

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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Current Data Parameters
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EXPNO 5
PROCNO 1

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Time_ 2.40
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PULPROG zg30
TD 54274
SOLVENT CDC13
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.0000000 sec
TD0 1

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P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
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SF 400.1300098 MHz
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SSB 0
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GB 0
PC 1.00

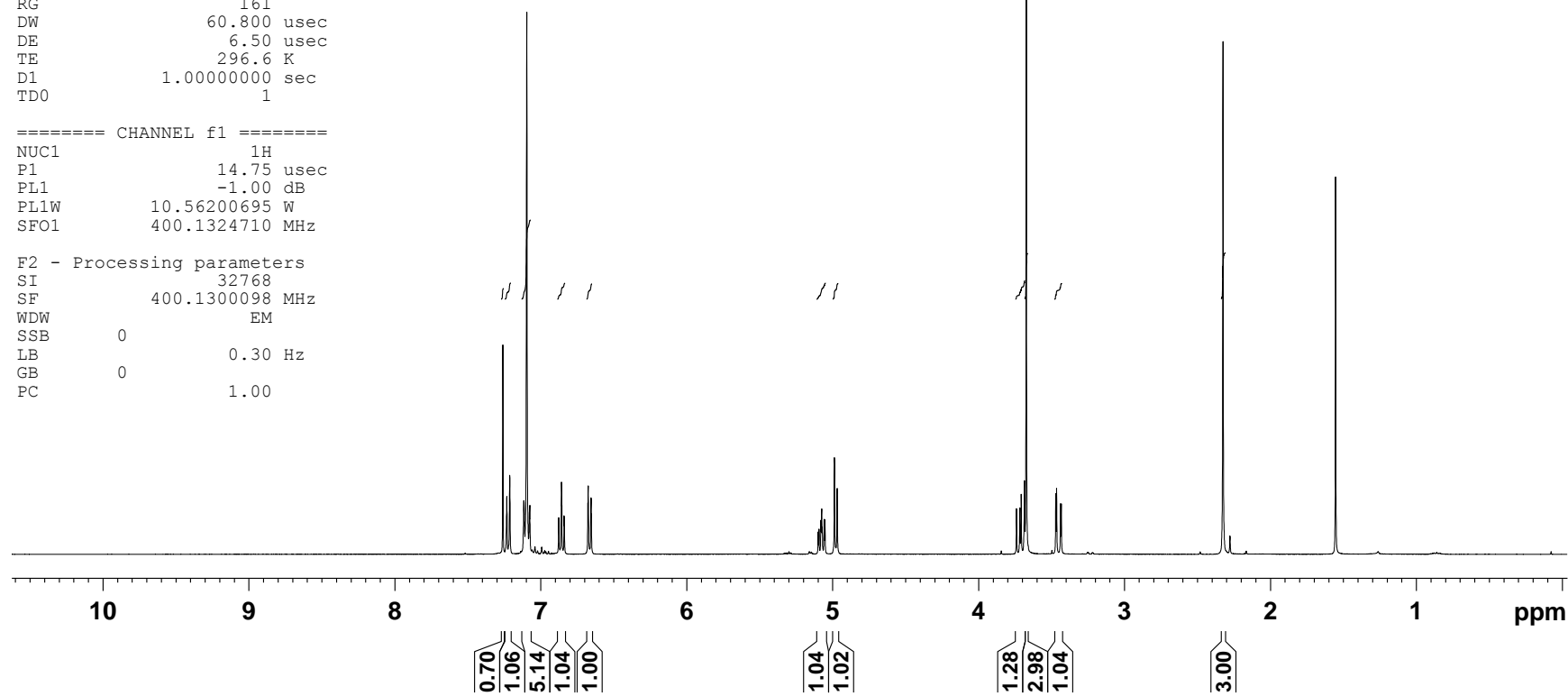
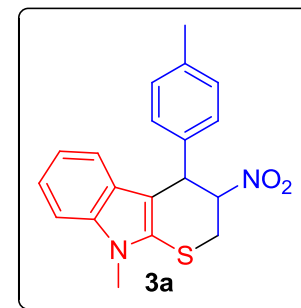
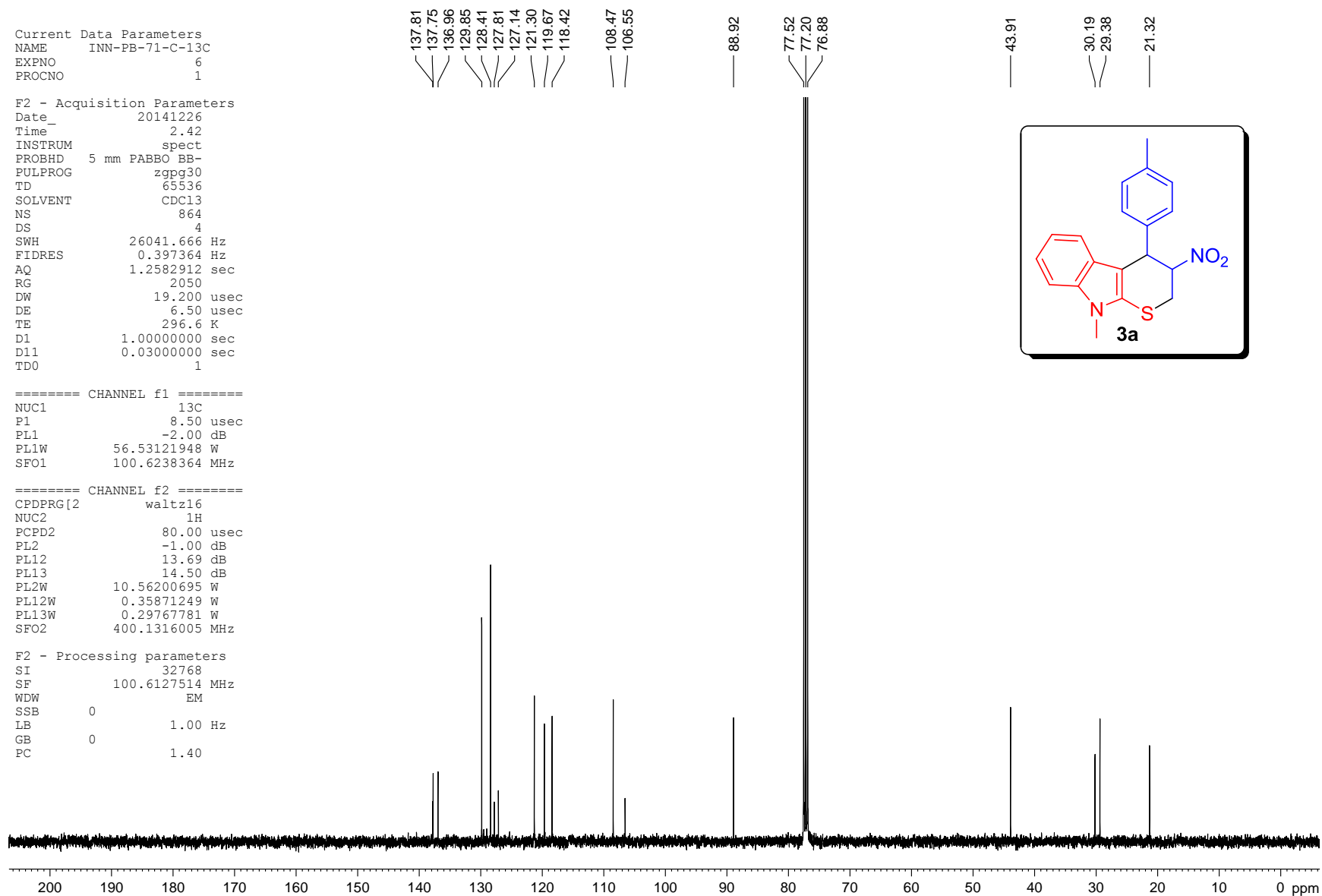


Figure S01. ¹H NMR Spectrum of 3a (Major isomer)

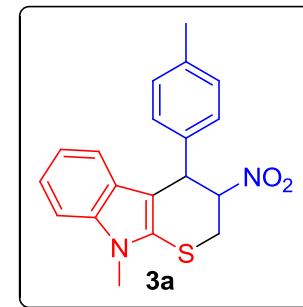
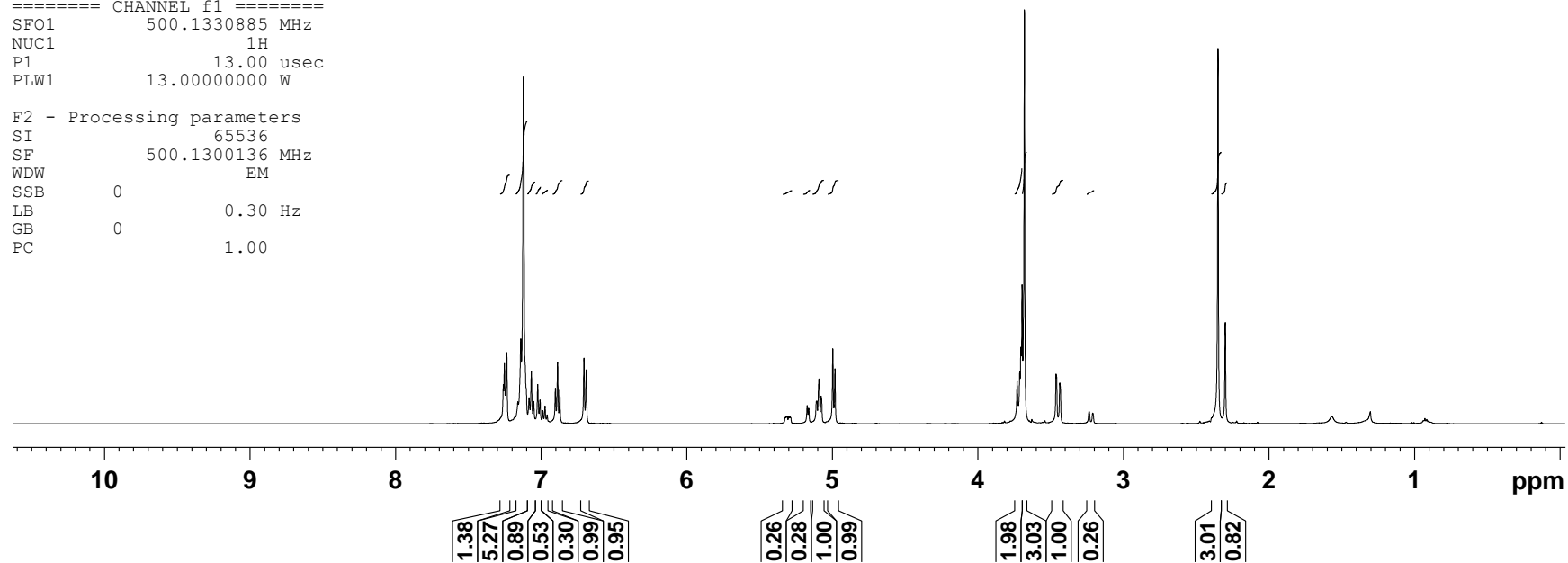


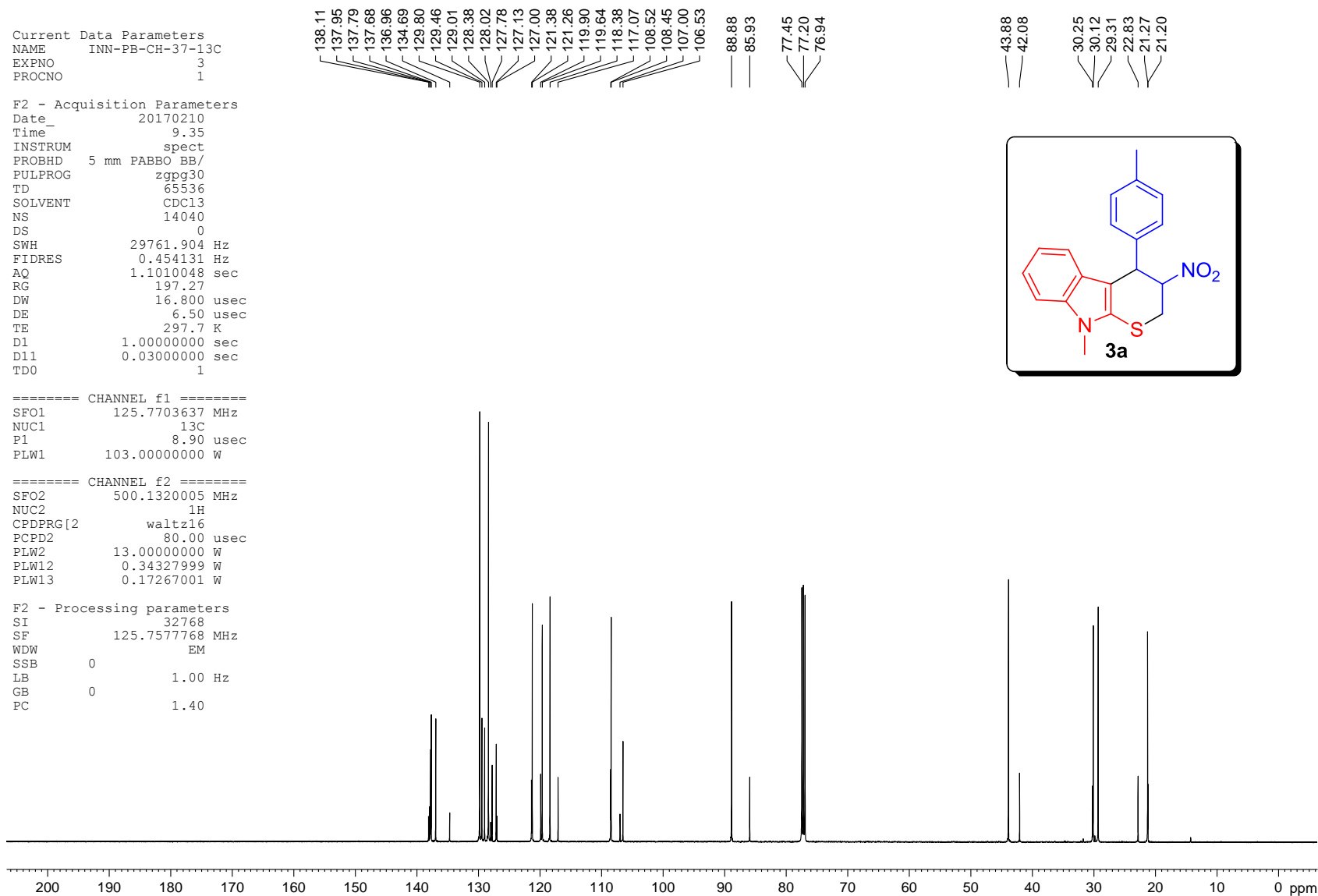
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 PROCNO 1

