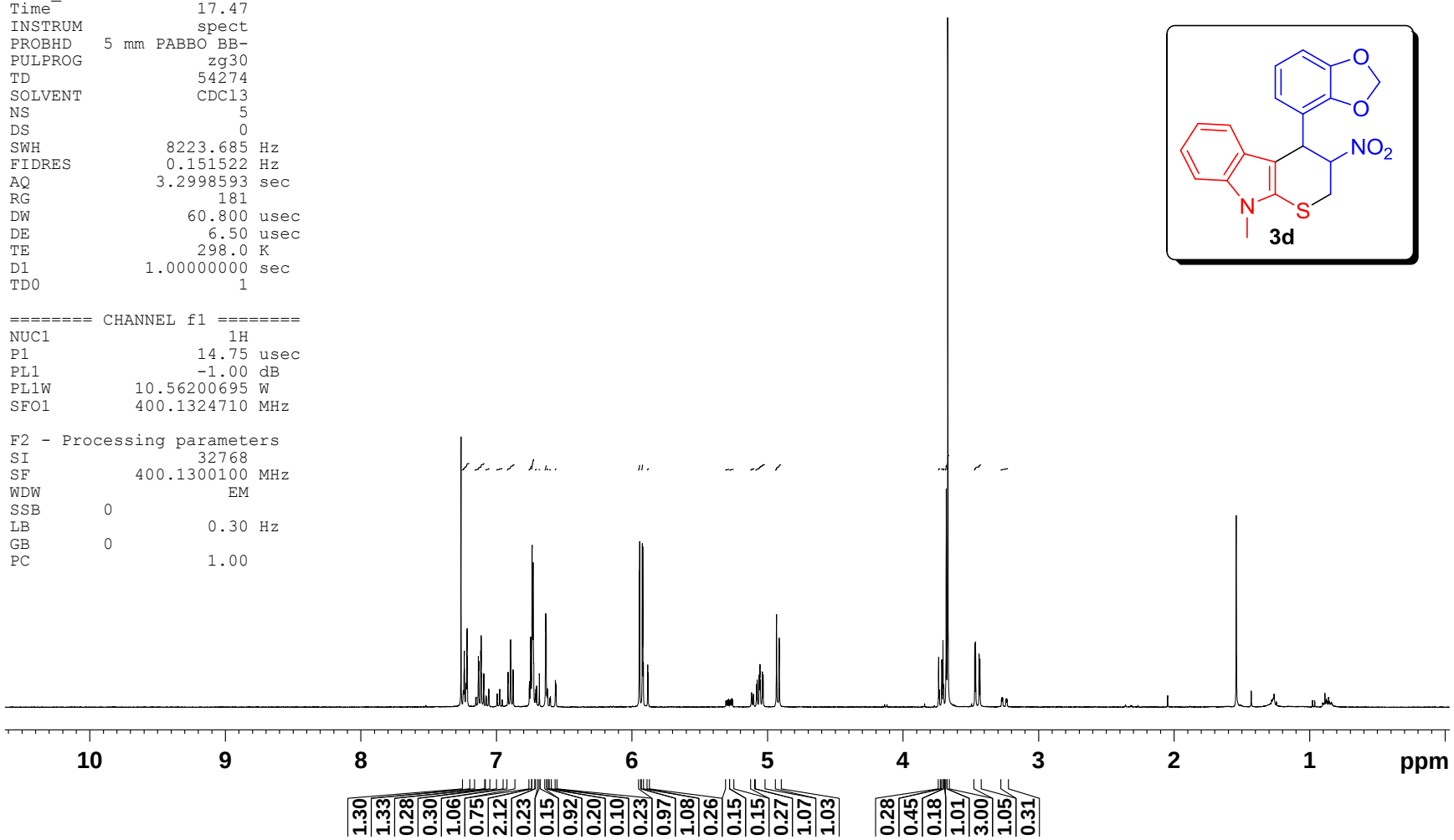

Figure S12. ^{1}H NMR Spectrum of 3d (major + minor, dr 78:22)

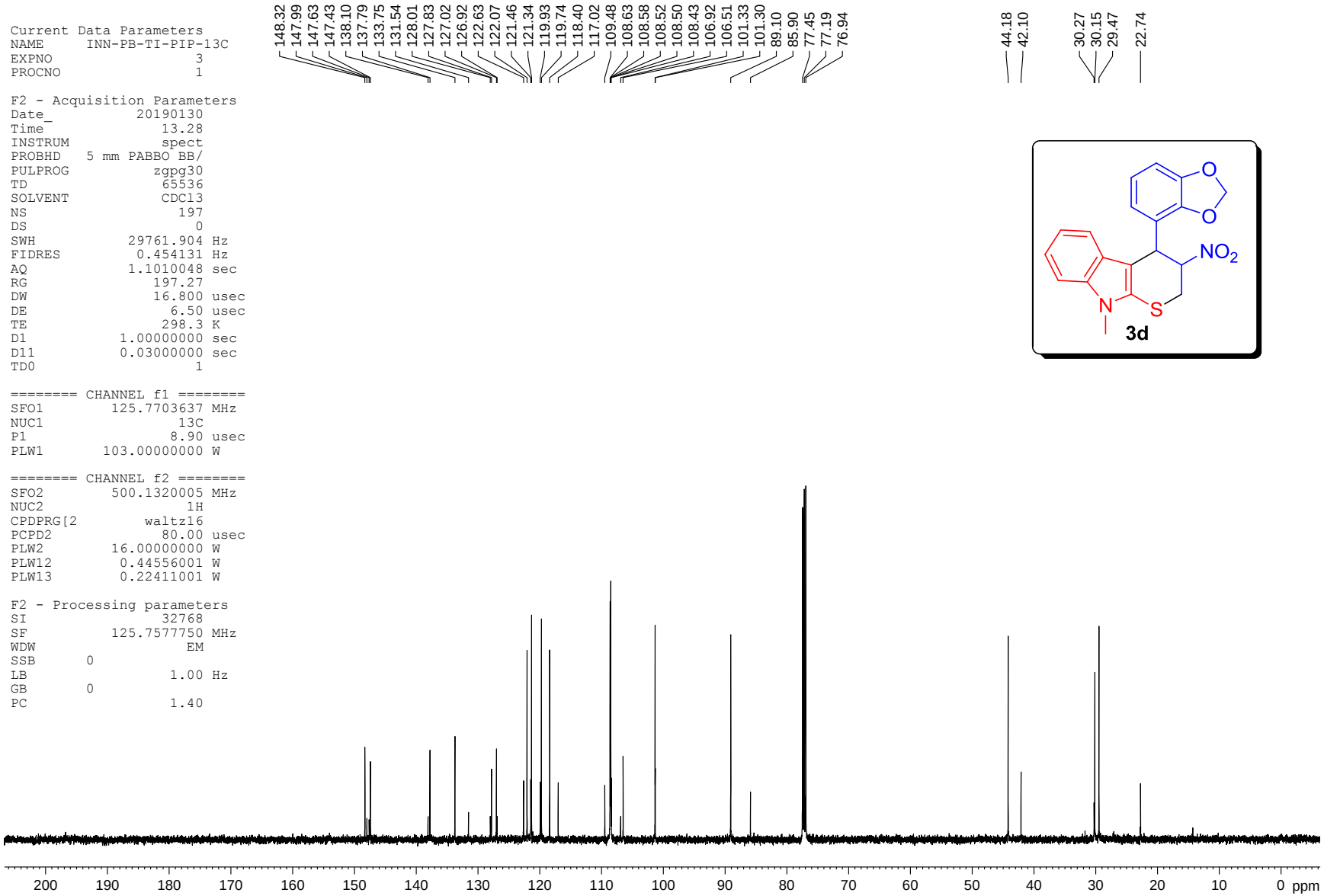

Figure S13. ^{13}C NMR Spectrum of 3d (major + minor, dr 78:22)

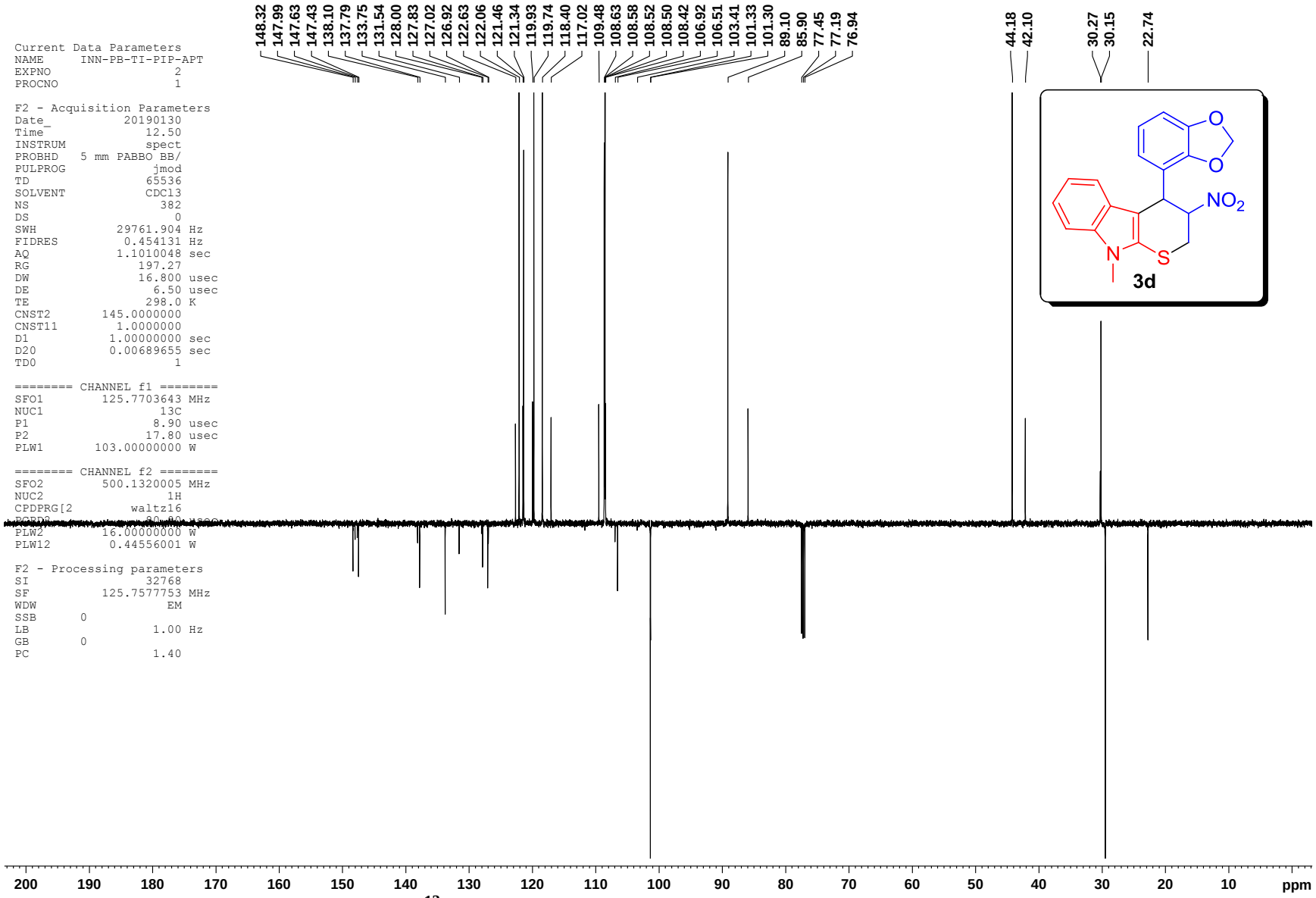

Figure S14. ^{13}C-APT NMR Spectrum of 3d (major + minor, dr 78:22)

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PROCNO                1

F2 - Acquisition Parameters
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INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                80.35
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                13.00 usec
PLW1        13.00000000 W

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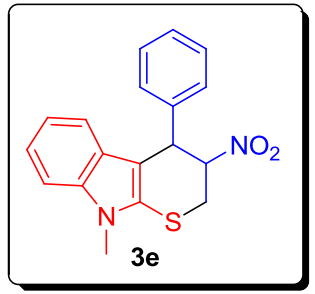



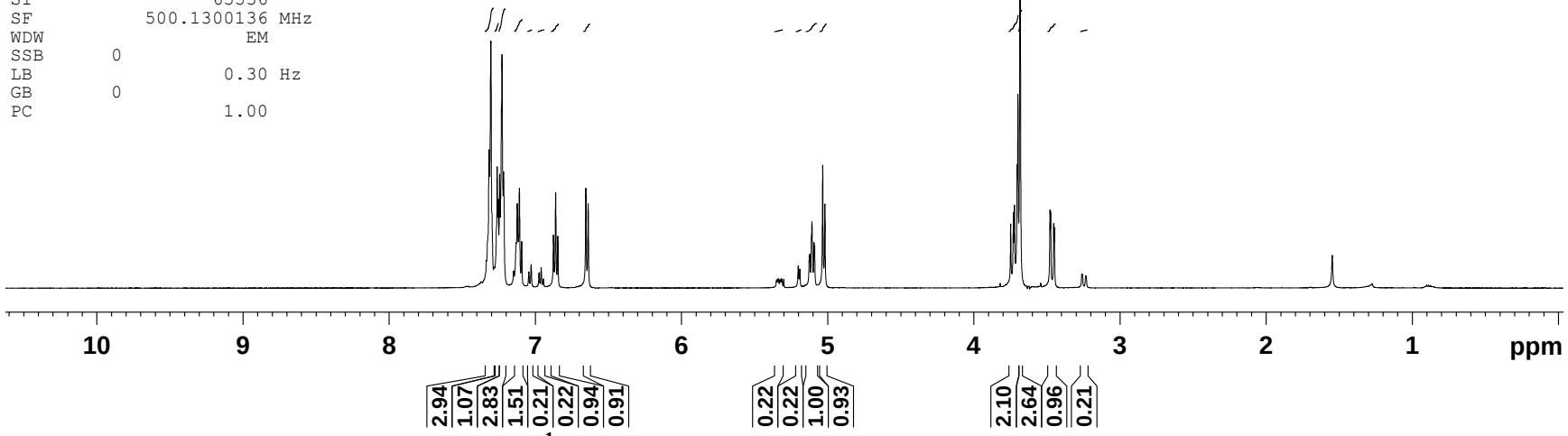


Figure S15. ^{1}H NMR Spectrum of 3e (major + minor, dr 82:18)

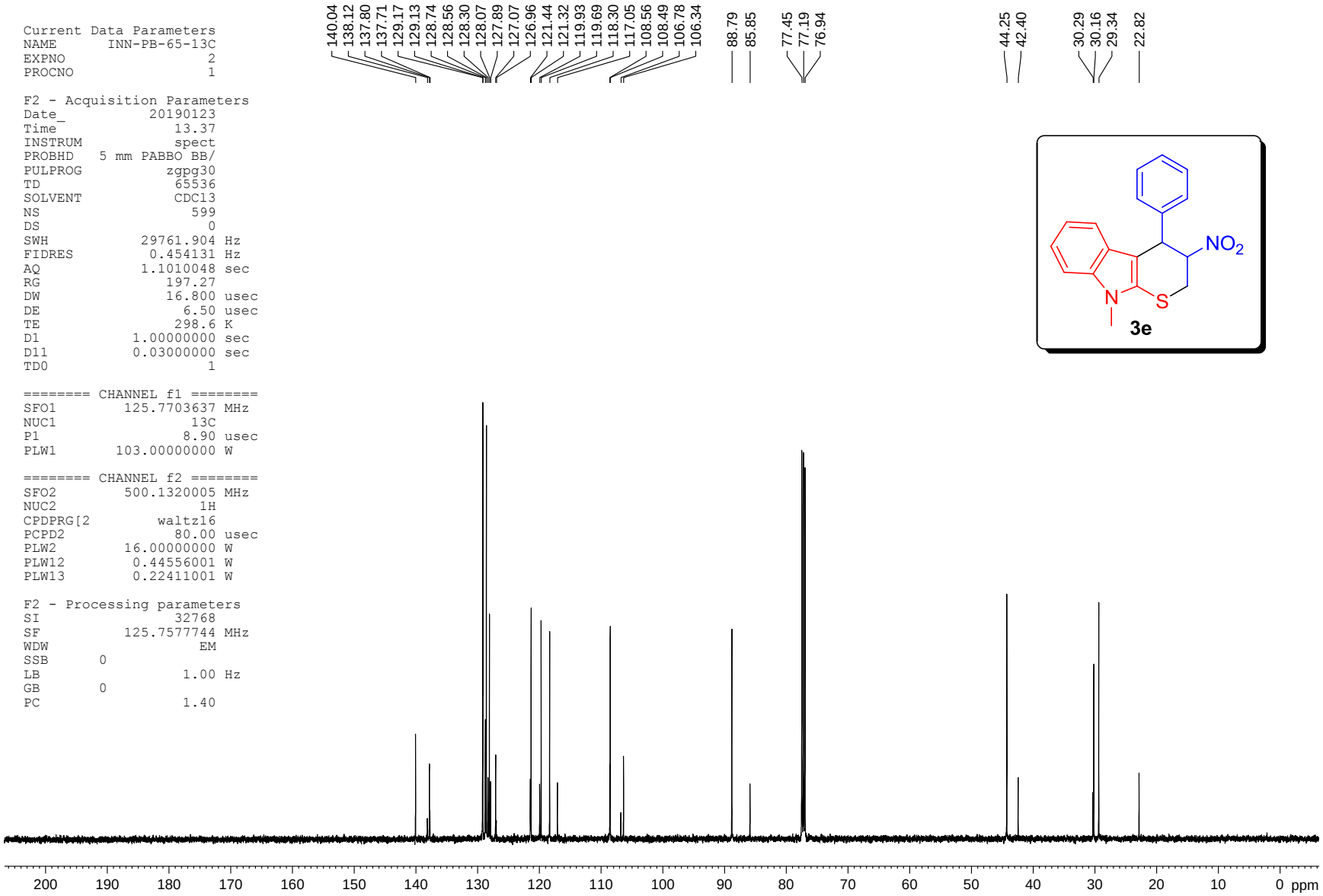


Figure S16. ^{13}C NMR Spectrum of 3e (major + minor, dr 82:18)

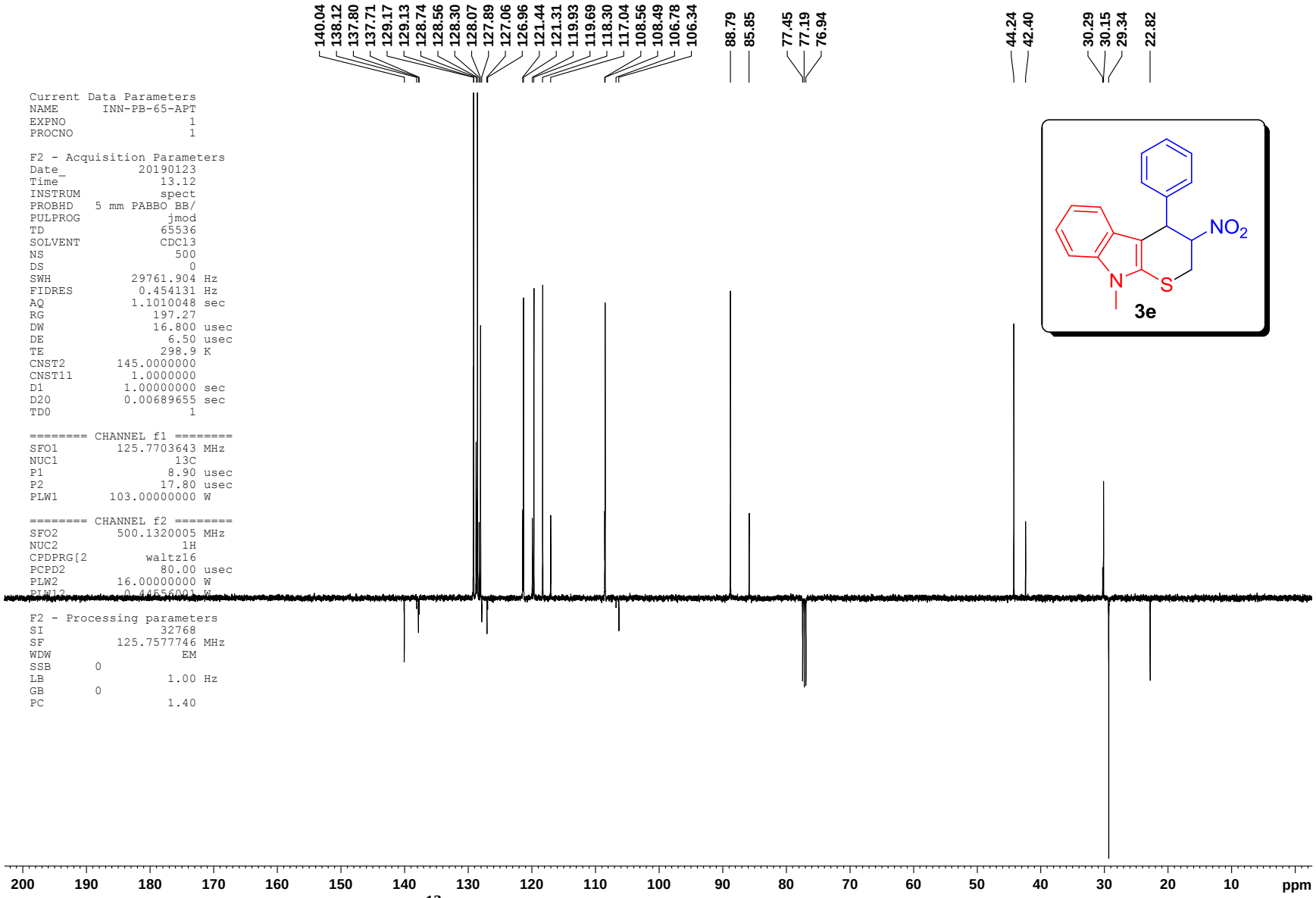


Figure S17. ^{13}C-APT NMR Spectrum of 3e (major + minor, dr 82:18)

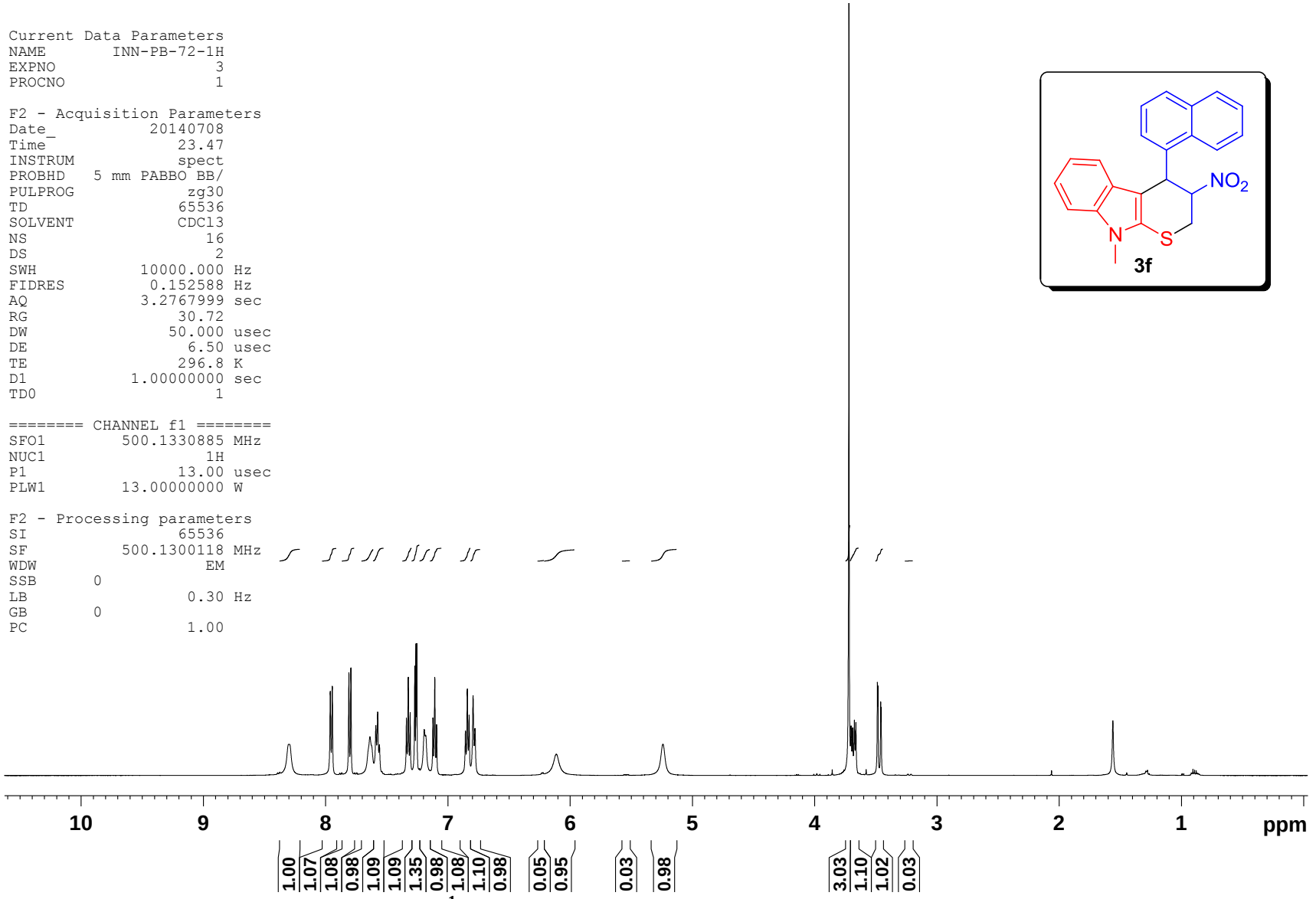
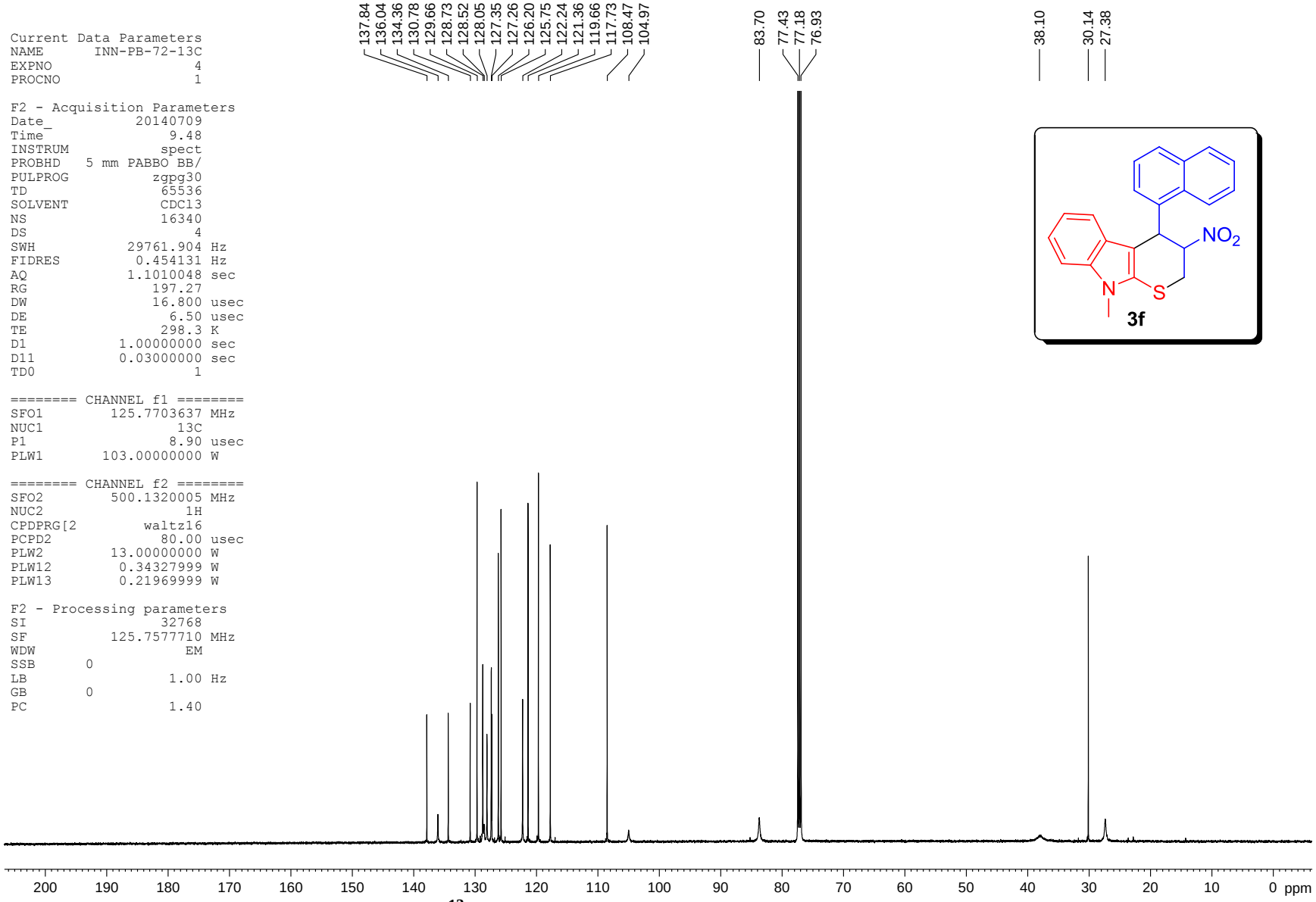


