Supporting Information
For

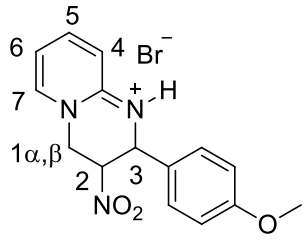
Regio- and Diastereoselective Synthesis of Dihydropyridopyrimidines *via* Cascade Reactions of 2-Aminopyridines with Morita-Baylis-Hillman Bromides of Nitroalkenes

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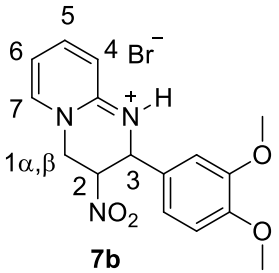
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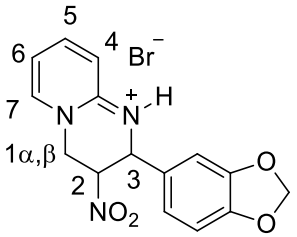
Table S1. ^{1}H NMR (δ, DMSO-d$_6$, 500 MHz, major) data of 7 and 10



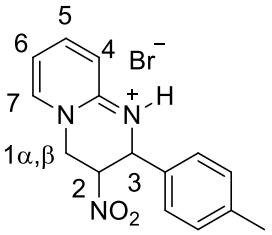
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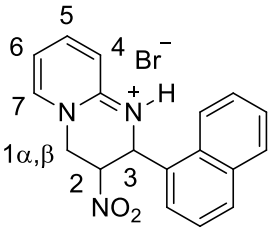
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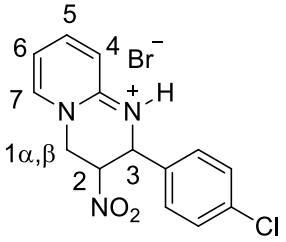
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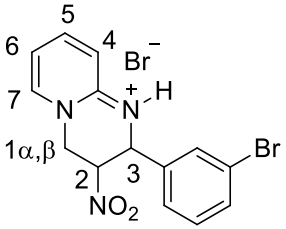
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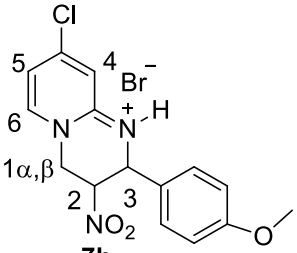
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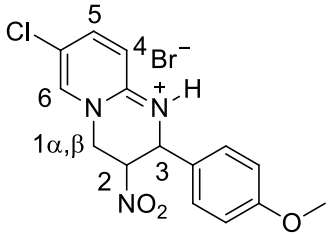
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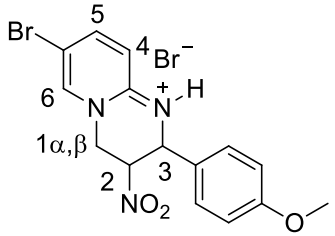
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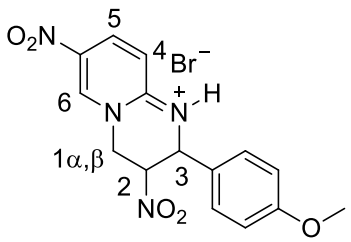
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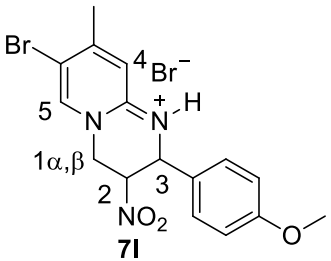
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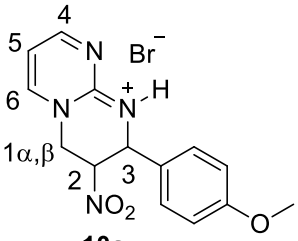
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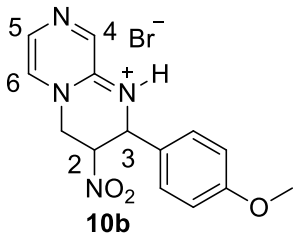
7k



7l



10a



10b

	7a	7b	7c	7d	7e	7f	7g	7h	7i	7j	7k	7l	10a	10b
1α	4.51 (d,1 *β*) *J* = 14.4	4.48 (d,1 *β*) *J* = 13.7	4.51 (d,1 *β*) *J* = 14.6	4.46 (dd, 1 *β* ,2) *J* = 15.4, 2.5	4.40 (d, 1 *β*) *J* = 14.6	4.48 (d, 1 *β*) *J* = 14.7	4.48 (dd, 1 *β*) *J* = 14.3, 2.2	4.48 (d, 1 *β*) *J* = 14.5	4.46 (dd, 1 *β*) *J* = 15.3, 2.8	4.47 (d, 1 *β*) *J* = 14.8	4.59 (d, 1 *β*) *J* = 15.0	4.42 (d, 1 *β*) *J* = 14.1	4.49 (dd, 1 *β*) *J* = 15.3, 3.0	4.50 (d, 1 *β*) *J* = 14.4
1 *β*	5.07 (d,1α) *J* = 14.4	5.07 (d, 1α) *J* = 13.7	5.06 (d, 1α) *J* = 16.6	5.06 (dd, 1α,2) *J* = 15.4, 2.5	5.09 (d, 1α) *J* = 14.6	5.10 (d, 1α) *J* = 14.7	5.09 (d, 1α) *J* = 14.3	5.10 (d, 1α) *J* = 14.5	5.05 (d, 1α) *J* = 15.3	5.06 (d, 1α) *J* = 14.8	5.28 (d, 1α) *J* = 15.0	5.07 (d, 1α) *J* = 14.1	5.12 (d, 1α) *J* = 15.3	5.09 (d, 1α) *J* = 14.4
2	5.80[a]	5.88[a]	5.77[a]	5.77-5.80 (m)	6.48[a]	5.87[a]	5.89[a]	5.78[a]	5.76[a]	5.78[a]	5.79[a]	5.79[a]	5.75 (d, 1α or 1 *β*) *J* = 2.5	5.76[a]
3	5.53[a]	5.51[a]	5.50[a]	5.56[a]	5.95[a]	5.66[a]	5.67[a]	5.56[a]	5.56[a]	5.55[a]	5.70[a]	5.54[a]	5.60[a]	5.63[a]

4	7.31[a]	7.34 (d, 8) *J* = 5.6	7.28 (d, 8) *J* = 7.2	7.24 (d, 7) *J* = 7.8	-	[b]	7.29 (d, 5) *J* = 8.8	7.45 (s)	7.31 (d, 5) *J* = 9.0	7.30 (d, 5) *J* = 9.1	7.36 (d, 5) *J* = 9.5	7.27 (s)	8.97-8.99 (m)	8.18[a]
5	7.97[b]	7.97[a]	7.96 (t,7,9) *J* = 7.3	7.97 (t, 6,8) *J* = 6.9	-	7.99[a]	7.99 (t, 4,6) *J* = 8.1	7.21 (d, 8) *J* = 5.5	8.07 (d, 4) *J* = 7.6	8.13 (d, 4) *J* = 9.1	8.58 (d, 4) *J* = 9.5	8.62 (s)	7.23-7.26 (m)	8.08[a]
6	7.02[b]	7.02[a]	7.02[a]	7.03 (t, 7,9) *J* = 6.9	-	7.05[a]	7.05 (t, 5,7) *J* = 6.9	8.27 (d,5) *J* = 5.5	8.55 (s)	8.60 (s)	9.50 (s)	-	8.67-8.69 (m)	8.87[a]
7	8.18[a]	8.16[a]	8.14 (d, 9) *J* = 7.2	8.13 (d, 8) *J* = 7.8	-	8.20[a]	8.17 (d, 6) *J* = 6.6	-	-	-	-	-	-	-

Chemical shifts, multiplicities (in parentheses) and *J* (Hz) are placed sequentially; confirmed by COSY (400 MHz) analysis; [a]Unresolved; [b]Merged; [c]Unsymmetrical pattern.

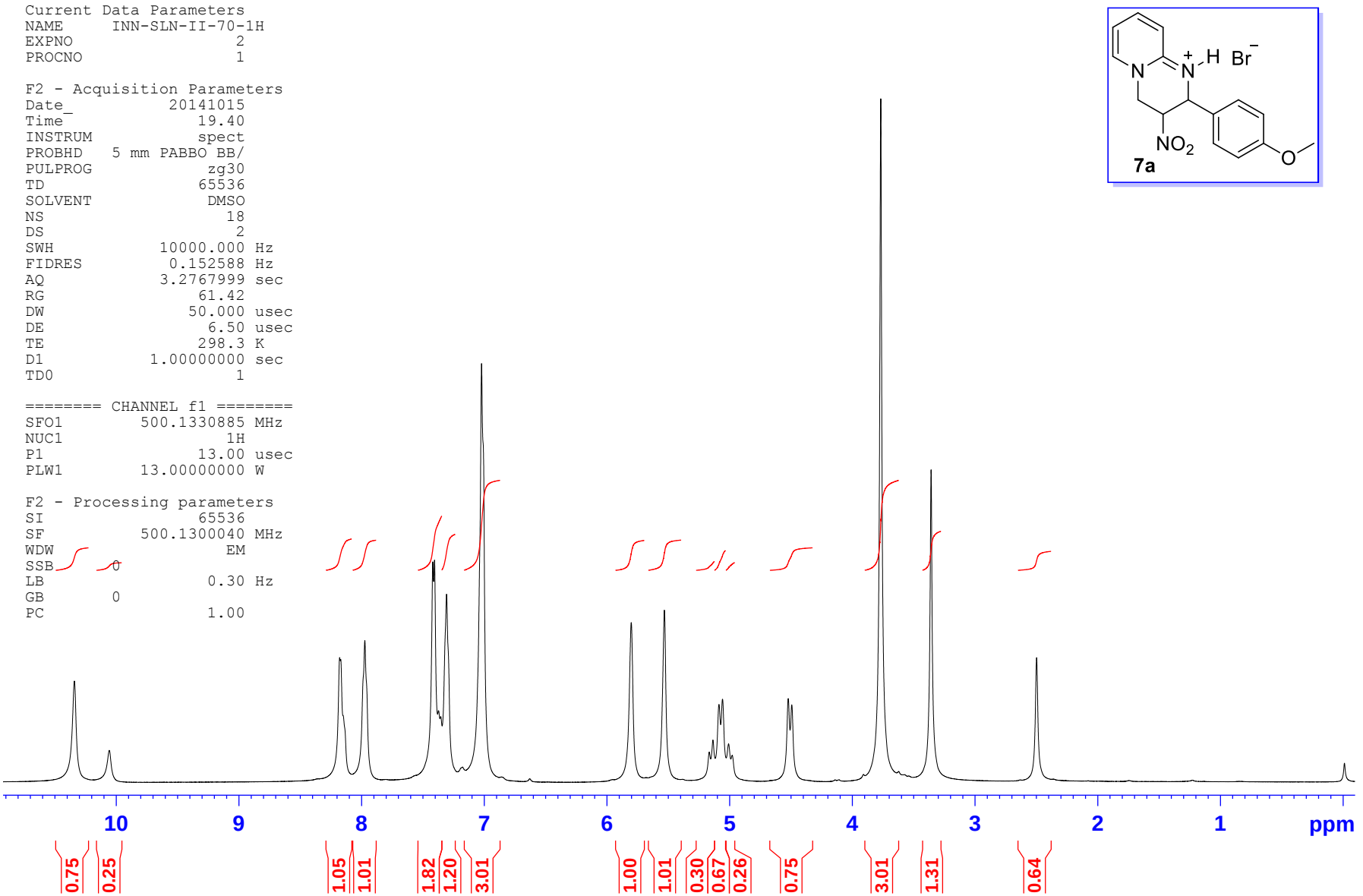


Fig S1. ^{1}H NMR Spectrum of 7a

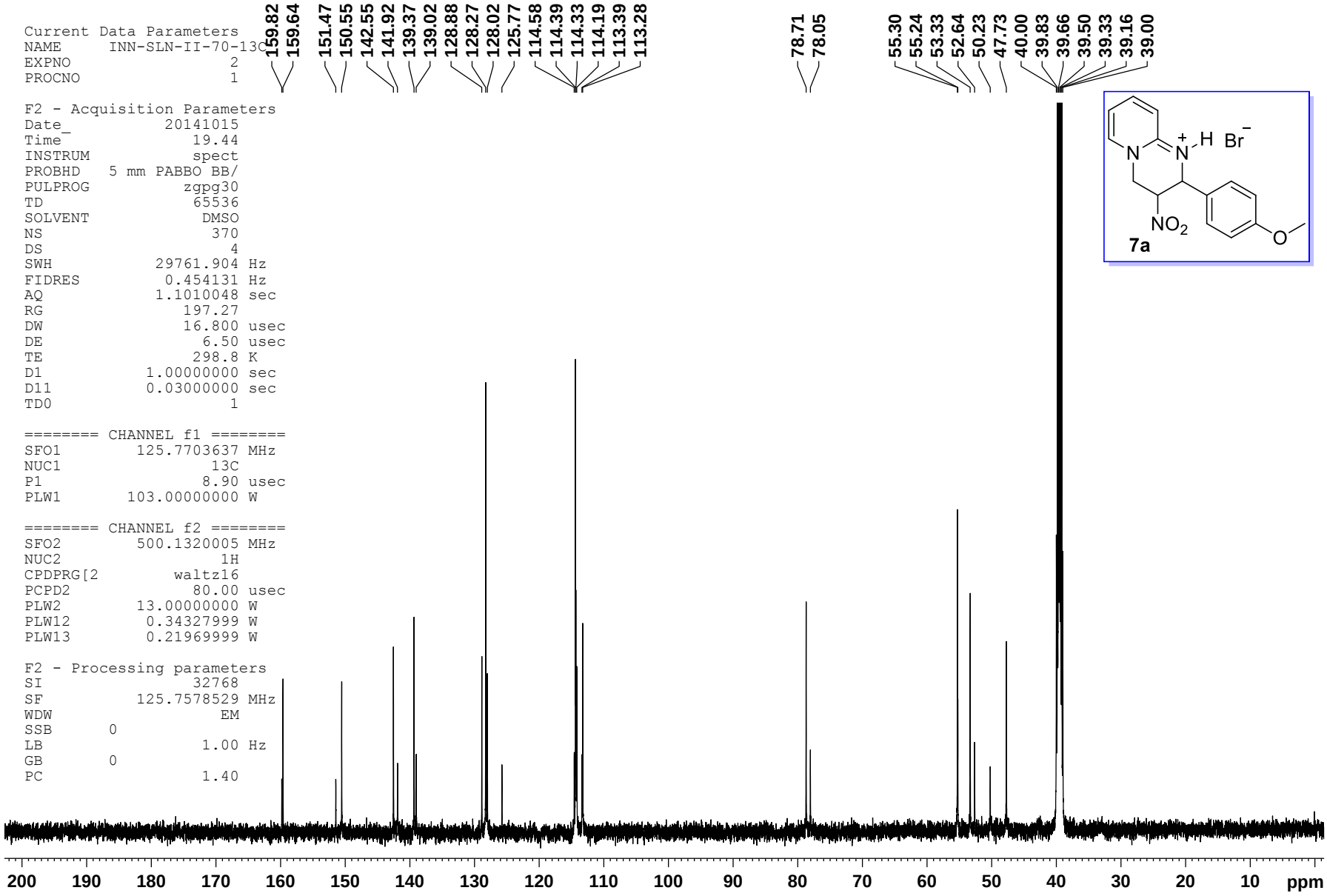


Fig S2. ^{13}C NMR Spectrum of 7a

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PROCNO                  1

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SOLVENT              DMSO
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DS                      2
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FIDRES          0.152588 Hz
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RG                  80.35
DW                 50.000 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                     1

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NUC1                   1H
P1                  13.00 usec
PLW1         13.00000000 W

F2 - Processing parameters
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WDW                    EM
SSB          0
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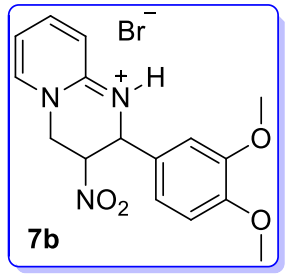