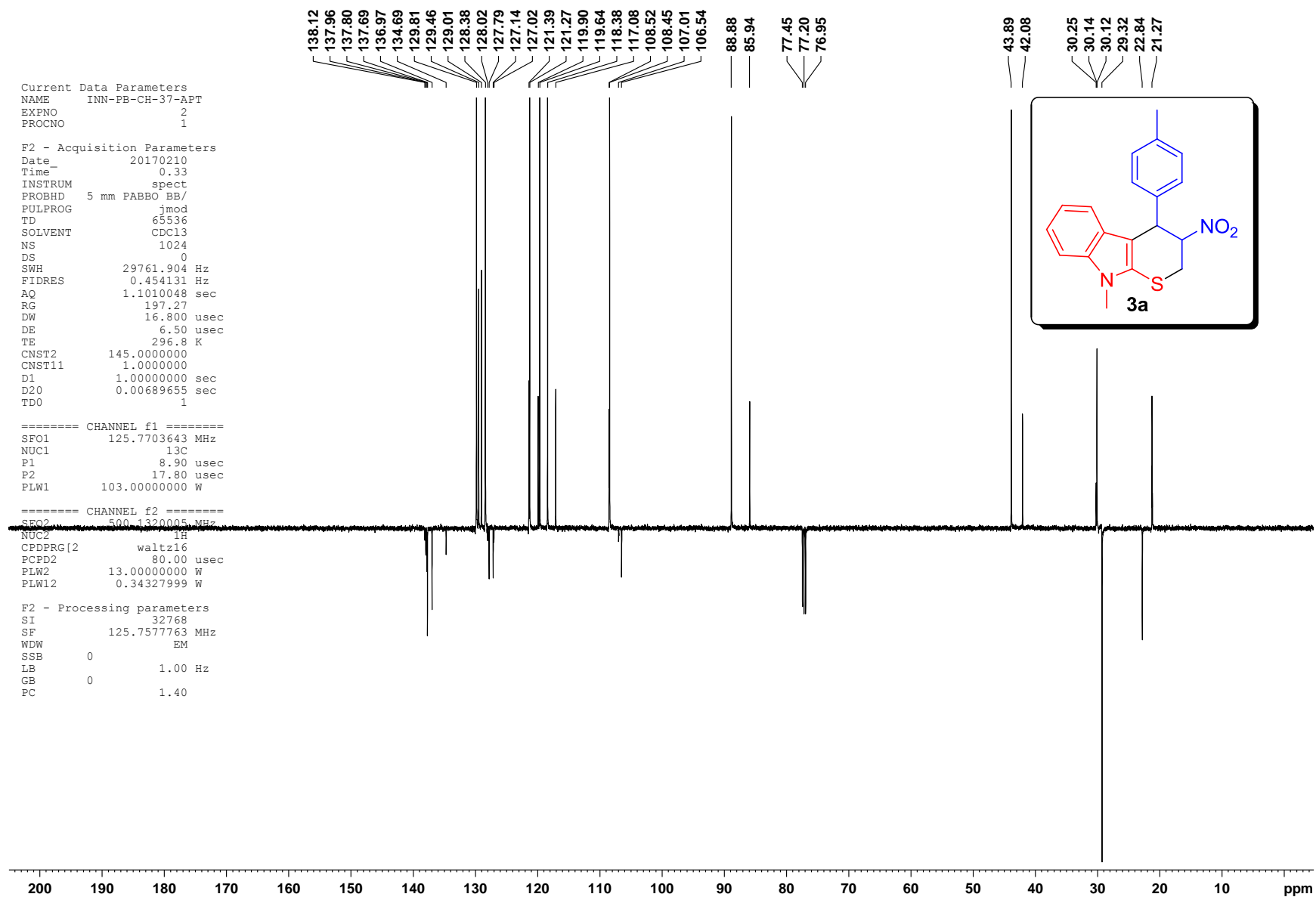
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 TD 65536
 SOLVENT CDC13
 NS 18
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 30.72
 DW 50.000 usec
 DE 6.50 usec
 TE 296.6 K
 D1 1.00000000 sec
 TD0 1

==== 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





Figure S05. ¹³C-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
 Time_ 19.44
 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
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 SF 500.1300122 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

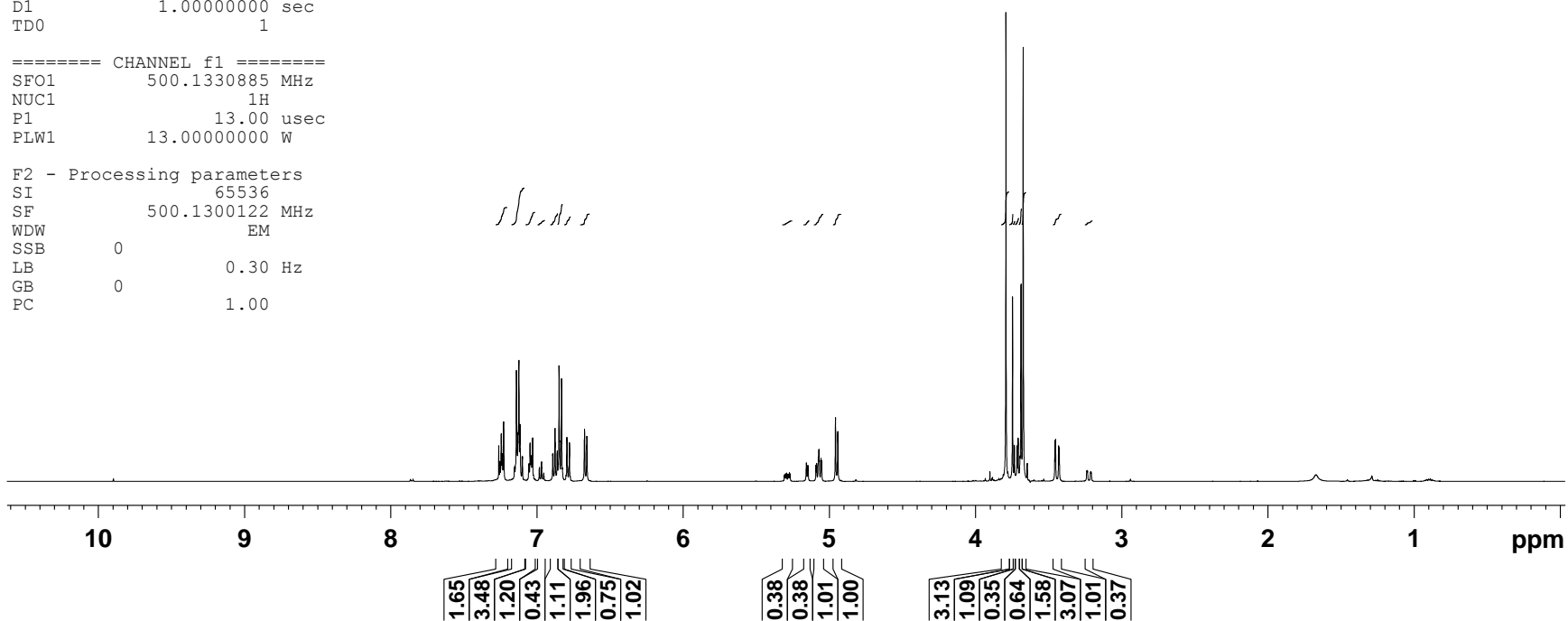


Figure S06. ¹H NMR Spectrum of 3b (major + minor, dr 73:27)

Current Data Parameters
 NAME INN-CH-67-13C
 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

159.48
 159.27
 138.06
 137.75
 131.80
 130.17
 129.66
 129.56
 127.97
 127.73
 127.04
 126.92
 121.38
 121.25
 119.87
 119.63
 118.43
 117.06
 114.43
 114.08
 108.53
 108.46
 107.04
 106.62
 89.06
 85.96
 77.45
 77.20
 76.95
 55.35
 55.27
 43.65
 41.67
 30.27
 30.14
 29.38
 22.75

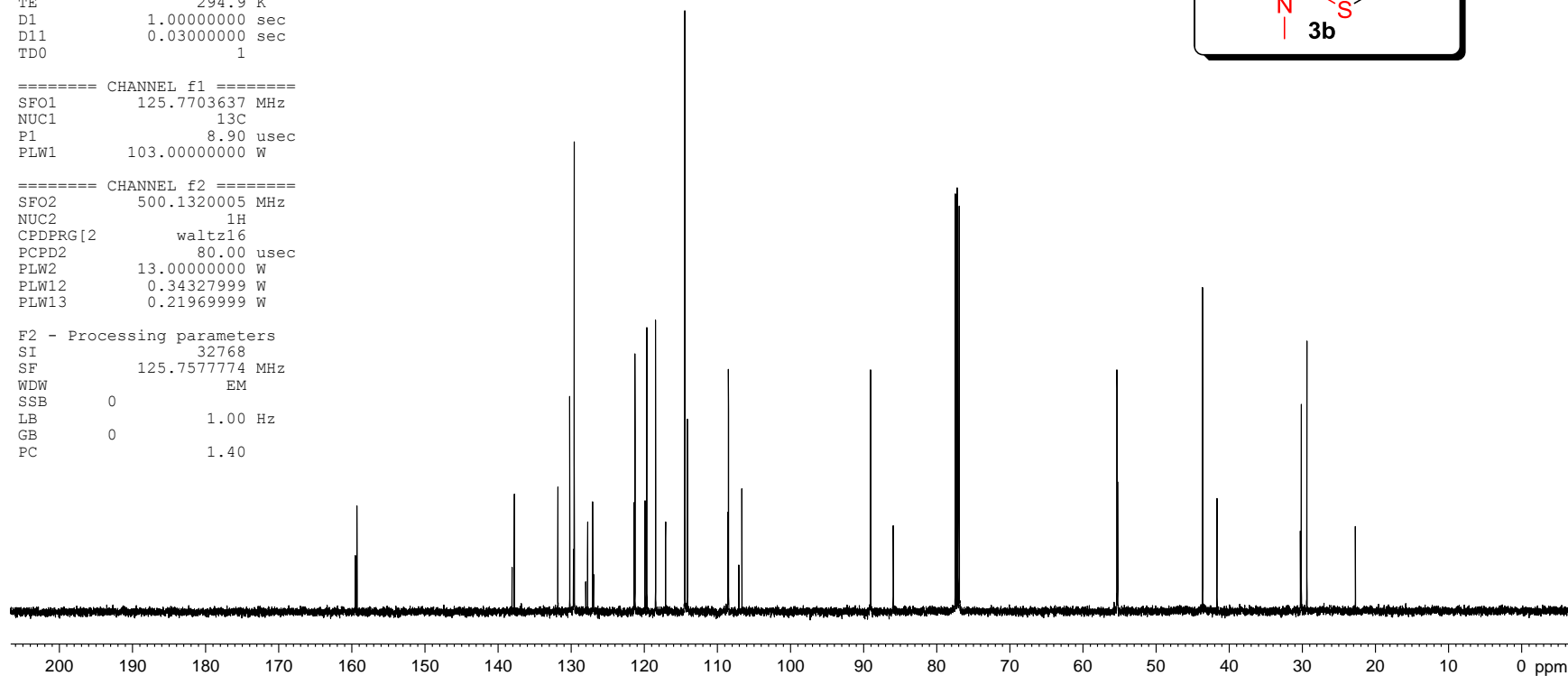
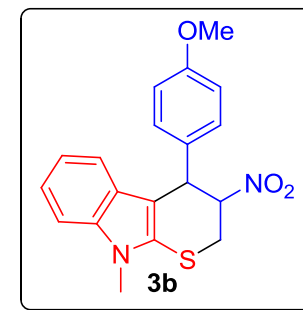
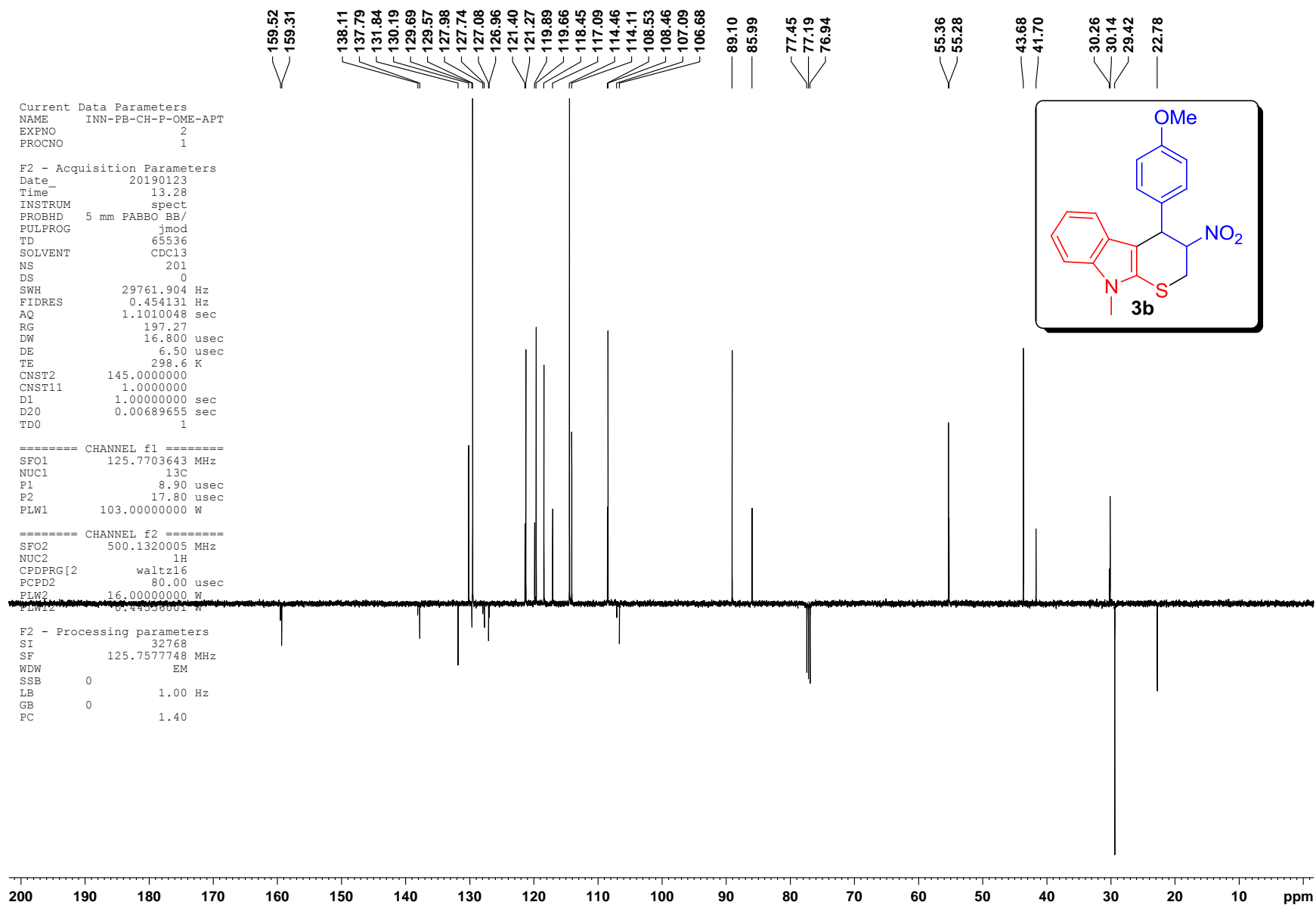