Figure S18. ^{1}H NMR Spectrum of 3f (major + minor, dr >95:05)

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Current Data Parameters
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EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
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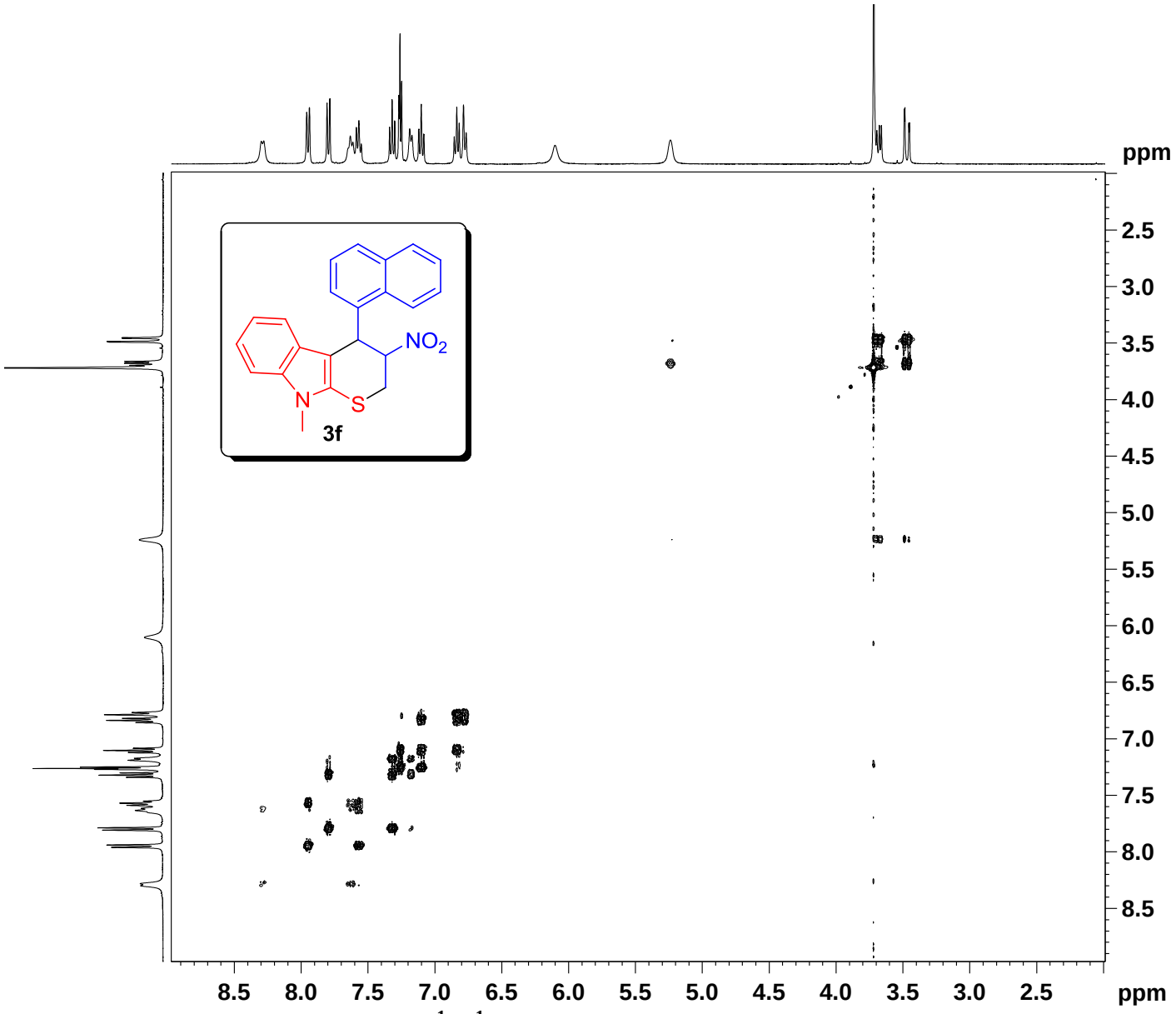
Time               9.48
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                16340
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE               298.3 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         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                32768
SF          125.7577710 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S19. ^{13}C NMR Spectrum of 3f (major + minor, dr >95:05)

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EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20181119
Time                 4.47
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG          cosygpqf
TD                   2048
SOLVENT              CDCl3
NS                     16
DS                      0
SWH              2794.337 Hz
FIDRES           1.364422 Hz
AQ               0.3664555 sec
RG                    1150
DW                178.933 usec
DE                  6.50 usec
TE                297.3 K
D0             0.00000300 sec
D1             1.00000000 sec
D13            0.00000400 sec
D16            0.00020000 sec
IN0            0.00035785 sec

======== CHANNEL f1 ========
NUC1                    1H
P0                  13.50 usec
P1                  13.50 usec
PL1                 -1.00 dB
PL1W         10.56200695 W
SFO1         400.1322023 MHz

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

F1 - Acquisition parameters
TD                     256
SFO1             400.1322 MHz
FIDRES          21.830650 Hz
SW                 6.984 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF           400.1300101 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF           400.1300101 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S20. ^{1}H-^{1}H COSY NMR Spectrum of 3f (major + minor, dr >95:05)

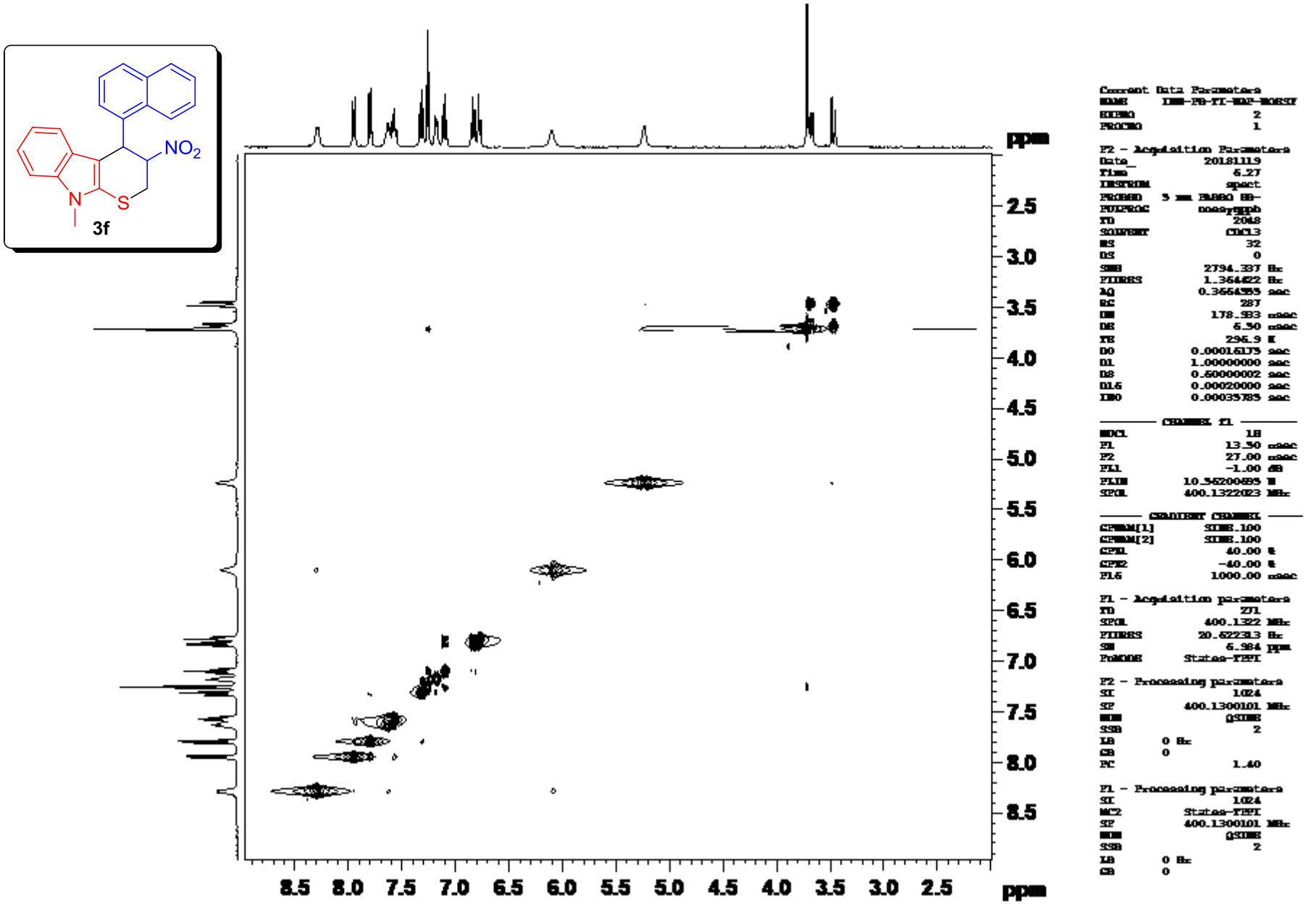


Figure S21. ^{1}H-^{1}H NOESY NMR Spectrum of 3f (major + minor, dr >95:05)

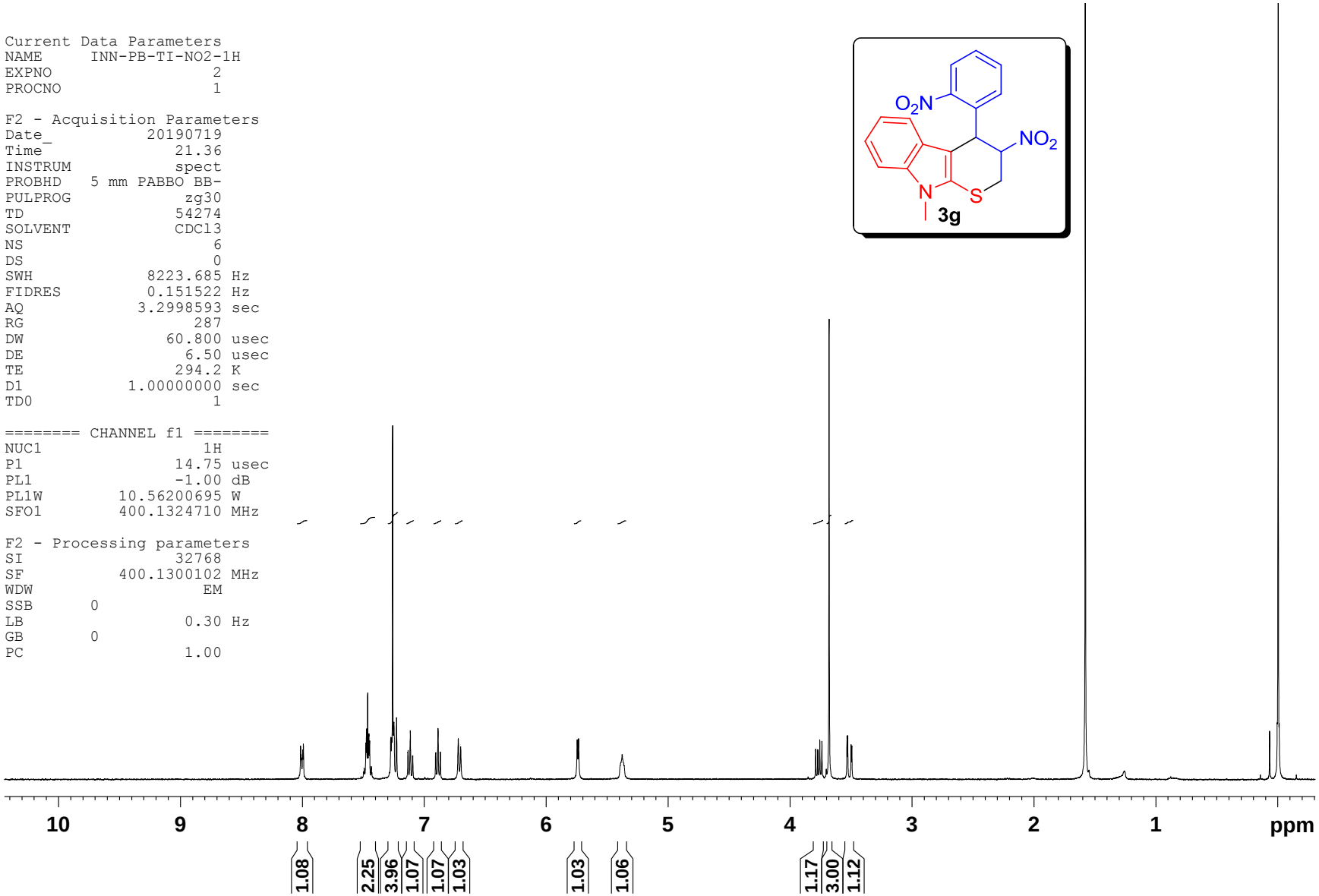
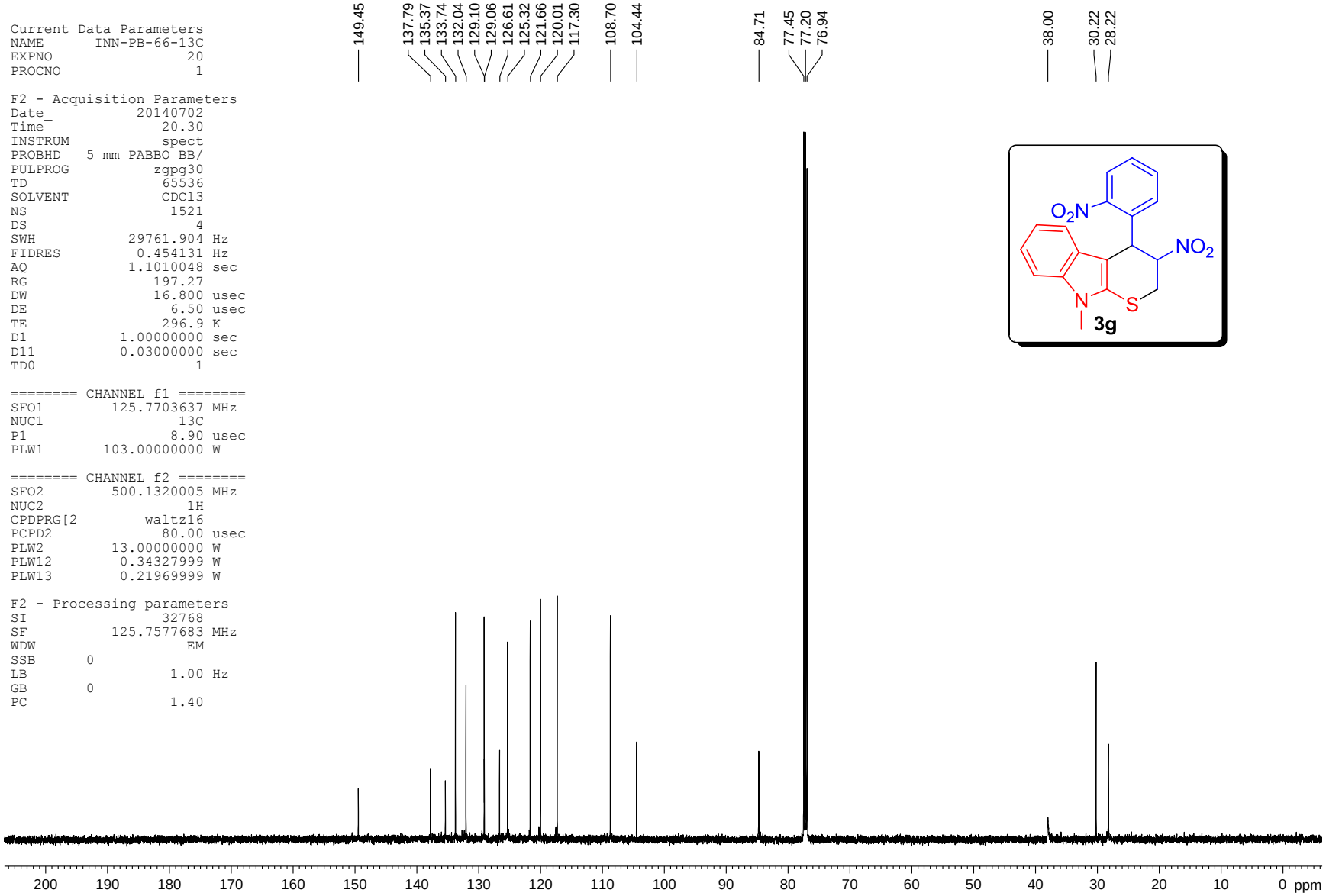


Figure S22. ^{1}H NMR Spectrum of 3g (major + minor, dr >95:05)




```
Current Data Parameters
NAME      INN-PB-66-13C
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20140702
Time              20.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1521
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                197.27
DW                16.800 usec
DE                 6.50 usec
TE                296.9 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         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                 32768
SF           125.7577683 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S23. ^{13}C NMR Spectrum of 3g (major + minor, dr >95:05)

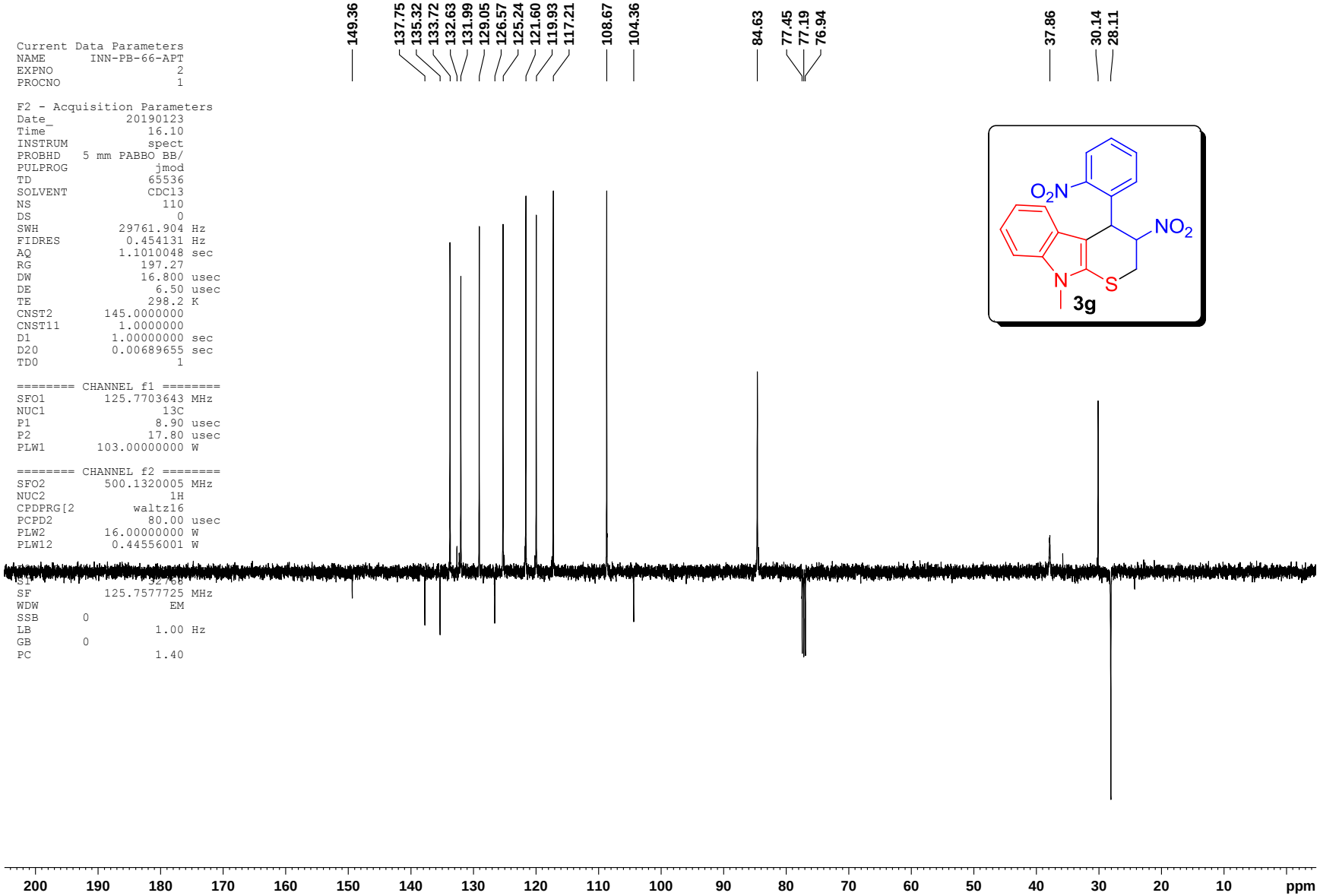


Figure S24. ^{13}C-APT NMR Spectrum of 3g (major + minor, dr >95:05)

```
Current Data Parameters
NAME       INN-CH-66-1H
EXPNO                 9
PROCNO                1

F2 - Acquisition Parameters
Date_           20140410
Time              17.59
INSTRUM           spect
PROBHD   5 mm SEI 1H/D-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9845889 sec
RG                   32
DW               60.800 usec
DE                6.50 usec
TE                297.0 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          400.1300095 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

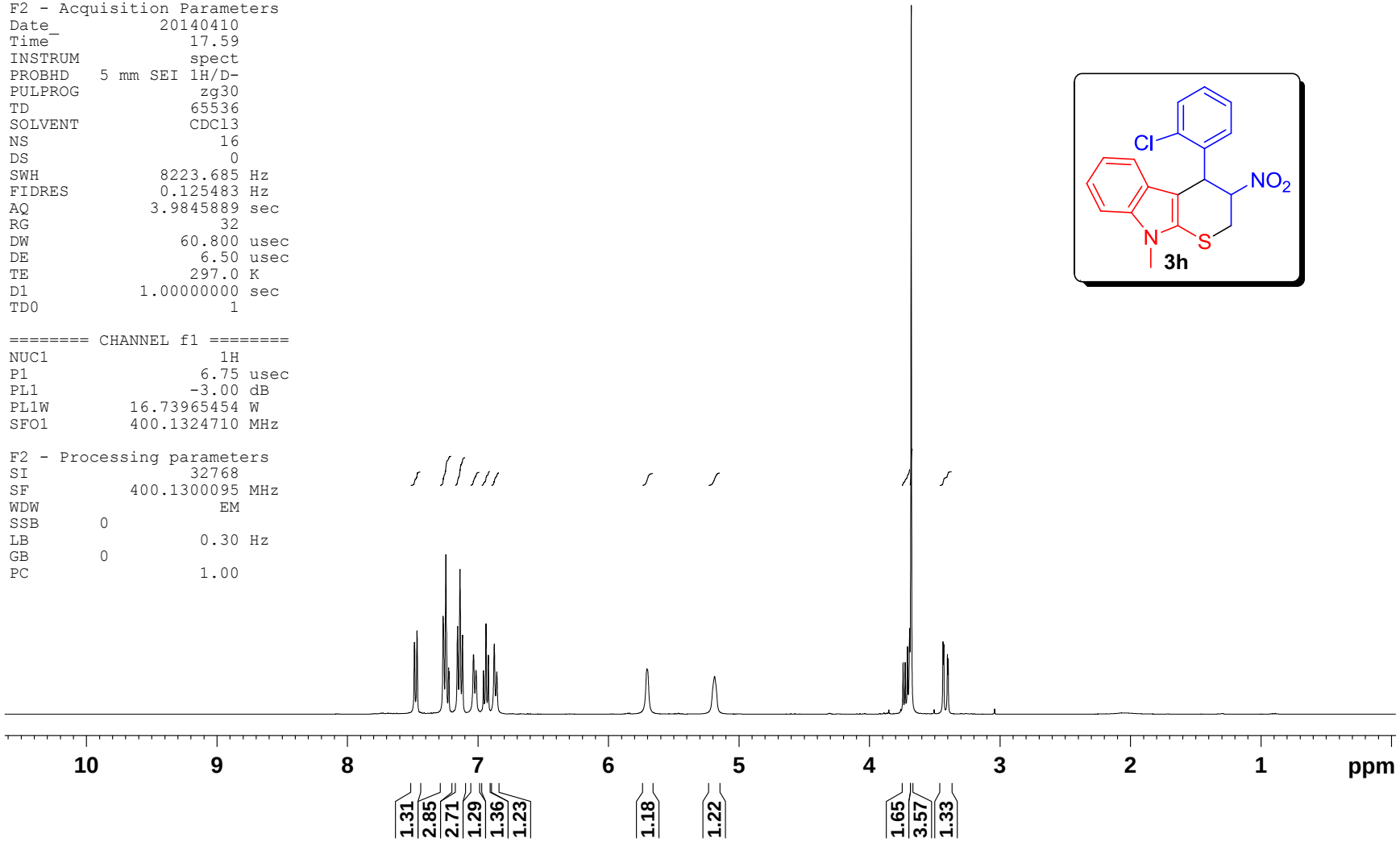
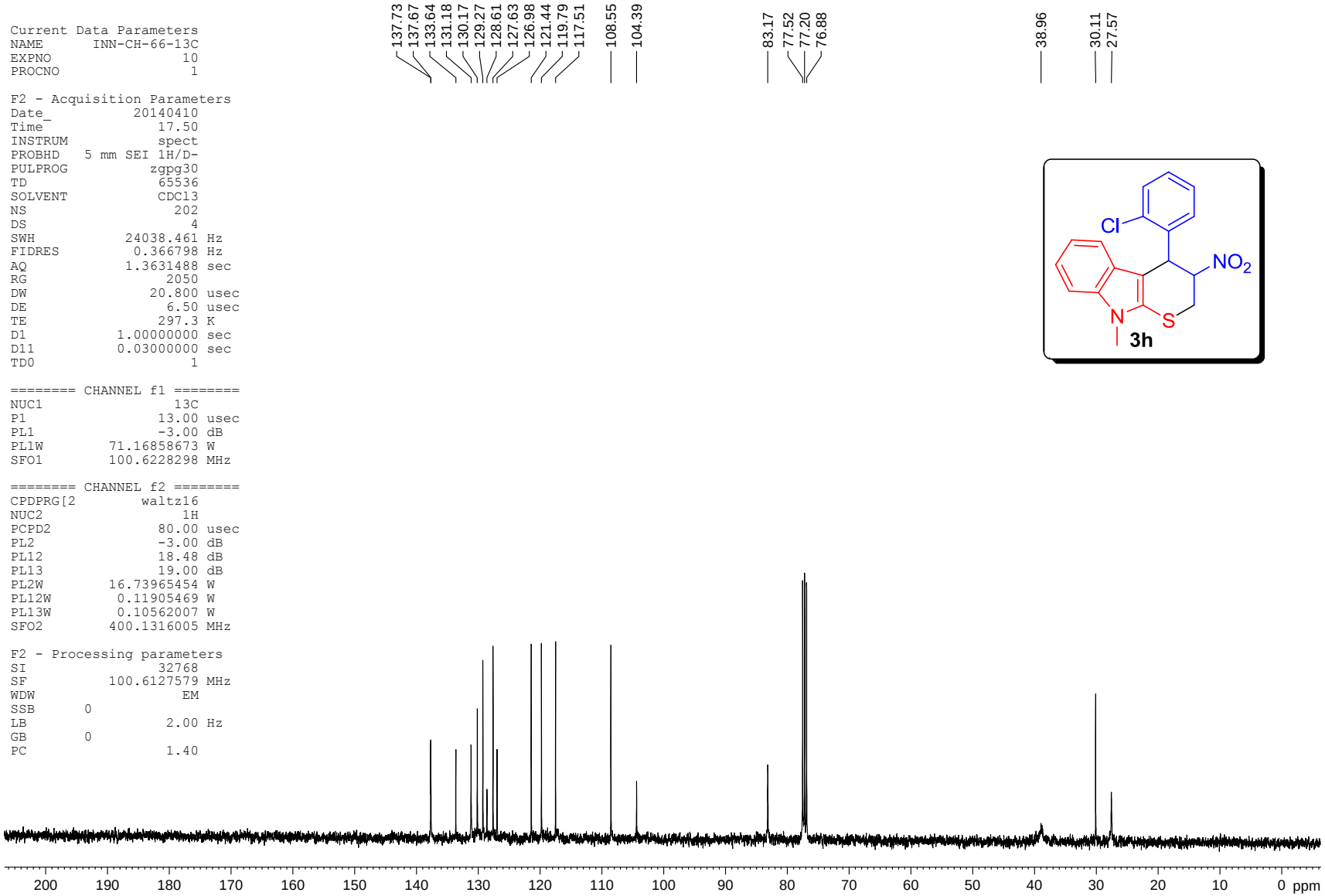