Fig S3. ^{1}H NMR Spectrum of 7b

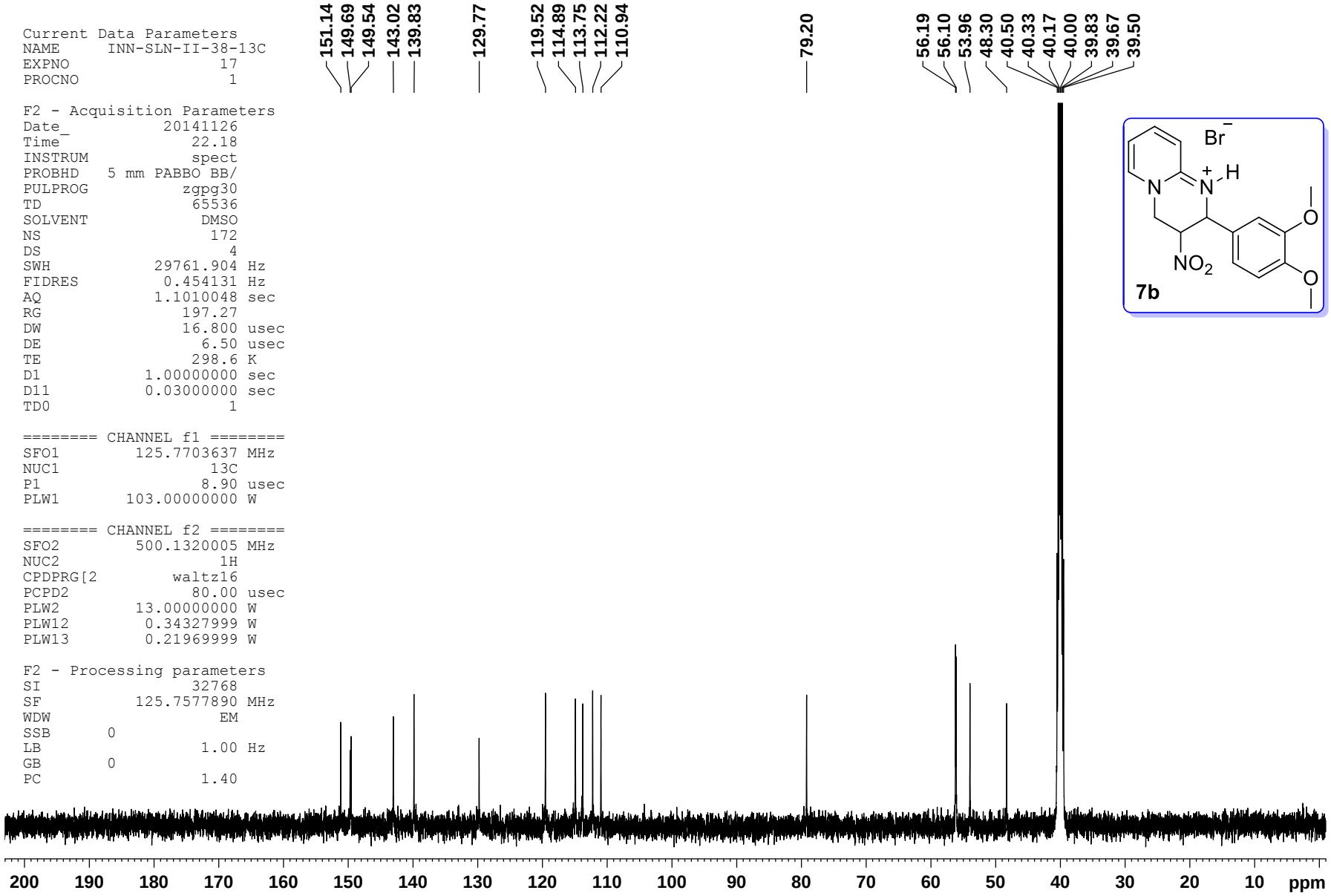
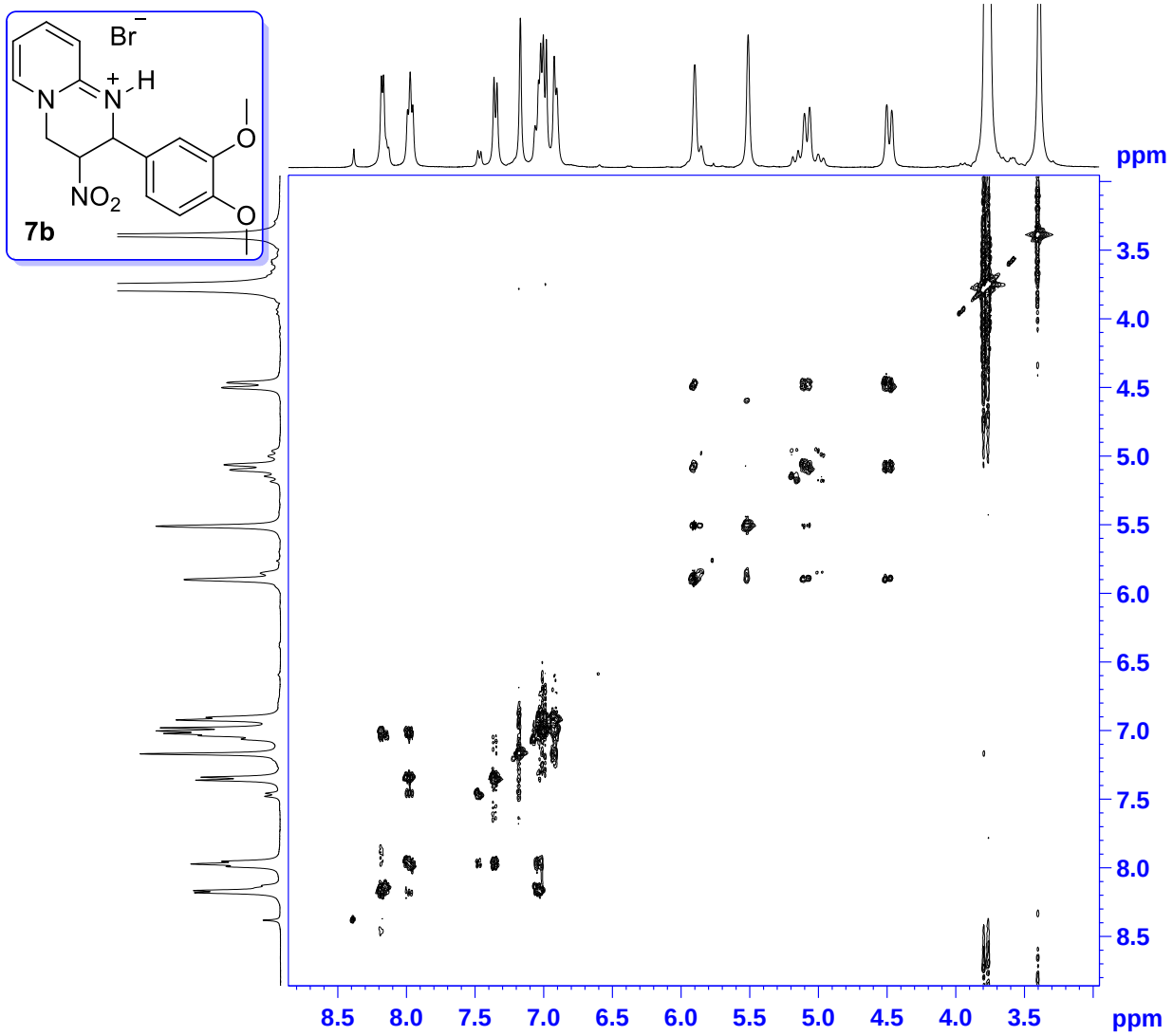


Fig S4. ^{13}C NMR Spectrum of 7b




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TD                   2048
SOLVENT              DMSO
NS                     16
DS                     16
SWH              2362.949 Hz
FIDRES           1.153784 Hz
AQ               0.4333568 sec
RG                    28.5
DW                211.600 usec
DE                  6.50 usec
TE                 295.1 K
D0            0.00000300 sec
D1            1.00000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00042320 sec

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P1                  14.75 usec
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SFO1        400.1323698 MHz

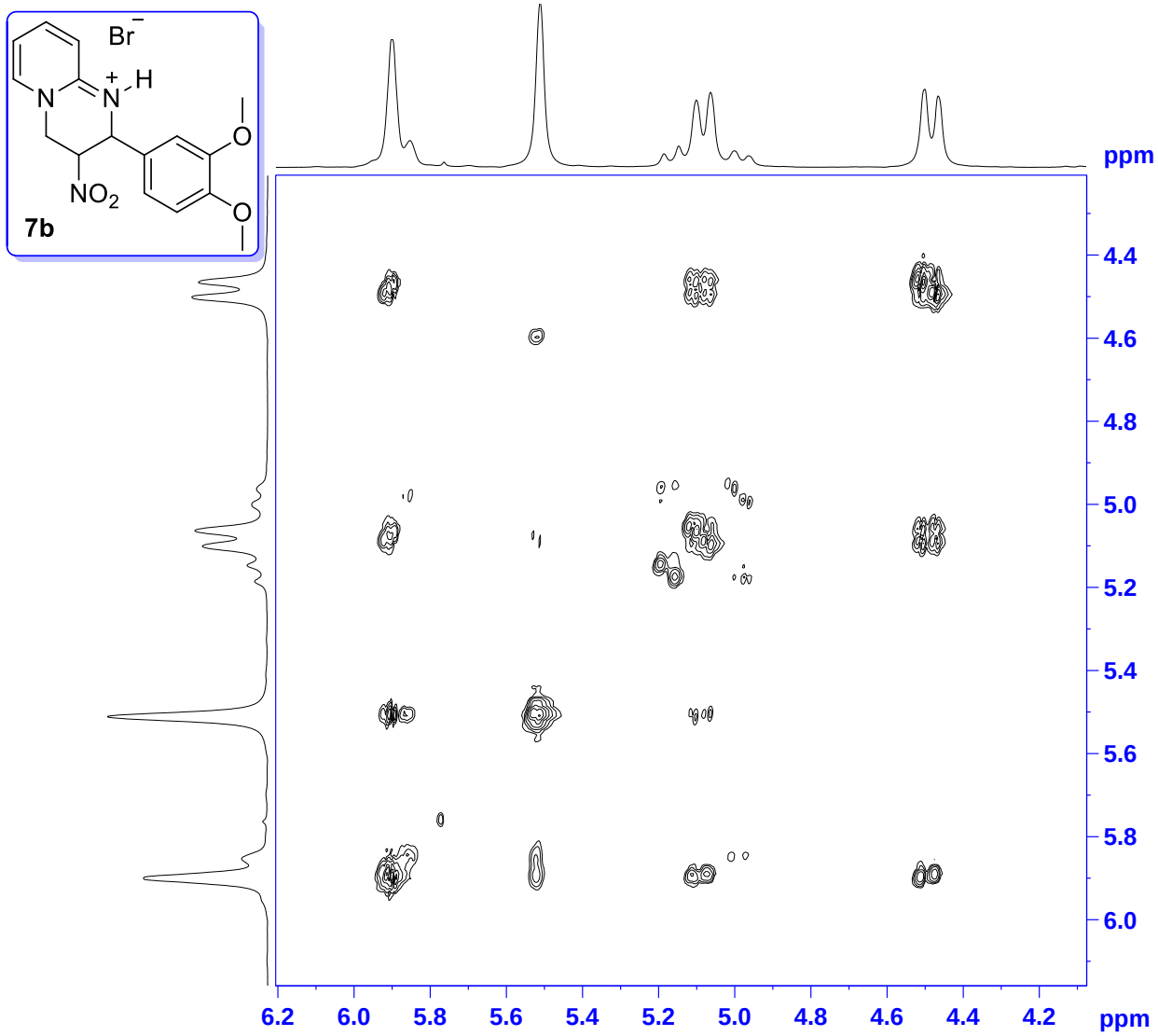
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FnMODE                 QF

F2 - Processing parameters
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SF          400.1300061 MHz
WDW                  SINE
SSB       0
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
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MC2                    QF
SF          400.1300061 MHz
WDW                  SINE
SSB       0
LB        0 Hz
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Fig S5. ^{1}H-^{1}H COSY NMR Spectrum of 7b




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PROCNO                     1

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TD                     2048
SOLVENT                DMSO
NS                       16
DS                       16
SWH                2362.949 Hz
FIDRES             1.153784 Hz
AQ                0.4333568 sec
RG                     28.5
DW                  211.600 usec
DE                    6.50 usec
TE                   295.1 K
D0              0.00000300 sec
D1              1.00000000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00042320 sec

======== CHANNEL f1 ========
NUC1                     1H
P0                    14.75 usec
P1                    14.75 usec
PL1                   -1.00 dB
PL1W          10.56200695 W
SFO1          400.1323698 MHz

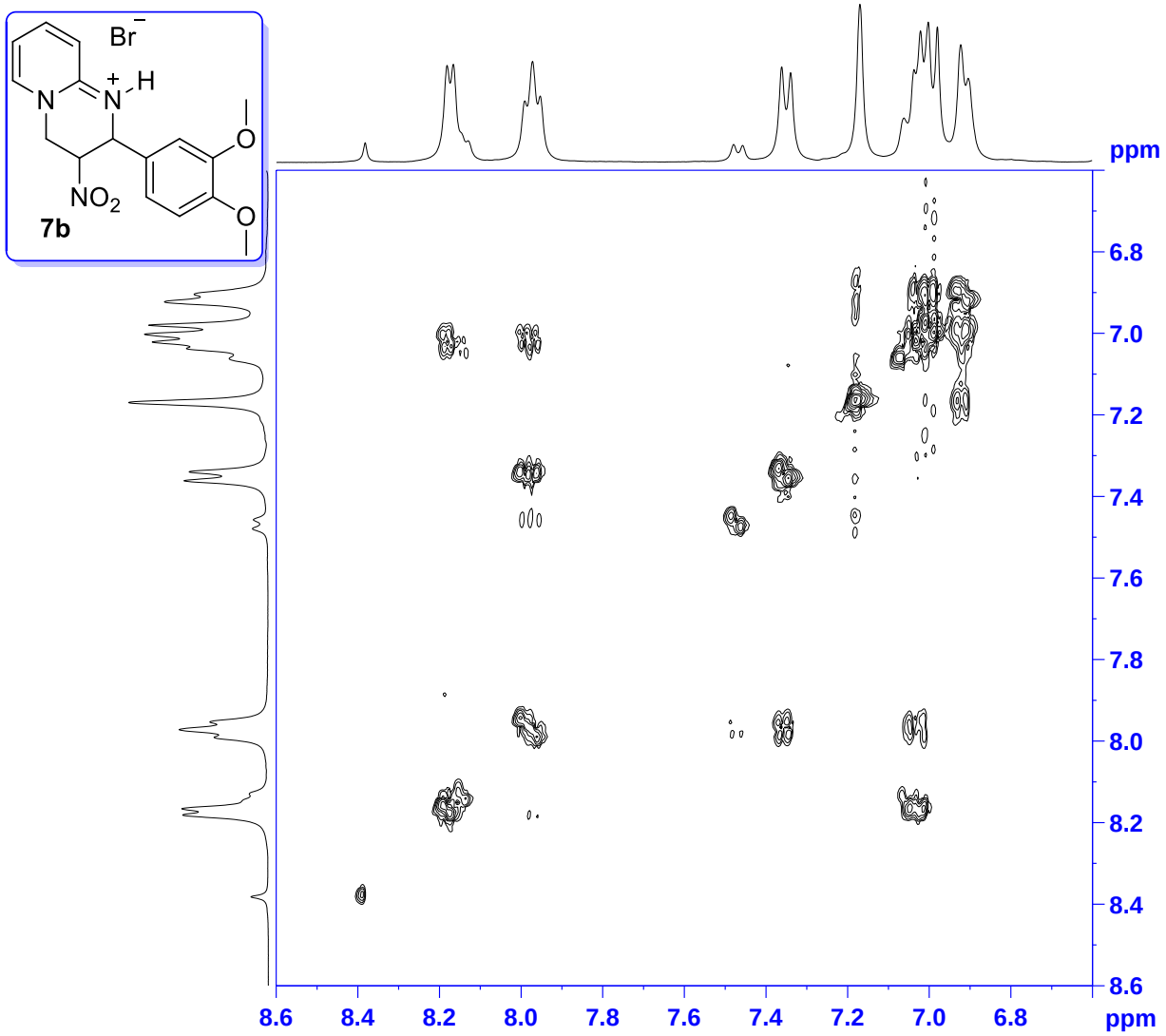
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P16                1000.00 usec

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FIDRES           12.117650 Hz
SW                   5.905 ppm
FnMODE                  QF

F2 - Processing parameters
SI                     2048
SF            400.1300061 MHz
WDW                    SINE
SSB       0
LB        0 Hz
GB        0
PC                     1.40

F1 - Processing parameters
SI                      512
MC2                      QF
SF            400.1300061 MHz
WDW                    SINE
SSB       0
LB        0 Hz
GB        0
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Fig S6. ^{1}H-^{1}H COSY NMR Spectrum of 7b (Expansion)