Figure S07. ^{13}C NMR Spectrum of 3b (major + minor, dr 73:27)

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

Current Data Parameters
 NAME INN-PB-70-C-1H
 EXPNO 8
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20150211
 Time_ 23.50
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 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 295.5 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 500.1300129 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

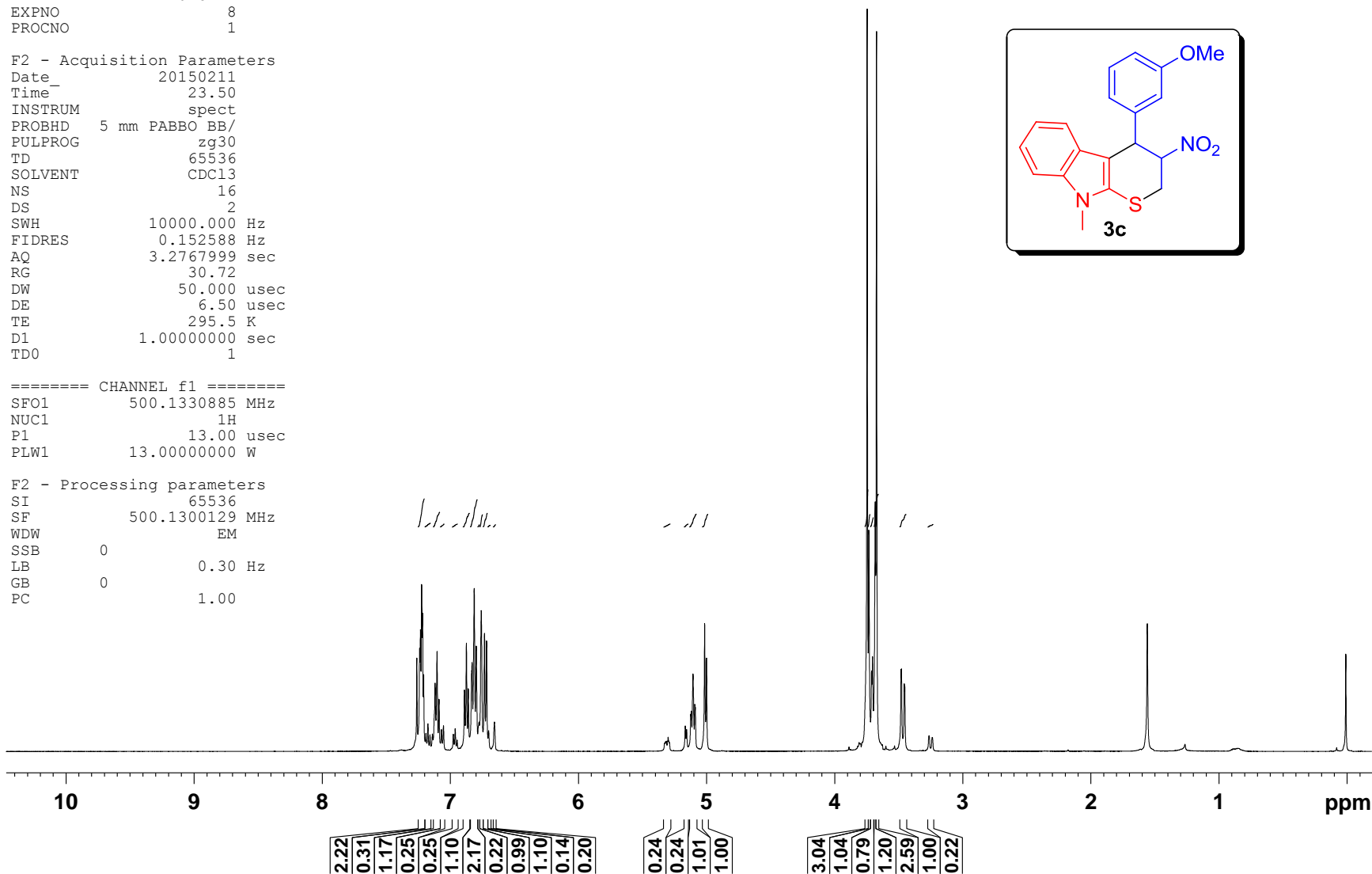


Figure S09. ¹H NMR Spectrum of 3c (major + minor, dr 80:20)

Current Data Parameters
 NAME INN-PB-70-13C
 EXPNO 15
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140519
 Time 22.28
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 159
 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 297.0 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 0.21969999 W

F2 - Processing parameters
 SI 32768
 SF 125.7577748 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

160.11
159.73
141.76
139.37
138.10
137.76
130.14
129.67
128.07
127.83
127.10
126.98
121.59
121.40
121.30
120.87
119.90
119.69
118.26
117.00
115.61
114.64
113.01
112.98
108.55
108.46
106.69
106.15
88.47
85.76
77.45
77.20
76.94

55.37
55.29

44.05
42.37

30.28
30.14
29.25

22.84

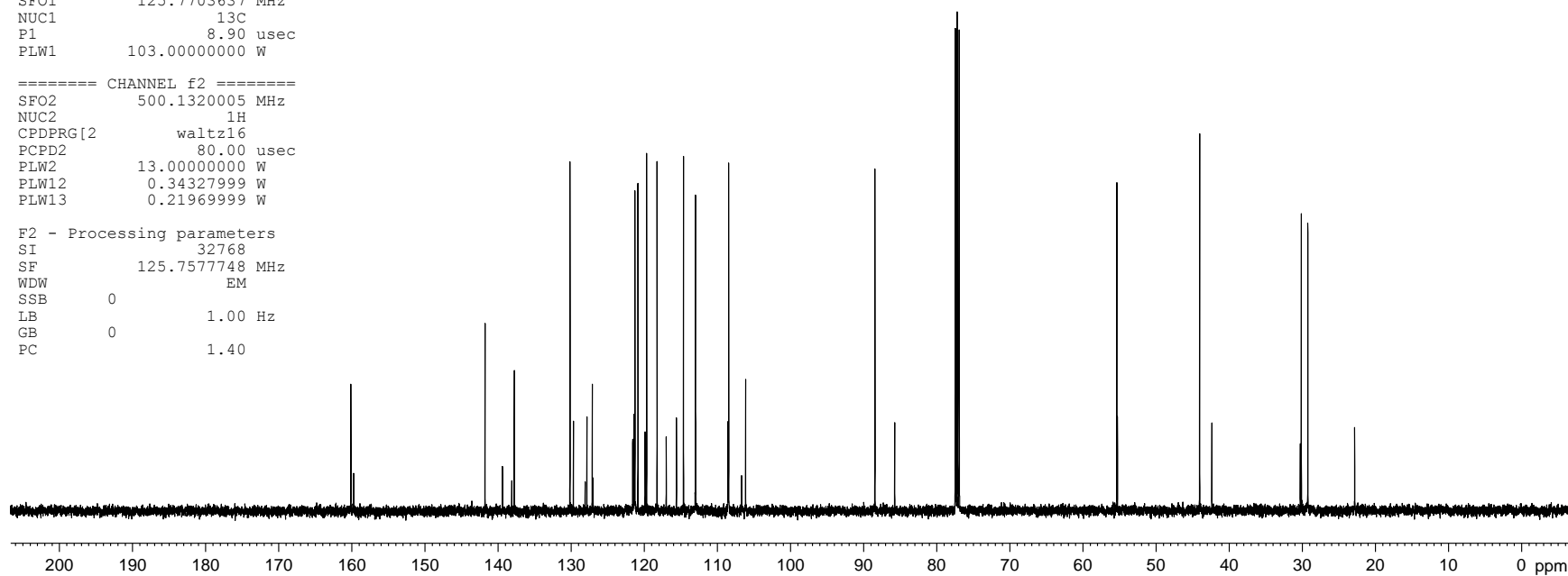
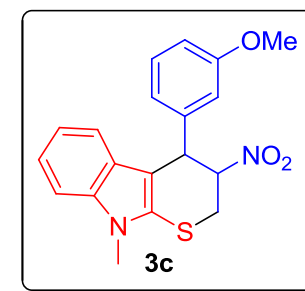
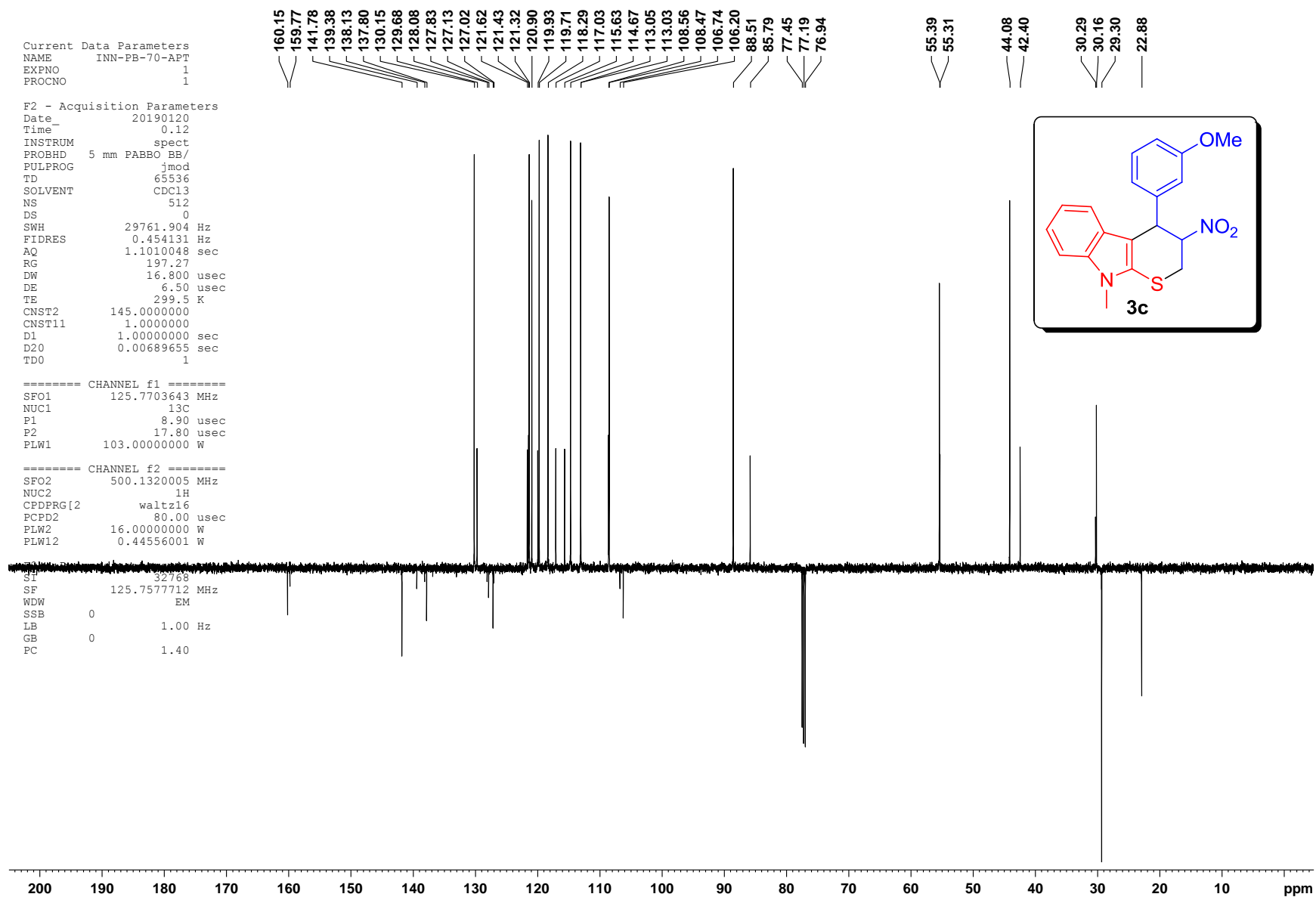