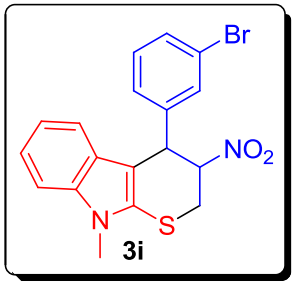
Figure S25. ^{1}H NMR Spectrum of 3h (major + minor, dr >95:05)




```
Current Data Parameters
NAME      INN-CH-66-13C
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20140410
Time              17.50
INSTRUM           spect
PROBHD   5 mm SEI 1H/D-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  202
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               297.3 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                13.00 usec
PL1               -3.00 dB
PL1W        71.16858673 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              18.48 dB
PL13              19.00 dB
PL2W        16.73965454 W
PL12W        0.11905469 W
PL13W        0.10562007 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127579 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```

Figure S26. ^{13}C NMR Spectrum of 3h (major + minor, dr >95:05)

```
Current Data Parameters
NAME      INN-PB-TI-5-BR-1H
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20190130
Time              13.14
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
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                297.6 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           500.1300111 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



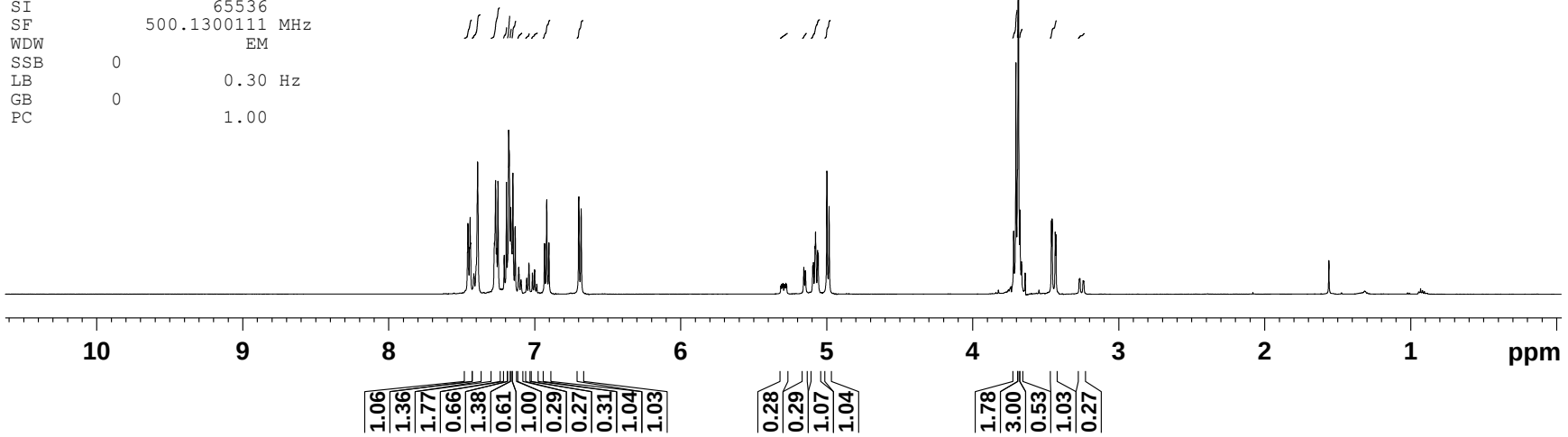


Figure S27. 1H NMR Spectrum of 3i (major + minor, dr 81:19)

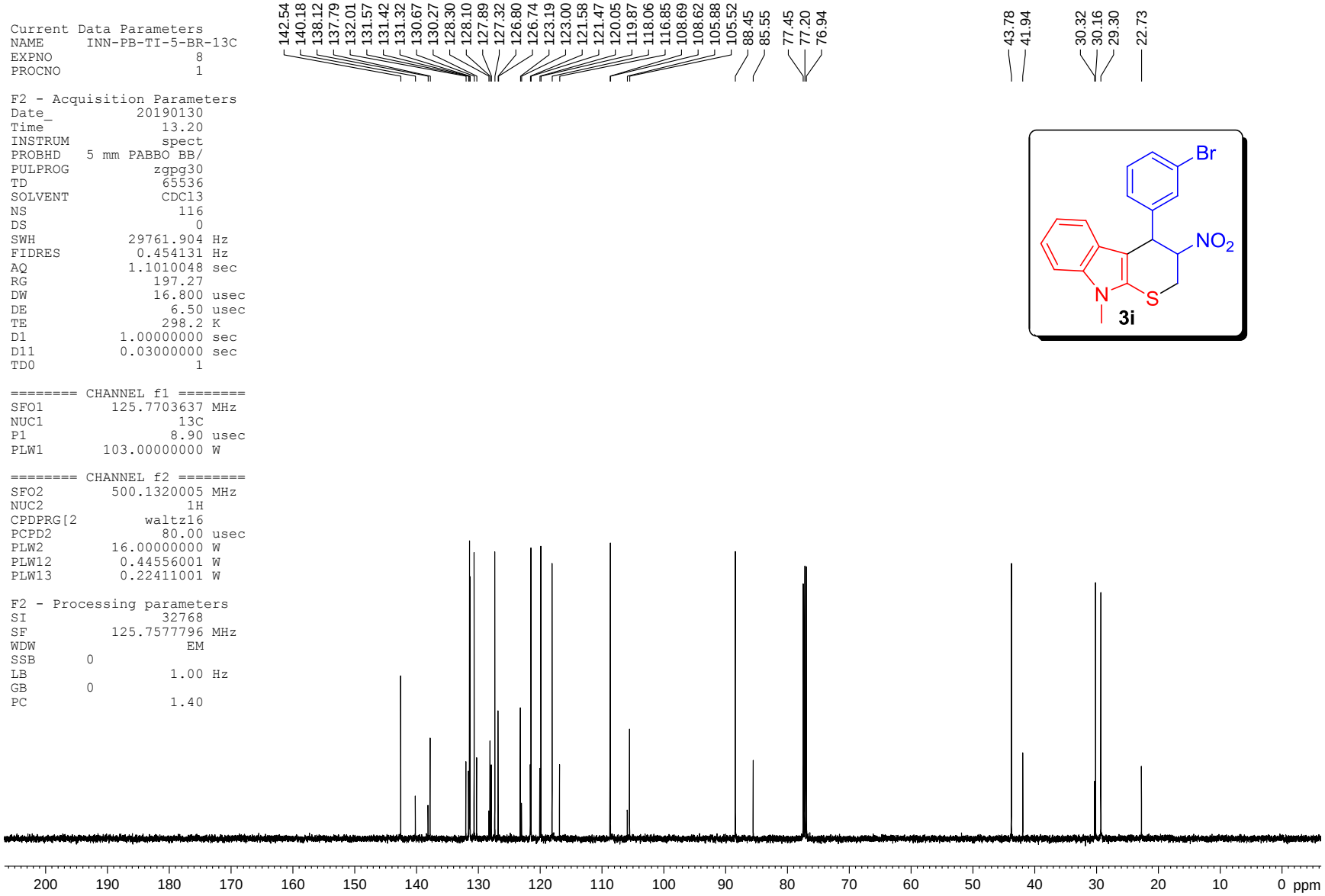


Figure S28. ^{13}C NMR Spectrum of 3i (major + minor, dr 81:19)

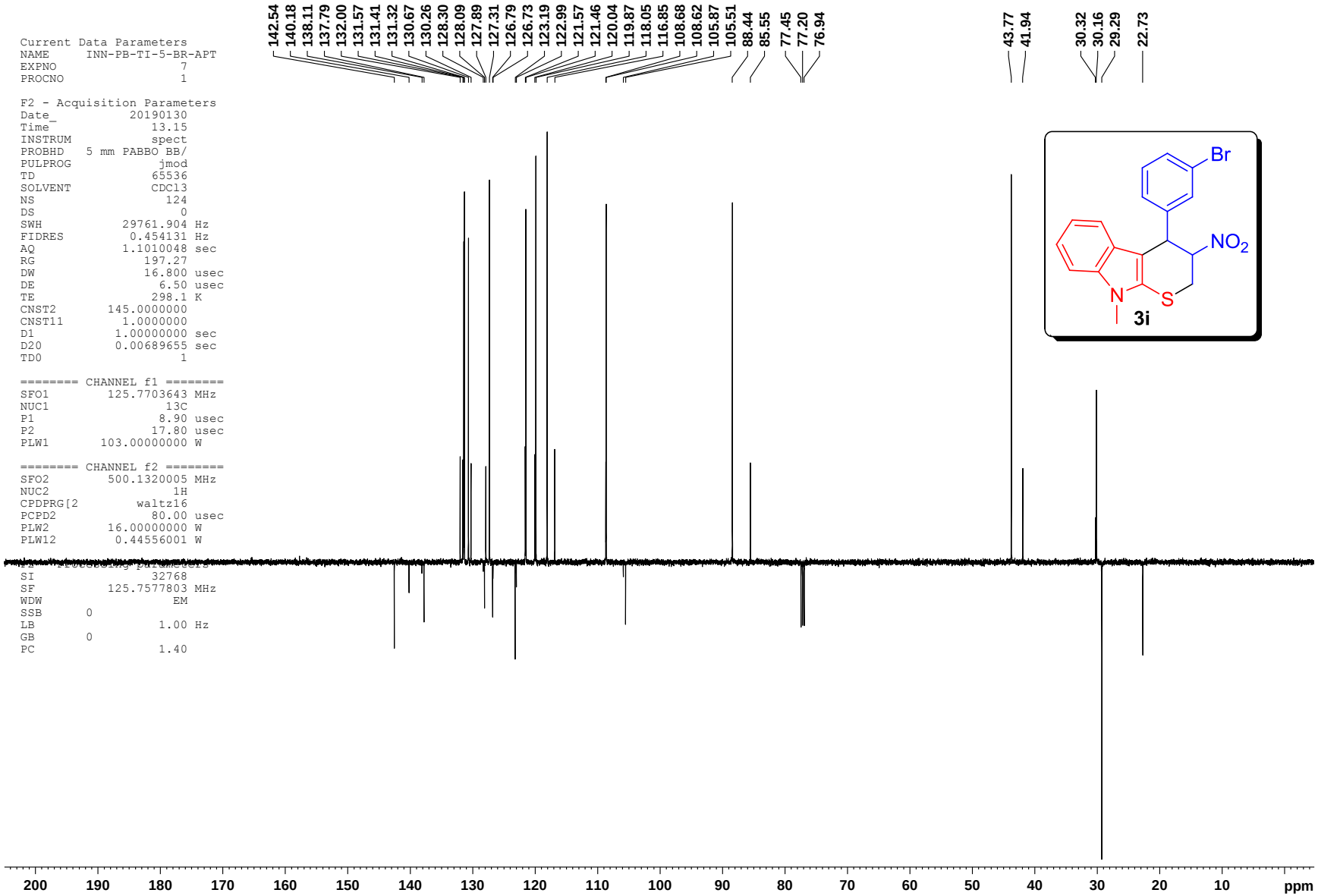


Figure S29. ^{13}C-APT NMR Spectrum of 3i (major + minor, dr 81:19)

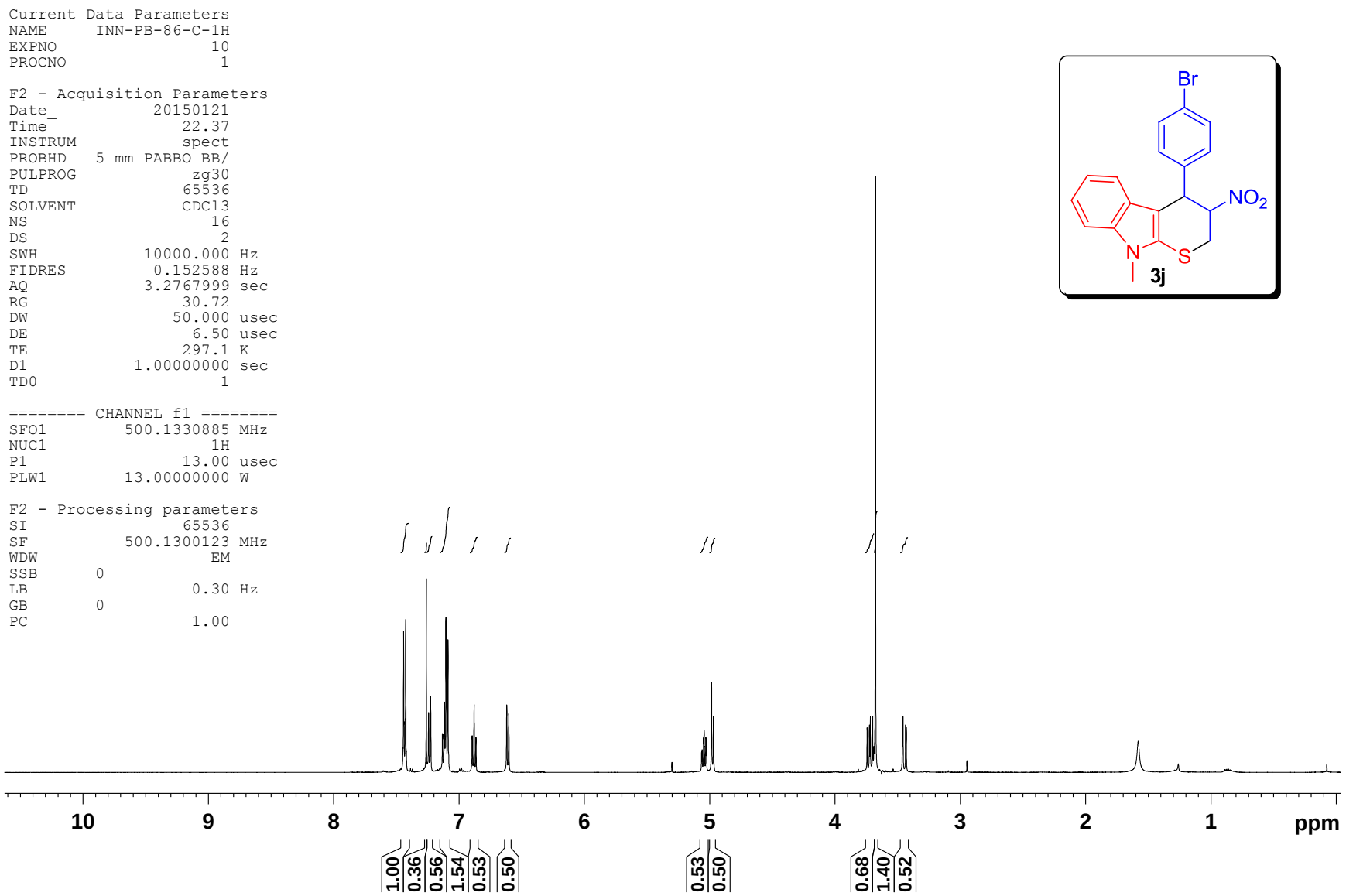


Figure S30. ^{1}H NMR Spectrum of 3j (Major isomer)

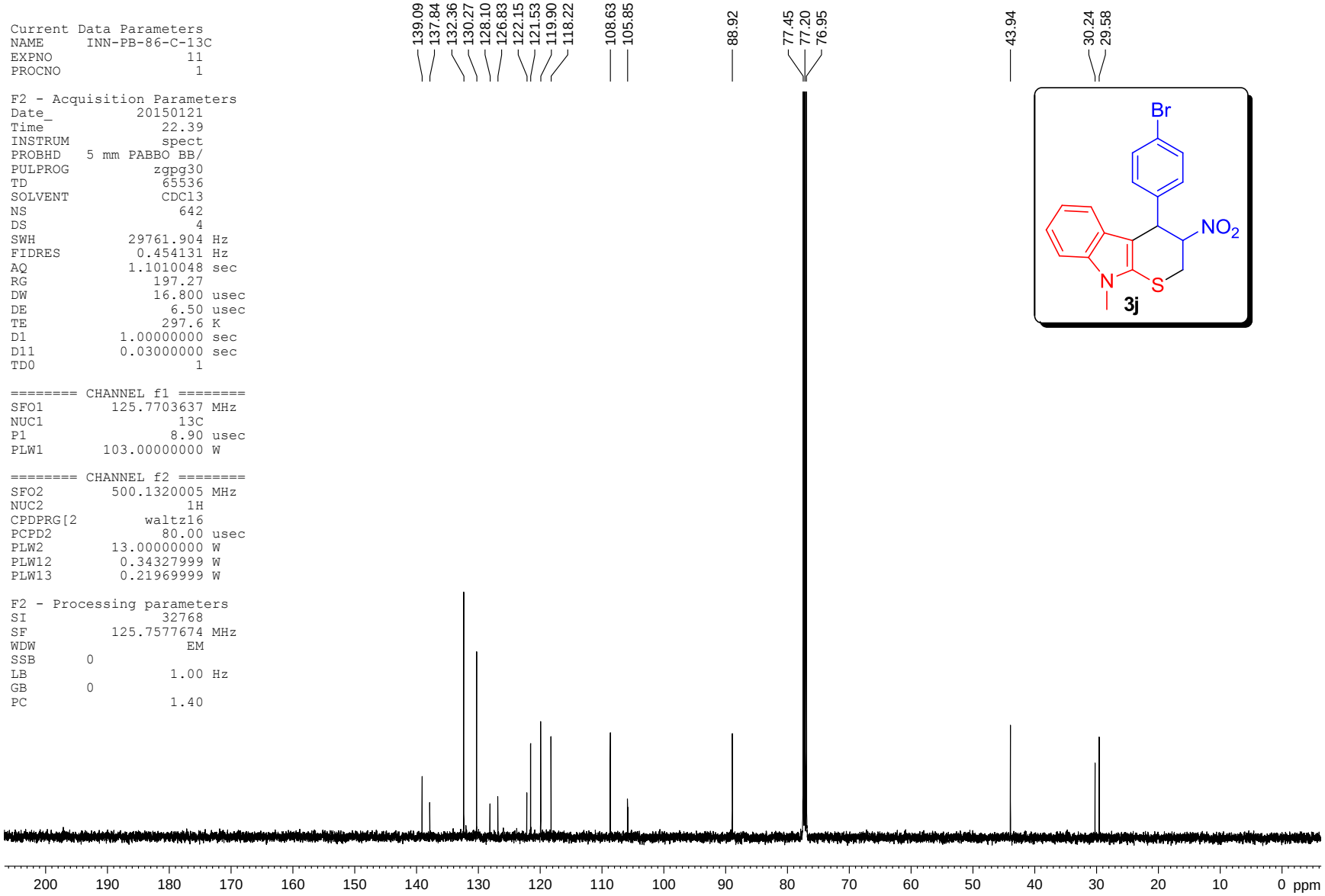
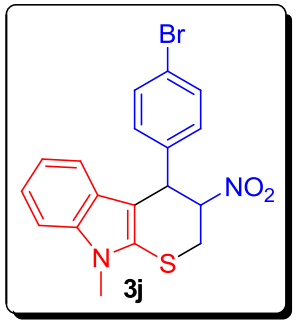


Figure S31. ^{13}C NMR Spectrum of 3j (Major isomer)

```
Current Data Parameters
NAME      INN-PB-TI-4-BR-1H
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170327
Time               0.10
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                119.07
DW                50.000 usec
DE                 6.50 usec
TE                298.6 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           500.1300130 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



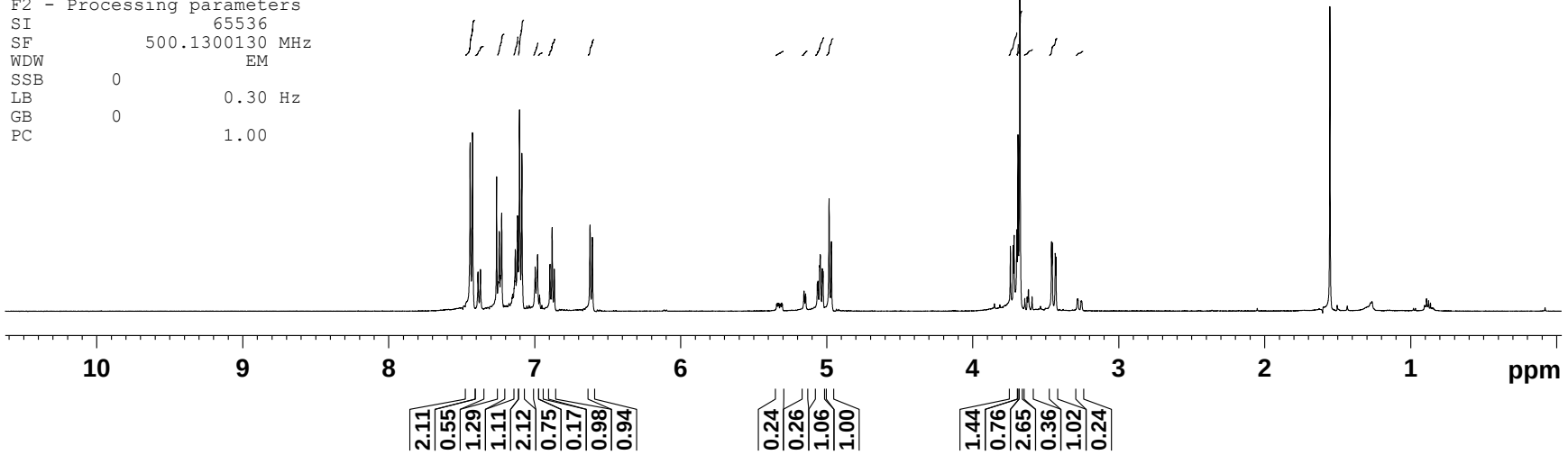


Figure S32. ^{1}H NMR Spectrum of 3j (major + minor, dr 87:13)

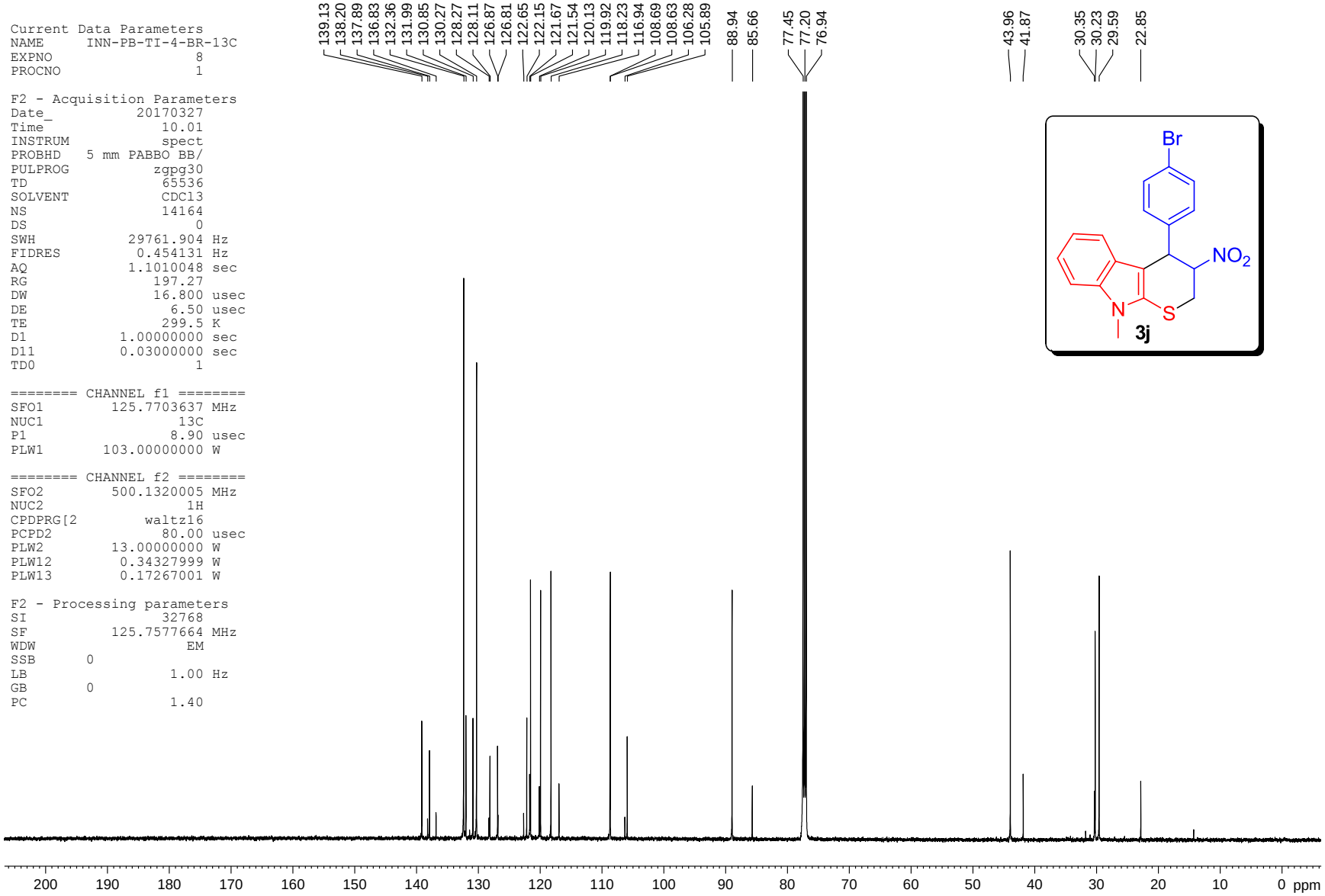


Figure S33. ^{13}C NMR Spectrum of 3j (major + minor, dr 87:13)

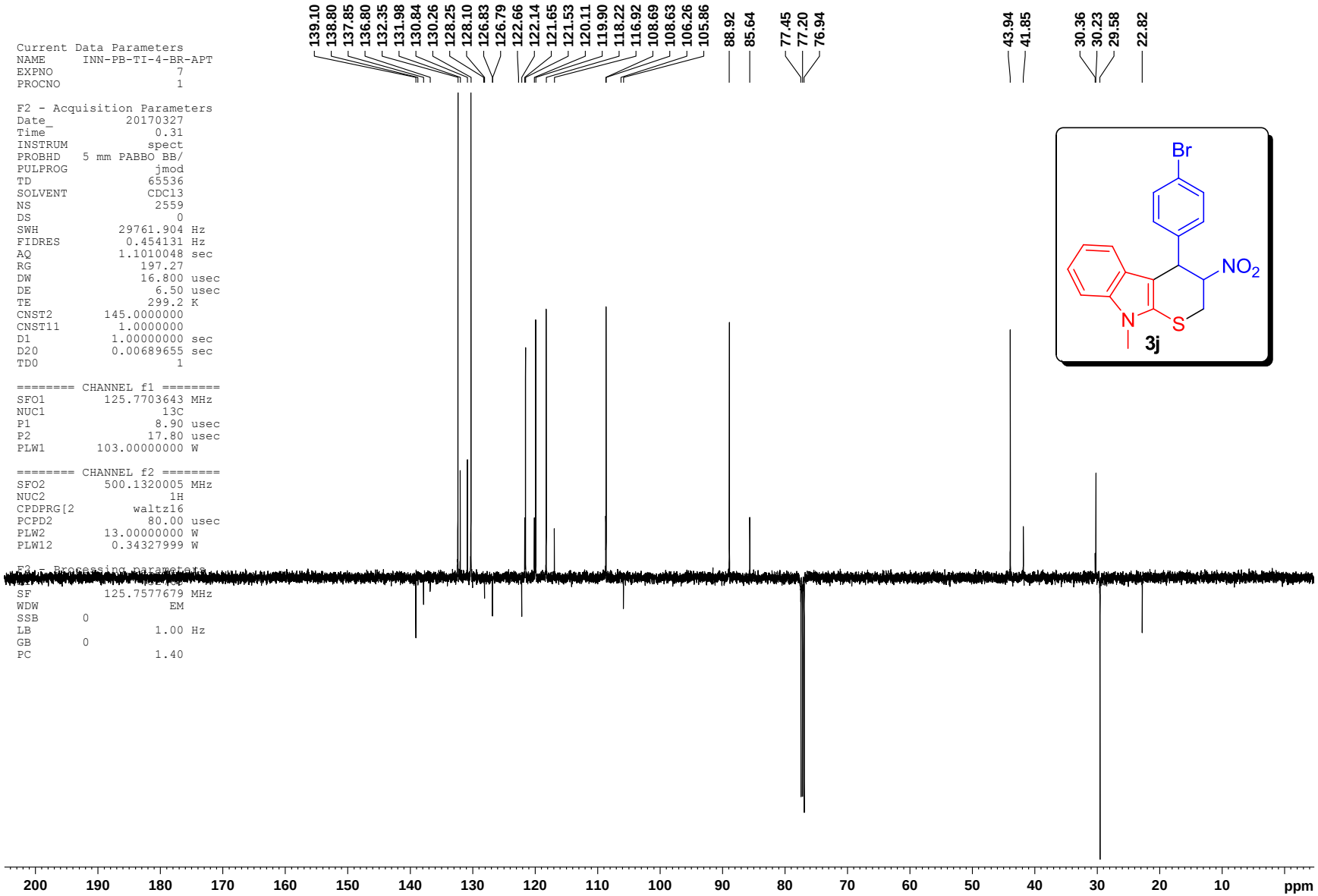
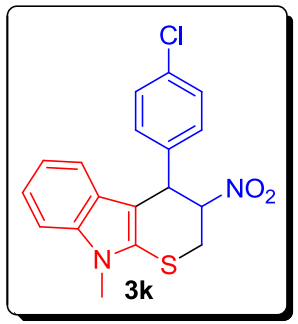


Figure S34. ^{13}C-APT NMR Spectrum of 3j (major + minor, dr 87:13)