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PROCNO                 1

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TD                 2048
SOLVENT             DMSO
NS                   16
DS                   16
SWH             2362.949 Hz
FIDRES          1.153784 Hz
AQ             0.4333568 sec
RG                  28.5
DW               211.600 usec
DE                 6.50 usec
TE                295.1 K
D0            0.00000300 sec
D1            1.00000000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00042320 sec

======== CHANNEL f1 ========
NUC1                 1H
P0                14.75 usec
P1                14.75 usec
PL1               -1.00 dB
PL1W        10.56200695 W
SFO1       400.1323698 MHz

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

F1 - Acquisition parameters
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SFO1           400.1324 MHz
FIDRES         12.117650 Hz
SW                5.905 ppm
FnMODE               QF

F2 - Processing parameters
SI                 2048
SF          400.1300061 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
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WDW                SINE
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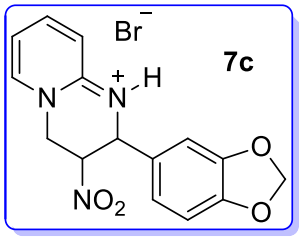
Fig S7. ^{1}H-^{1}H COSY NMR Spectrum of 7b (Expansion)

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SOLVENT             DMSO
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RG                 85.91
DW                50.000 usec
DE                 6.50 usec
TE                301.7 K
D1             1.00000000 sec
TD0                    1

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

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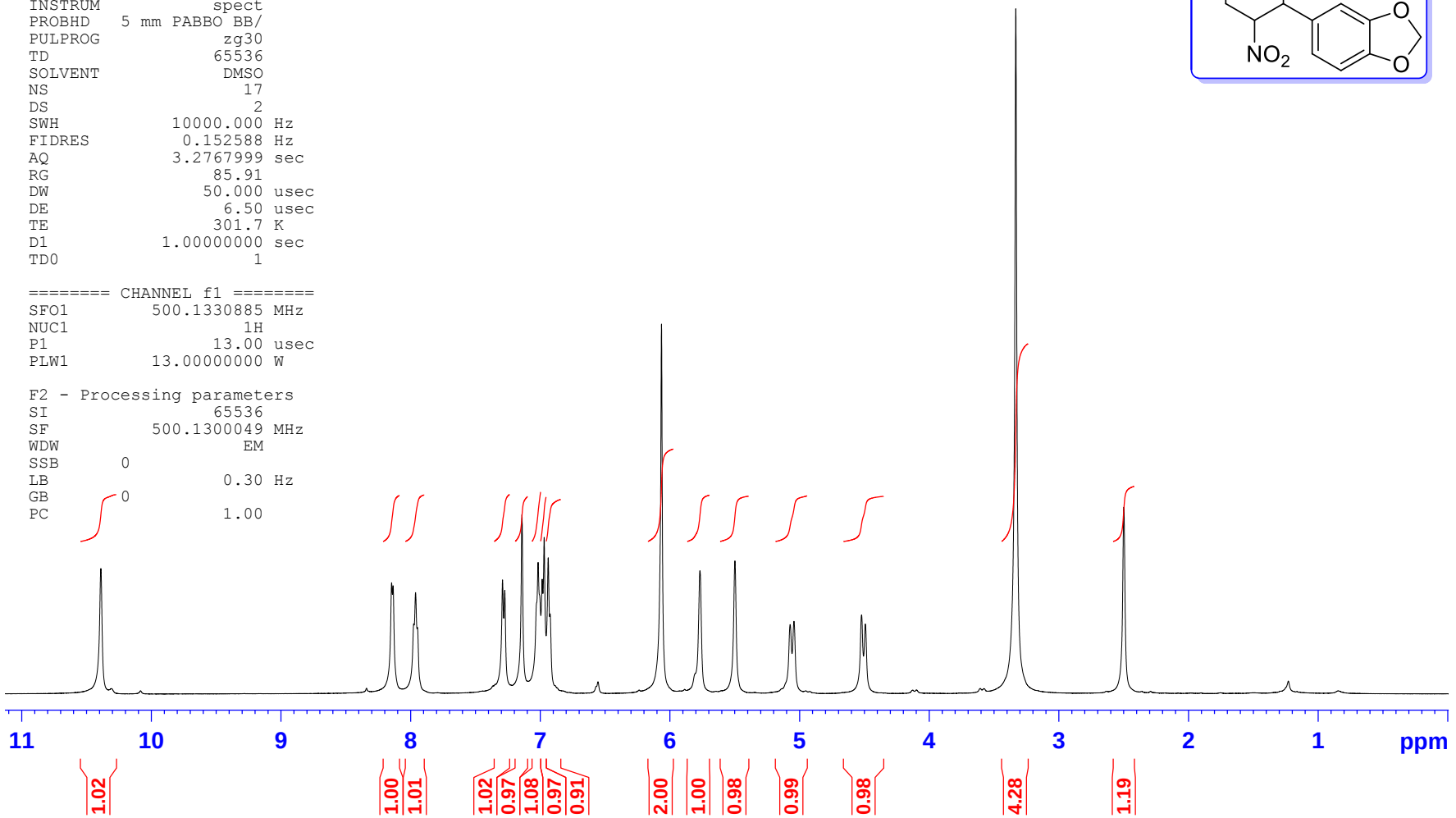