Figure S10. ¹³C NMR Spectrum of 3c (major + minor, dr 80:20)



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 CDC13
 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

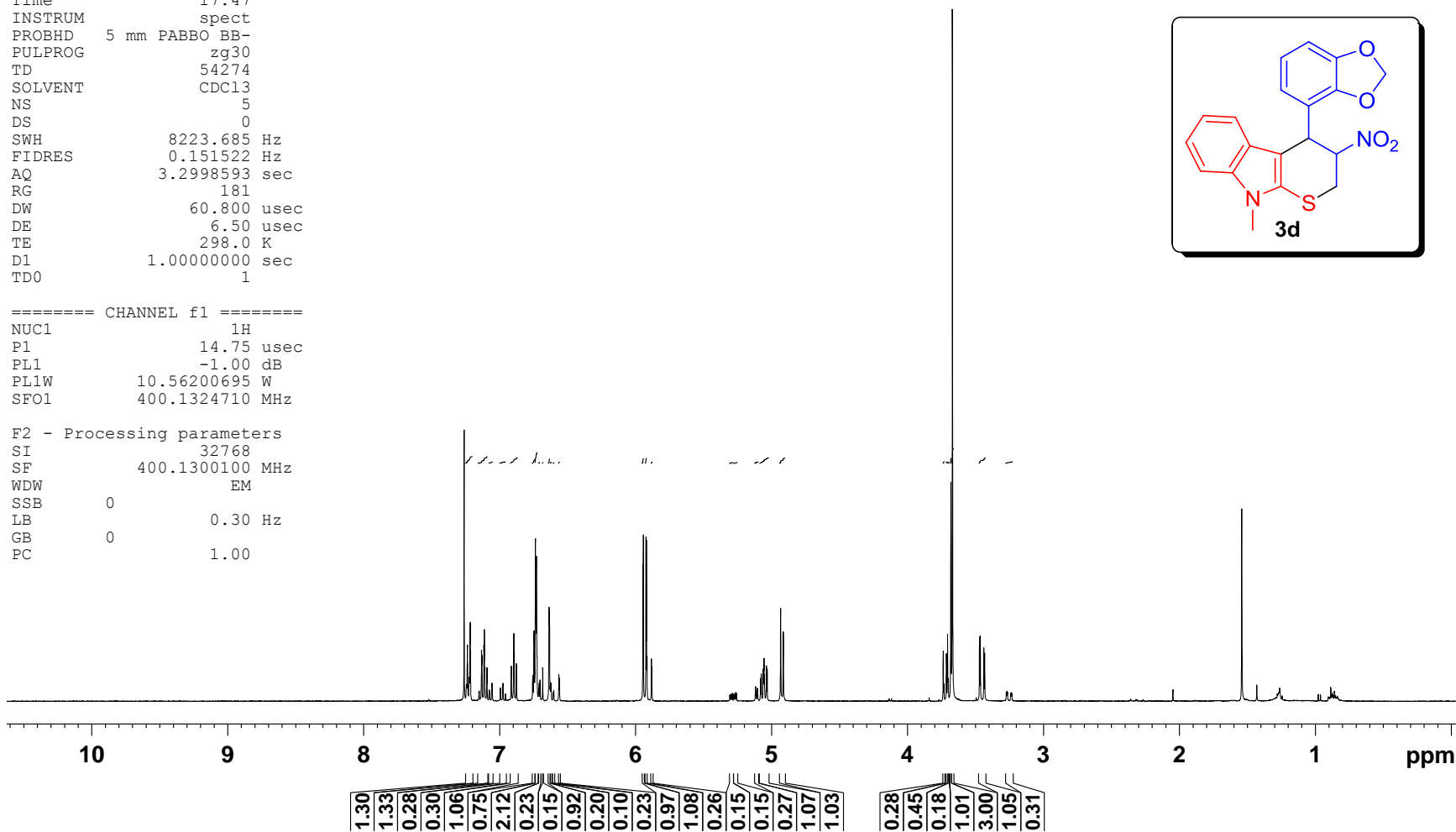


Figure S12. ¹H NMR Spectrum of 3d (major + minor, dr 78:22)

Current Data Parameters
 NAME INN-PB-TI-PIP-13C
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20190130
 Time_ 13.28
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 197
 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 103.0000000 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 125.7577750 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

148.32
 147.99
 147.63
 147.43
 138.10
 137.79
 133.75
 131.54
 128.01
 127.83
 127.02
 126.92
 122.63
 122.07
 121.46
 121.34
 119.93
 119.74
 118.40
 117.02
 109.48
 108.63
 108.58
 108.52
 108.50
 108.43
 106.92
 106.51
 101.33
 101.30
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 85.90
 77.45
 77.19
 76.94

44.18
 42.10

30.27
 30.15
 29.47
 22.74

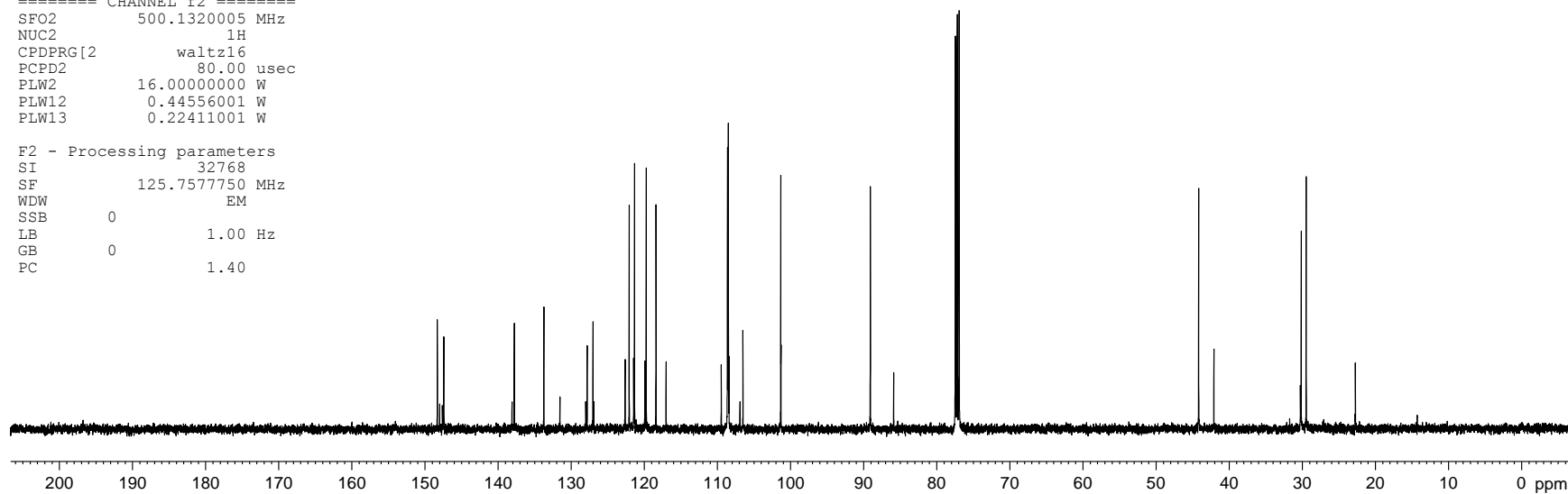
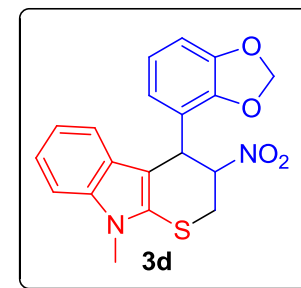
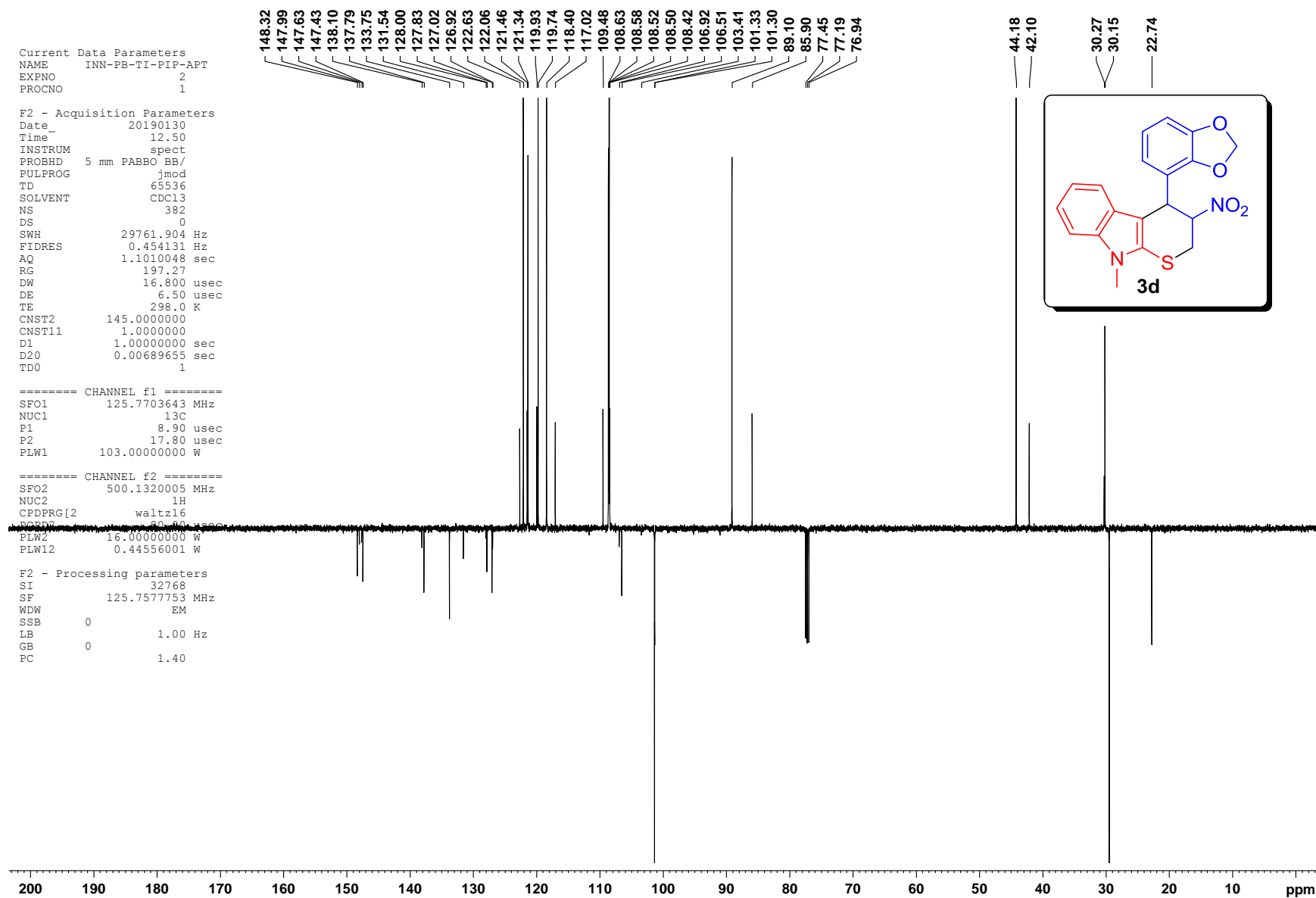


Figure S13. ^{13}C NMR Spectrum of 3d (major + minor, dr 78:22)



Current Data Parameters
 NAME INN-PB-65-1H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20170212
 Time_ 1.41
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 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