```
Current Data Parameters
NAME      INN-PB-P-CL-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190125
Time              13.15
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
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               298.0 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
```



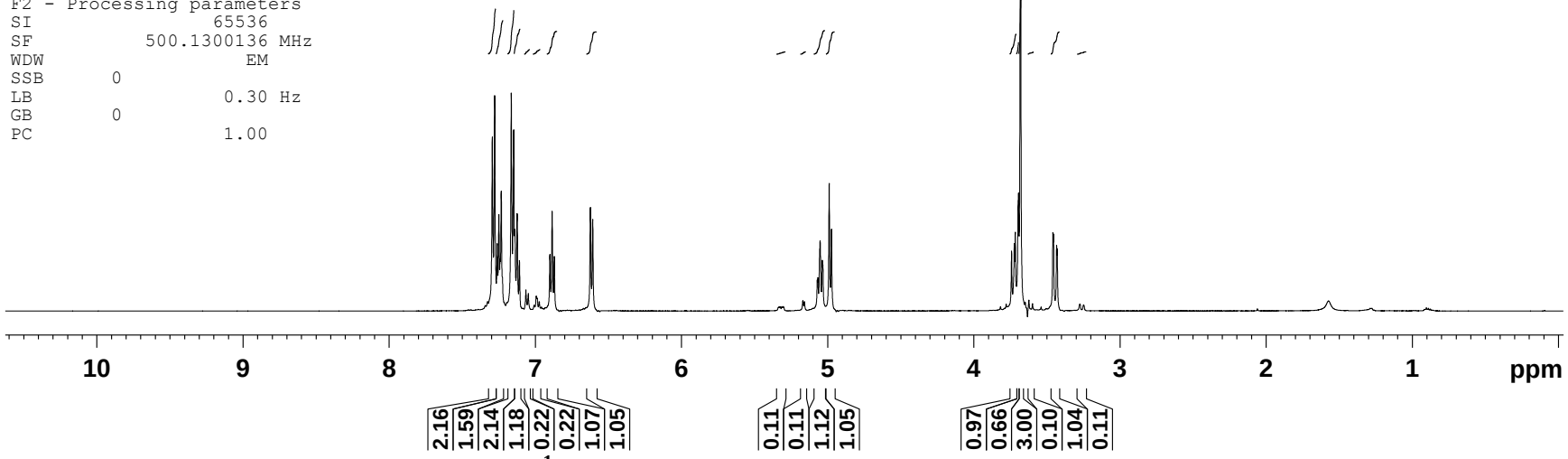
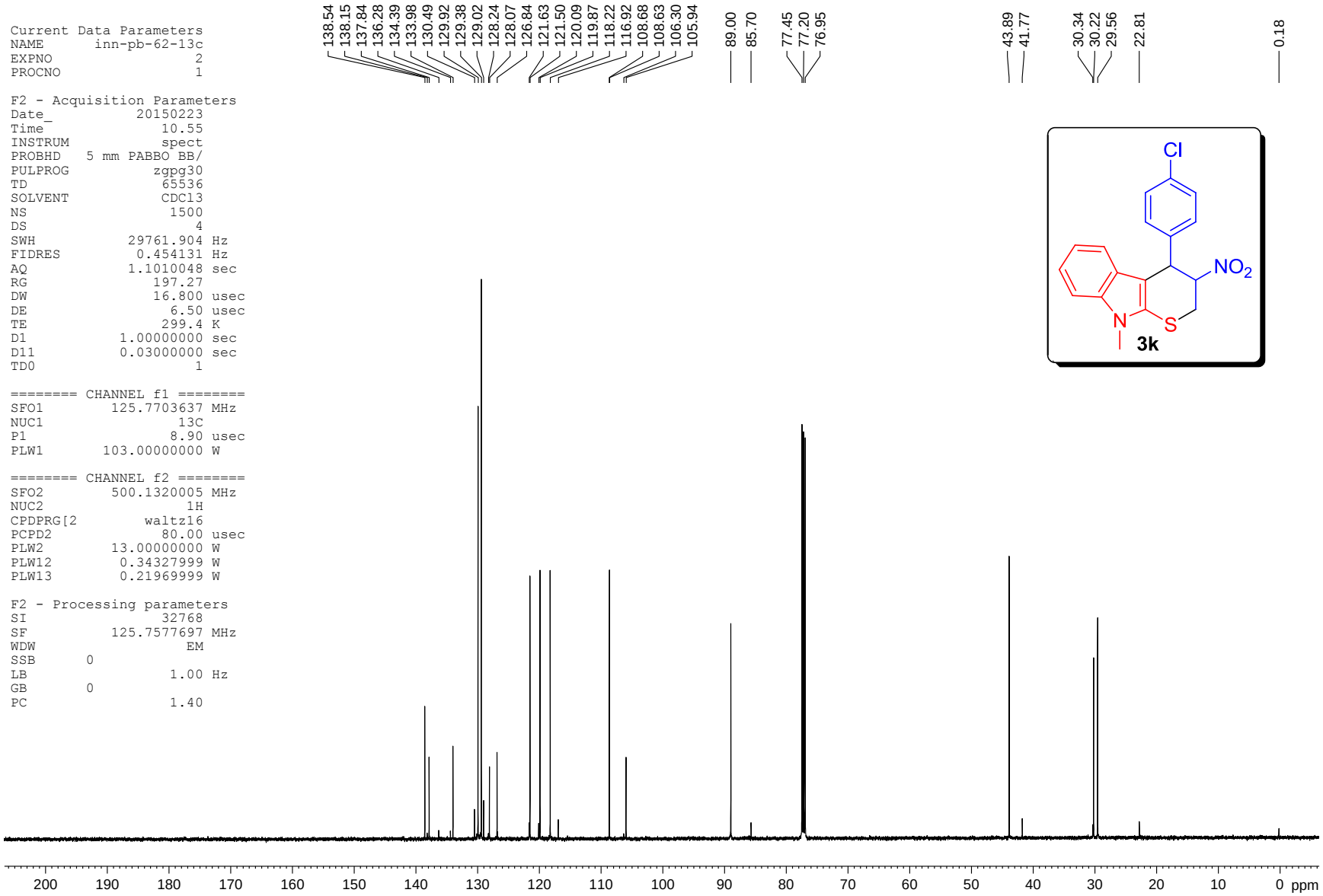


Figure S35. ^{1}H NMR Spectrum of 3k (major + minor, dr 90:10)




```
Current Data Parameters
NAME      inn-pb-62-13c
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150223
Time              10.55
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1500
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE               299.4 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         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                 32768
SF           125.7577697 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S36. ^{13}C NMR Spectrum of 3k (major + minor, dr 90:10)

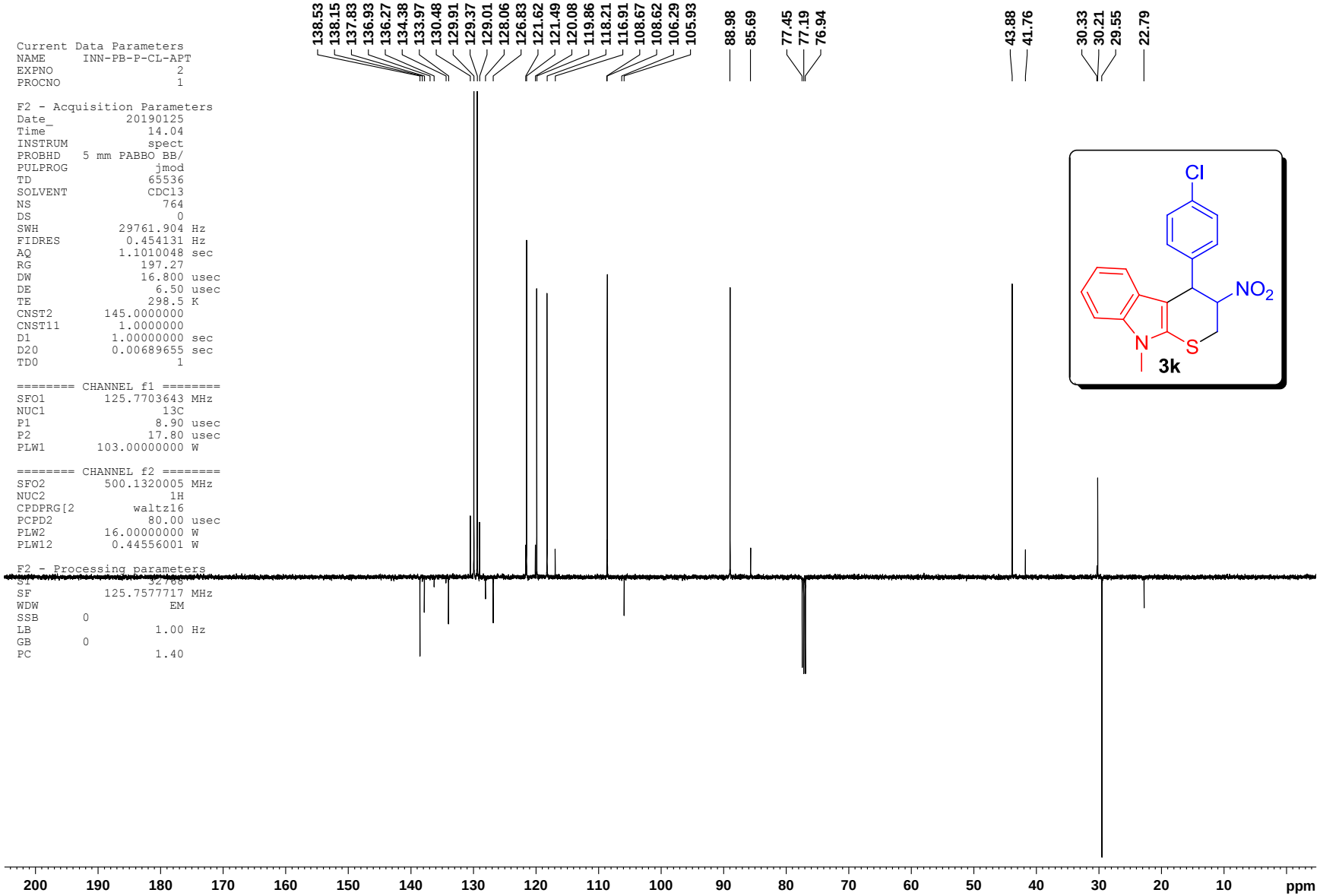


Figure S37. ^{13}C-APT NMR Spectrum of 3k (major + minor, dr 90:10)

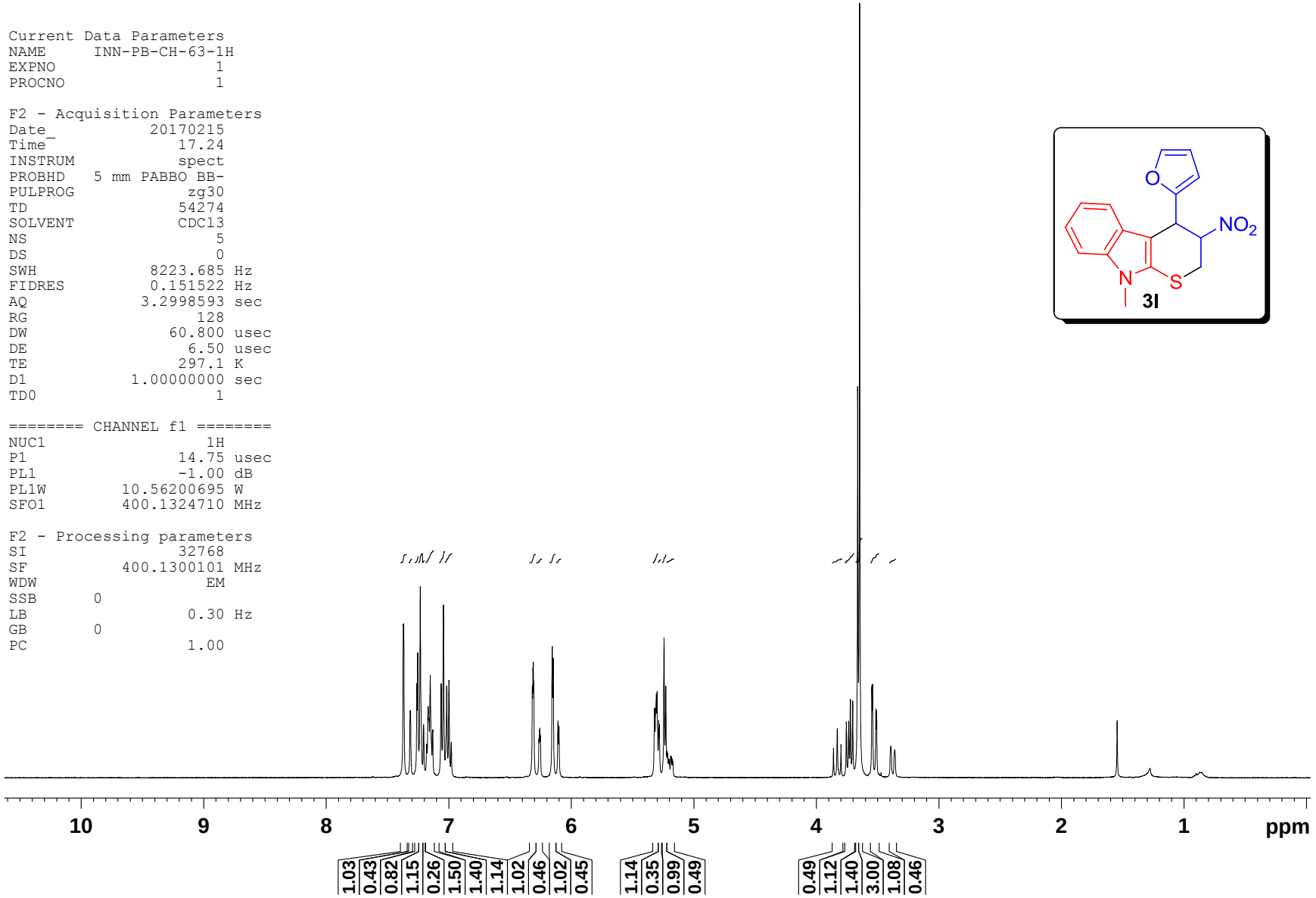


Figure S38. ^{1}H NMR Spectrum of 3l (major + minor, dr 70:30)

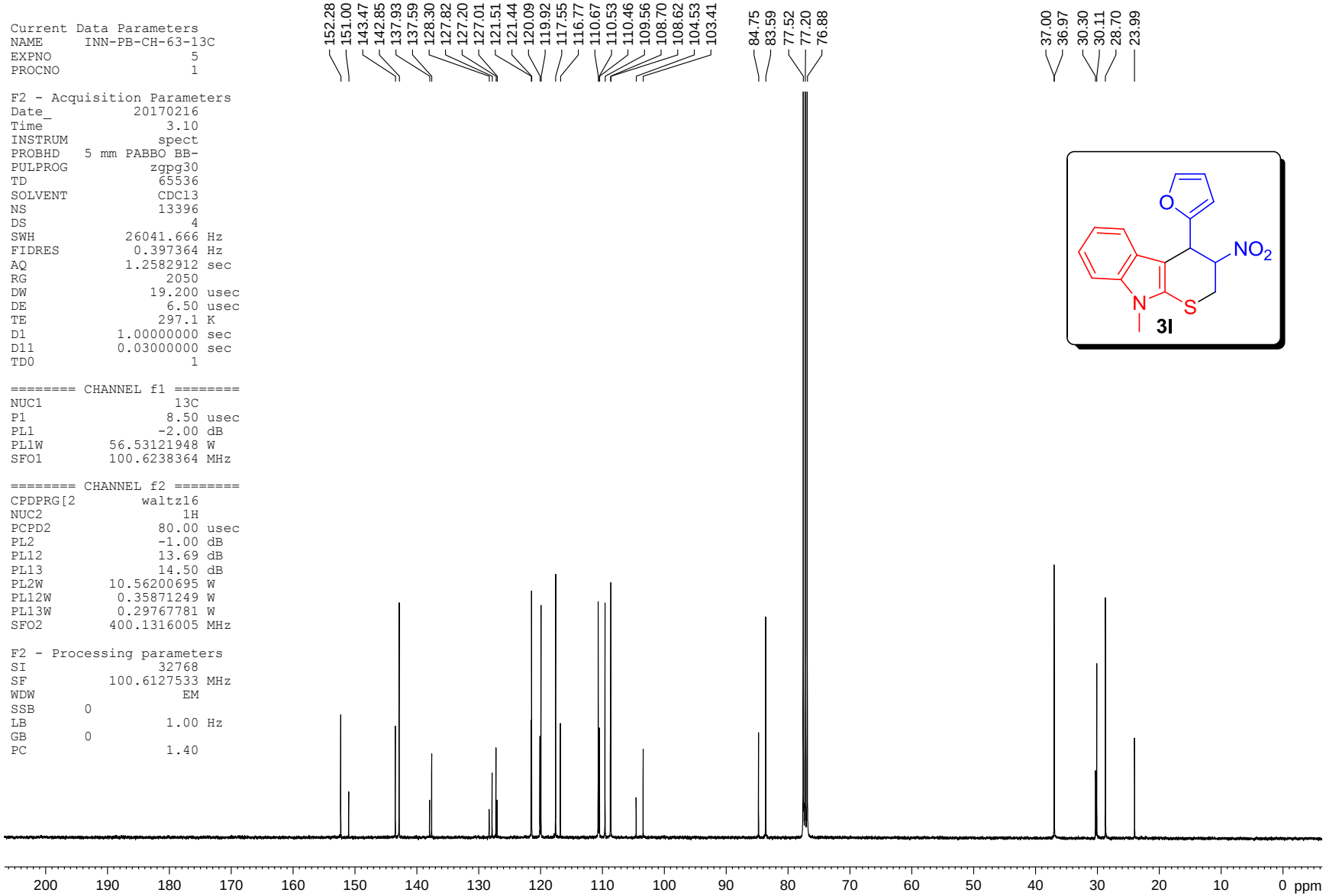


Figure S39. ^{13}C NMR Spectrum of 3l (major + minor, dr 70:30)

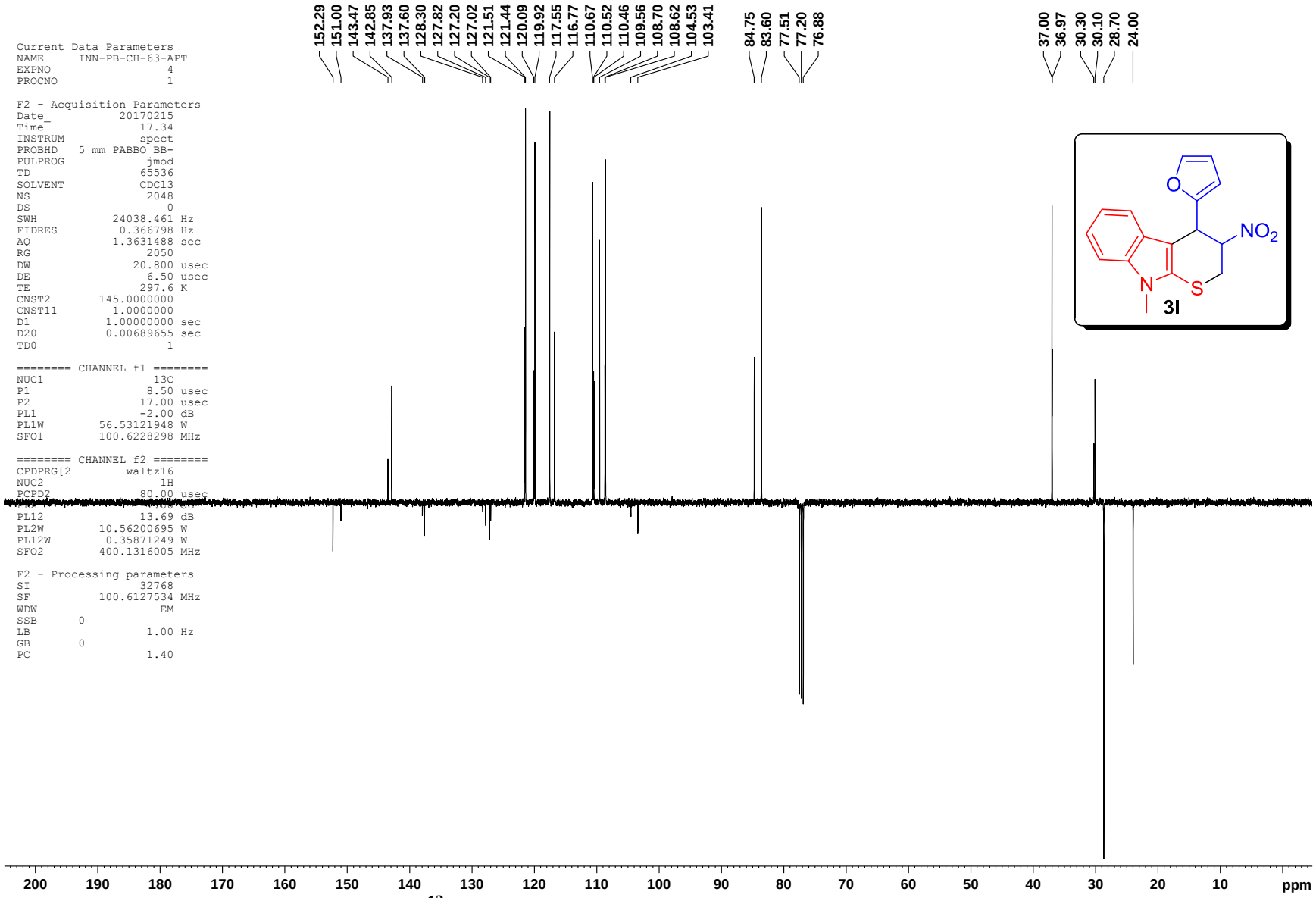
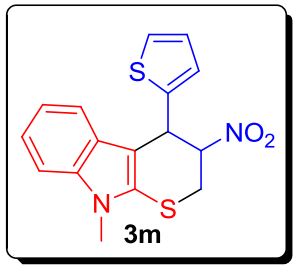