Fig S8. ^{1}H NMR Spectrum of 7c

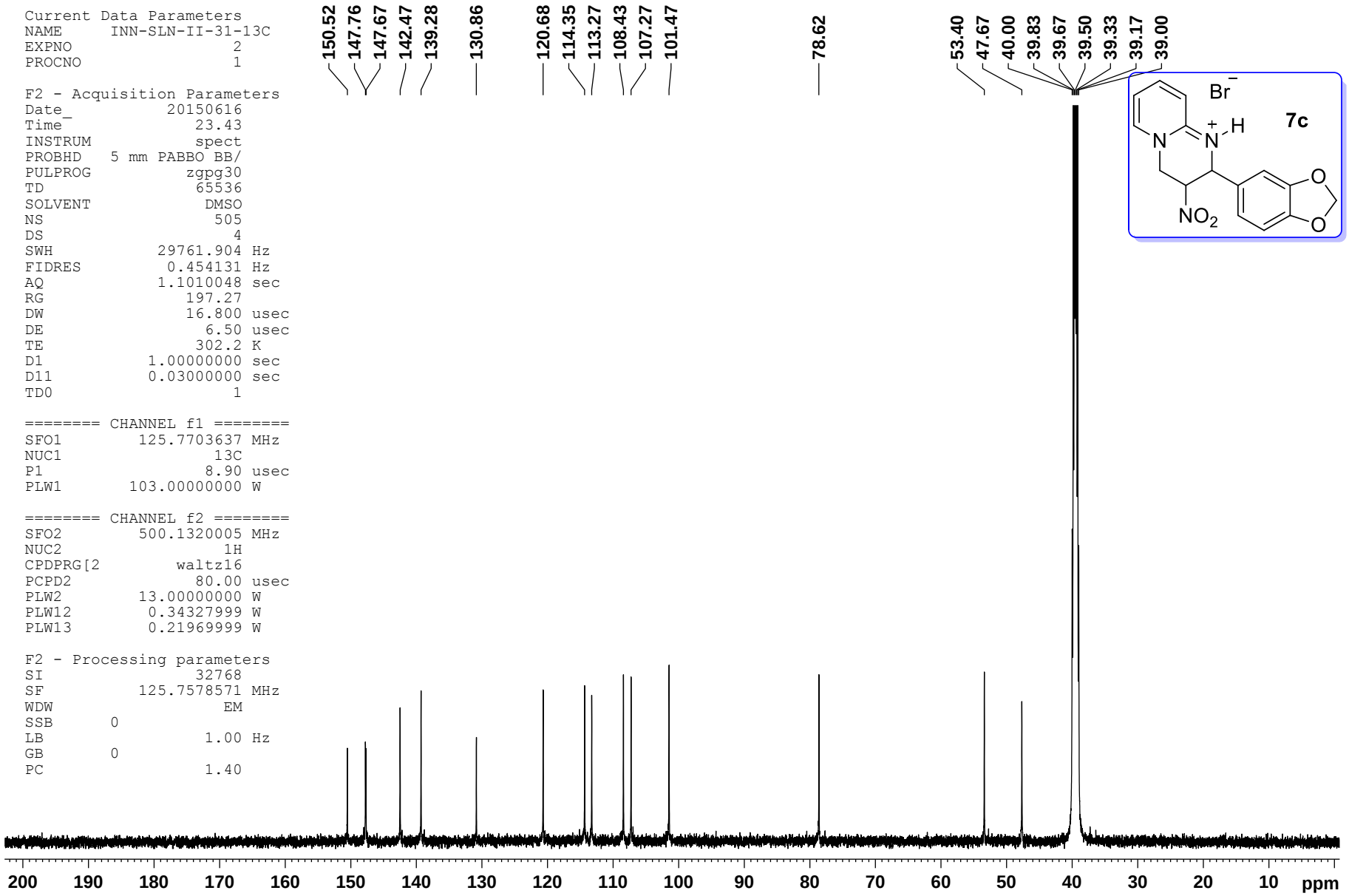


Fig S9. ^{13}C NMR Spectrum of 7c

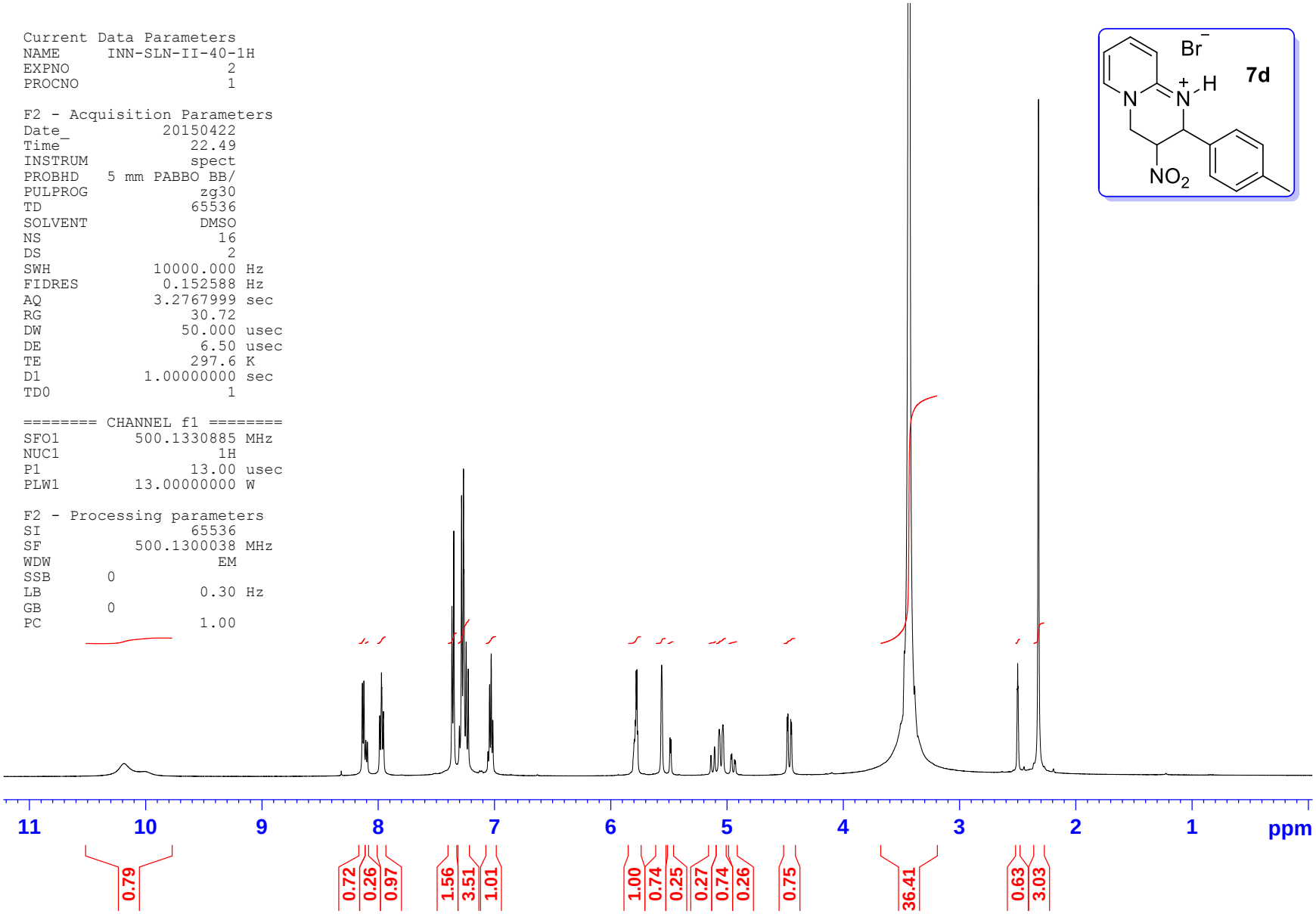


Fig S10. ^{1}H NMR Spectrum of 7d

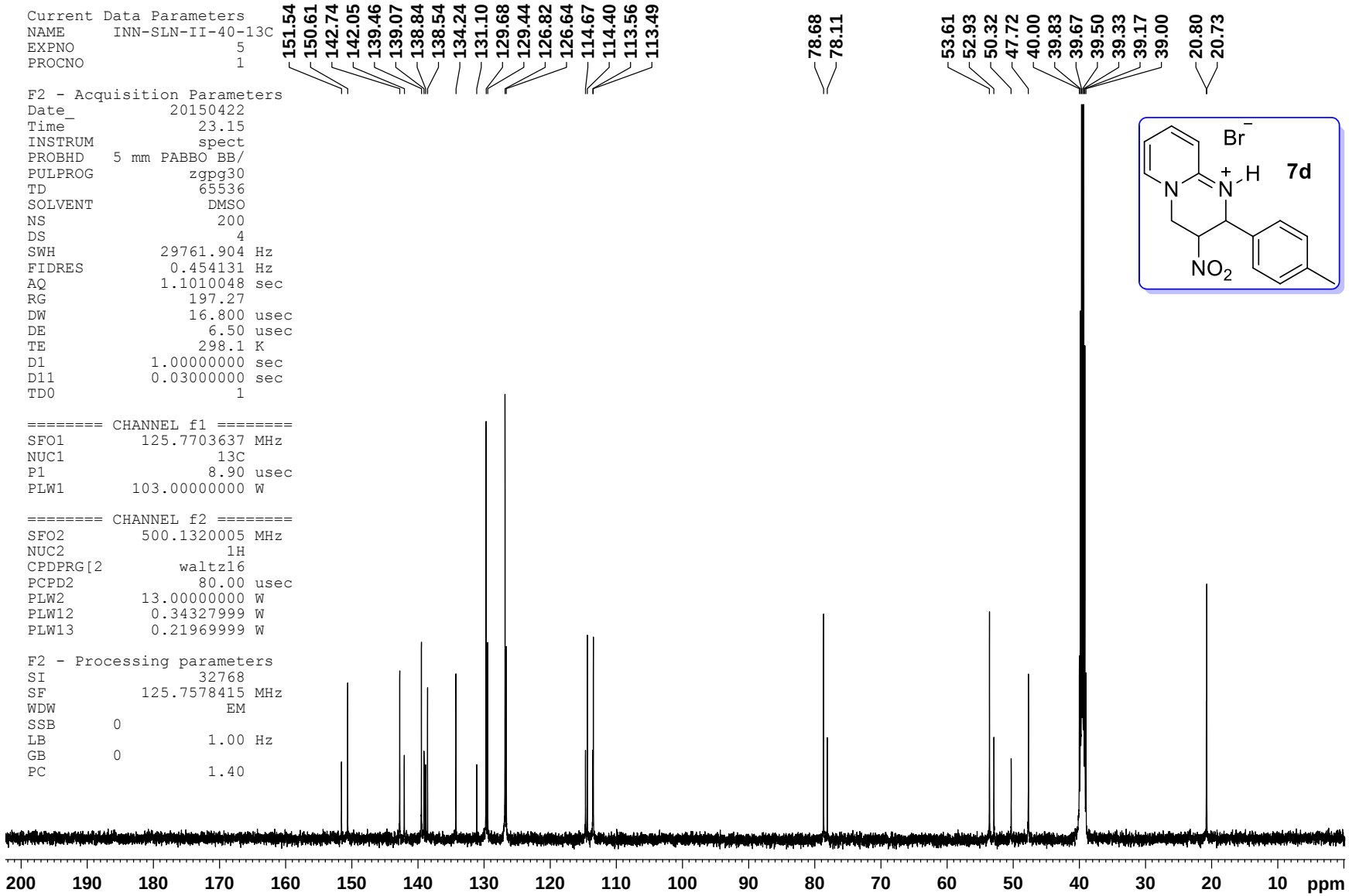


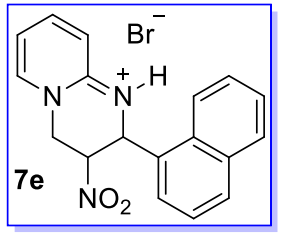
Fig S11. ^{13}C NMR Spectrum of 7d

```
Current Data Parameters
NAME      INN-SLN-II-111-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20150225
Time                22.51
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 85.91
DW                50.000 usec
DE                 6.50 usec
TE                 297.5 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           500.1300035 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



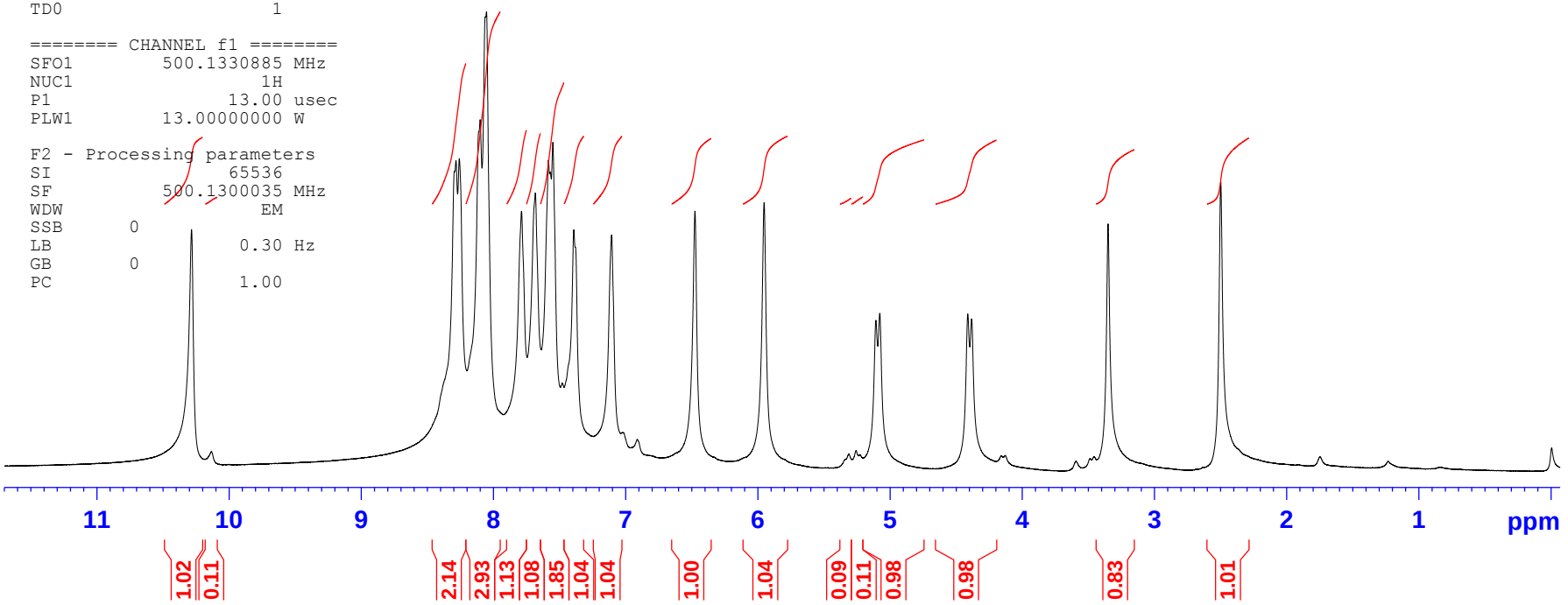


Fig S12. ^{1}H NMR Spectrum of 7e

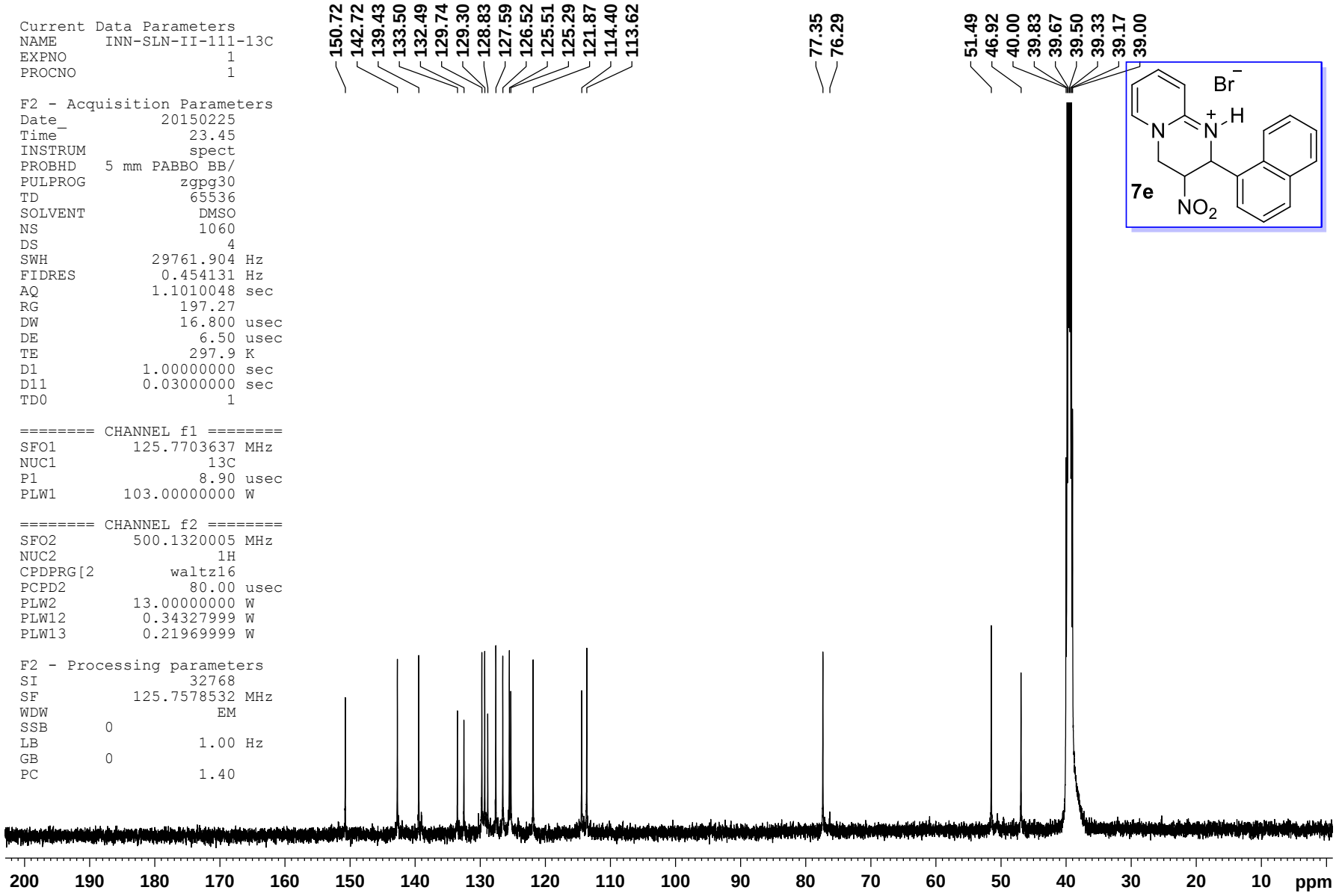


Fig S13. ^{13}C NMR Spectrum of 7e

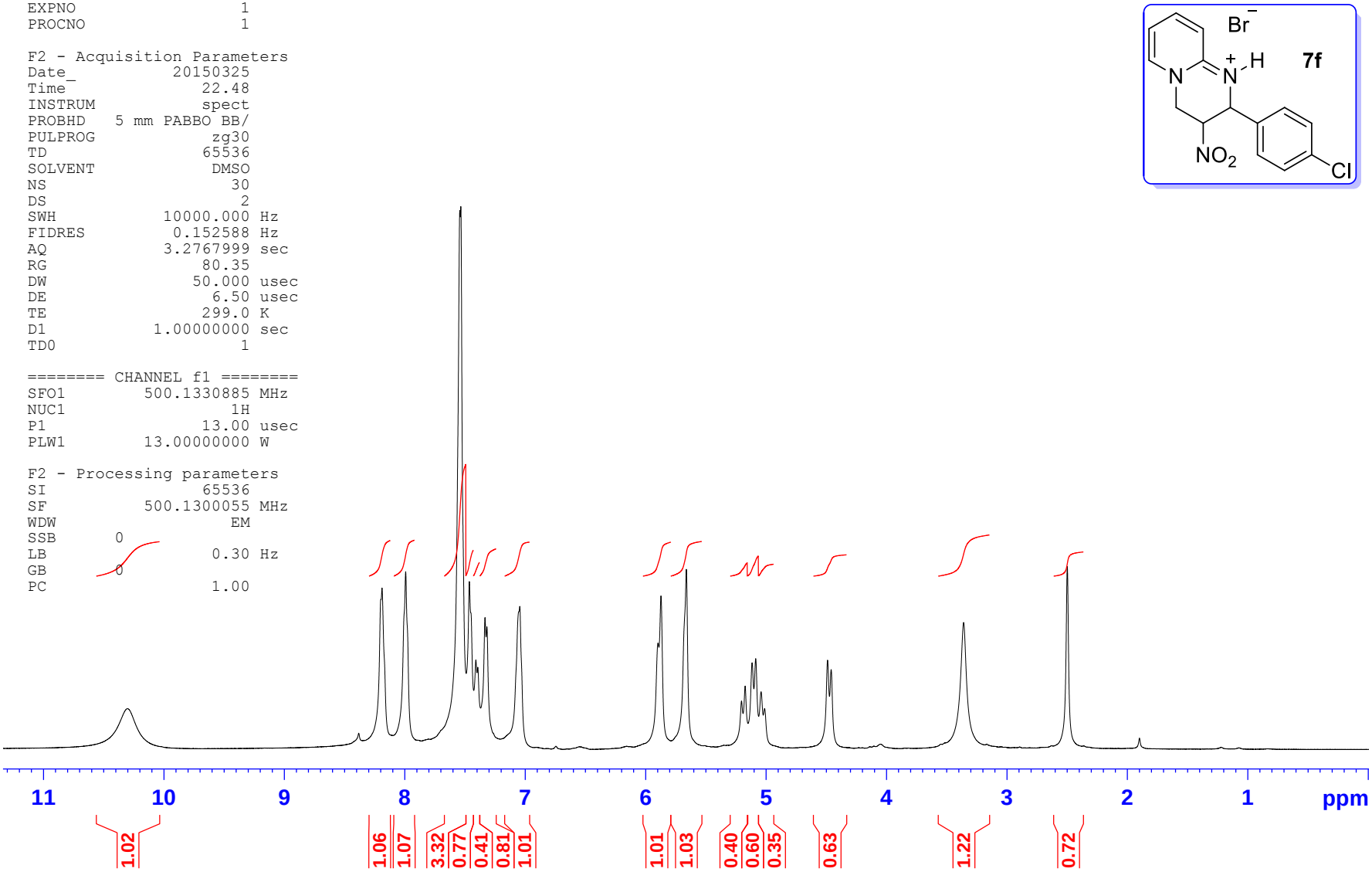


Fig S14. ^{1}H NMR Spectrum of 7f

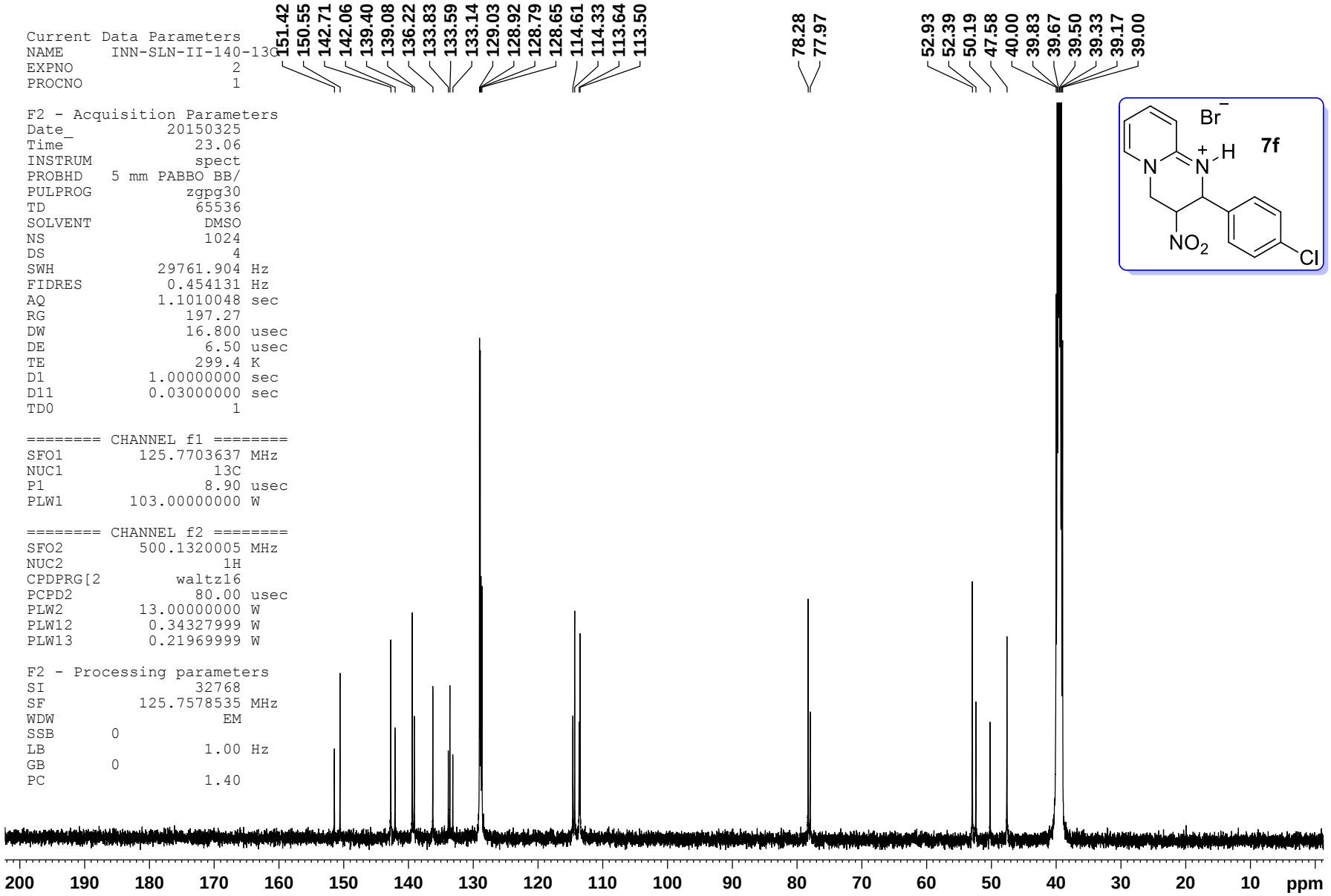


Fig S15. ^{13}C NMR Spectrum of 7f

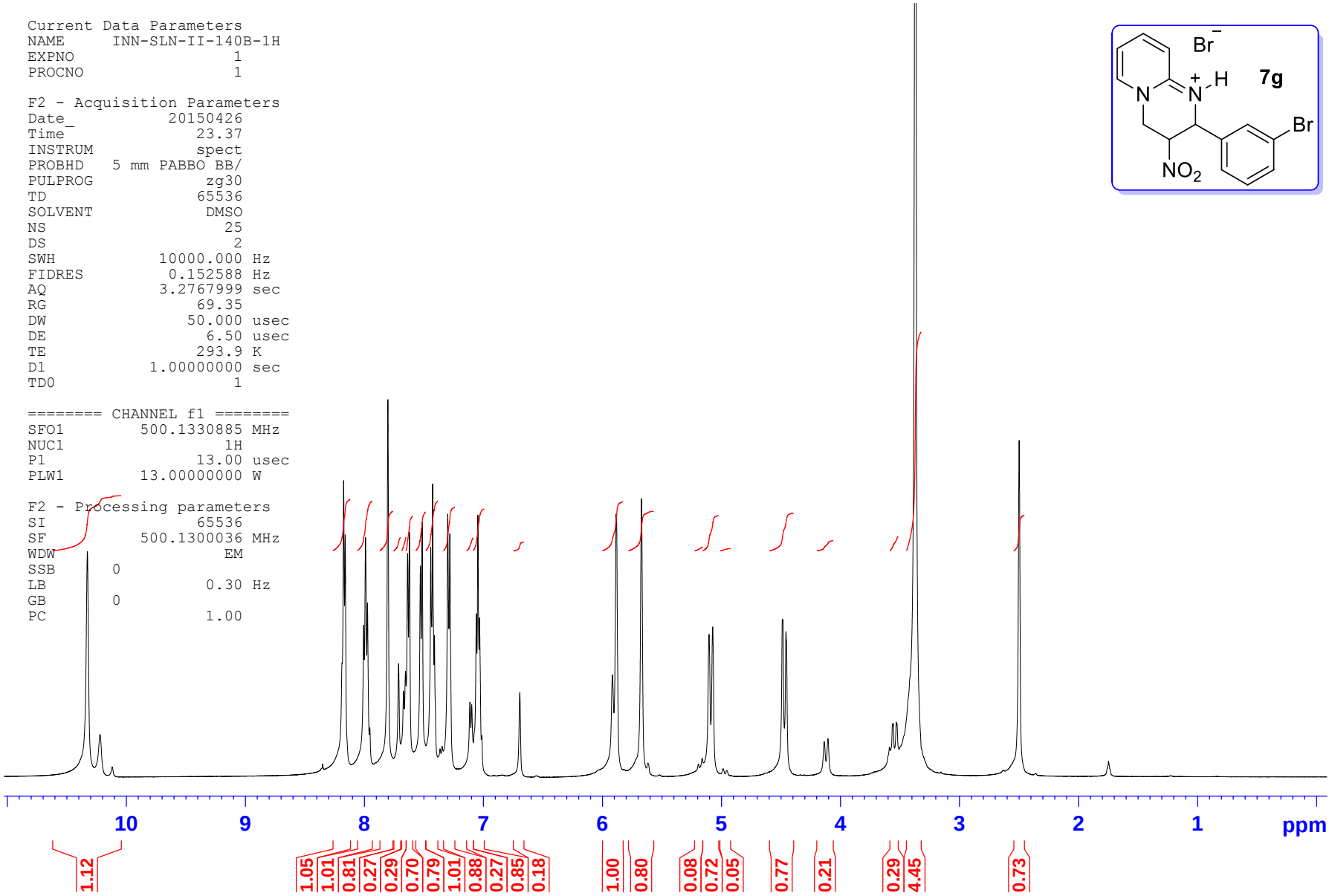


Fig S16. ^{1}H NMR Spectrum of 7g

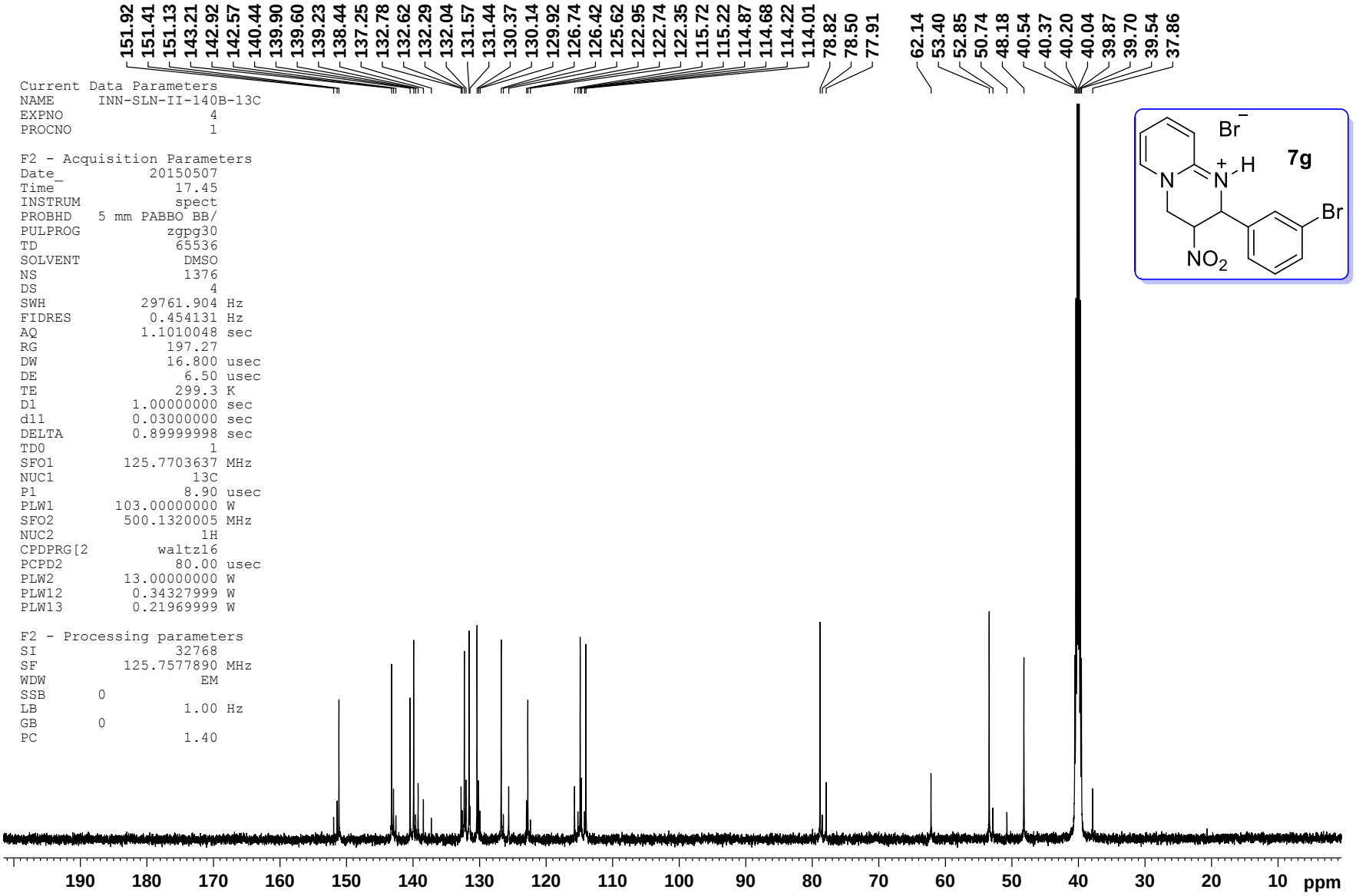


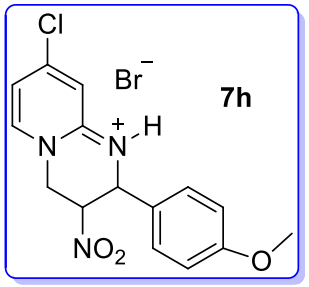
Fig S17. ^{13}C NMR Spectrum of 7g