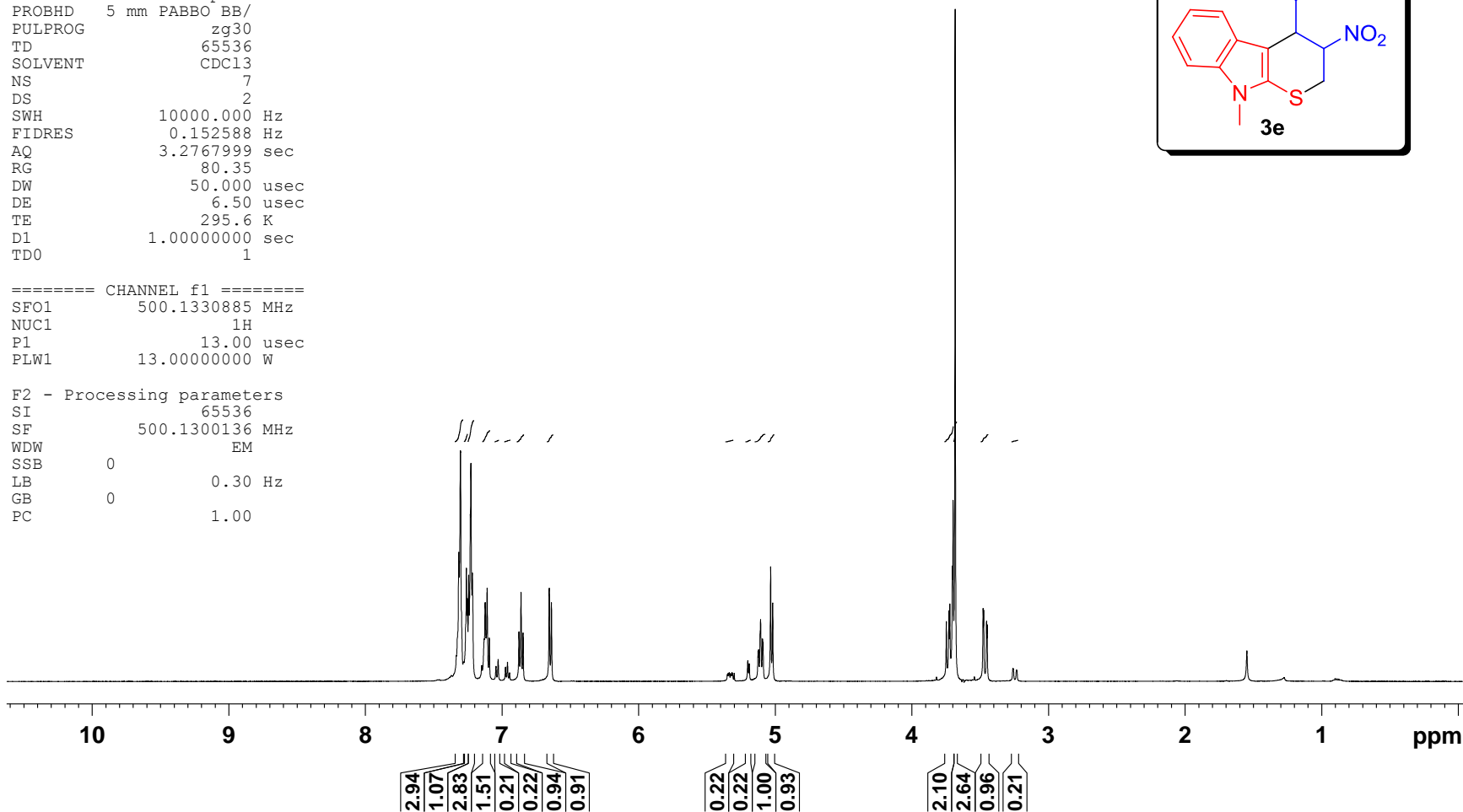
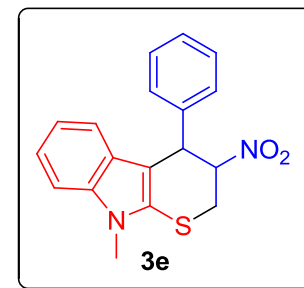
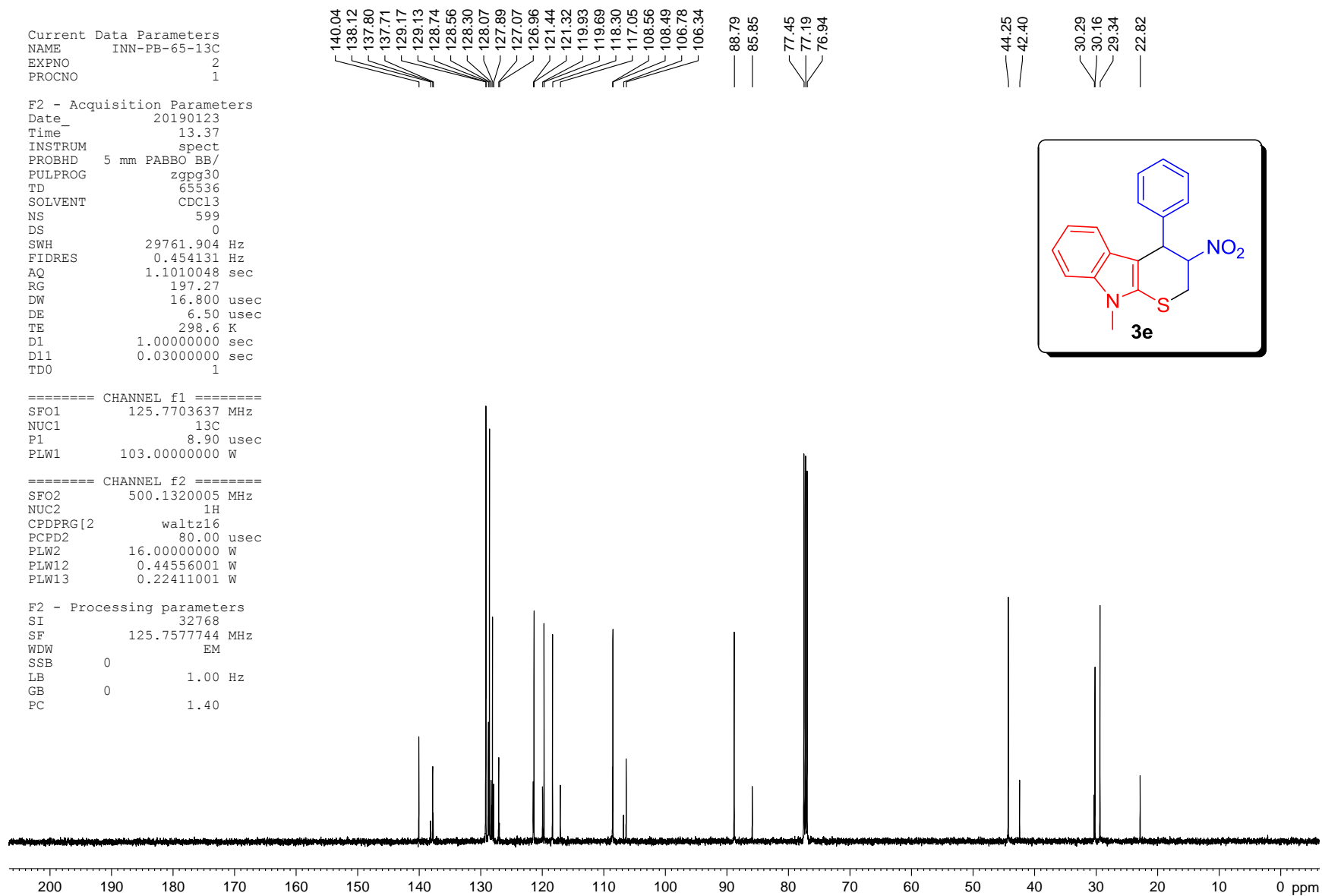
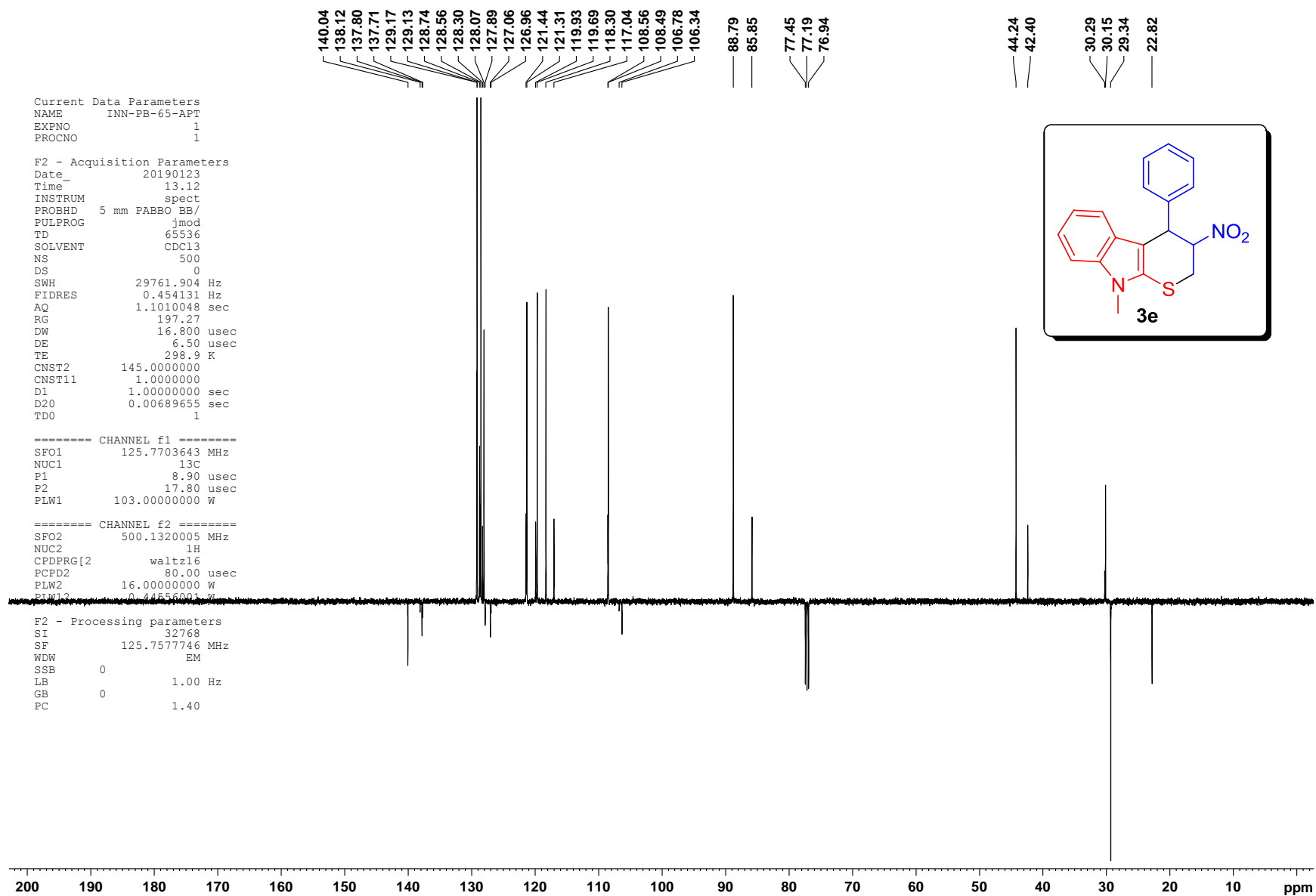


Figure S15. ¹H NMR Spectrum of 3e (major + minor, dr 82:18)

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



Current Data Parameters
 NAME INN-PB-72-1H
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140708
 Time_ 23.47
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 30.72
 DW 50.000 usec
 DE 6.50 usec
 TE 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 500.1300118 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

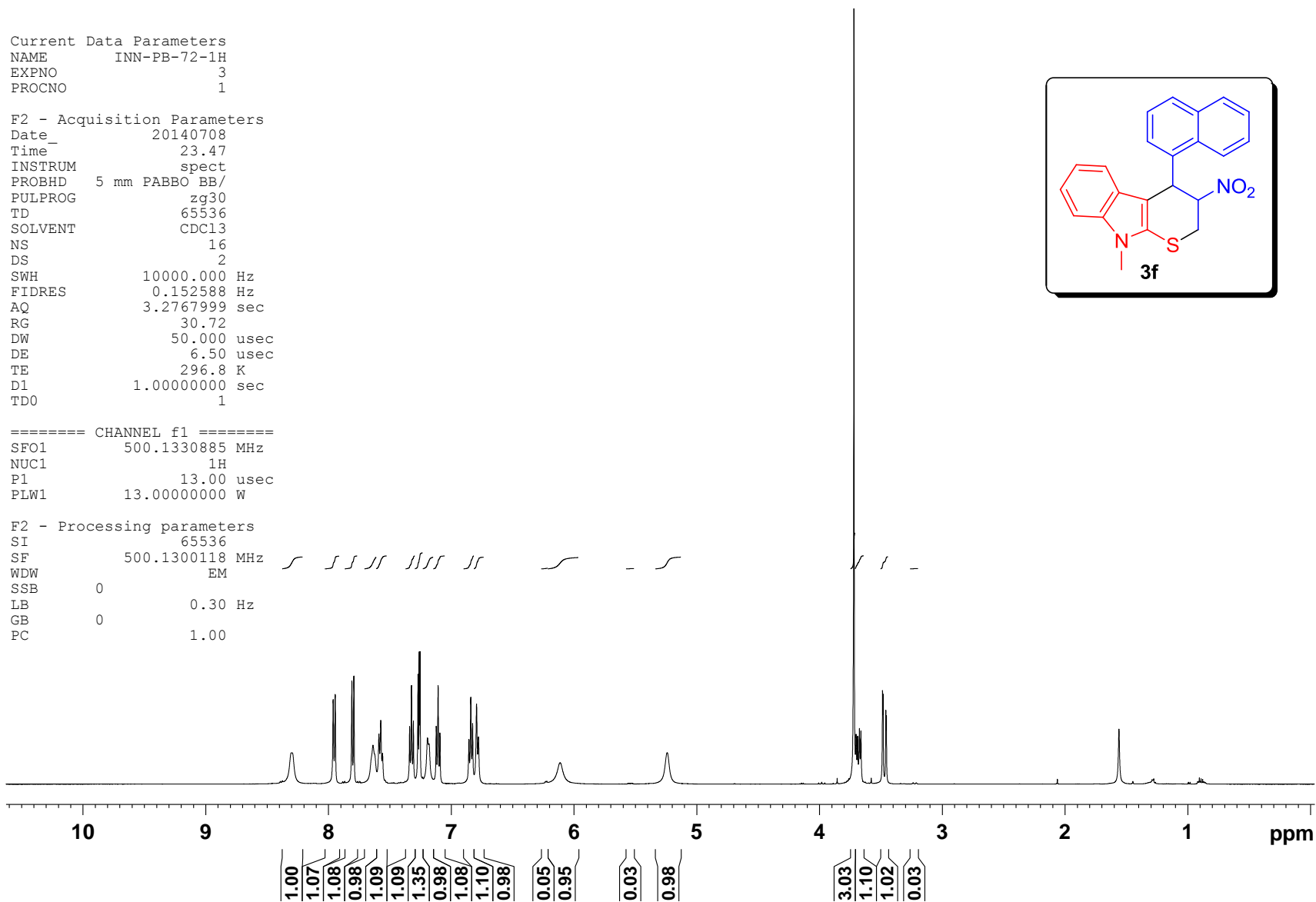


Figure S18. ^1H NMR Spectrum of 3f (major + minor, dr >95:05)