Figure S40. ^{13}C-APT NMR Spectrum of 3l (major + minor, dr 70:30)

```
Current Data Parameters
NAME      INN-PB-CH-62-1H
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170129
Time              20.51
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
DS                    2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG               119.07
DW               50.000 usec
DE                6.50 usec
TE                296.9 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          500.1300136 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



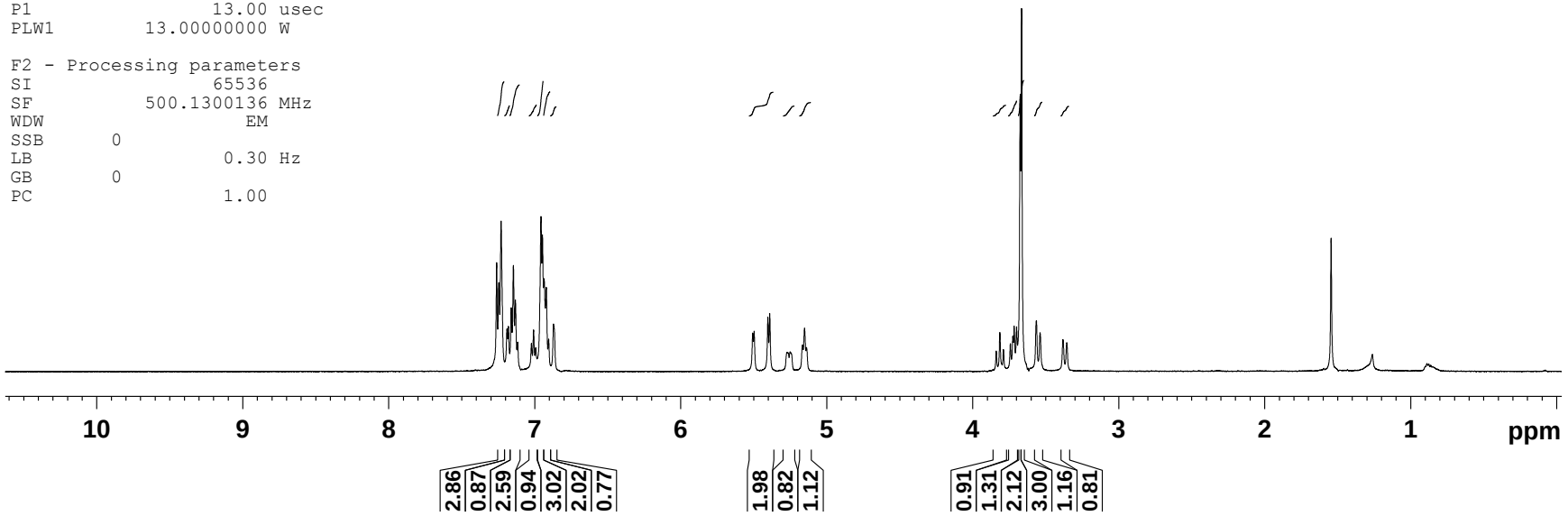
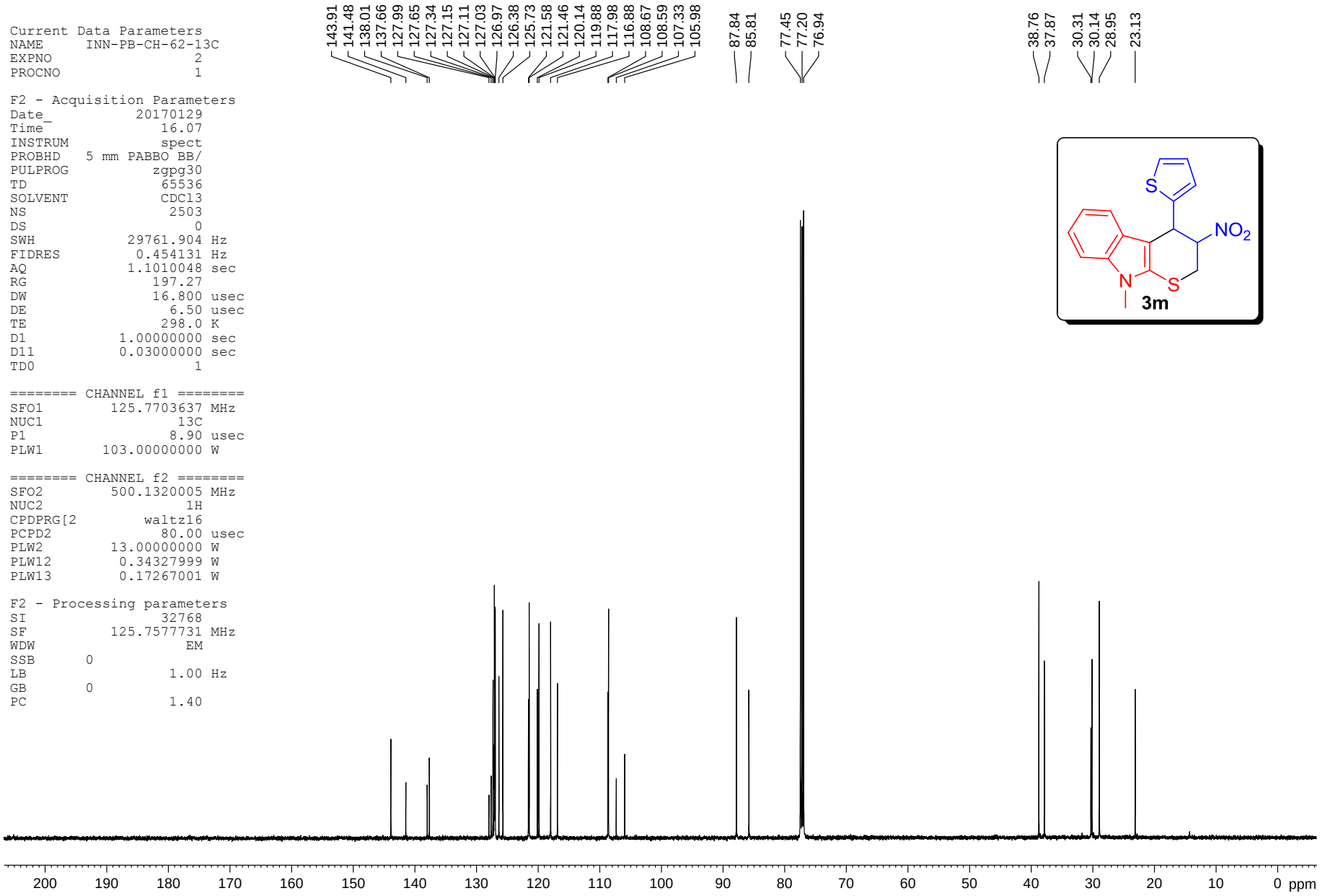
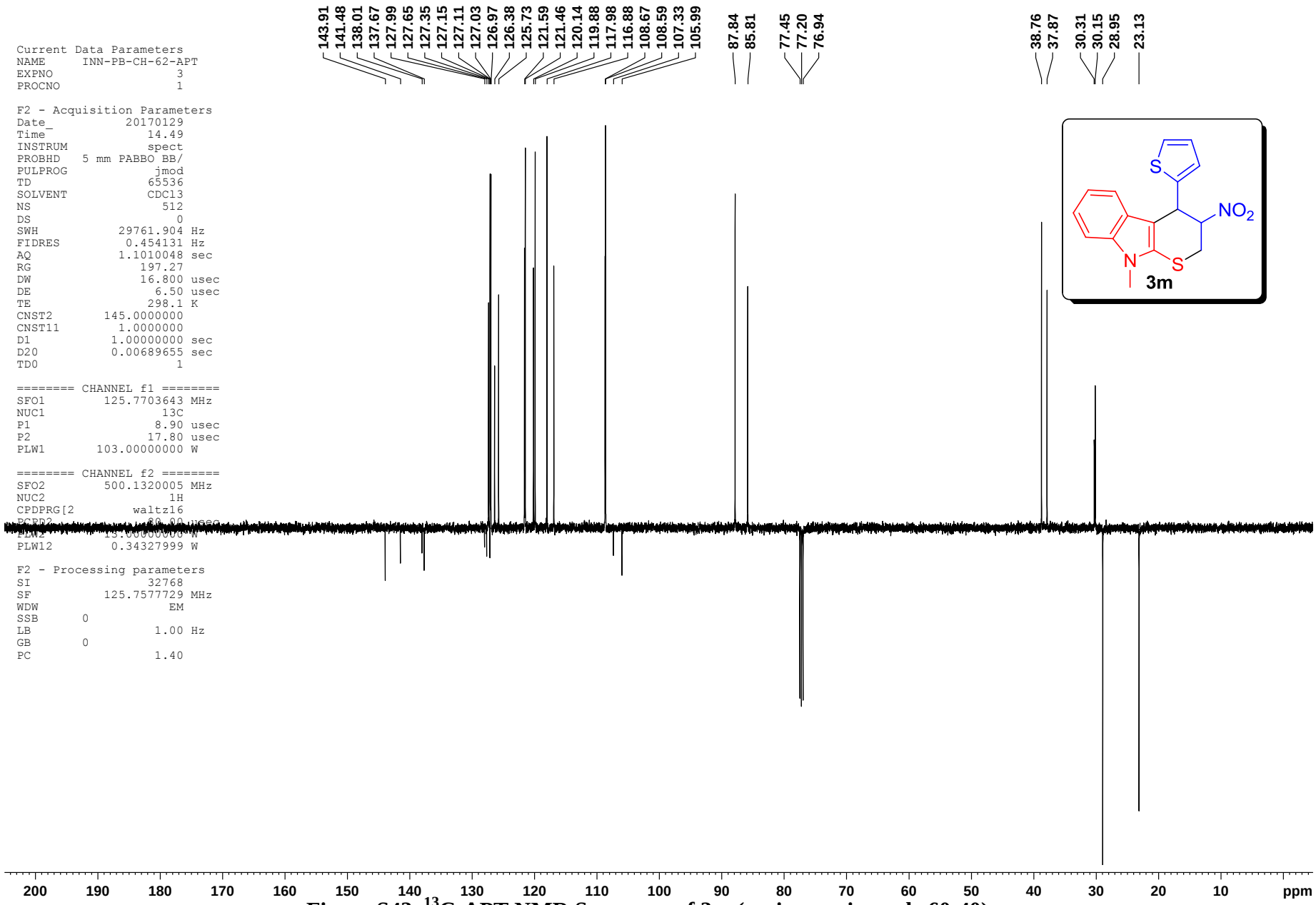


Figure S41. ^{1}H NMR Spectrum of 3m (major + minor, dr 60:40)




```
Current Data Parameters
NAME      INN-PB-CH-62-13C
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20170129
Time               16.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2503
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE               298.0 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        13.00000000 W
PLW12        0.34327999 W
PLW13        0.17267001 W

F2 - Processing parameters
SI                 32768
SF          125.7577731 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

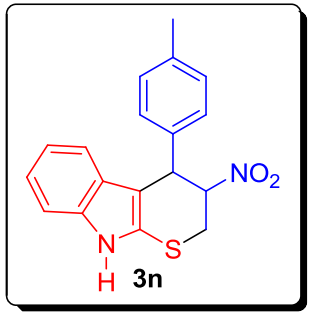
Figure S42. ^{13}C NMR Spectrum of 3m (major + minor, dr 60:40)




```
Current Data Parameters
NAME      INN-PB-CH-62-APT
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170129
Time               14.49
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                 197.27
DW                 16.800 usec
DE                   6.50 usec
TE                  298.1 K
CNST2          145.0000000
CNST11           1.0000000
D1             1.00000000 sec
D20            0.00689655 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703643 MHz
NUC1                  13C
P1                   8.90 usec
P2                  17.80 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           13.0000000 W
PLW12          0.34327999 W

F2 - Processing parameters
SI                  32768
SF           125.7577729 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Figure S43. ^{13}C-APT NMR Spectrum of 3m (major + minor, dr 60:40)

```
Current Data Parameters
NAME       INN-PB-74-1H
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_           20170220
Time              17.34
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                 90.5
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          400.1300094 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



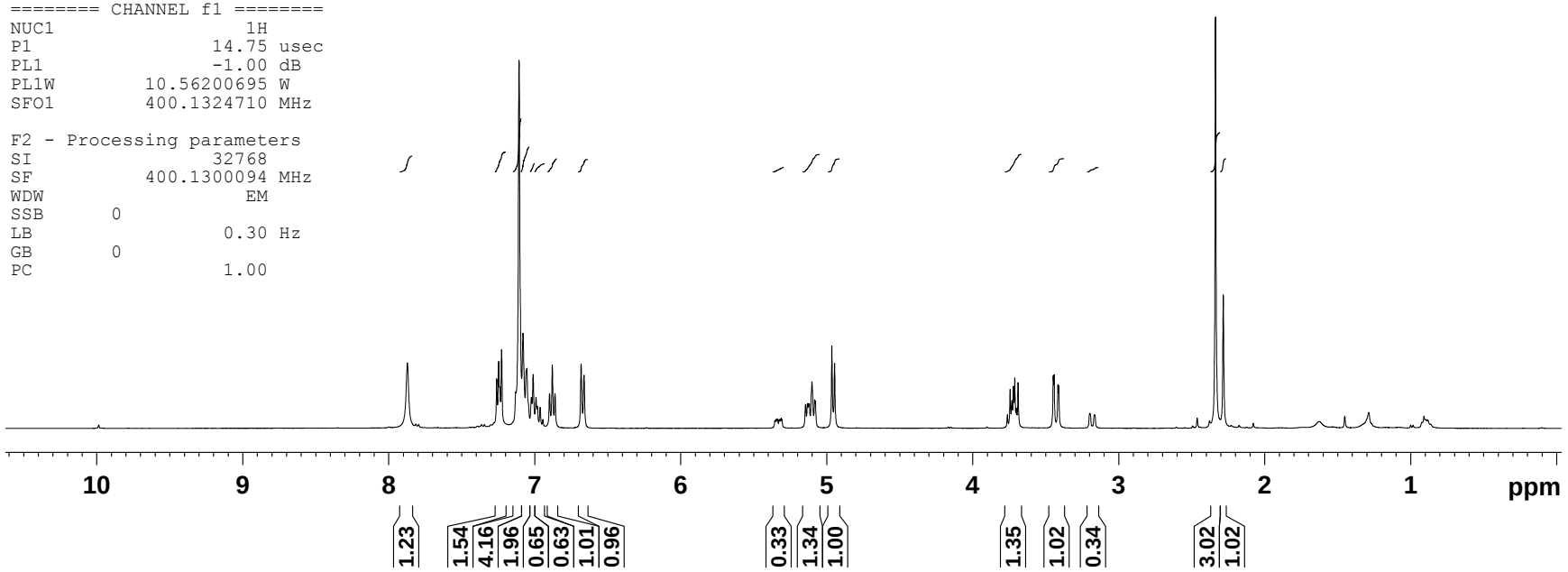
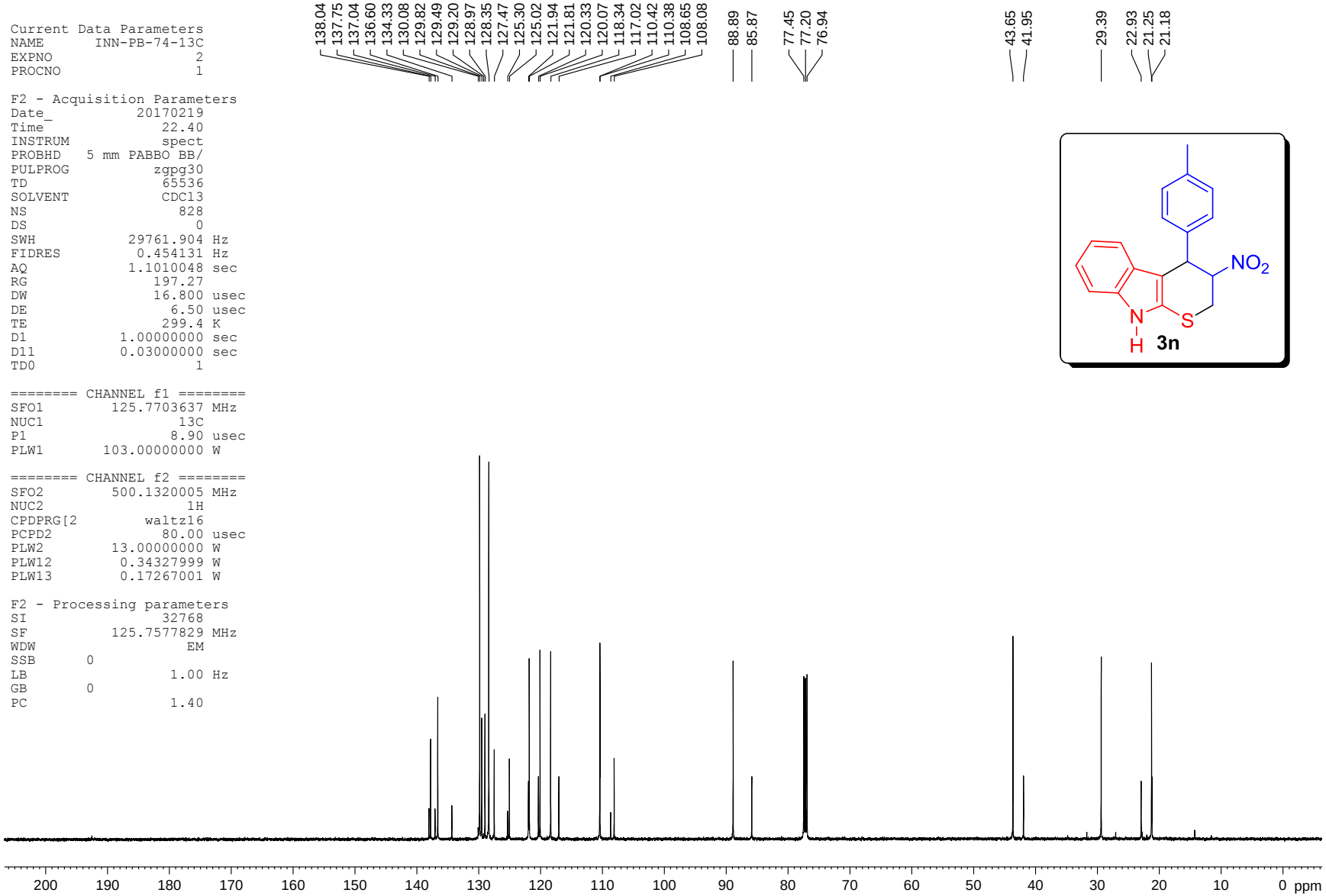


Figure S44. ^{1}H NMR Spectrum of 3n (major + minor, dr 77:23)




```
Current Data Parameters
NAME      INN-PB-74-13C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20170219
Time              22.40
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  828
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                197.27
DW                16.800 usec
DE                 6.50 usec
TE                299.4 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         13.00000000 W
PLW12         0.34327999 W
PLW13         0.17267001 W

F2 - Processing parameters
SI                 32768
SF           125.7577829 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S45. ^{13}C NMR Spectrum of 3n (major + minor, dr 77:23)

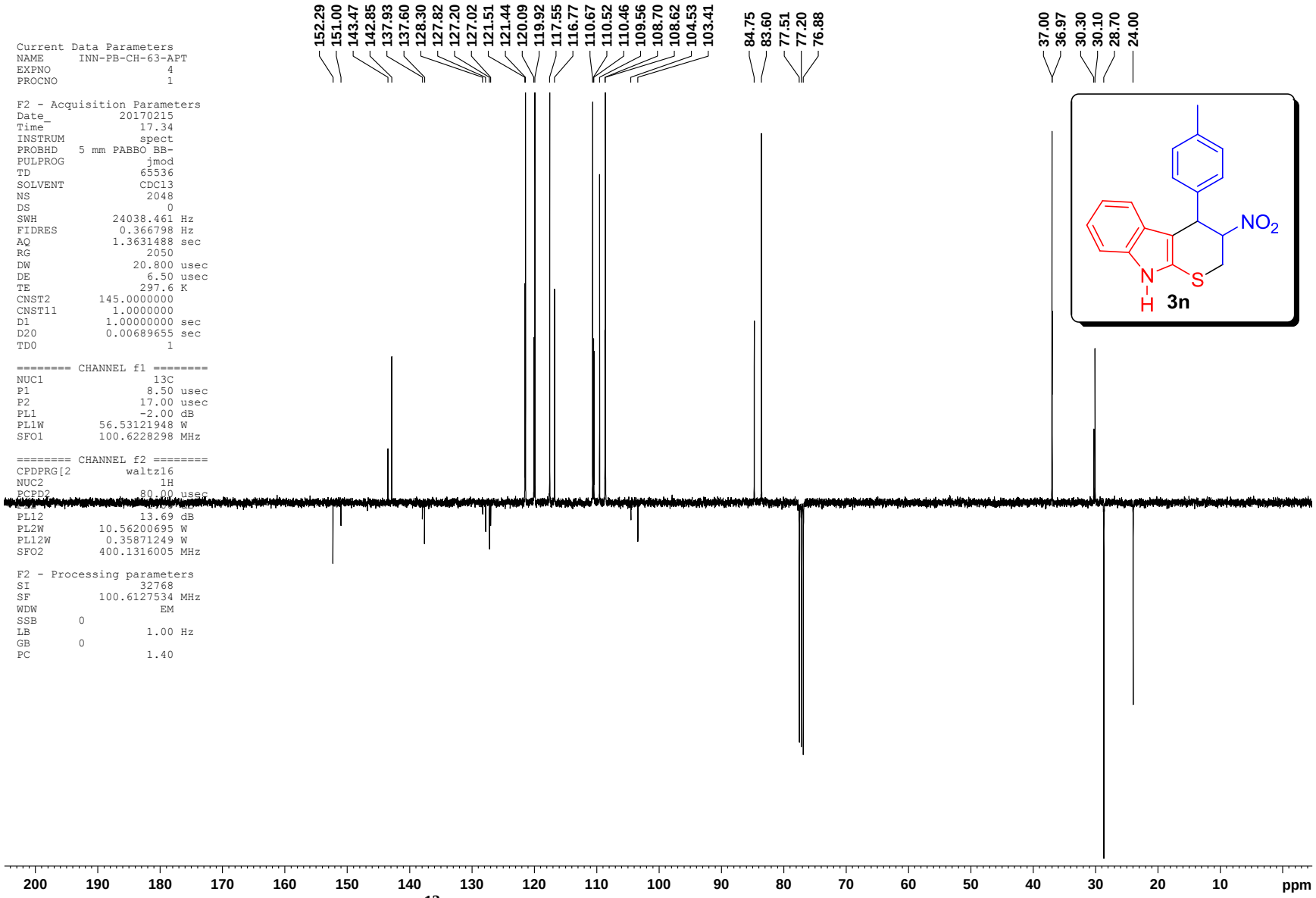
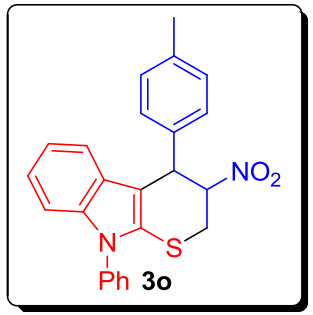


Figure S46. ^{13}C-APT NMR Spectrum of 3n (major + minor, dr 77:23)

```
Current Data Parameters
NAME       INN-PB-73-1H
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20170129
Time              22.33
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    6
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                296.8 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           500.1300129 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



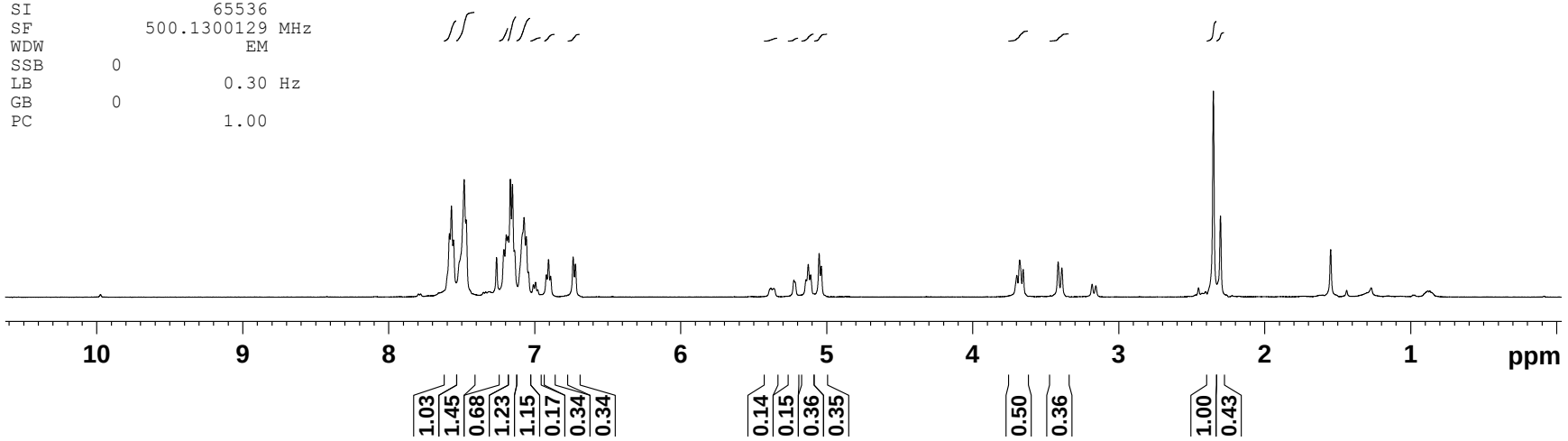


Figure S47. ^{1}H NMR Spectrum of 3o (major + minor, dr 75:25)

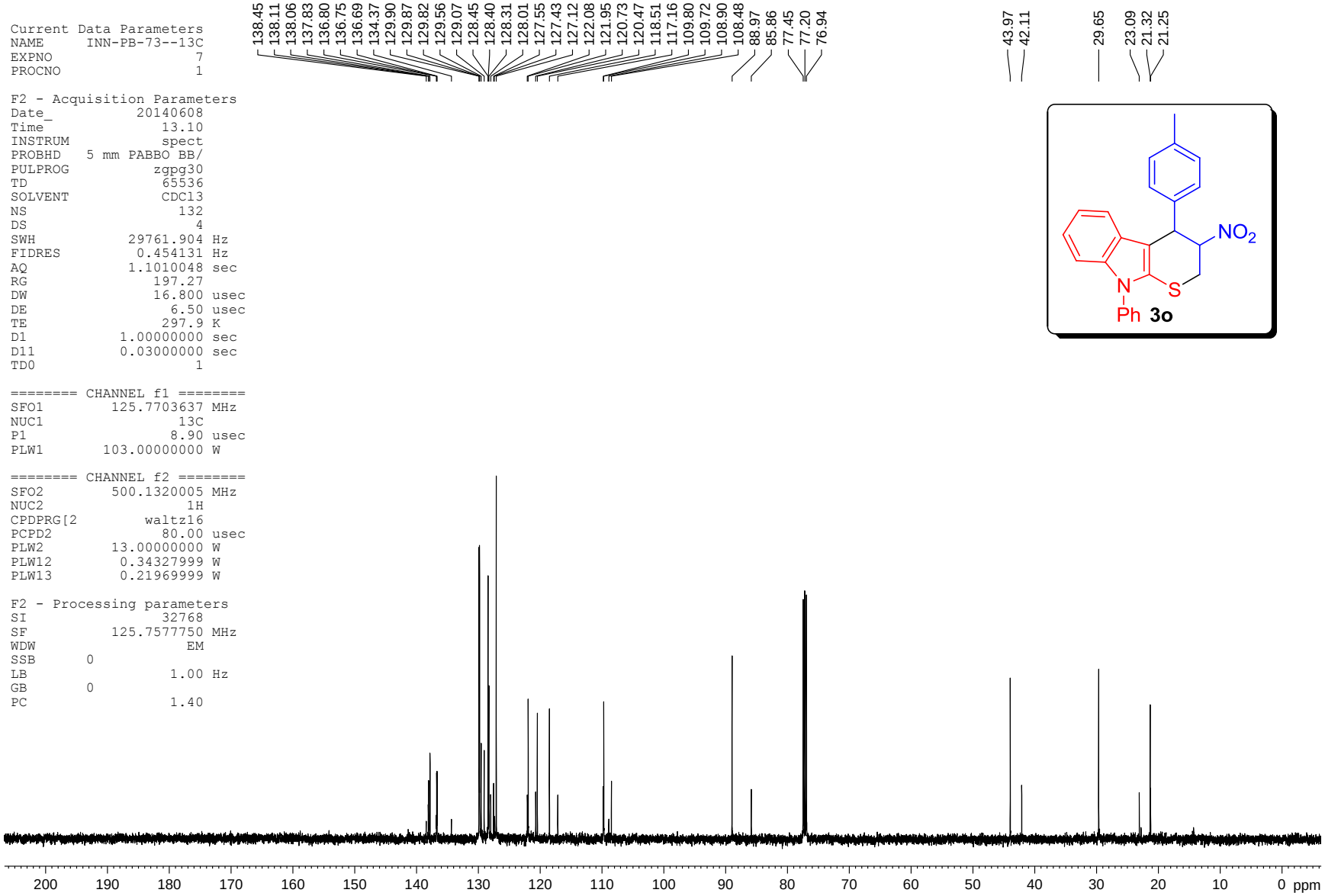


Figure S48. ^{13}C NMR Spectrum of 3o (major + minor, dr 75:25)