```
Current Data Parameters
NAME      INN-SLN-II-142A-1H
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150410
Time               16.57
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 54274
SOLVENT             DMSO
NS                    30
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                 295.2 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          400.1300037 MHz
WDW                   EM
SSB        0
LB                  0.30 Hz
GB         0
PC                  1.00
```



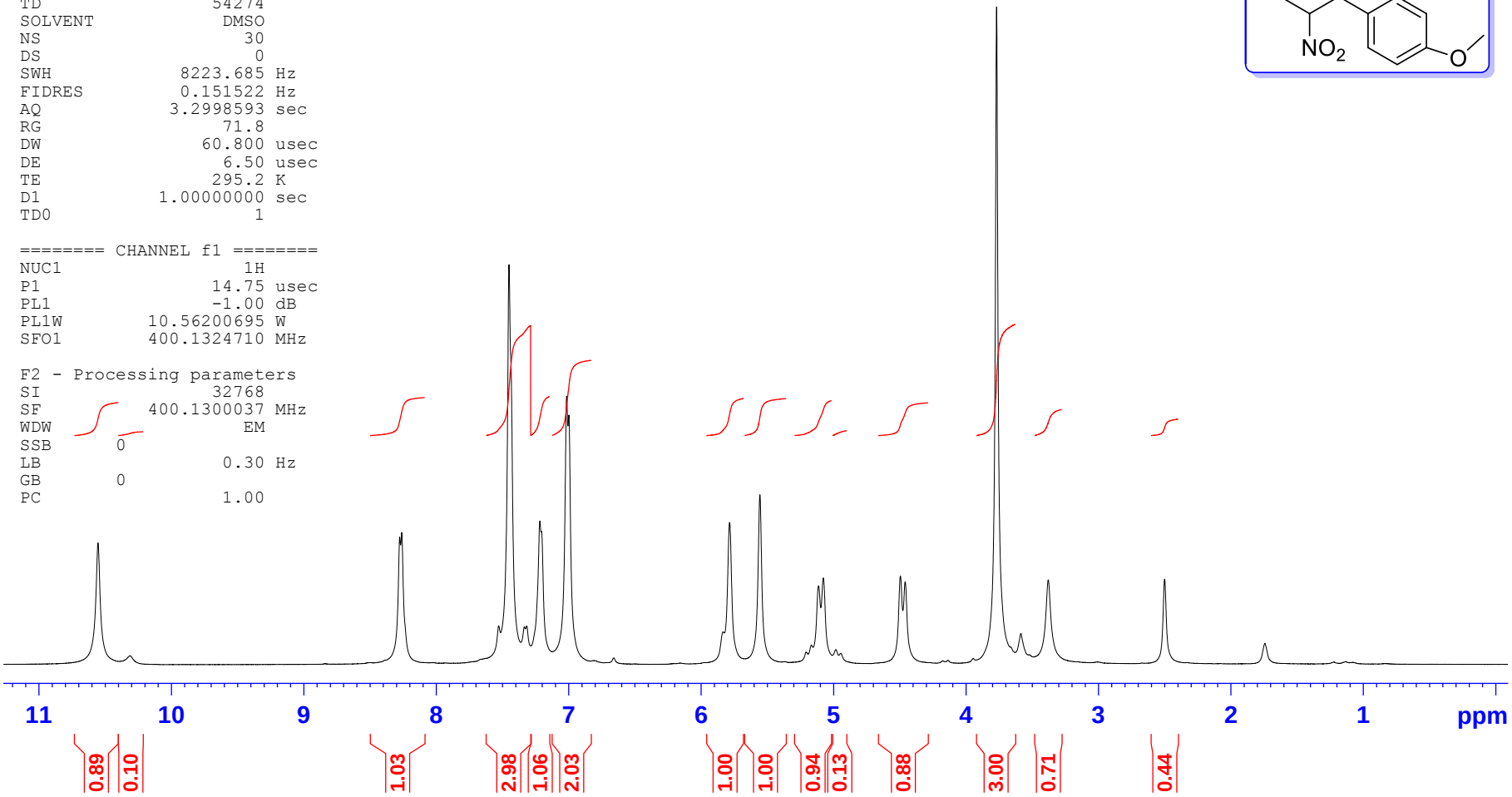


Fig S18. ^{1}H NMR Spectrum of 7h

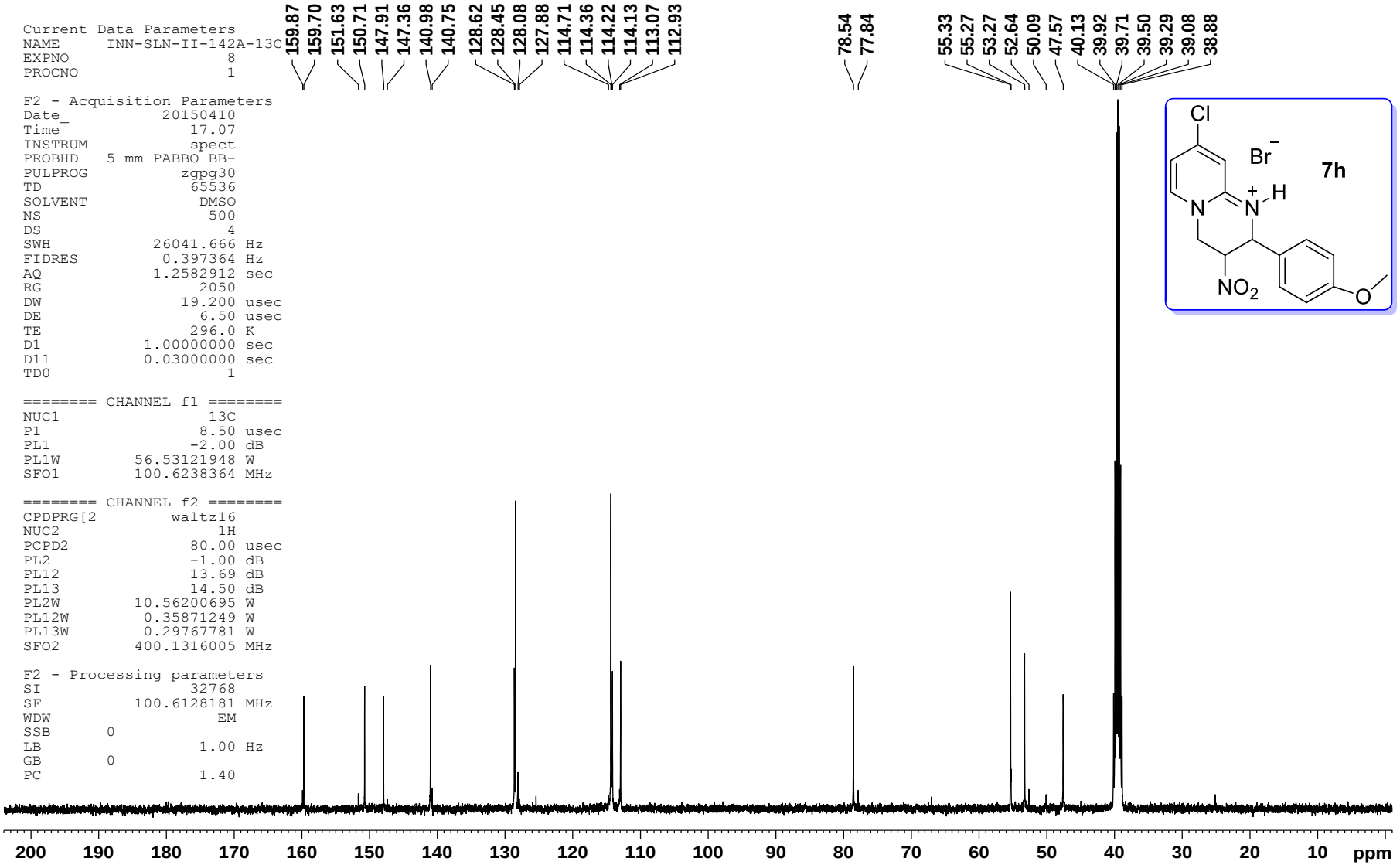


Fig S19. ^{13}C NMR Spectrum of 7h

```
Current Data Parameters
NAME      inn-sln-ii-20-1h
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20150126
Time               11.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
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                295.5 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           500.1300041 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