Current Data Parameters
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 EXPNO 4
 PROCNO 1

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 Date_ 20140709
 Time_ 9.48
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 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

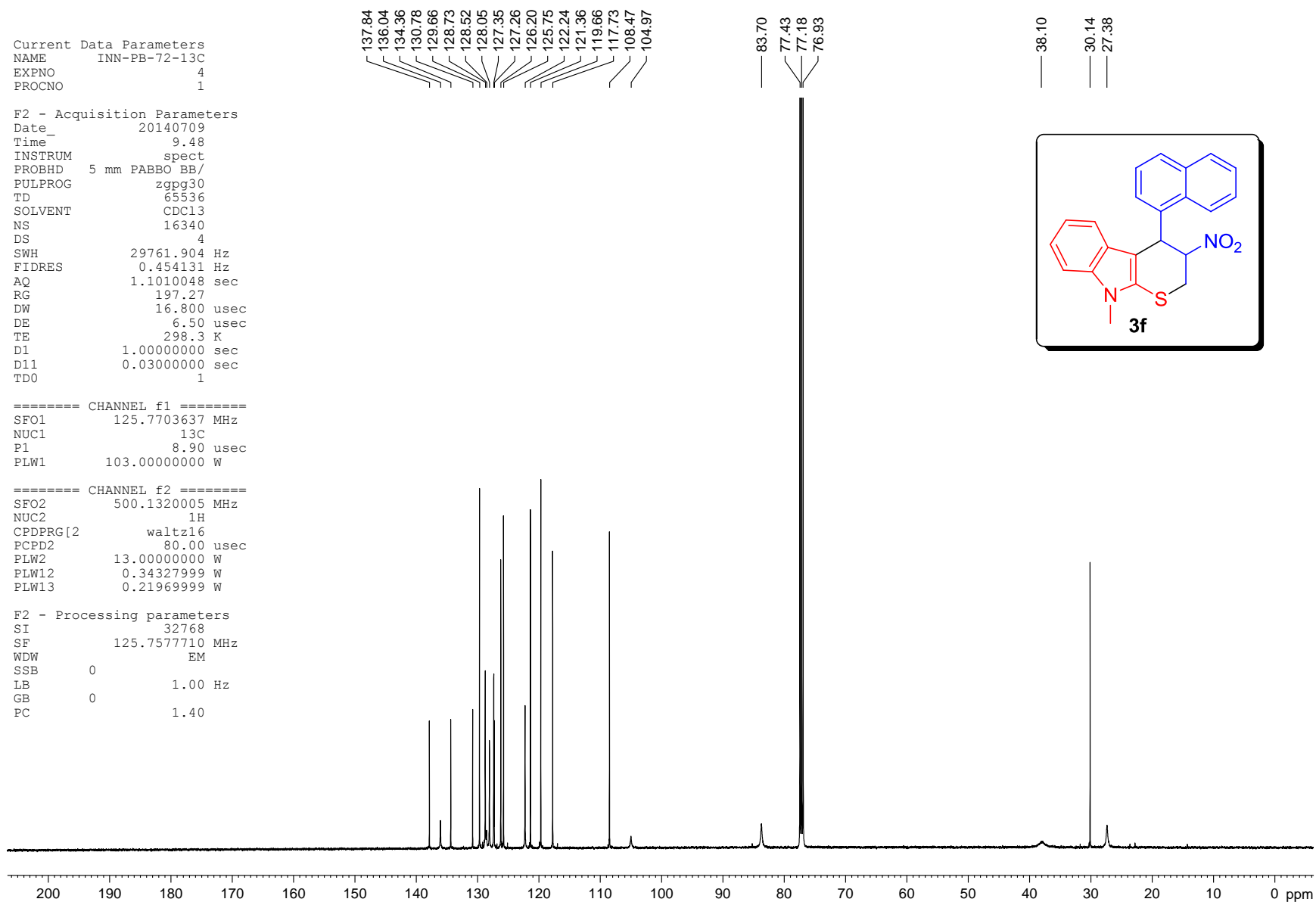
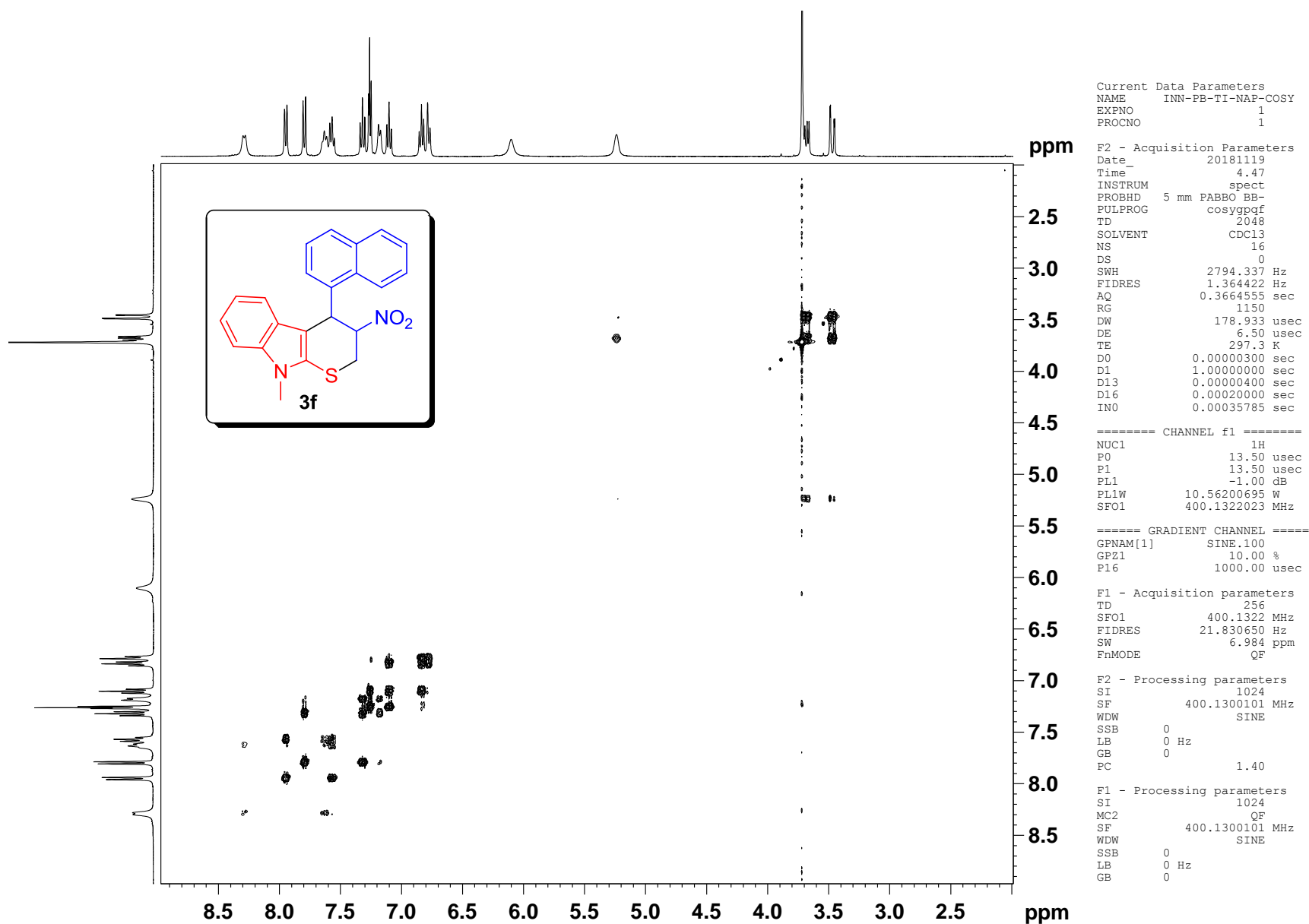
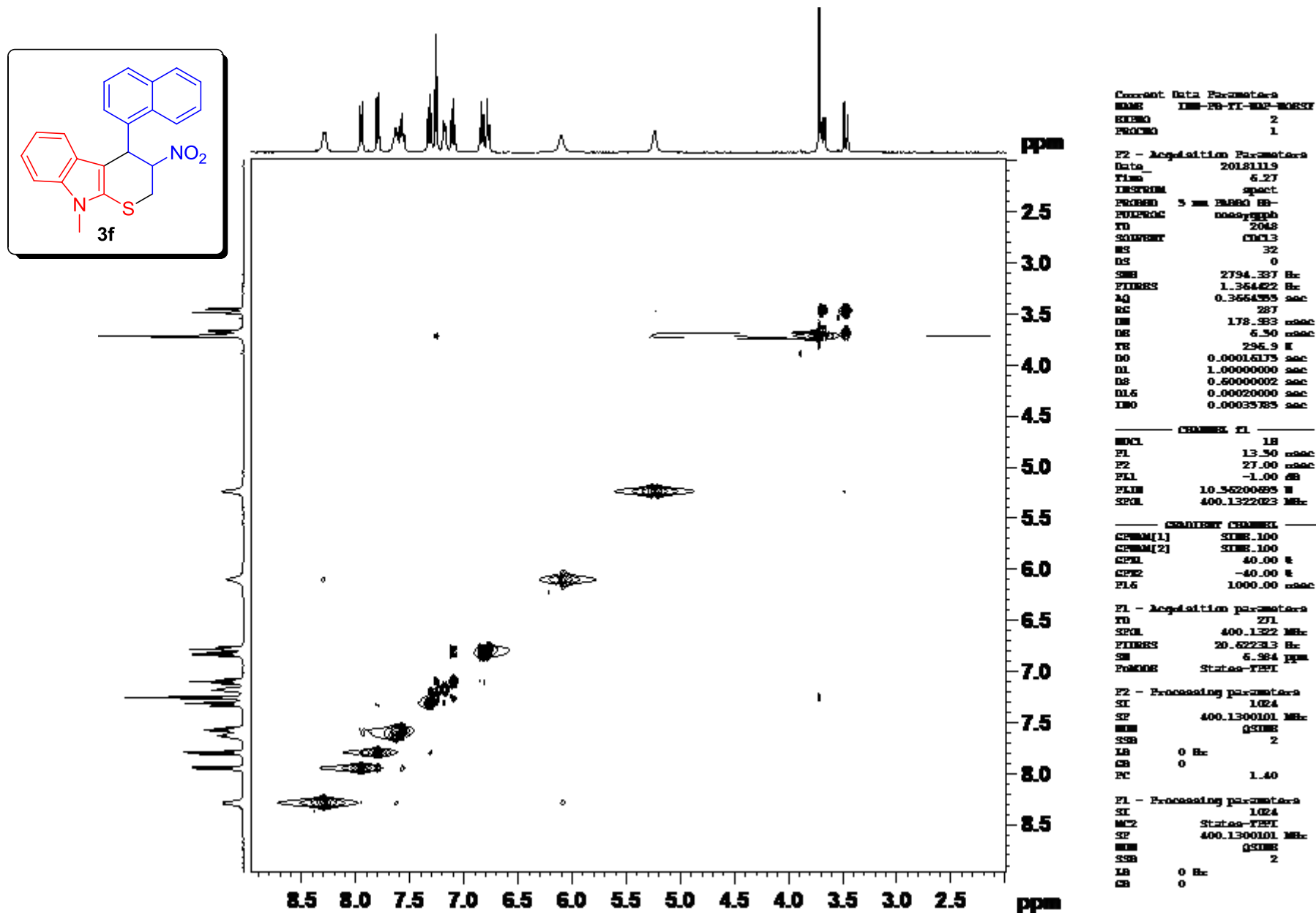


Figure S19. ¹³C NMR Spectrum of 3f (major + minor, dr >95:05)

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

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

Current Data Parameters
NAME INN-PB-TI-NO2-1H
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190719
Time_ 21.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 6
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 294.2 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 400.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