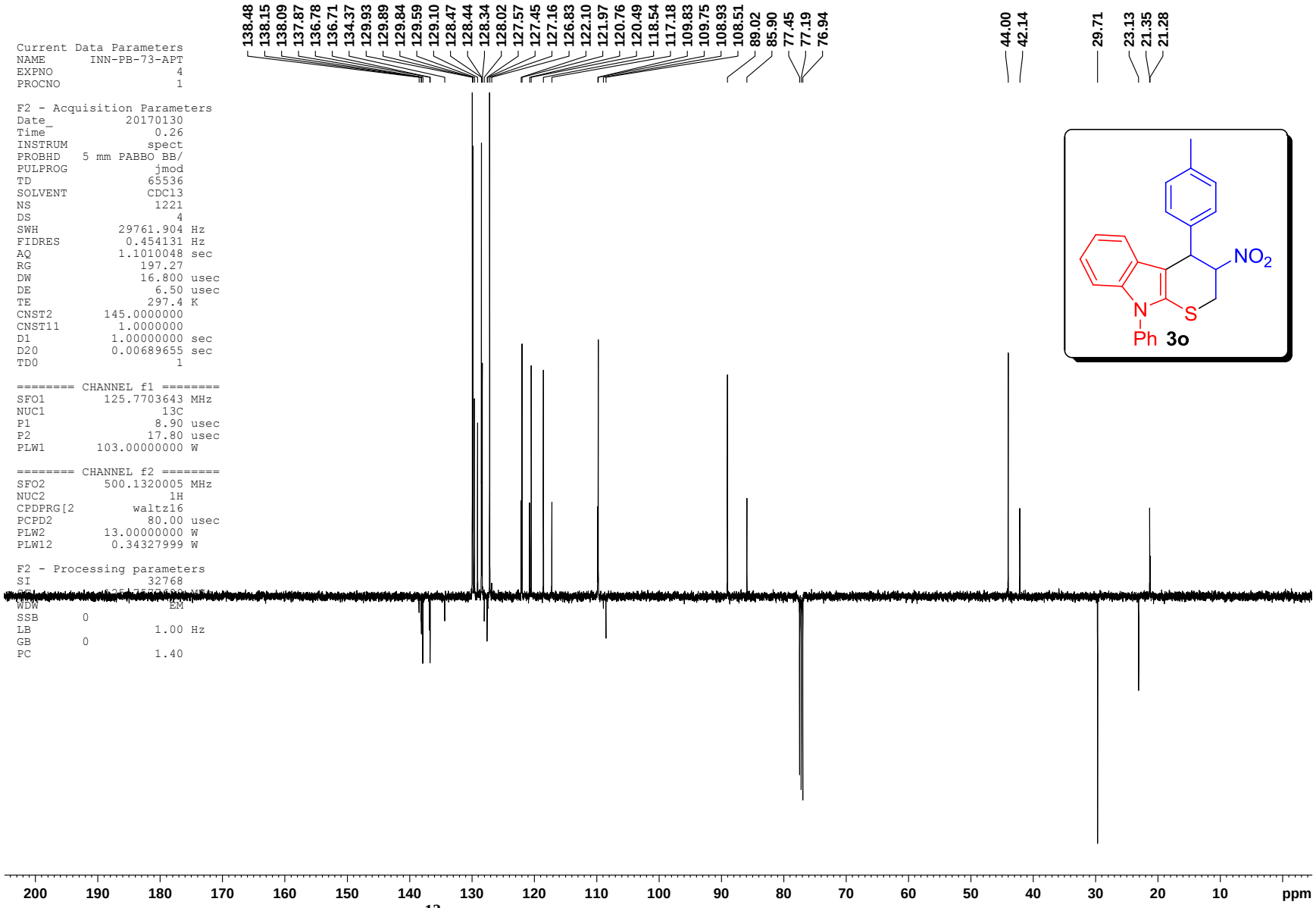


Figure S49. ^{13}C-APT NMR Spectrum of 3o (major + minor, dr 75:25)

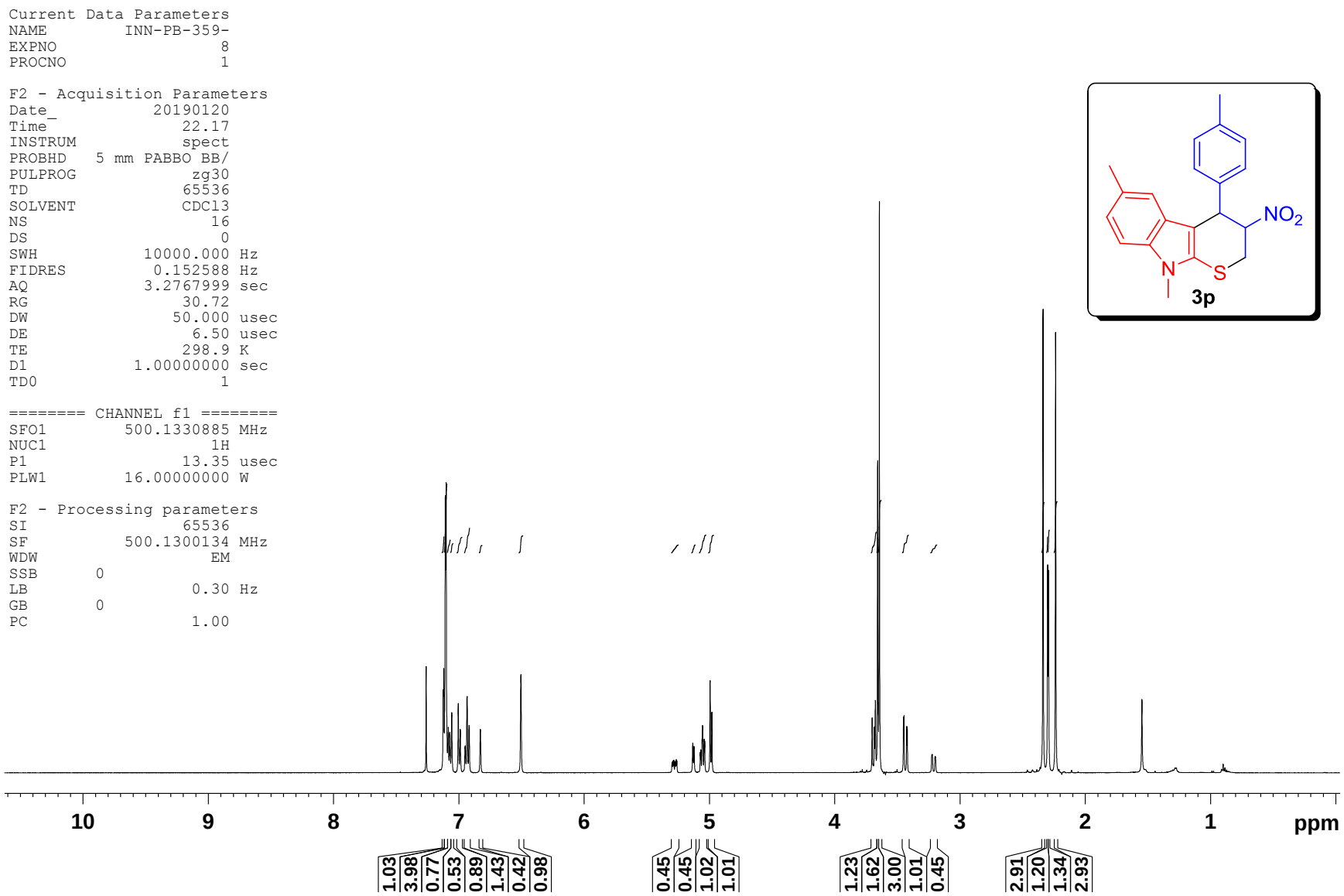


Figure S50. ^{1}H NMR Spectrum of 3p (major + minor, dr 69:31)

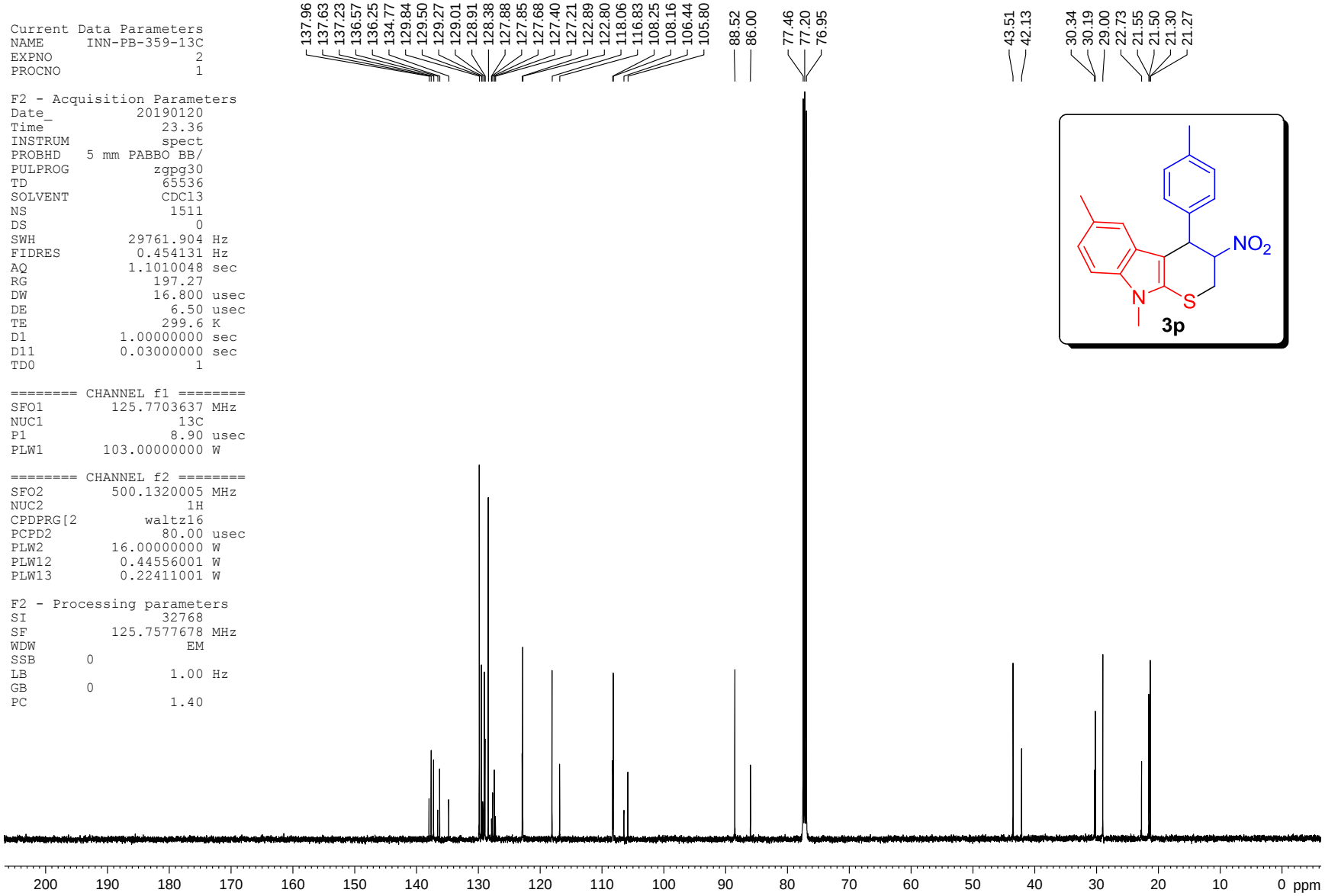
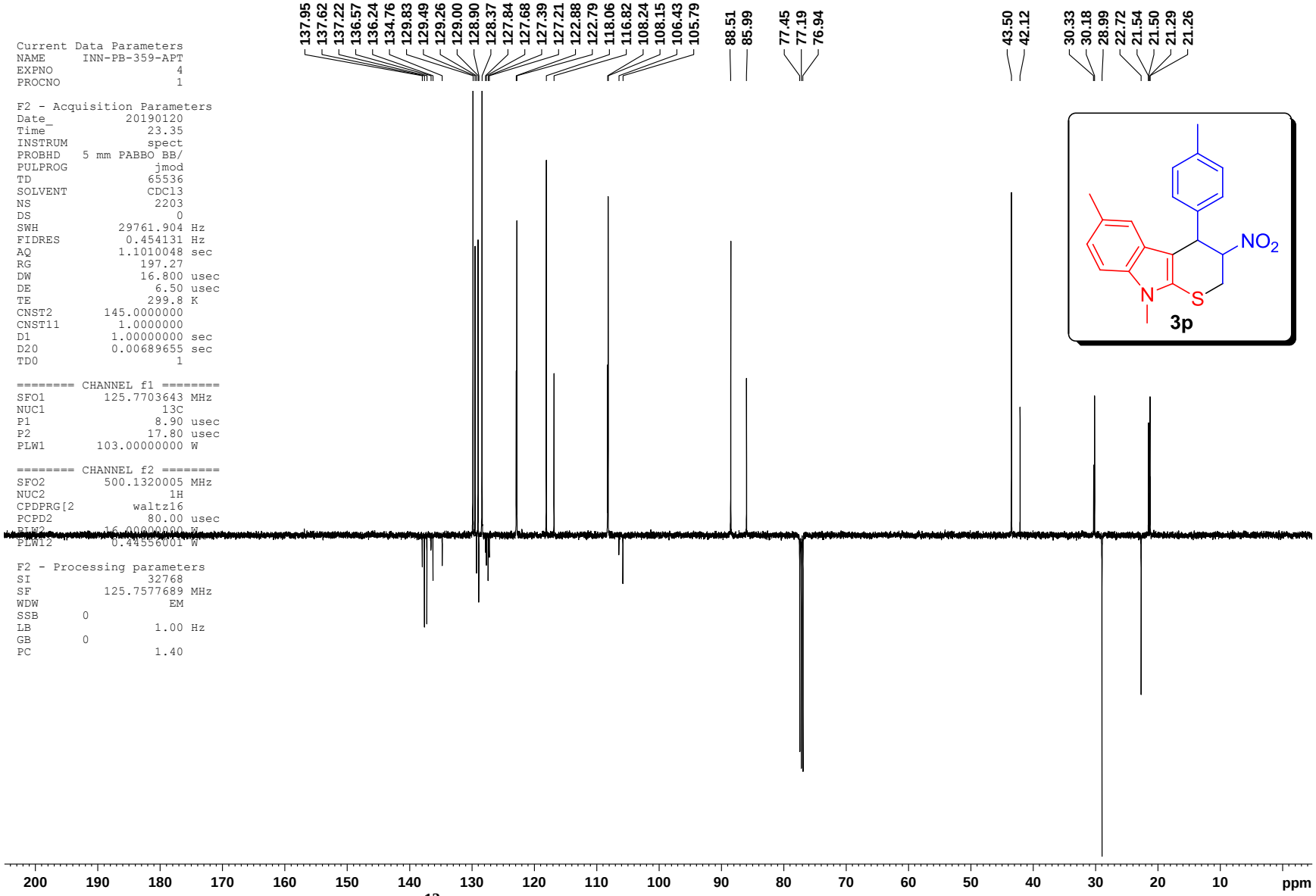


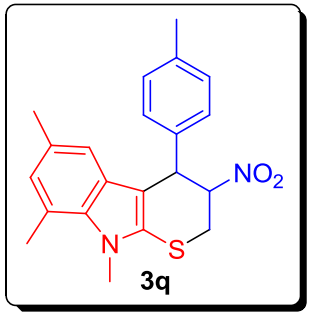
Figure S51. ^{13}C NMR Spectrum of 3o (major + minor, dr 69:31)




```
Current Data Parameters
NAME      INN-PB-359-APT
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20190120
Time              23.35
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           jmod
TD               65536
SOLVENT          CDCl3
NS                2203
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010048 sec
RG              197.27
DW              16.800 usec
DE                6.50 usec
TE               299.8 K
CNST2       145.0000000
CNST11        1.0000000
D1           1.00000000 sec
D20          0.00689655 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        125.7703643 MHz
NUC1                13C
P1                 8.90 usec
P2                17.80 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

F2 - Processing parameters
SI                32768
SF          125.7577689 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S52. ^{13}C-APT NMR Spectrum of 3p (major + minor, dr 69:31)

```
Current Data Parameters
NAME      INN-PB-360-1H
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_           20190120
Time              19.34
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
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                299.1 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           500.1300135 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



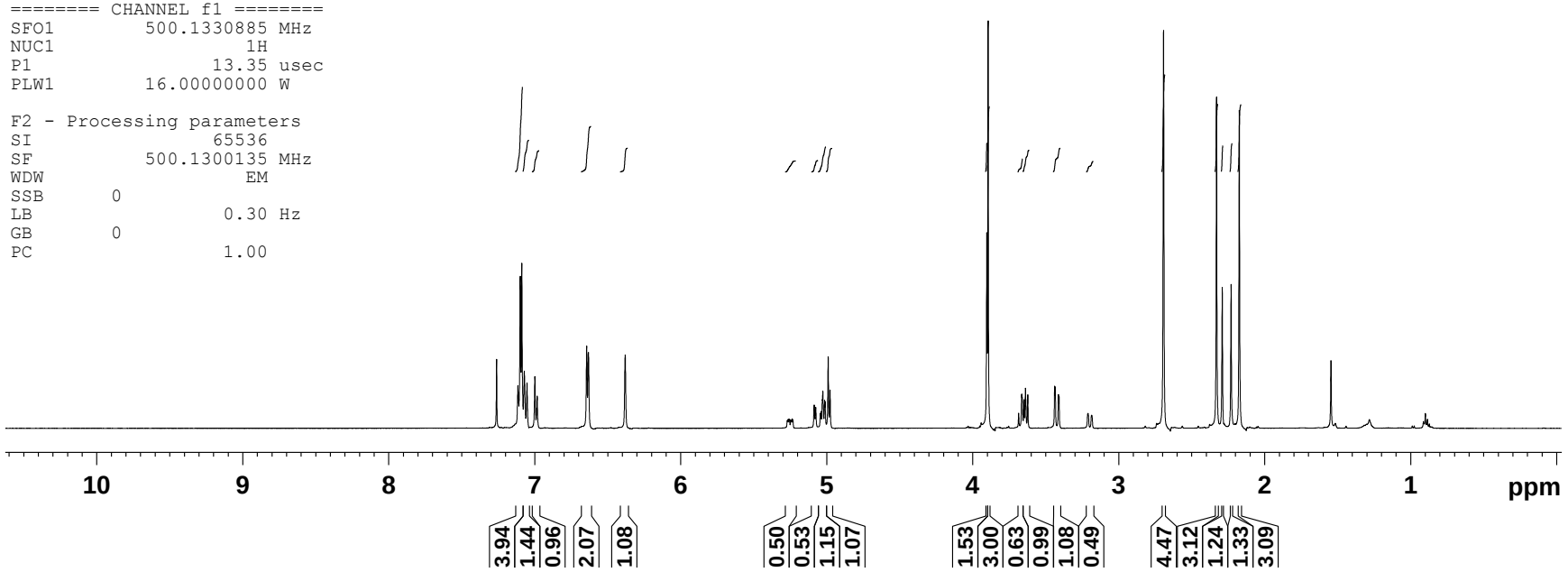
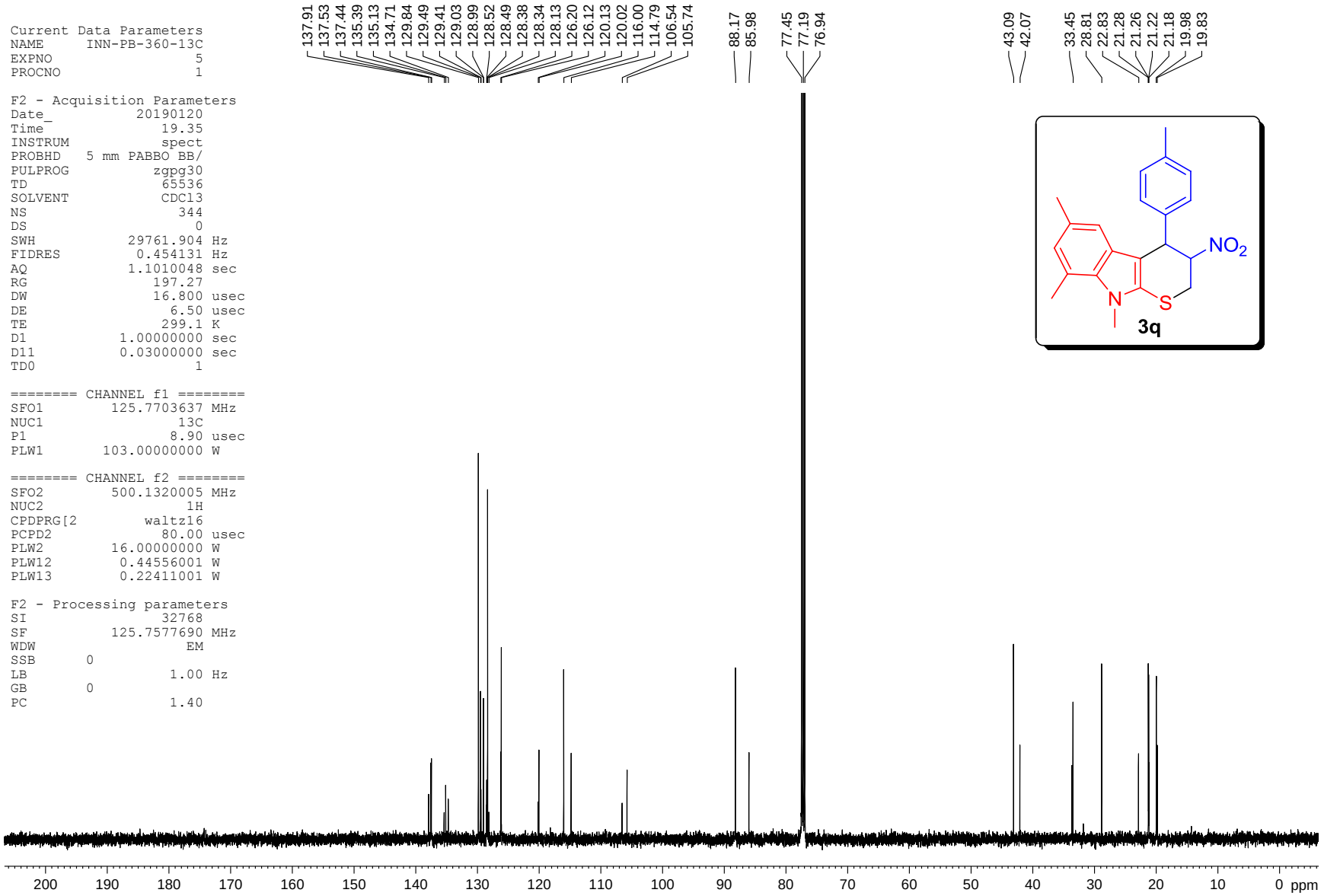


Figure S53. ^{1}H NMR Spectrum of 3q (major + minor, dr 66:34)




```
Current Data Parameters
NAME      INN-PB-360-13C
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20190120
Time              19.35
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 344
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE                299.1 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          125.7577690 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S54. ^{13}C NMR Spectrum of 3q (major + minor, dr 66:34)

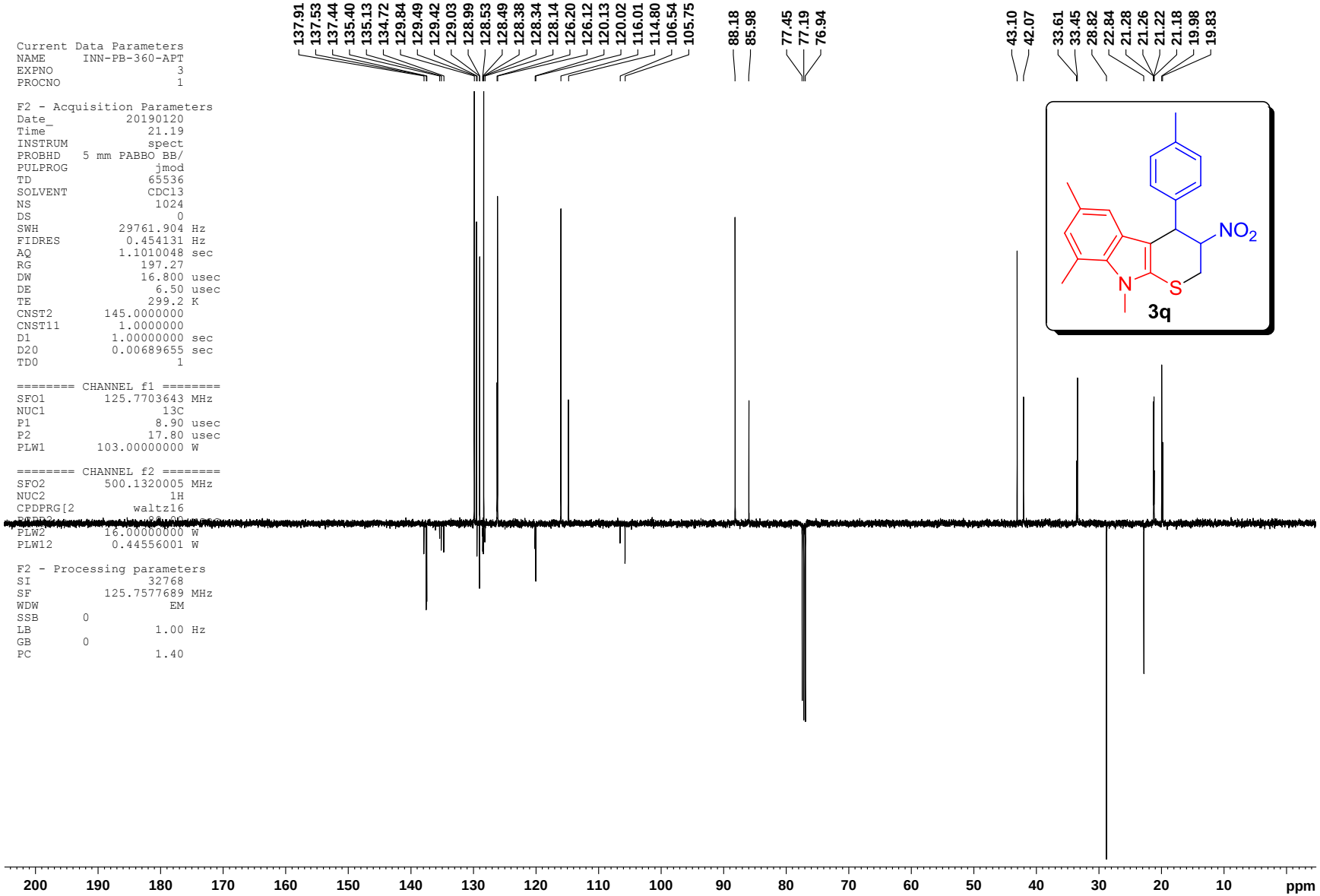
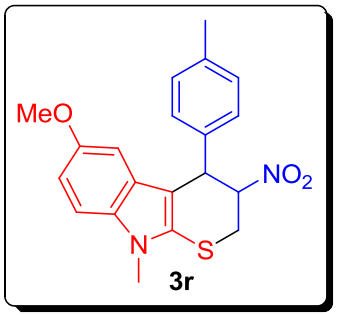


Figure S55. ^{13}C-APT NMR Spectrum of 3q (major + minor, dr 66:34)

```
Current Data Parameters
NAME      INN-PB-361-1H
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_           20190125
Time              13.55
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   15
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              298.7 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          500.1300133 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```