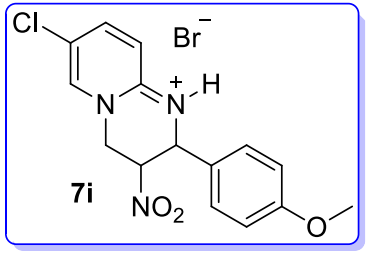


Fig S20. ^{1}H NMR Spectrum of 7i

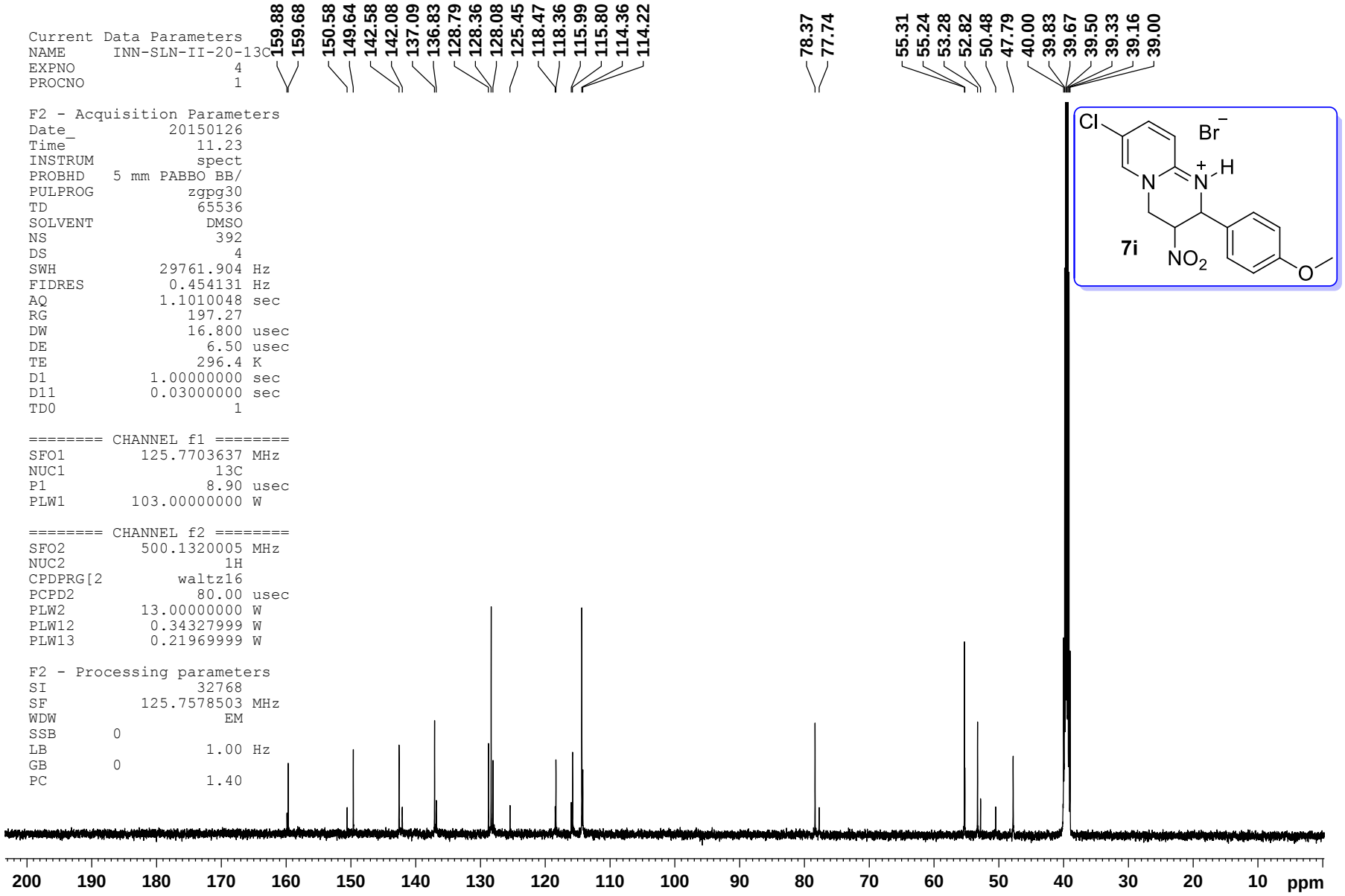


Fig S21. ^{13}C NMR Spectrum of 7i

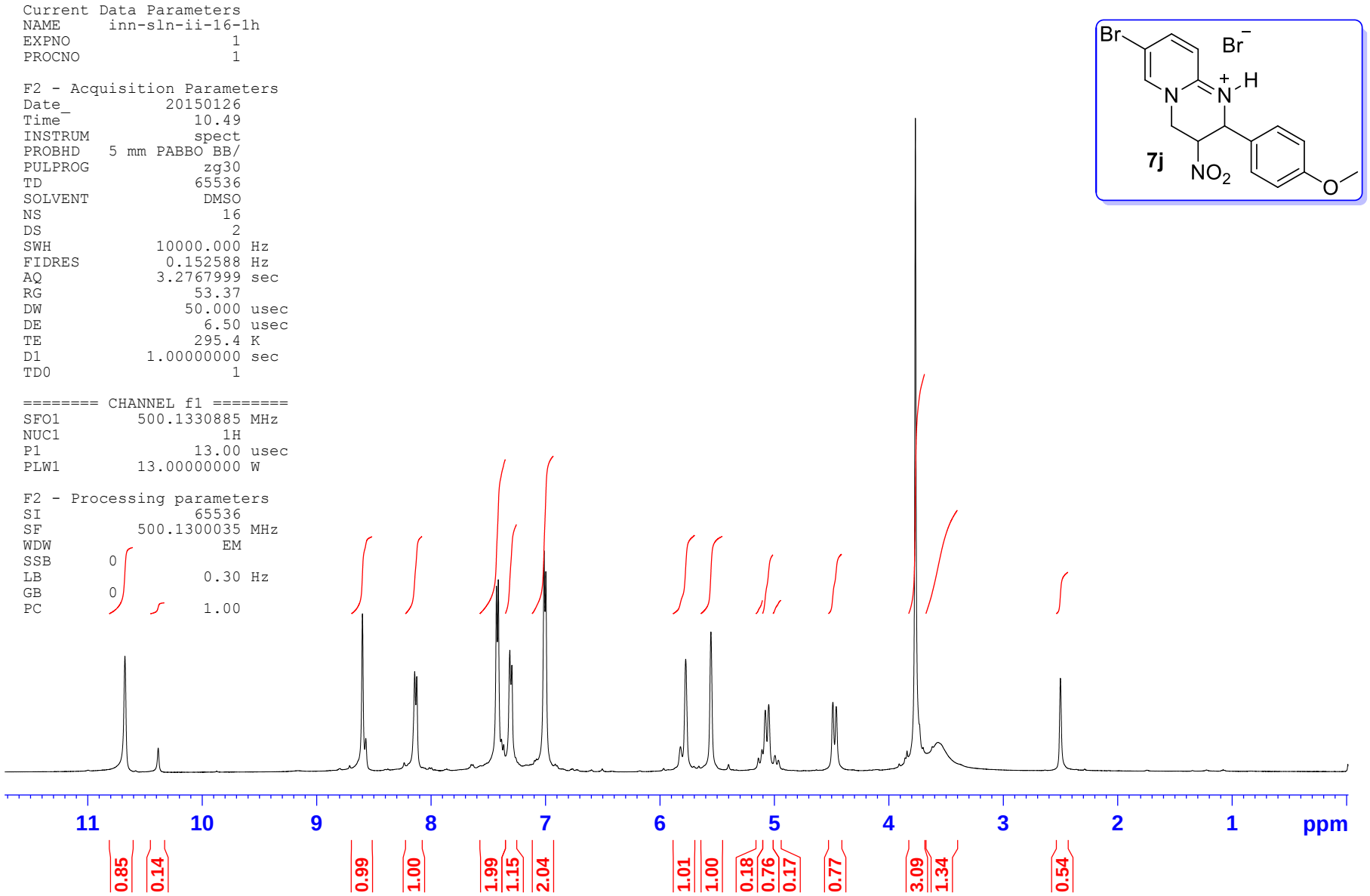


Fig S22. ^{1}H NMR Spectrum of 7j

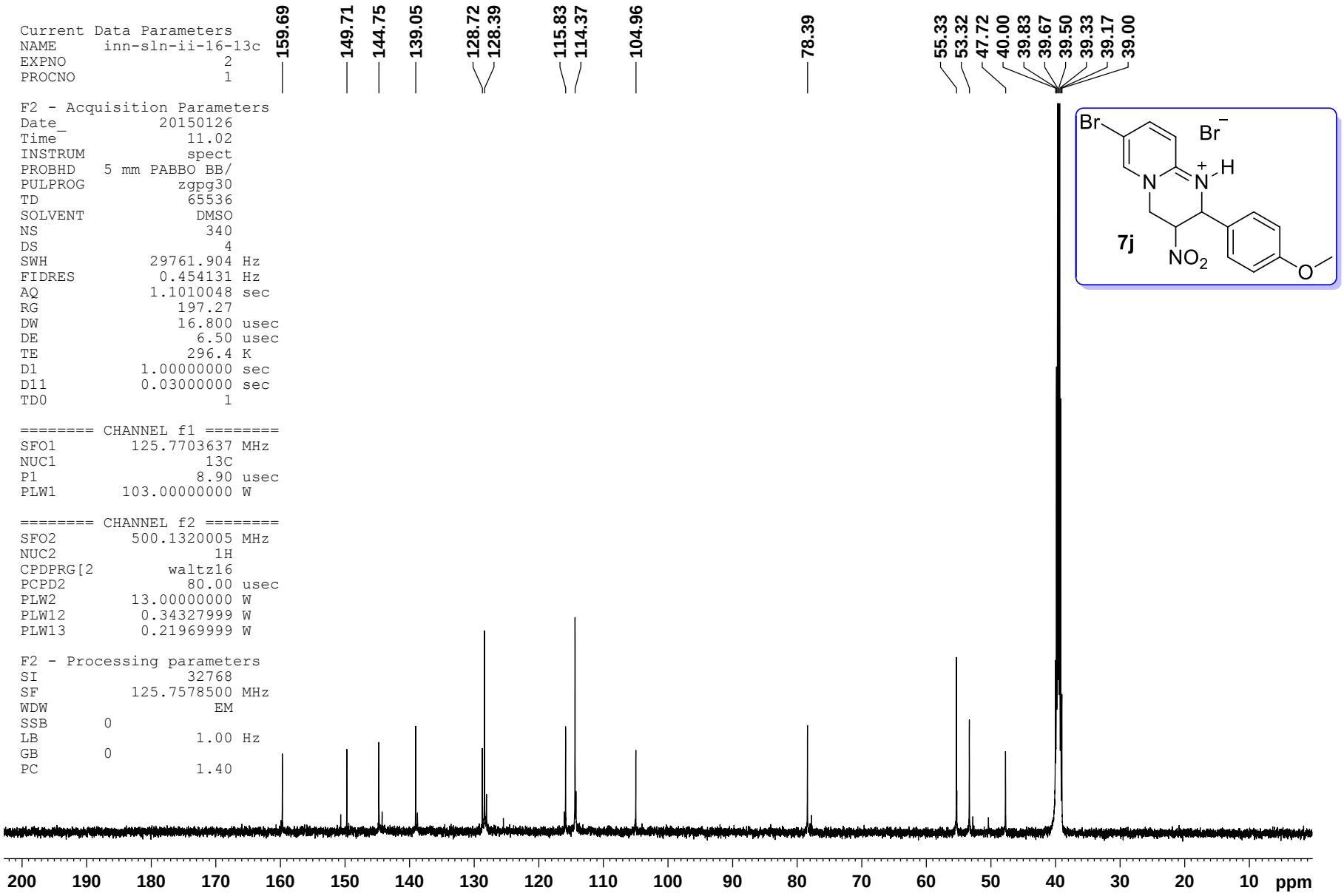


Fig S23. ^{13}C NMR Spectrum of 7j

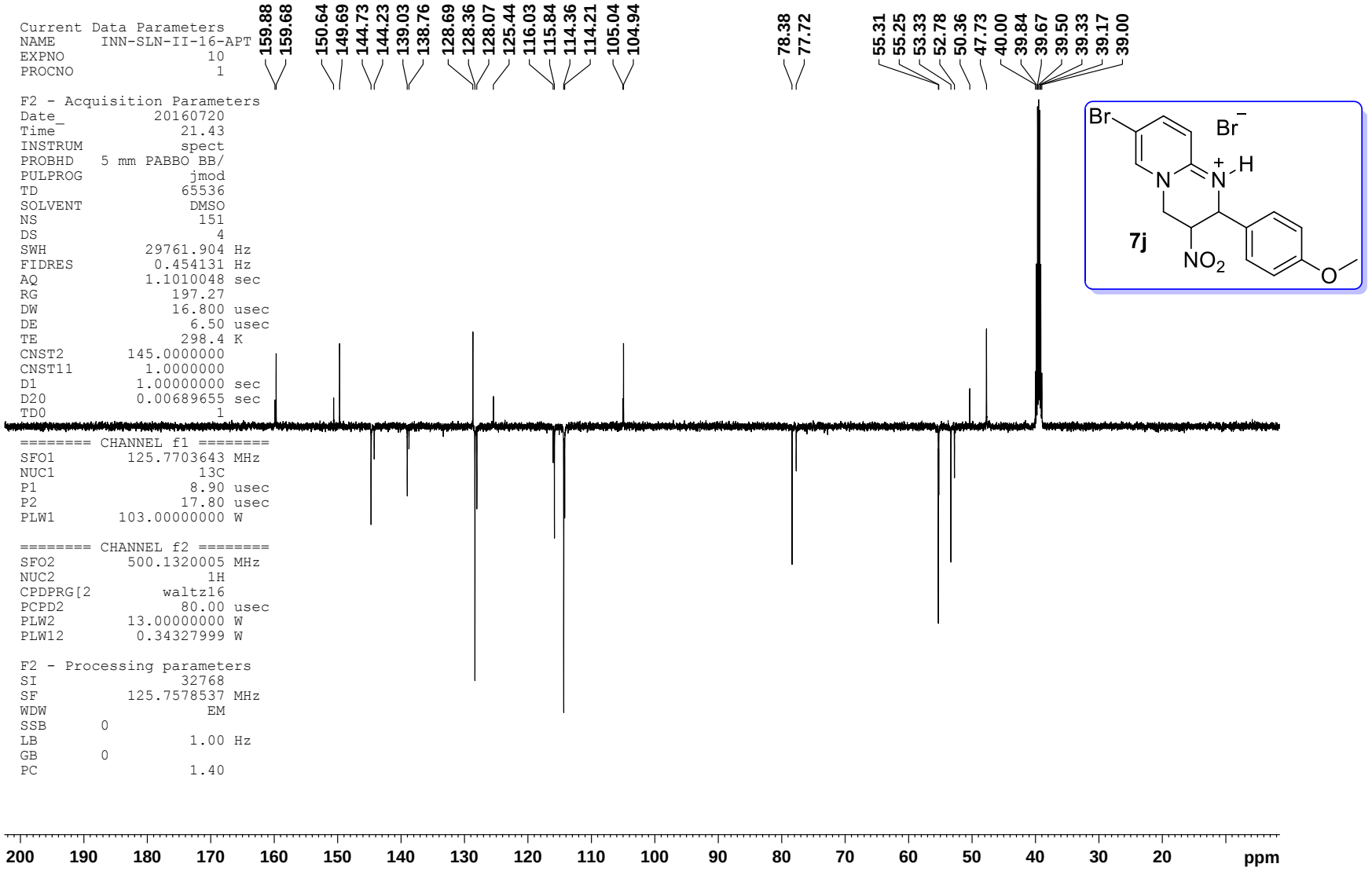


Fig S24. ^{13}C-APT NMR Spectrum of 7j

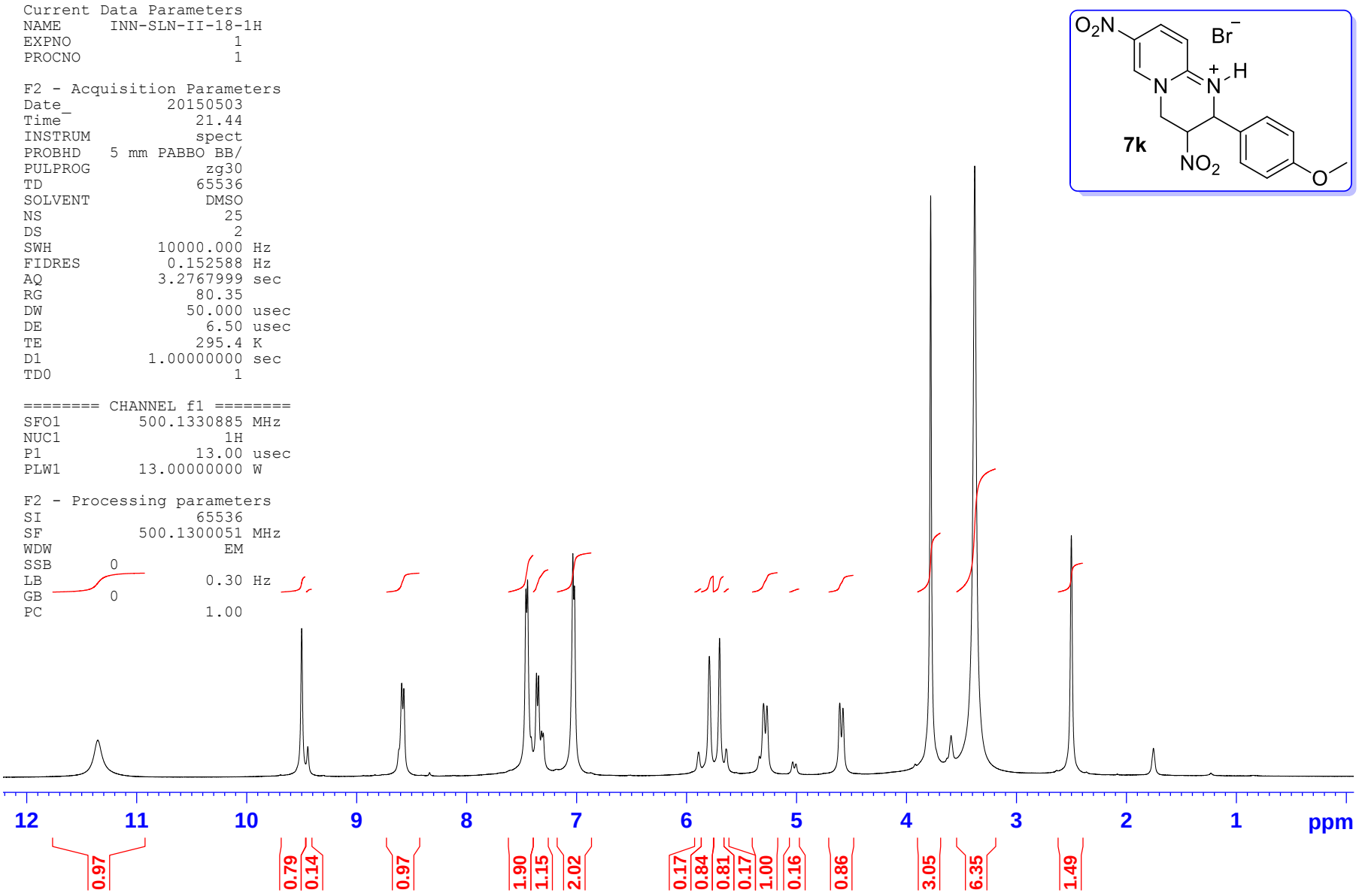


Fig S25. ^{1}H NMR Spectrum of 7k

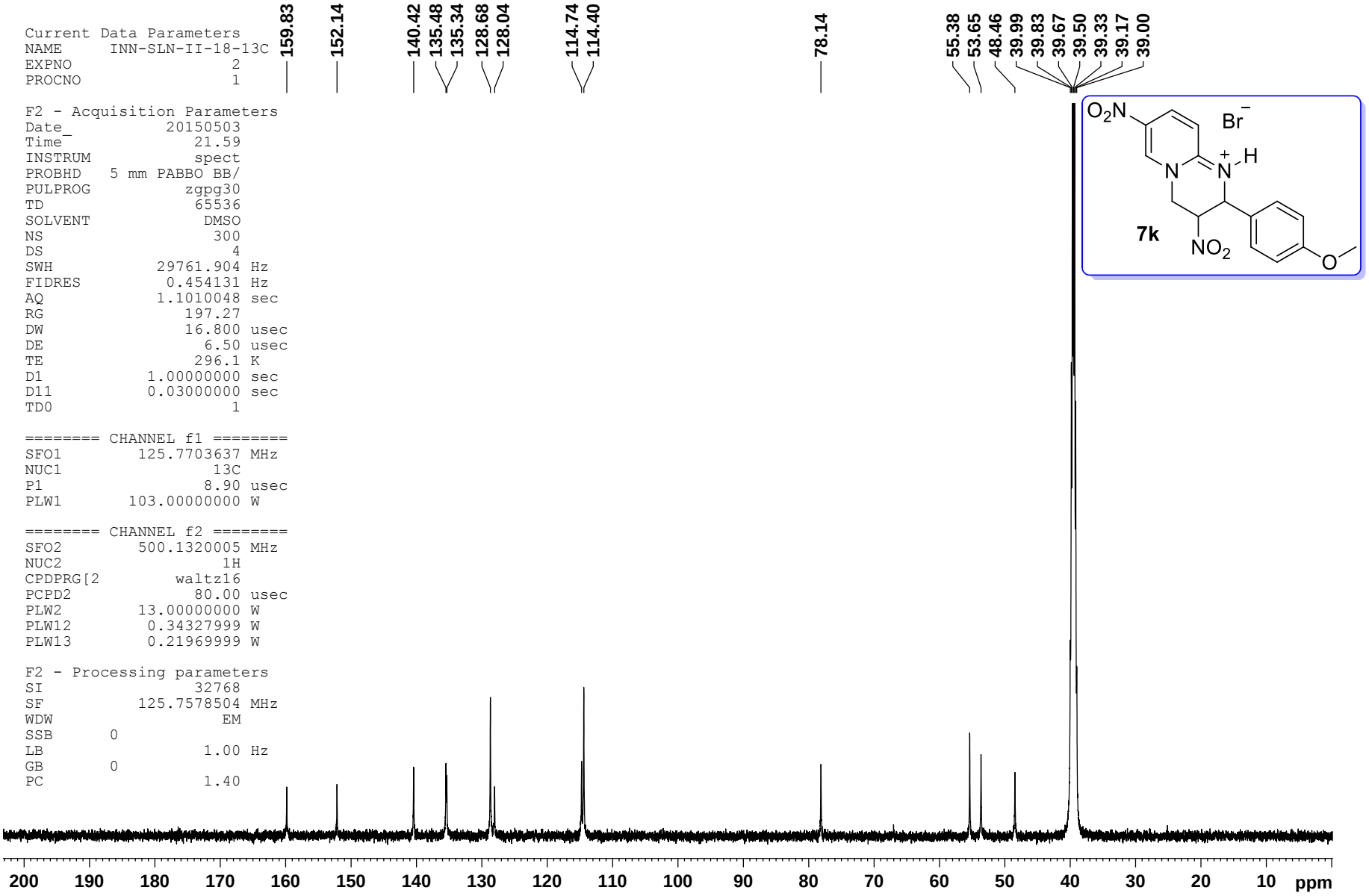


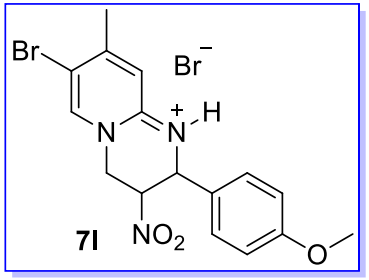
Fig S26. ^{13}C NMR Spectrum of 7k

```
Current Data Parameters
NAME      INN-SLN-II-142-B
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20150403
Time               12.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