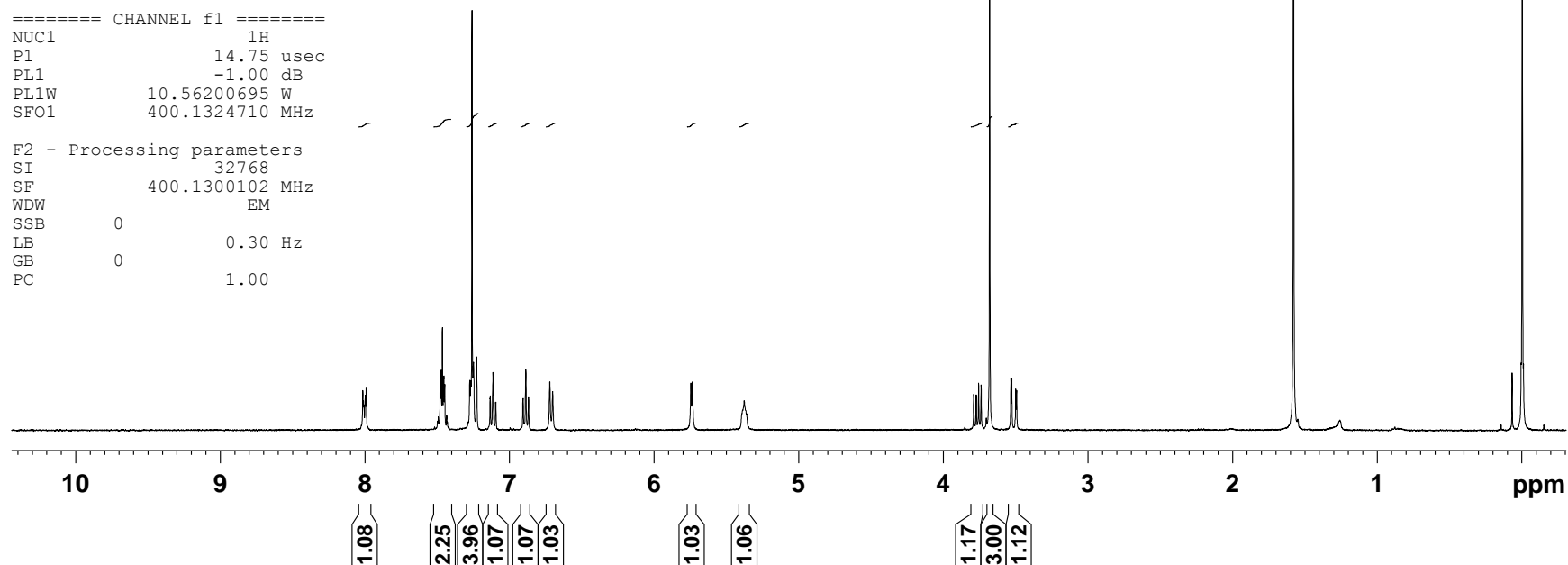
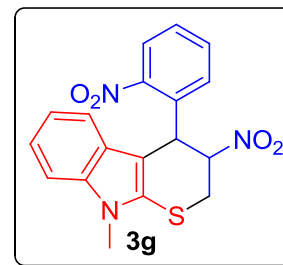
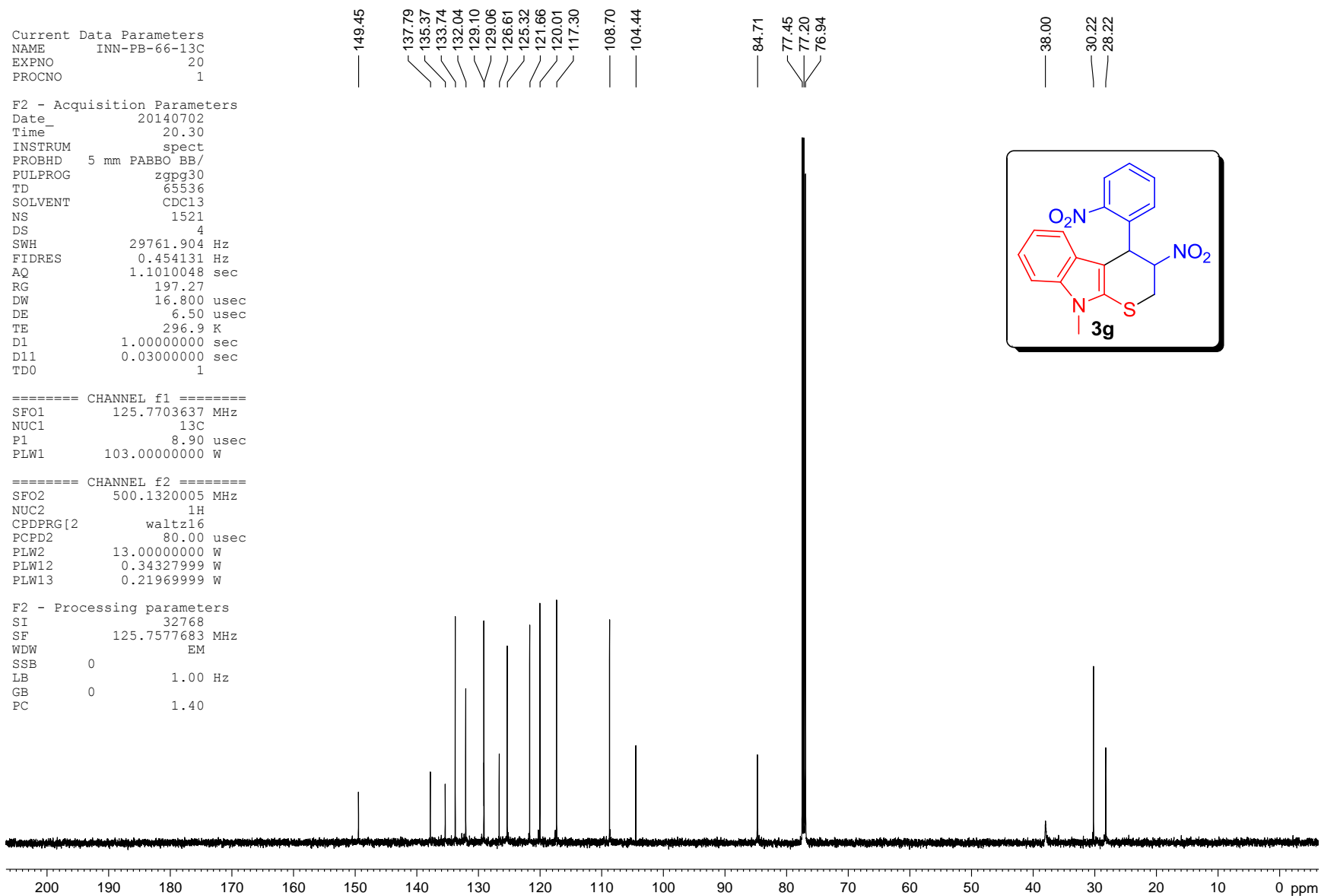
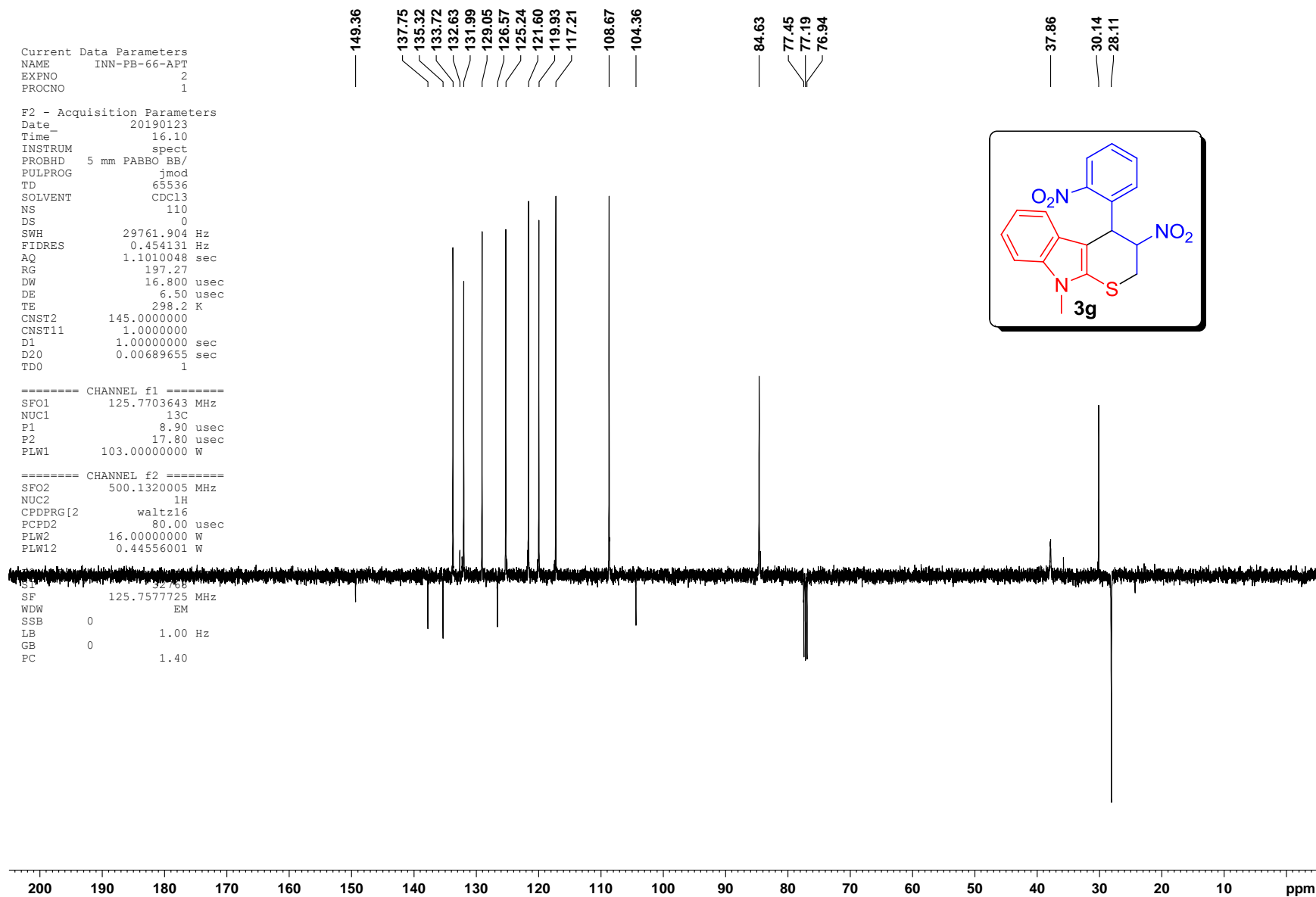


Figure S22. ¹H NMR Spectrum of 3g (major + minor, dr >95:05)

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

Figure S24. ¹³C-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

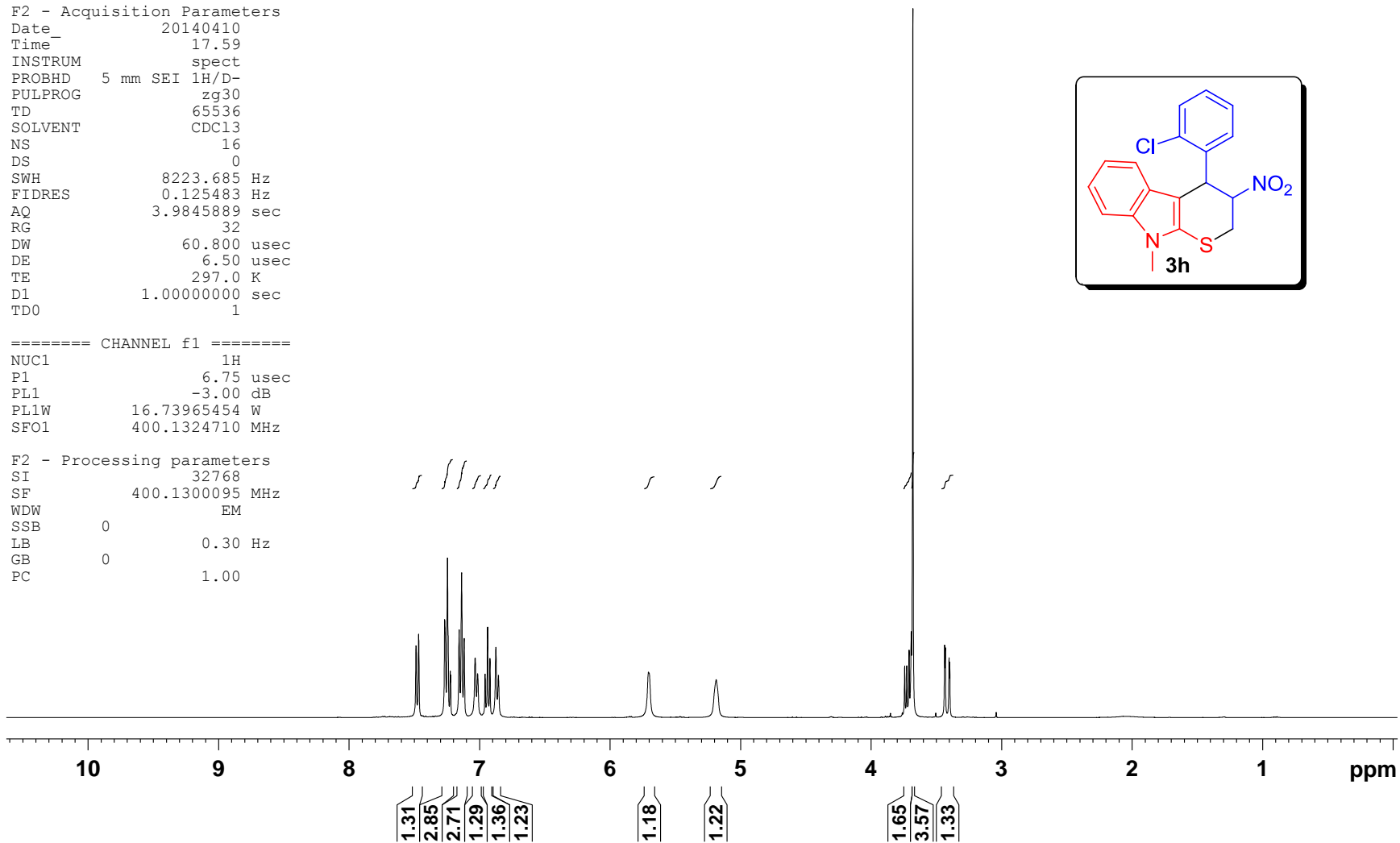


Figure S25. ¹H NMR Spectrum of 3h (major + minor, dr >95:05)