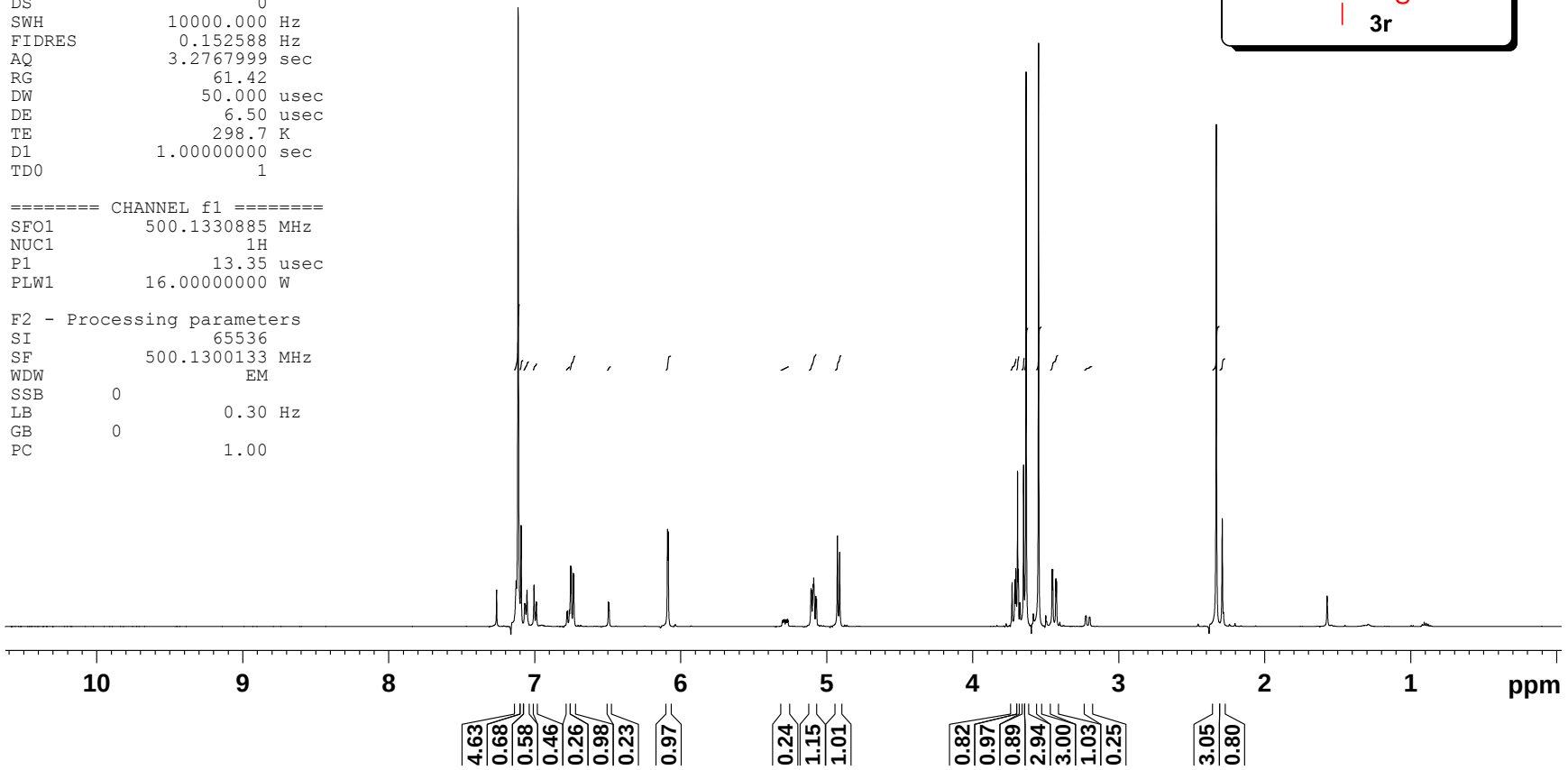
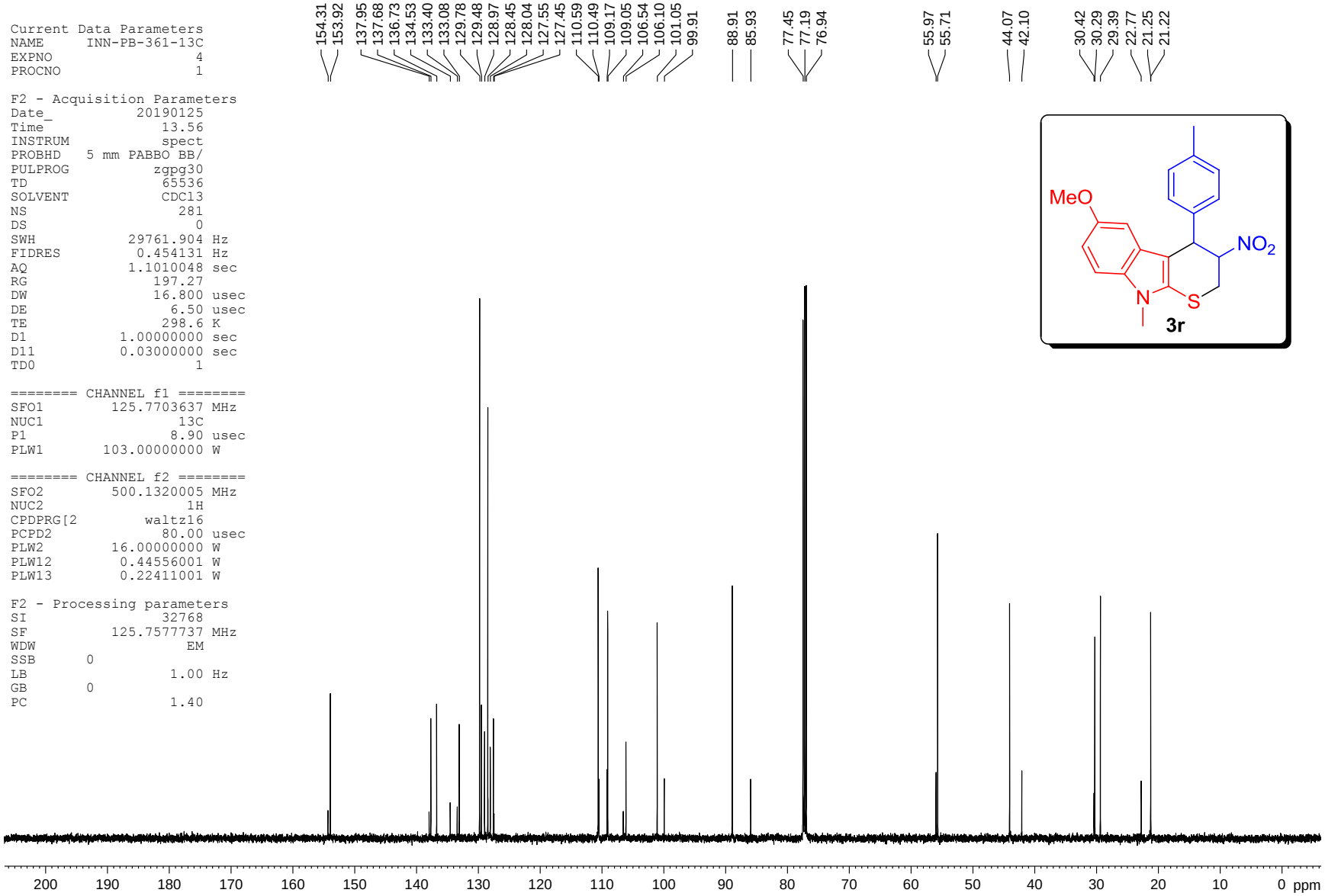


Figure S56. ^{1}H NMR Spectrum of 3r (major + minor, dr 79:21)




```
Current Data Parameters
NAME      INN-PB-361-13C
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20190125
Time              13.56
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 281
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE               298.6 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          125.7577737 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S57. ^{13}C NMR Spectrum of 3r (major + minor, dr 79:21)

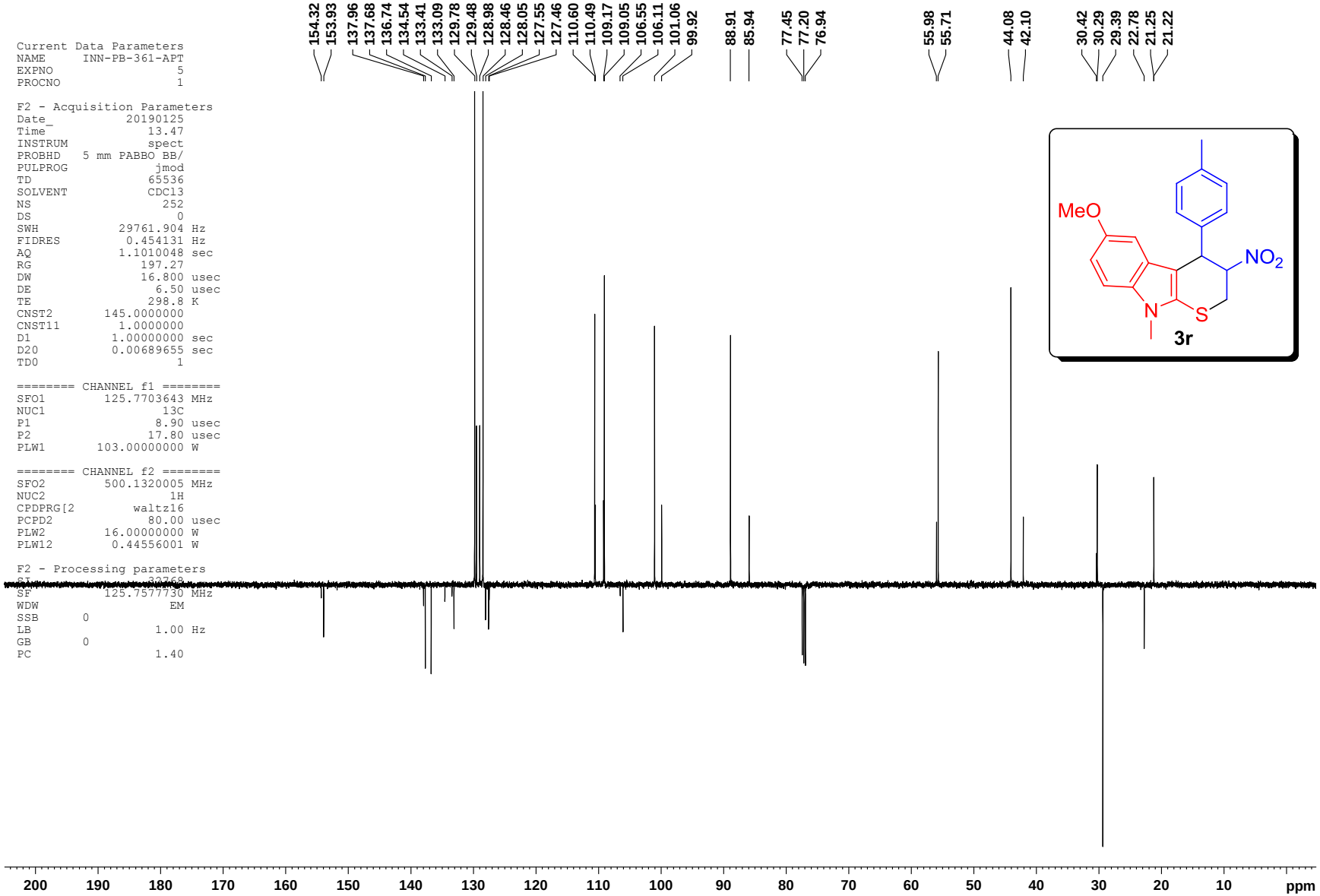
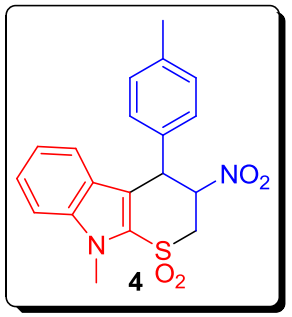


Figure S58. ^{13}C-APT NMR Spectrum of 3r (major + minor, dr 79:21)

```
Current Data Parameters
NAME      INN-2-PB-SO2-1H
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170222
Time              15.00
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                69.35
DW               50.000 usec
DE                 6.50 usec
TE                297.9 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          500.1300103 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



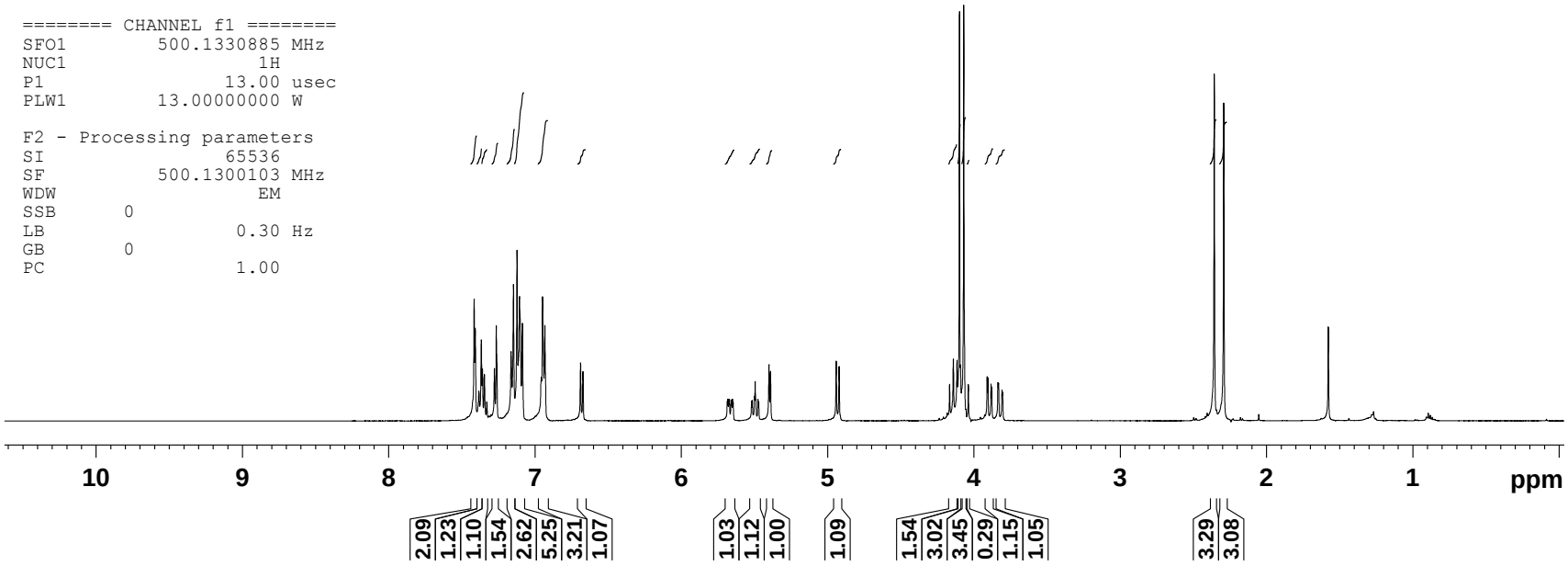


Figure S59. ^{1}HNMR Spectrum of 4 (major + minor, dr 50:50)

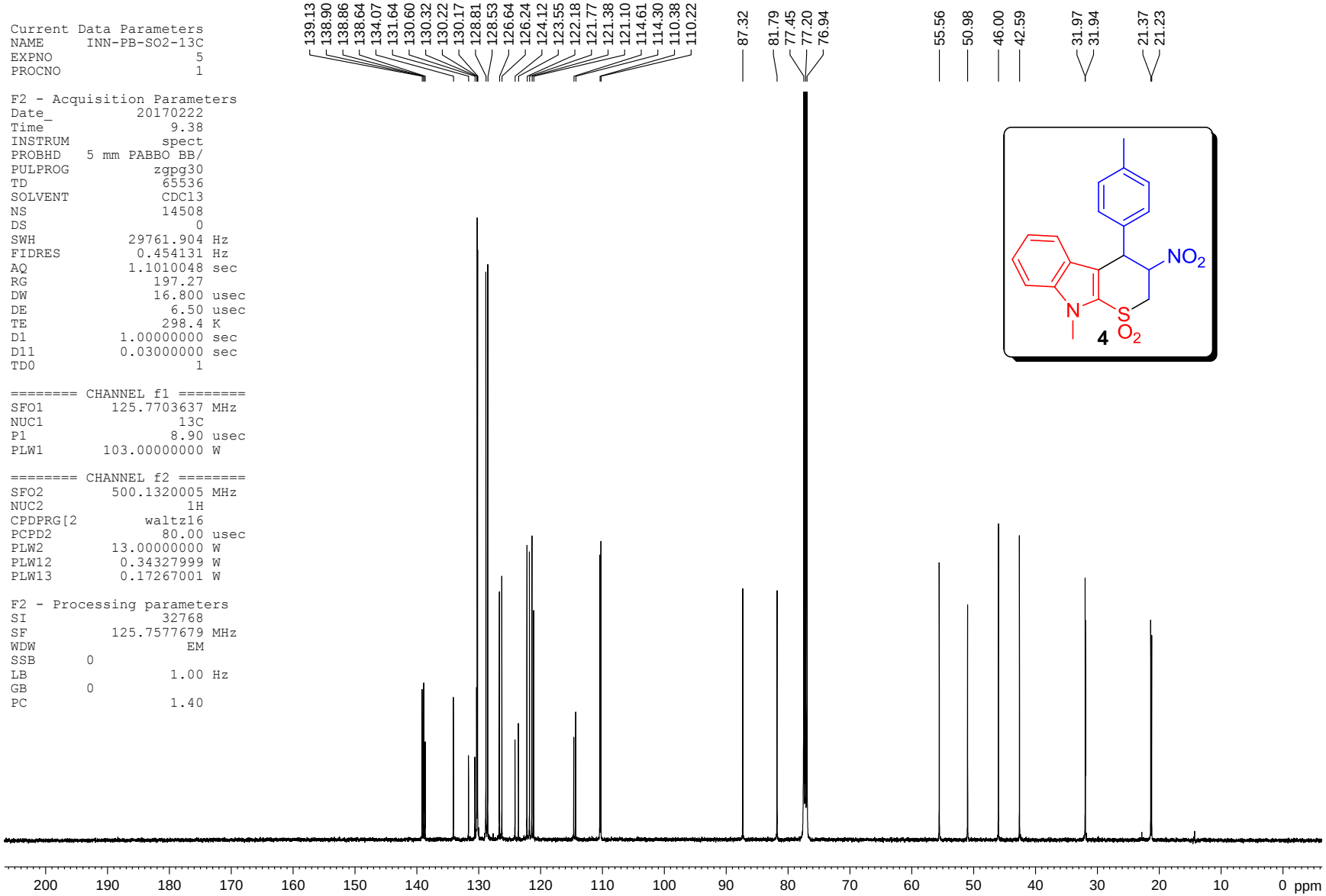
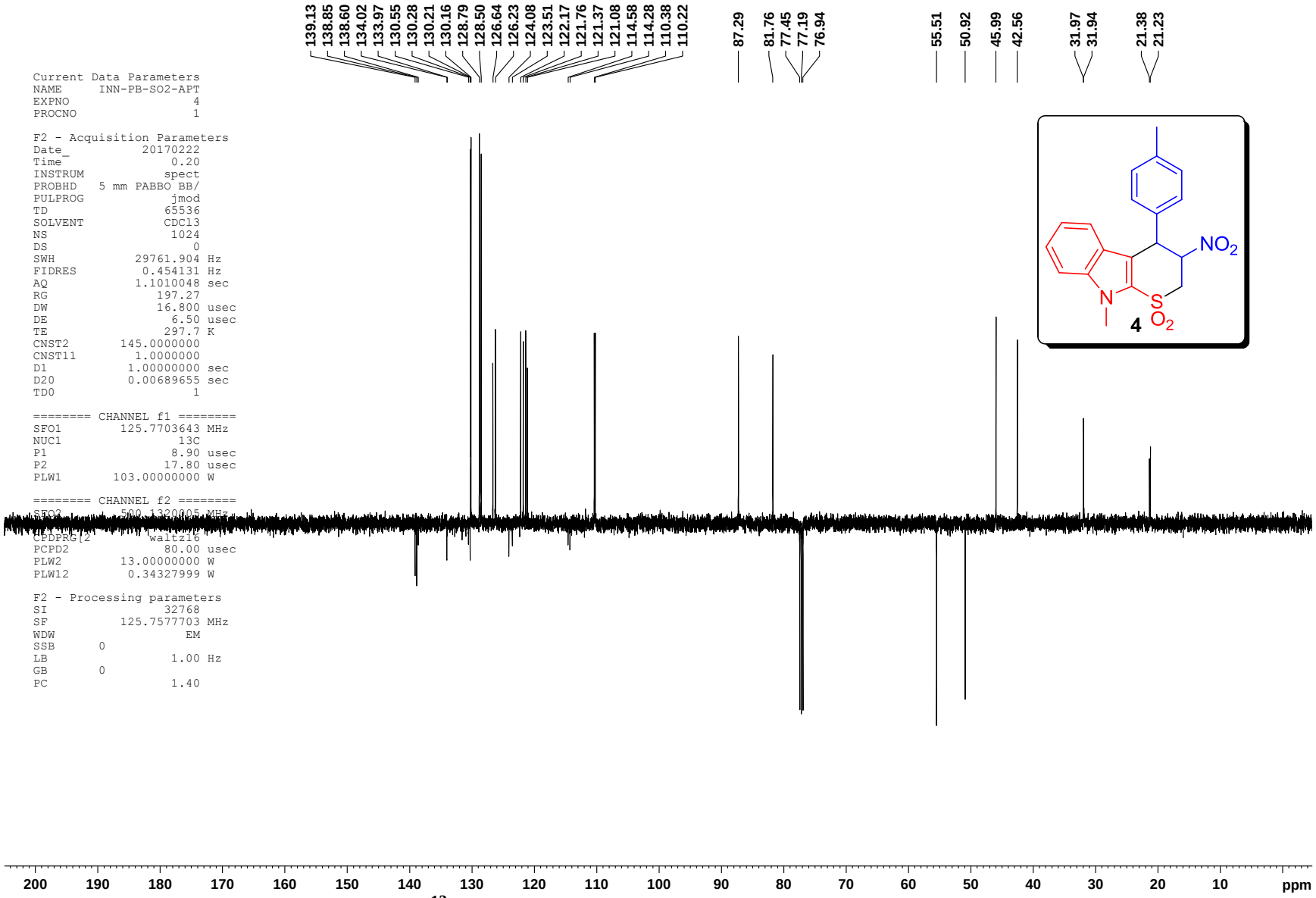


Figure S60. ^{13}C NMR Spectrum of 4 (major + minor, dr 50:50)




```
Current Data Parameters
NAME      INN-PB-SO2-APT
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20170222
Time              0.20
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           jmod
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                6.50 usec
TE                297.7 K
CNST2        145.0000000
CNST11         1.0000000
D1           1.00000000 sec
D20          0.00689655 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       125.7703643 MHz
NUC1               13C
P1                8.90 usec
P2               17.80 usec
PLW1      103.00000000 W

======== CHANNEL f2 ========
SFO2       500.1320005 MHz
CPDPRG[2          waltz16
PCPD2            80.00 usec
PLW2       13.00000000 W
PLW12       0.34327999 W

F2 - Processing parameters
SI                32768
SF         125.7577703 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

Figure S61. ^{13}C-APT NMR Spectrum of 4 (major + minor, dr 50:50)

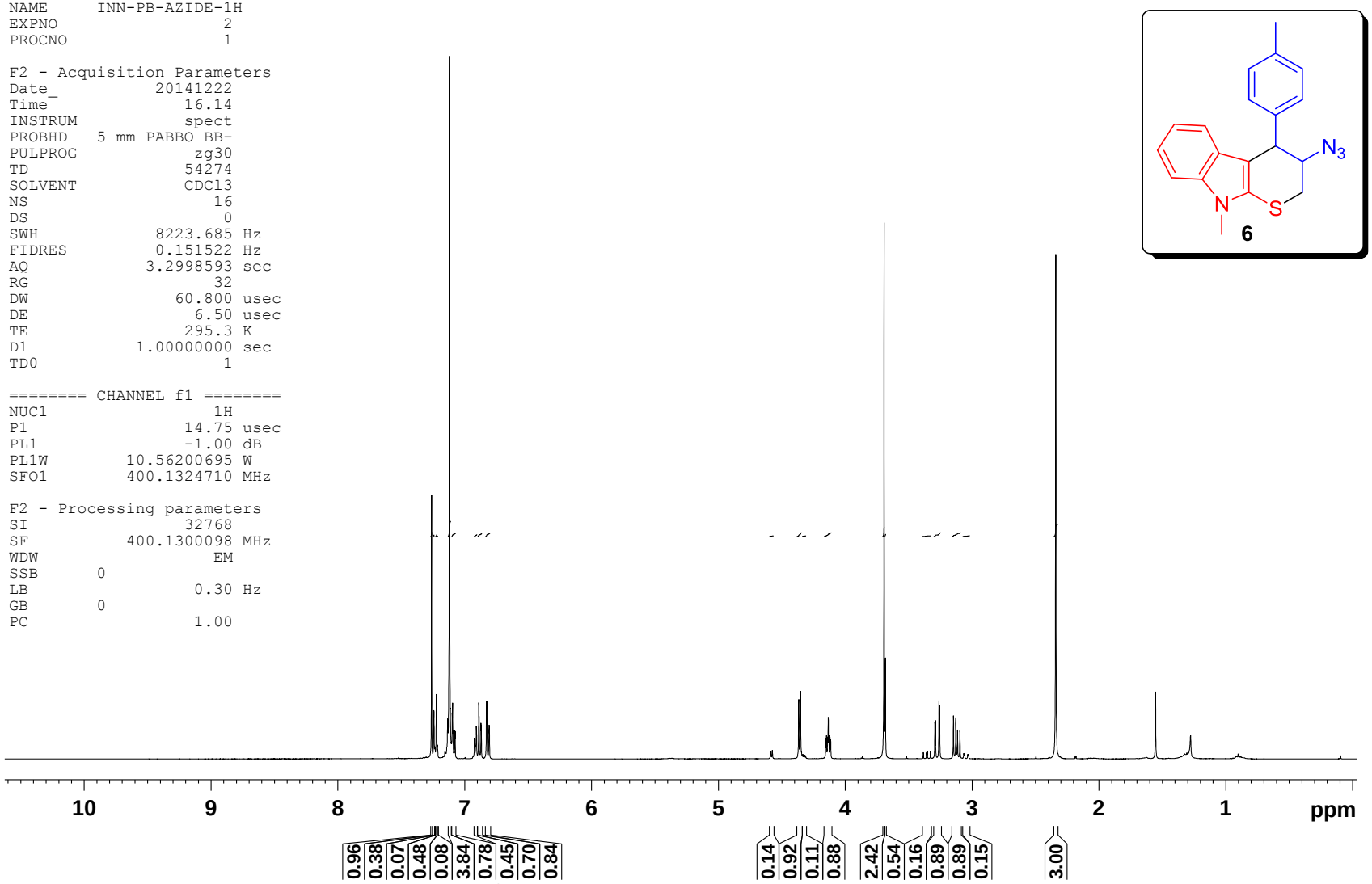


Figure S62. ^{1}H NMR Spectrum of 6 (major + minor, dr 85:15)

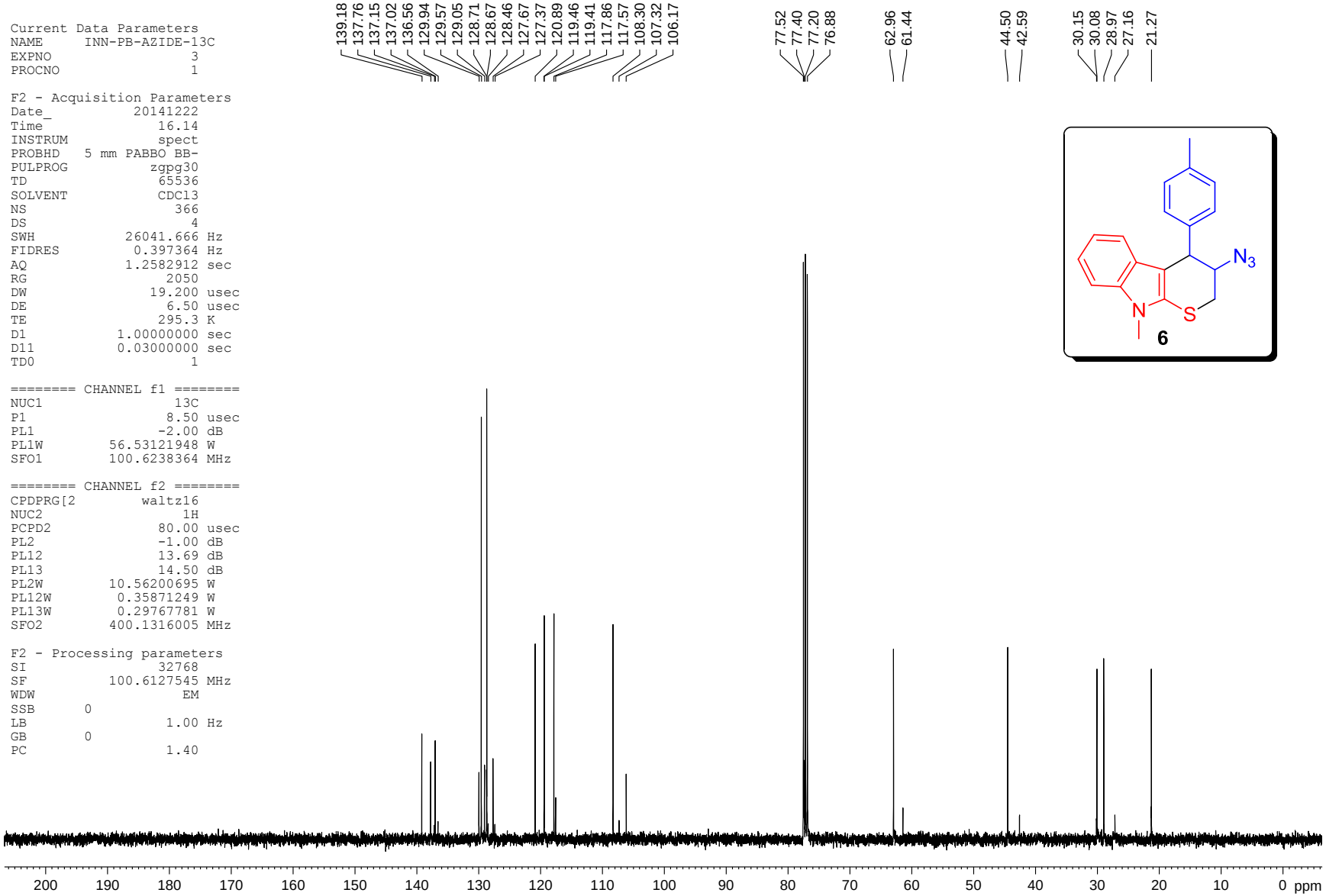
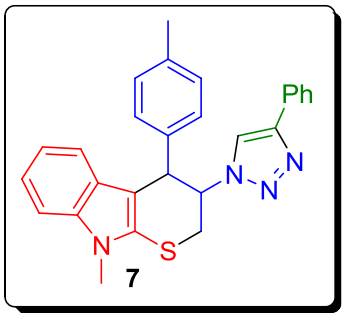


Figure S63. ^{13}C NMR Spectrum of 6 (major + minor, dr 85:15)