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                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          500.1300034 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



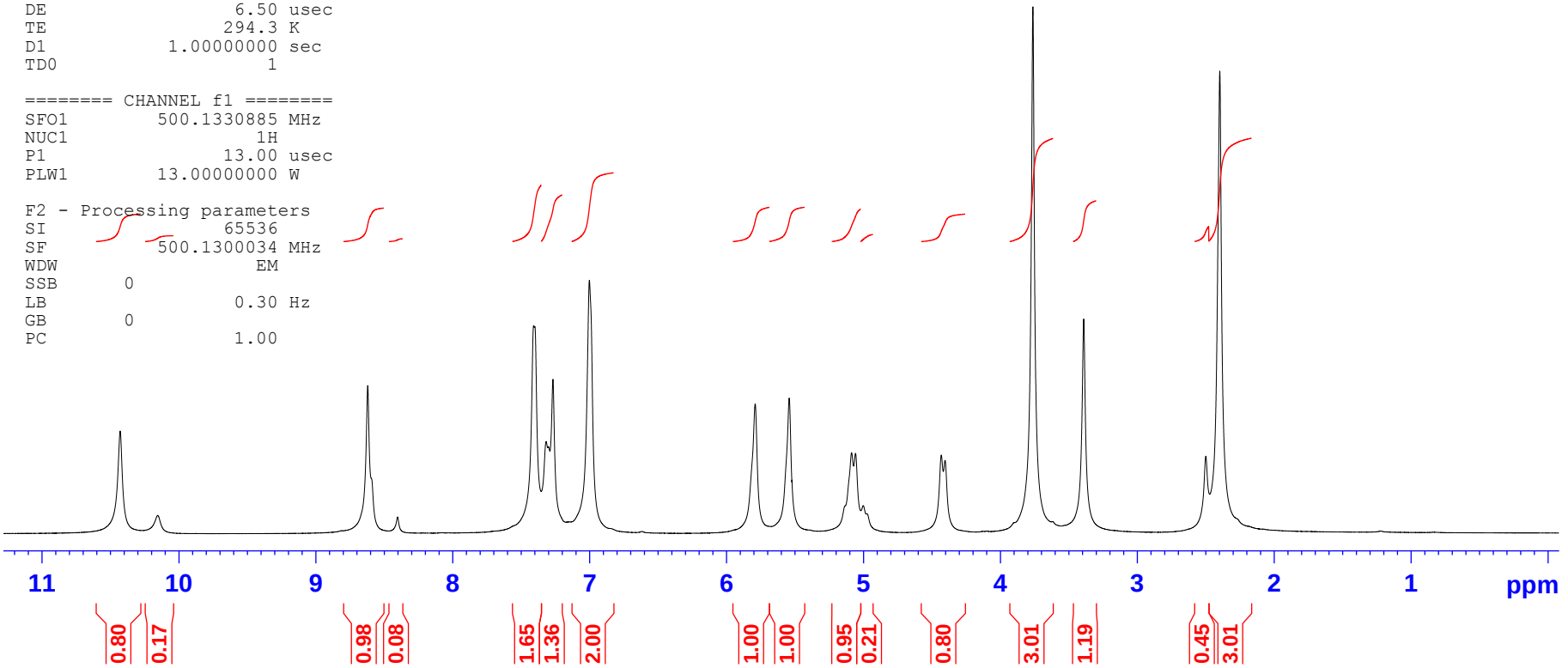


Fig S27. ^{1}H NMR Spectrum of 7l

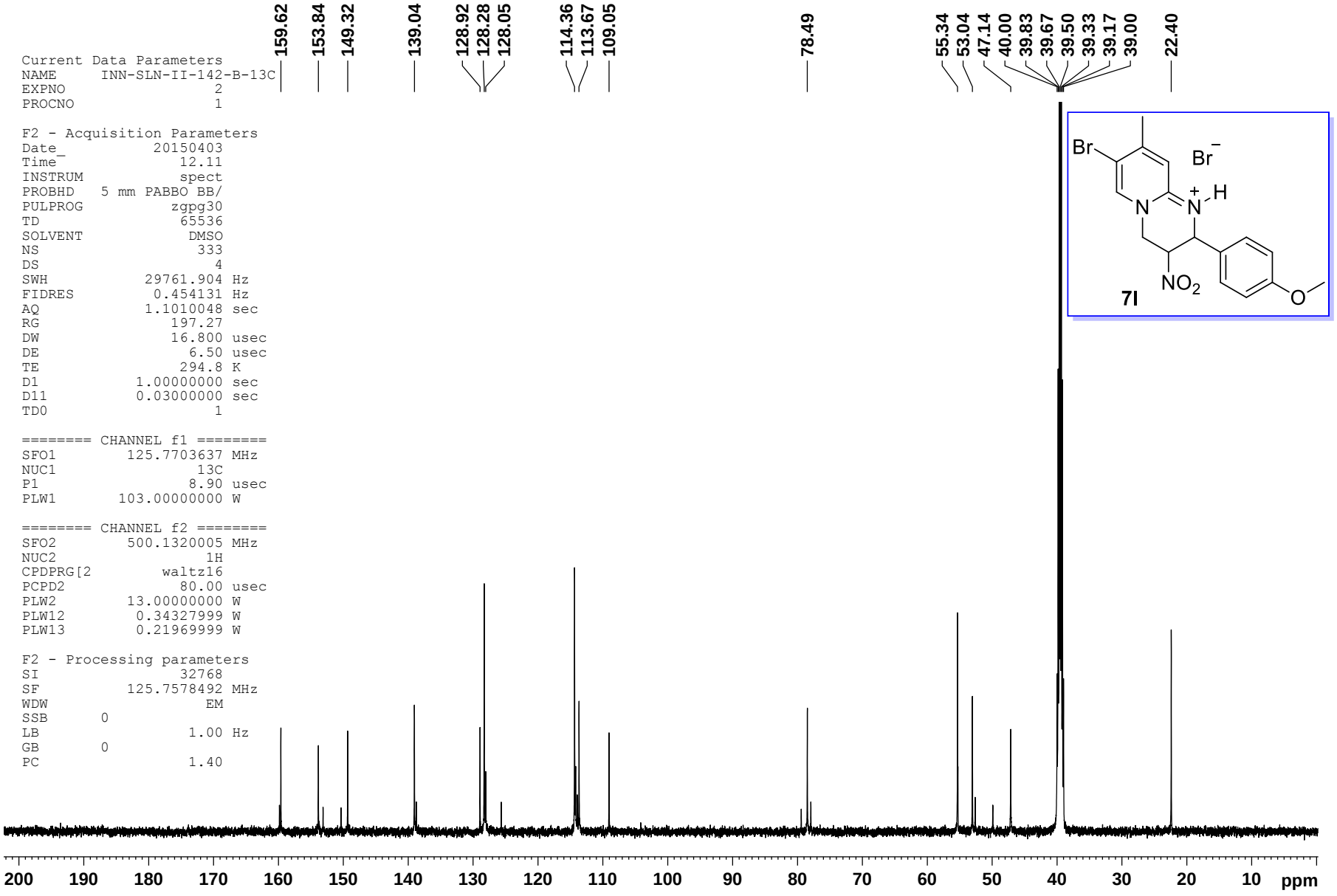


Fig S28. ^{13}C NMR Spectrum of 7l

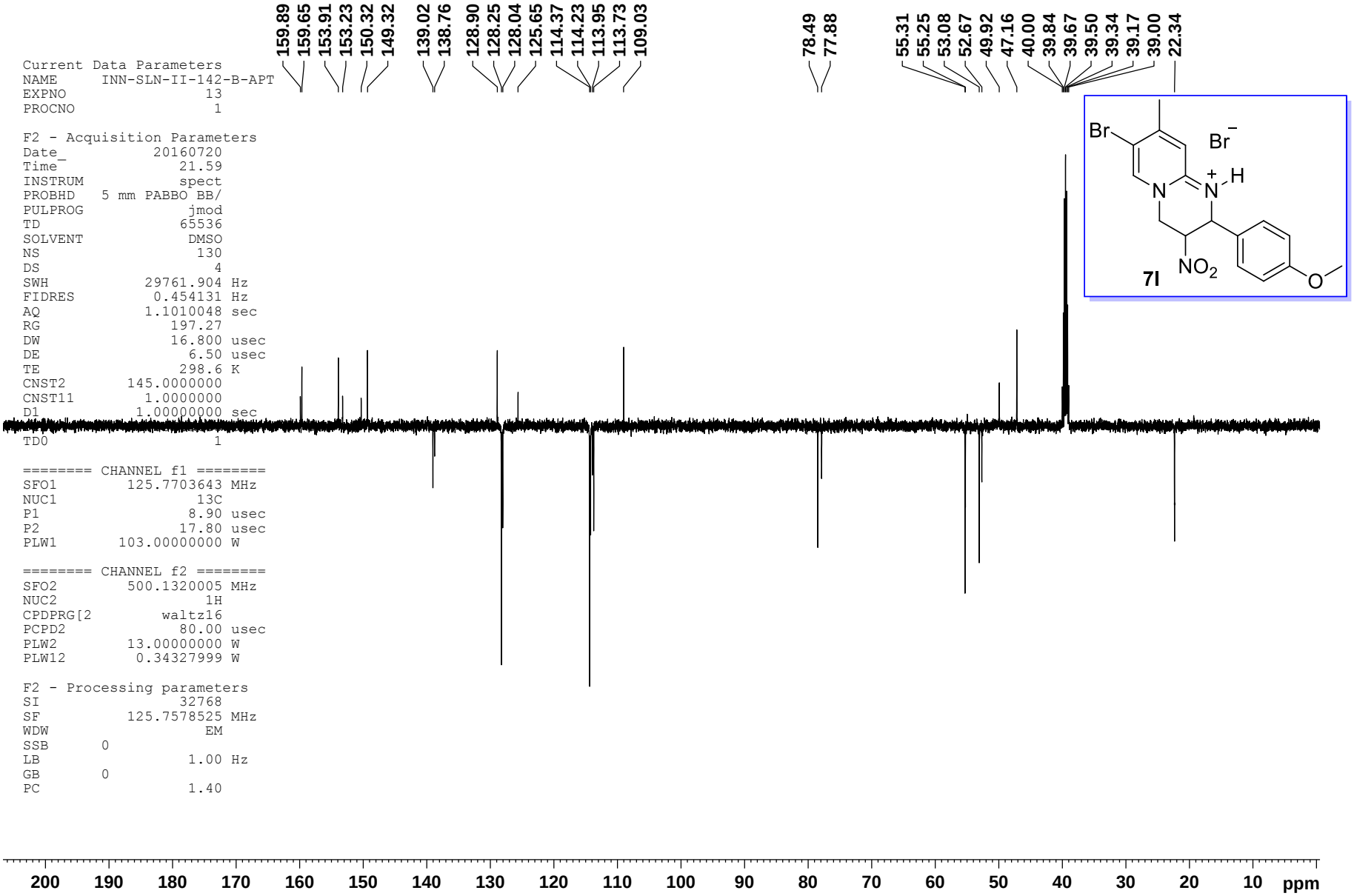
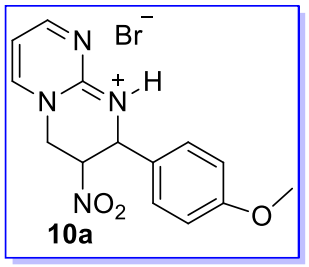


Fig S29. ^{13}C-APT NMR Spectrum of 7l




```
Current Data Parameters
NAME      INN-SLN-II-23-1H
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140727
Time                 16.03
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
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                295.7 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           500.1300038 MHz
WDW                    EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