```
Current Data Parameters
NAME     inn-pb-triazole-1h
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20141229
Time              21.40
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                  114
DW                60.800 usec
DE                 6.50 usec
TE                296.4 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          400.1300451 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



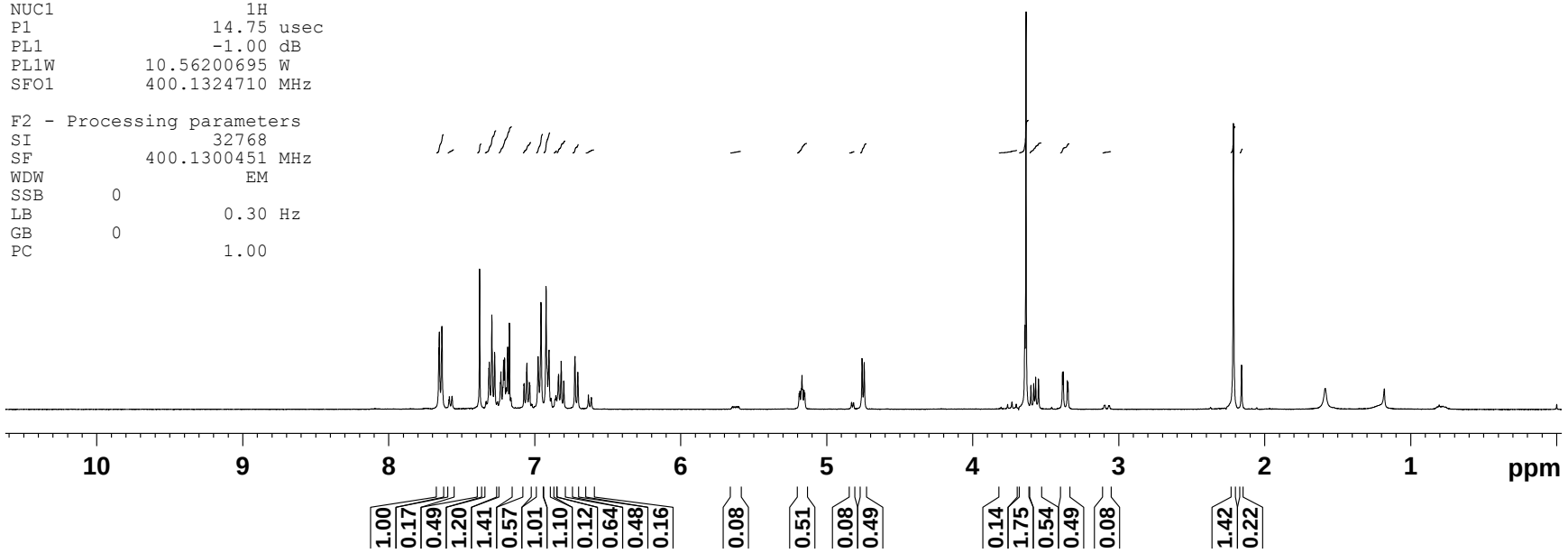
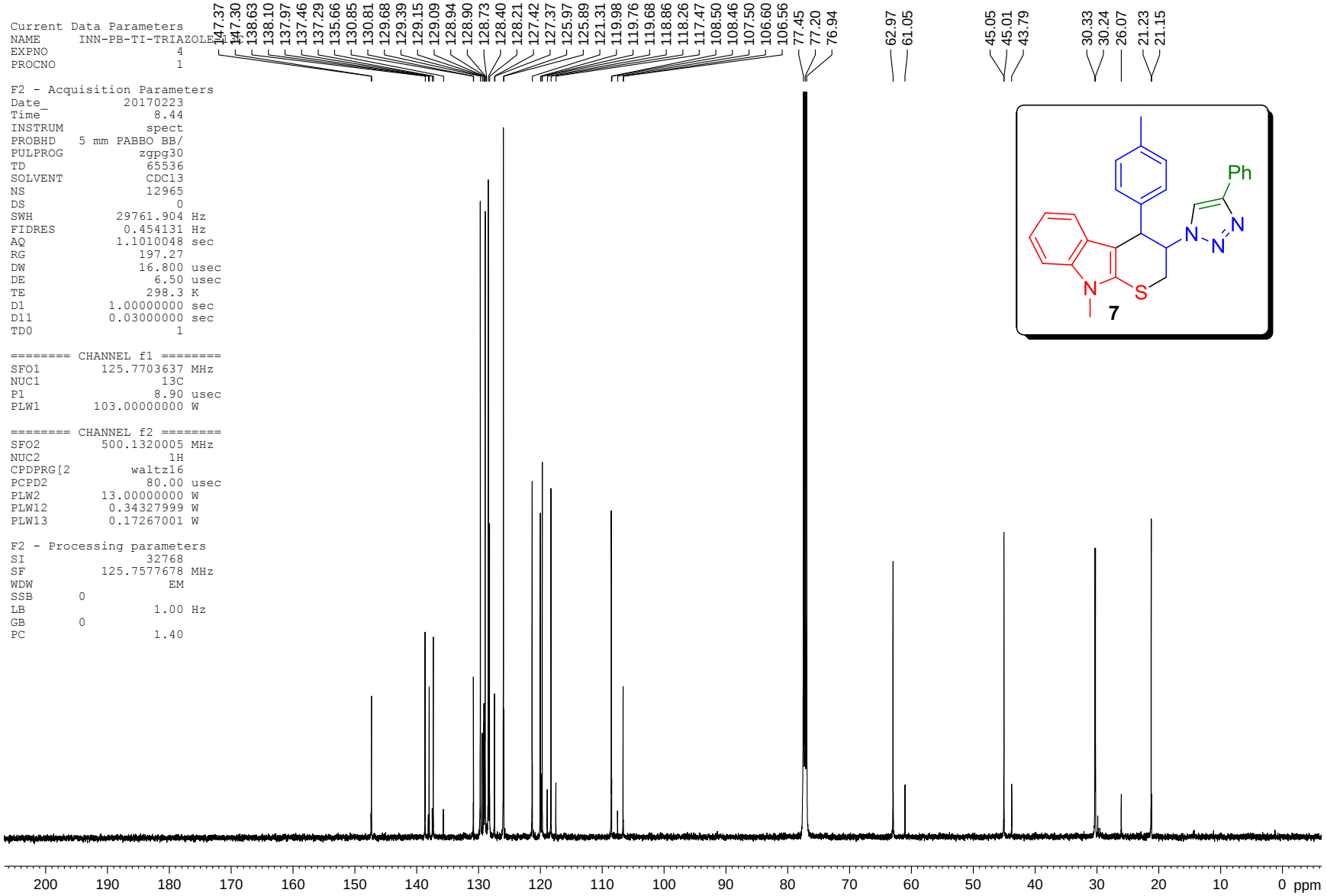


Figure S64. ^{1}H NMR Spectrum of 7 (major + minor, dr 86:14)




```
Current Data Parameters
NAME      INN-PB-TI-TRIAZOLE-1
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_           20170223
Time               8.44
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                12965
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                197.27
DW                16.800 usec
DE                 6.50 usec
TE                298.3 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        13.00000000 W
PLW12         0.34327999 W
PLW13         0.17267001 W

F2 - Processing parameters
SI                32768
SF          125.7577678 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

Figure S65. ^{13}C NMR Spectrum of 7 (major + minor, dr 86:14)

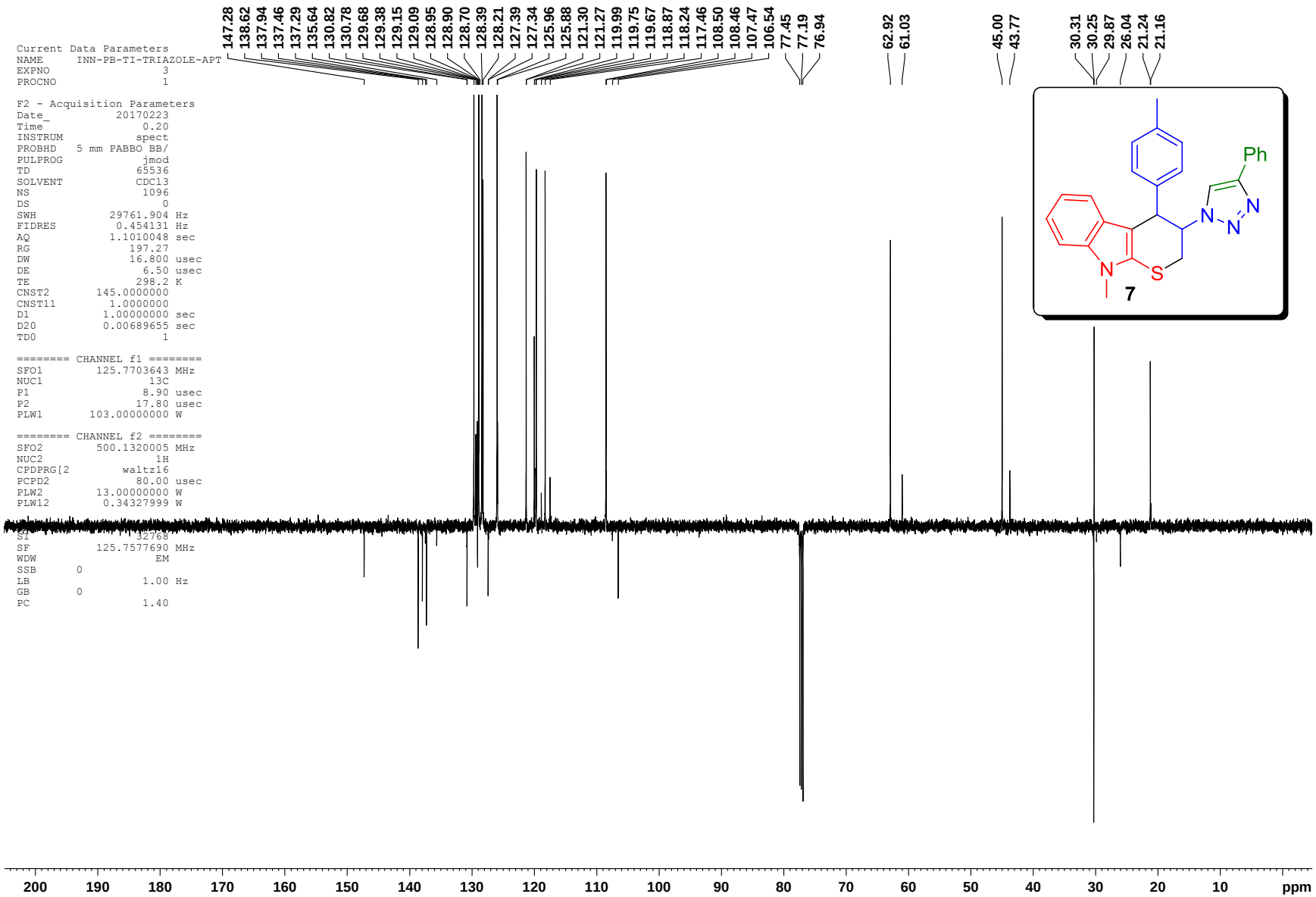
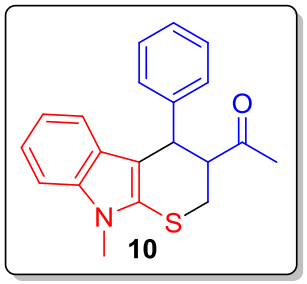


Figure S66. ^{13}C-APT NMR Spectrum of 7 (major + minor, dr 86:14)

```
Current Data Parameters
NAME      INN-PB-384-1H
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           20191126
Time              15.05
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                30.72
DW               50.000 usec
DE                6.50 usec
TE                296.4 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           500.1300064 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



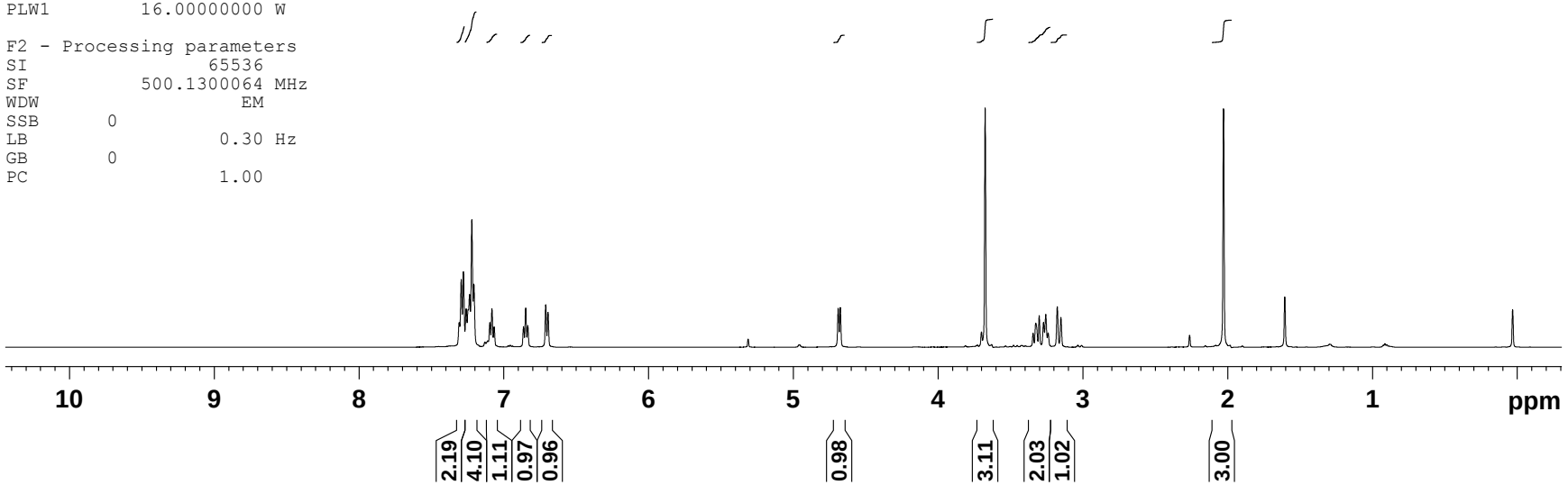


Figure S67. ^{1}H NMR Spectrum of 10 (major + minor, dr > 95:05)

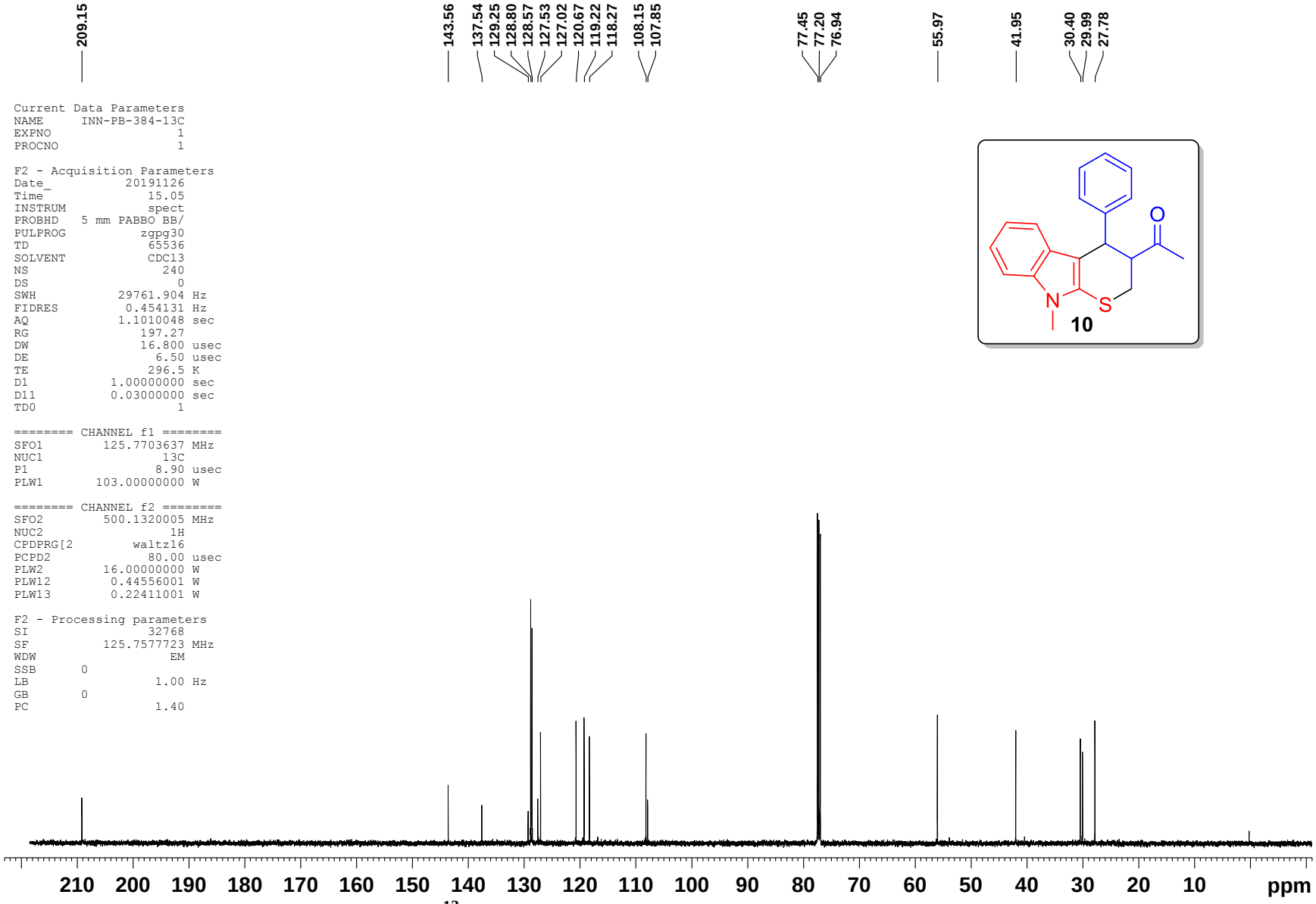


Figure S68. ^{13}C NMR Spectrum of 10 (major + minor, > dr 95:05)

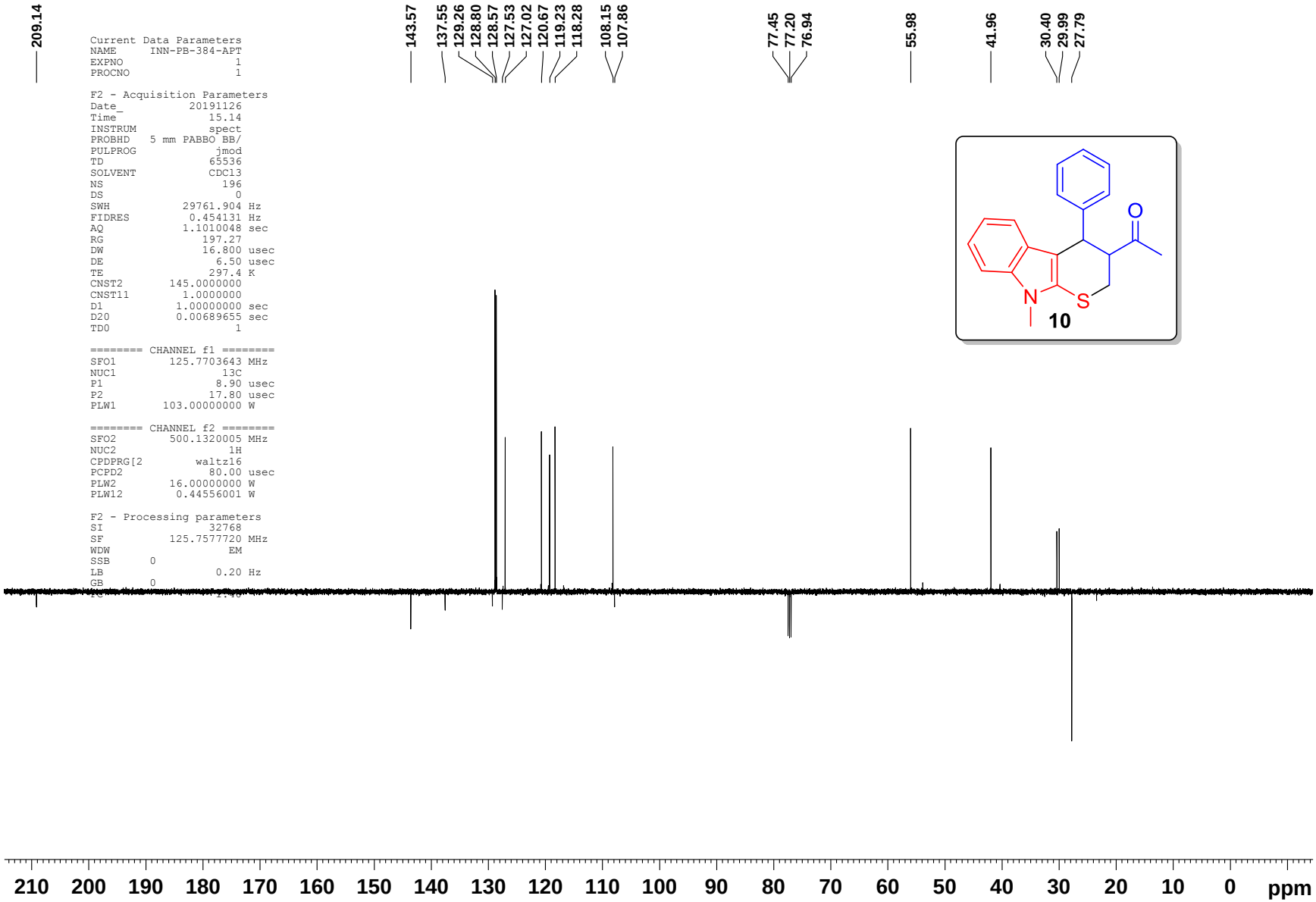
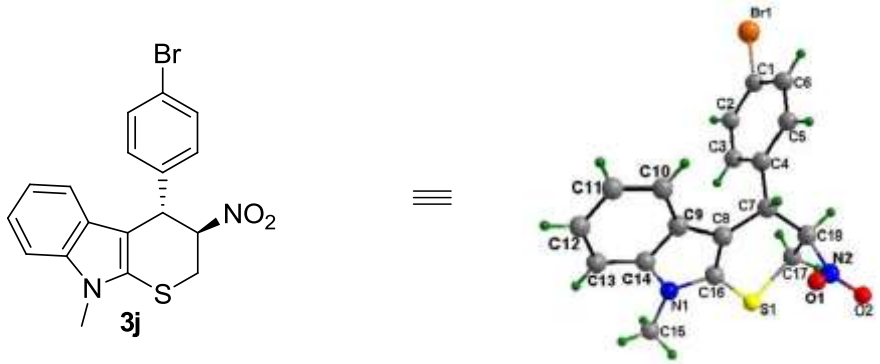


Figure S69. ^{13}C-APT NMR Spectrum of 10 (major + minor, dr 95:05)

Table S1. Crystal data and structure refinement for thiopyranoindole **3j**



Identification code	INN-PB-86C	
Empirical formula	$C_{18}H_{15}BrN_2O_2S$	
Formula weight	403.29	
Temperature	293(2) K	
Wavelength	0.71070 Å	
Crystal system, space group	Trigonal, R -3	
Unit cell dimensions	a = 29.728(9) Å	α= 90°.
	b = 29.728(9) Å	β= 90°.
	c = 9.928(3) Å	γ = 120°.
Volume	7598(4) $Å^3$	
Z, Density (calculated)	18, 1.586 Mg/m^3	
Absorption coefficient	2.571 mm^{-1}	
F(000)	3672	
Crystal size	0.066 x 0.086 x 0.434 mm^3	
Theta range for data collection	3.51 to 24.99°.	
Index ranges	-35<=h<=34, -35<=k<=35, -11<=l<=11	
Reflections collected	19656	
Independent reflections	2968 [R(int) = 0.1924]	
Completeness to theta	= 24.99° 99.8 %	

Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2968 / 0 / 217
Goodness-of-fit on F^2	1.115
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1497
R indices (all data)	R1 = 0.0630, wR2 = 0.1566
Largest diff. peak and hole	1.145 and -0.822 e.$Å^{-3}$