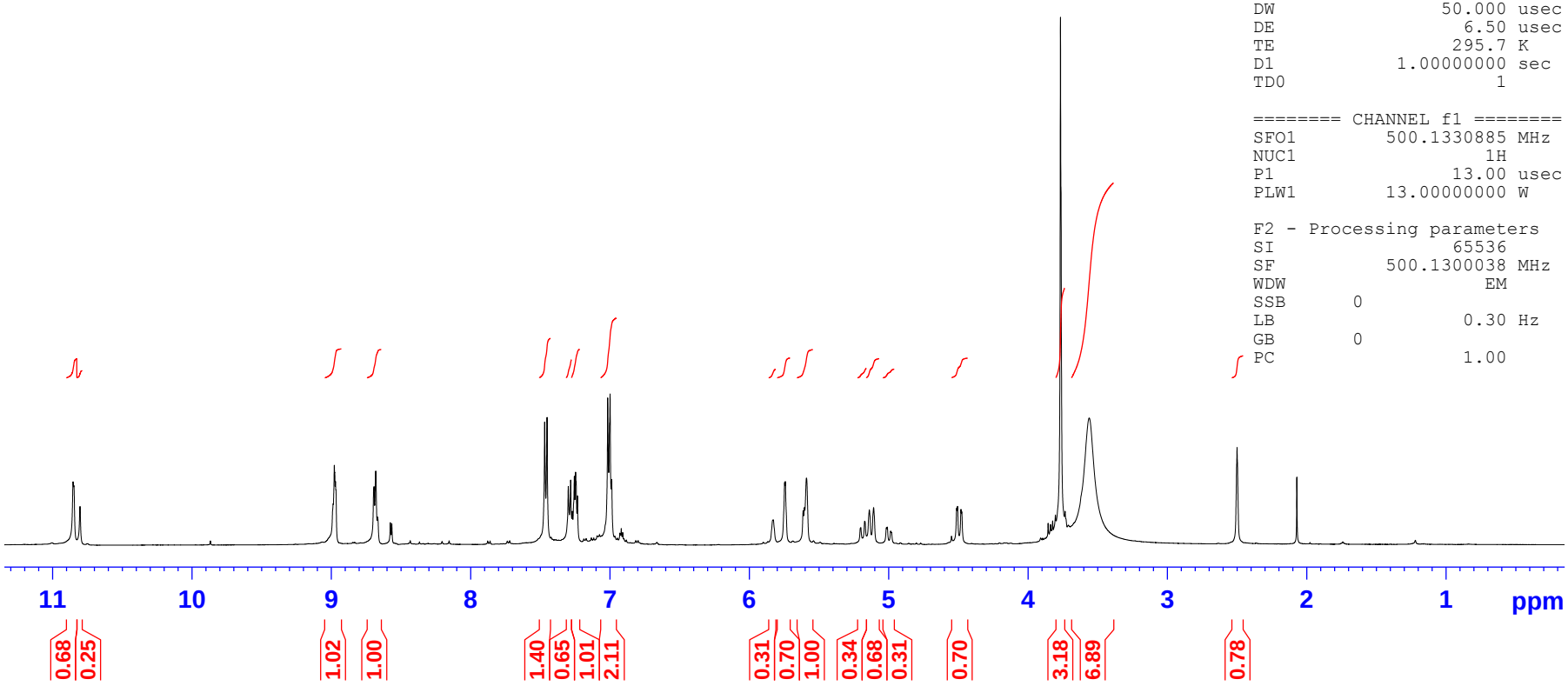


Fig S30. ^{1}H NMR Spectrum of 10a

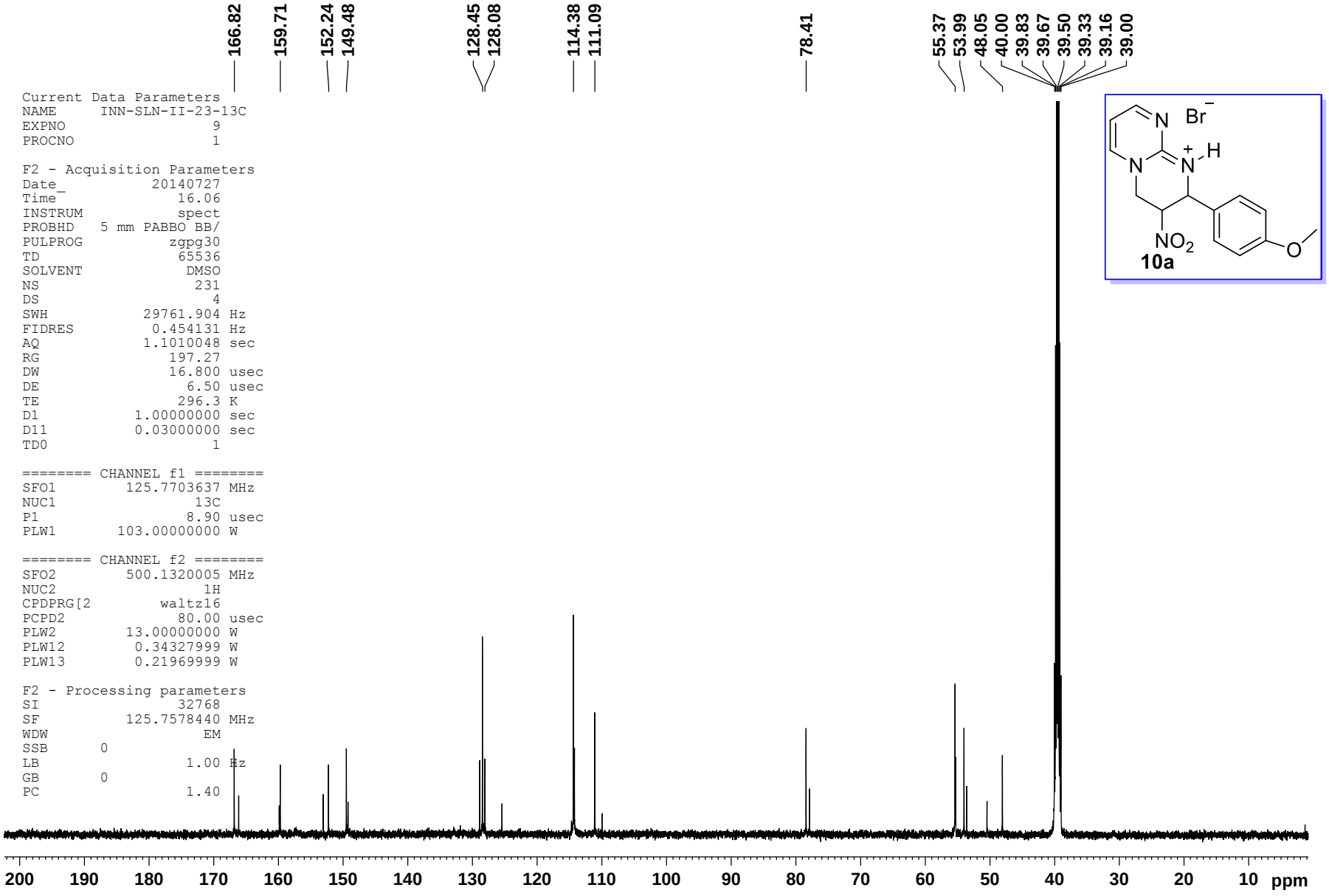


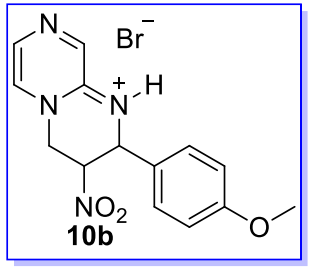
Fig S31. ^{13}C NMR Spectrum of 10a

```
Current Data Parameters
NAME      INN-SLN-II-39-1H
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20141116
Time                16.53
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                      12
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                   295.7 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            500.1300054 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



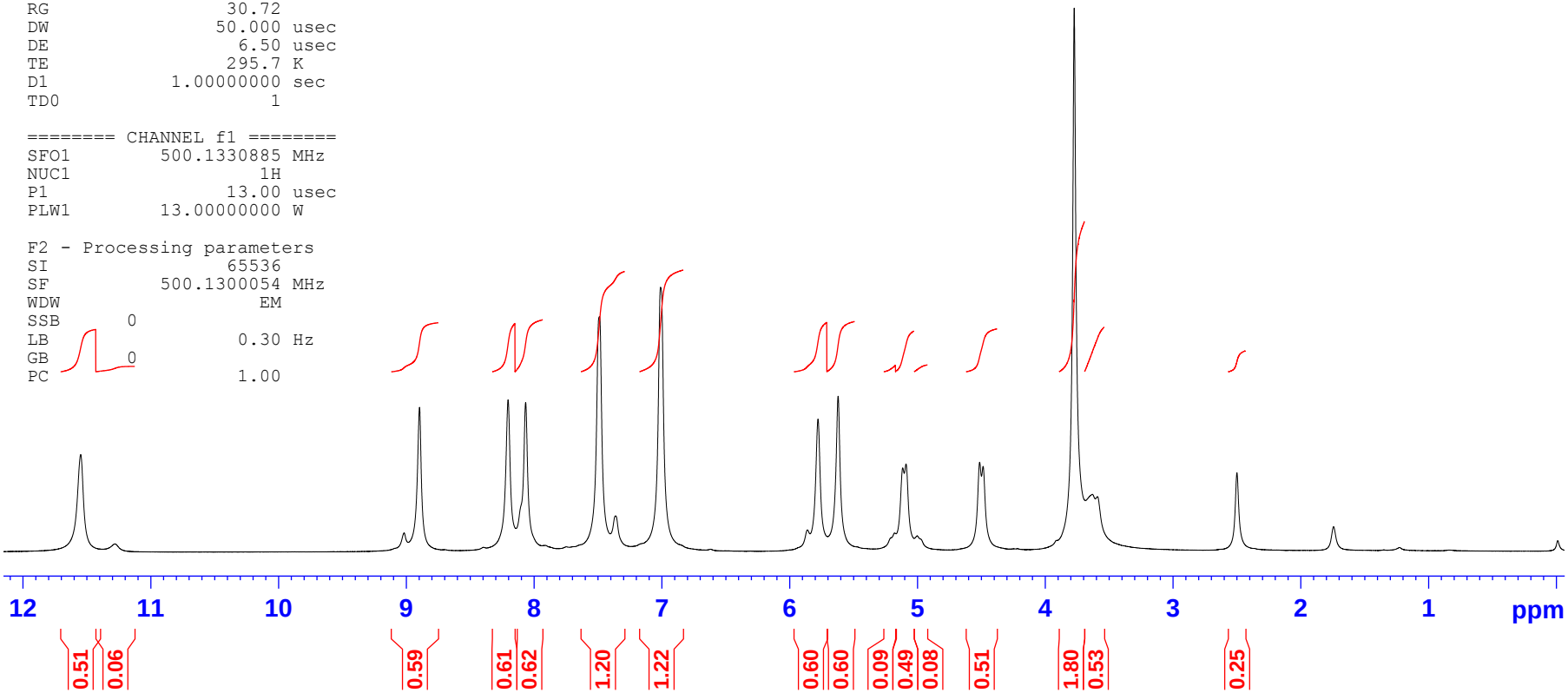


Fig S32. ^{1}H NMR Spectrum of 10b

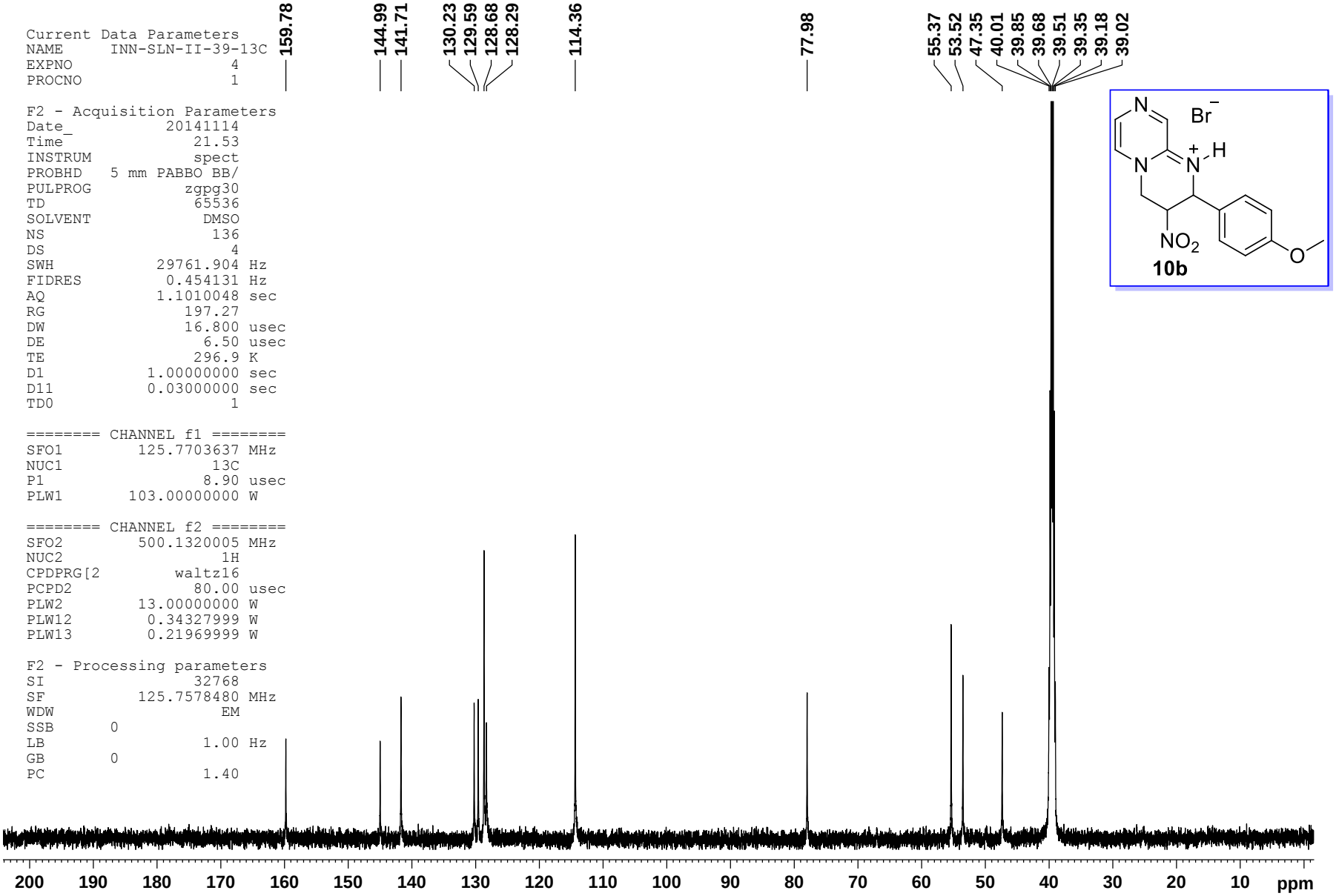
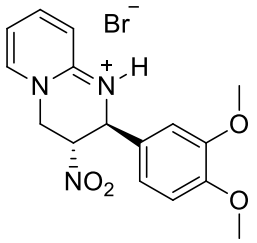
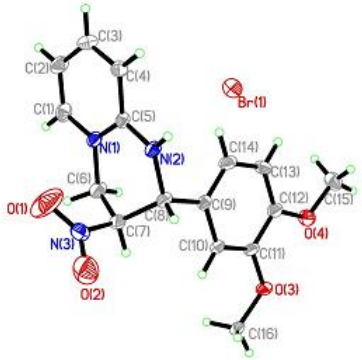


Fig S33. ^{13}C NMR Spectrum of 10b

Table S2. Selected X-ray data of 7b with 50% probability for the ellipsoid contour





Empirical formula	$C_{16}H_{18}BrN_3O_4$
Formula weight	396.24
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
A Å	10.7705(7)
B Å	10.1713(6)
C Å	15.4078(9)
αdeg	90
β deg	β = 97.569(6)°
γ	90
V Å^3	1673.21(17)
Z	4
Density (calc), g/m^3)	1.573
Absorption coefficient, mm^{-1}	2.482

F(000)	808
Crystal size, mm^3	0.14 x 0.17 x 0.30
θ range, deg	2.41 to 25.00°
Index ranges	-9<=h<=12, -12<=k<=8, -18<=l<=14
Reflections collected / unique	7073 / 2944 [R(int) = 0.0430]
Absorption correction	Full-matrix least-squares on F^2
Max. and min. transmission	0.7709 and 0.5214
Refinement method	Full-matrix least-squares on F^2
No. of data / restraints / parameters	2944 / 0 / 217
Goodness-of-fit on F2	1.075
Final R indices [I>2σ(I)]	R1 = 0.0497, wR2 = 0.1412
R indices (all data)	R1 = 0.0606, wR2 = 0.1499
Largest diff. peak and hole e.$Å^3$	0.871 and -0.594