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

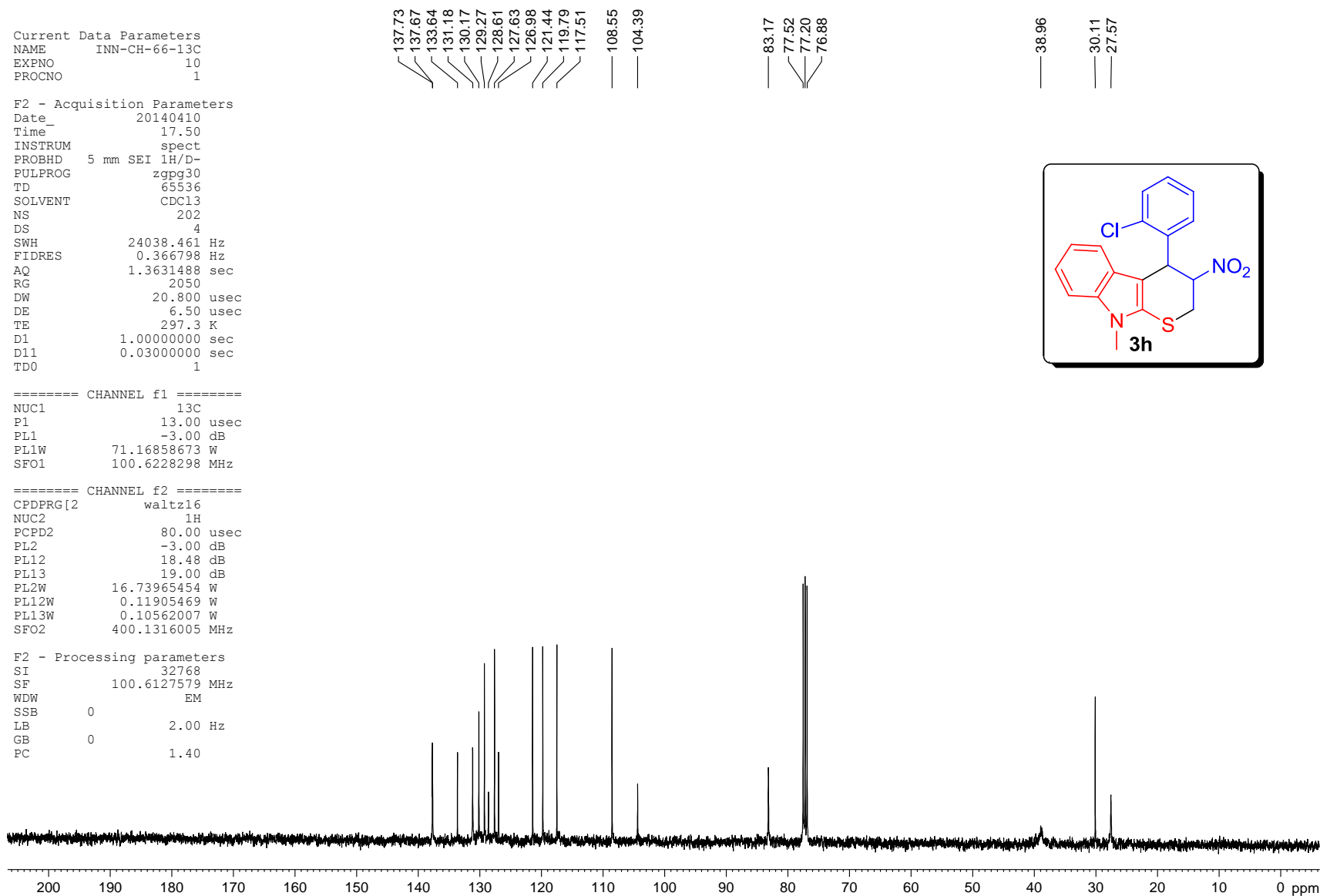


Figure S26. ¹³C NMR Spectrum of 3h (major + minor, dr >95:05)

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

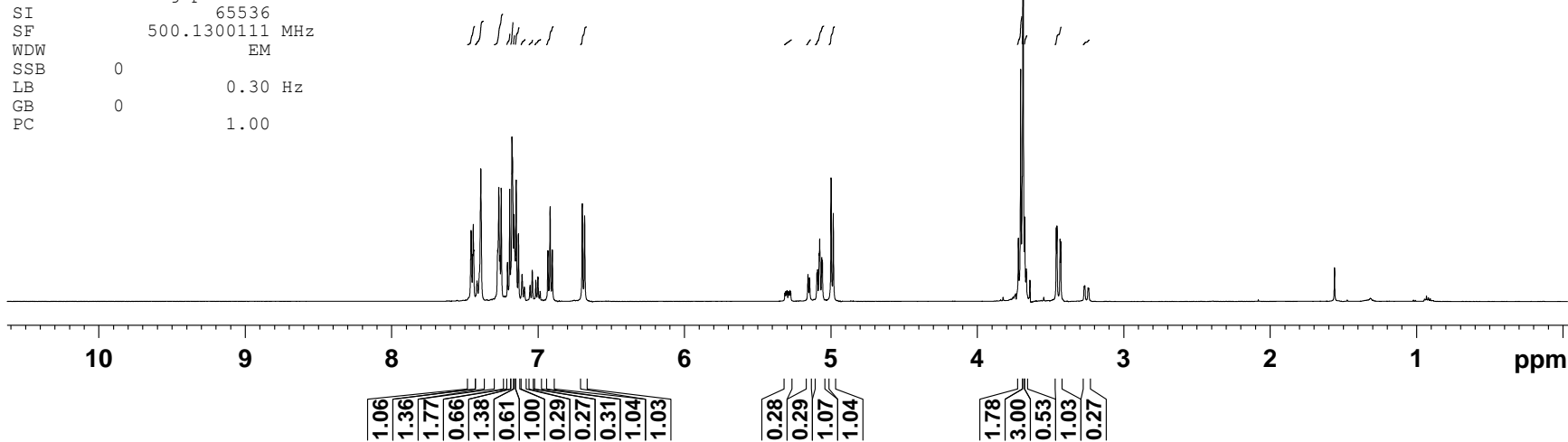
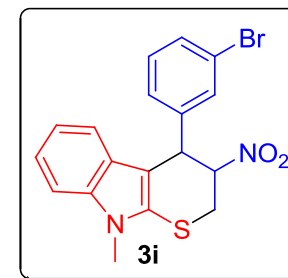


Figure S27. ¹H NMR Spectrum of 3i (major + minor, dr 81:19)

Current Data Parameters
 NAME INN-PB-TI-5-BR-13C
 EXPNO 8
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20190130
 Time_ 13.20
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 116
 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 298.2 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
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 16.00000000 W
 PLW12 0.44556001 W
 PLW13 0.22411001 W

F2 - Processing parameters
 SI 32768
 SF 125.7577796 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

142.54
 140.18
 138.12
 137.79
 132.01
 131.57
 131.42
 131.32
 130.67
 130.27
 128.30
 128.10
 127.89
 127.32
 126.80
 126.74
 123.19
 123.00
 121.58
 121.47
 120.05
 119.87
 118.06
 116.85
 108.69
 108.62
 105.88
 105.52
 88.45
 85.55
 77.45
 77.20
 76.94

43.78
 41.94

30.32
 30.16
 29.30
 22.73

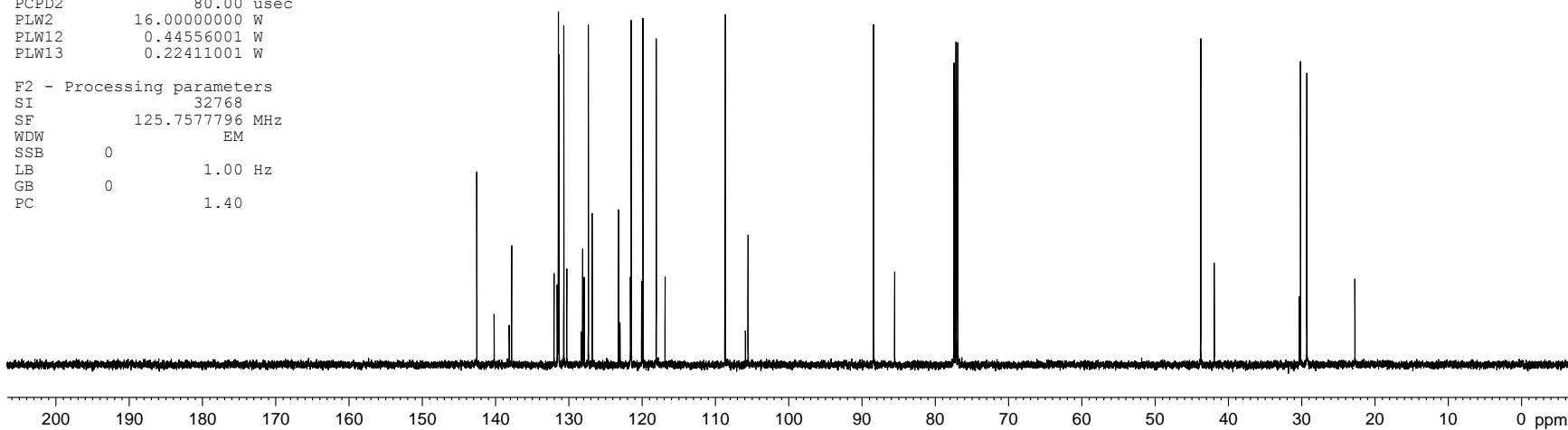
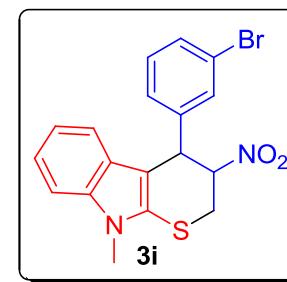


Figure S28. ^{13}C NMR Spectrum of 3i (major + minor, dr 81:19)

Current Data Parameters
NAME INN-PB-86-C-1H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150121
Time_ 22.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
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 297.1 K
D1 1.00000000 sec
TD0 1

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

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

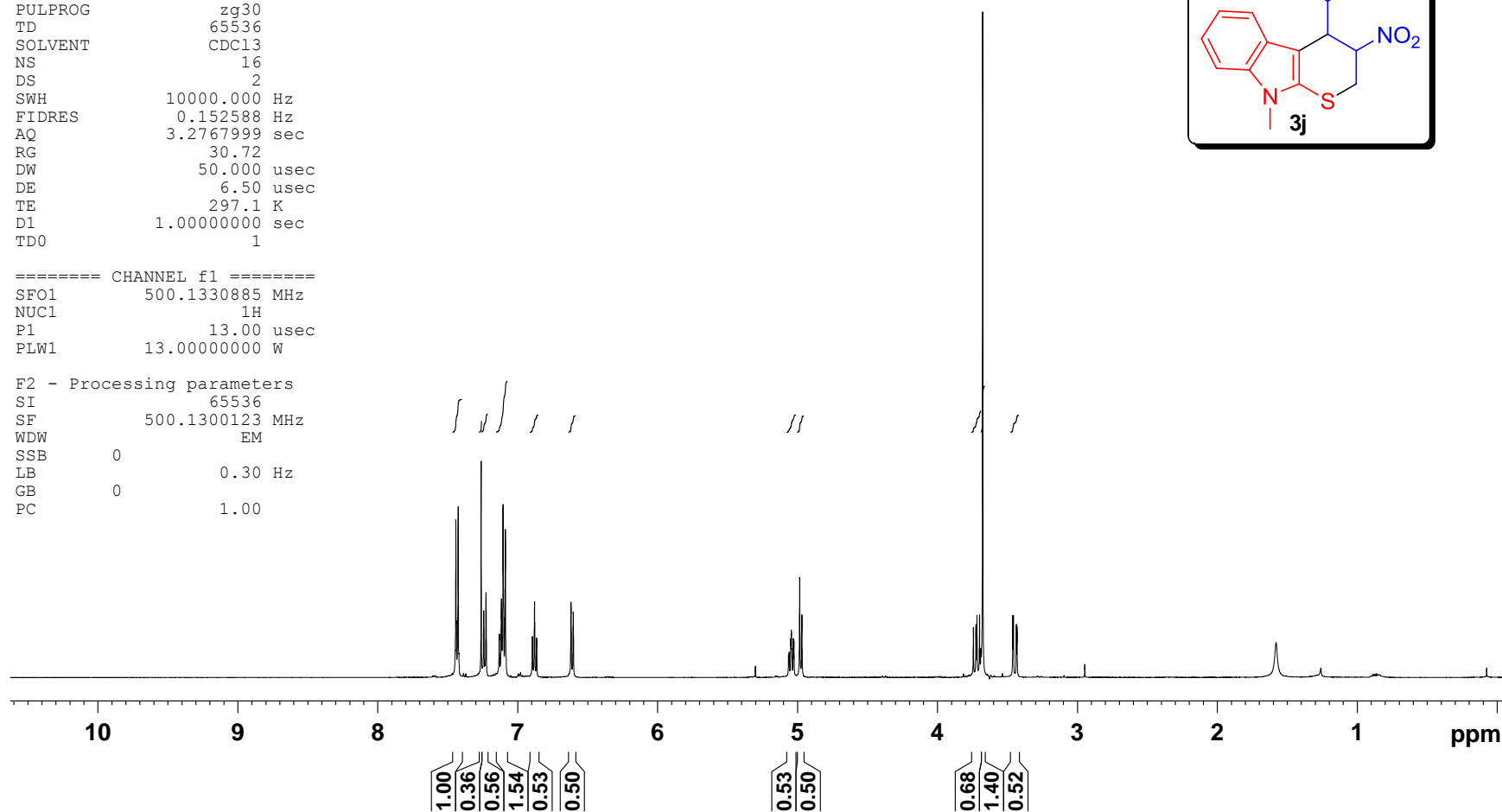
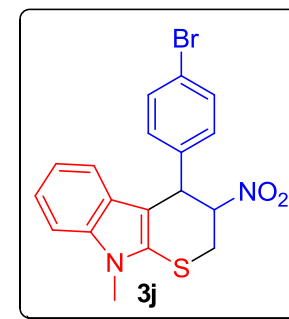
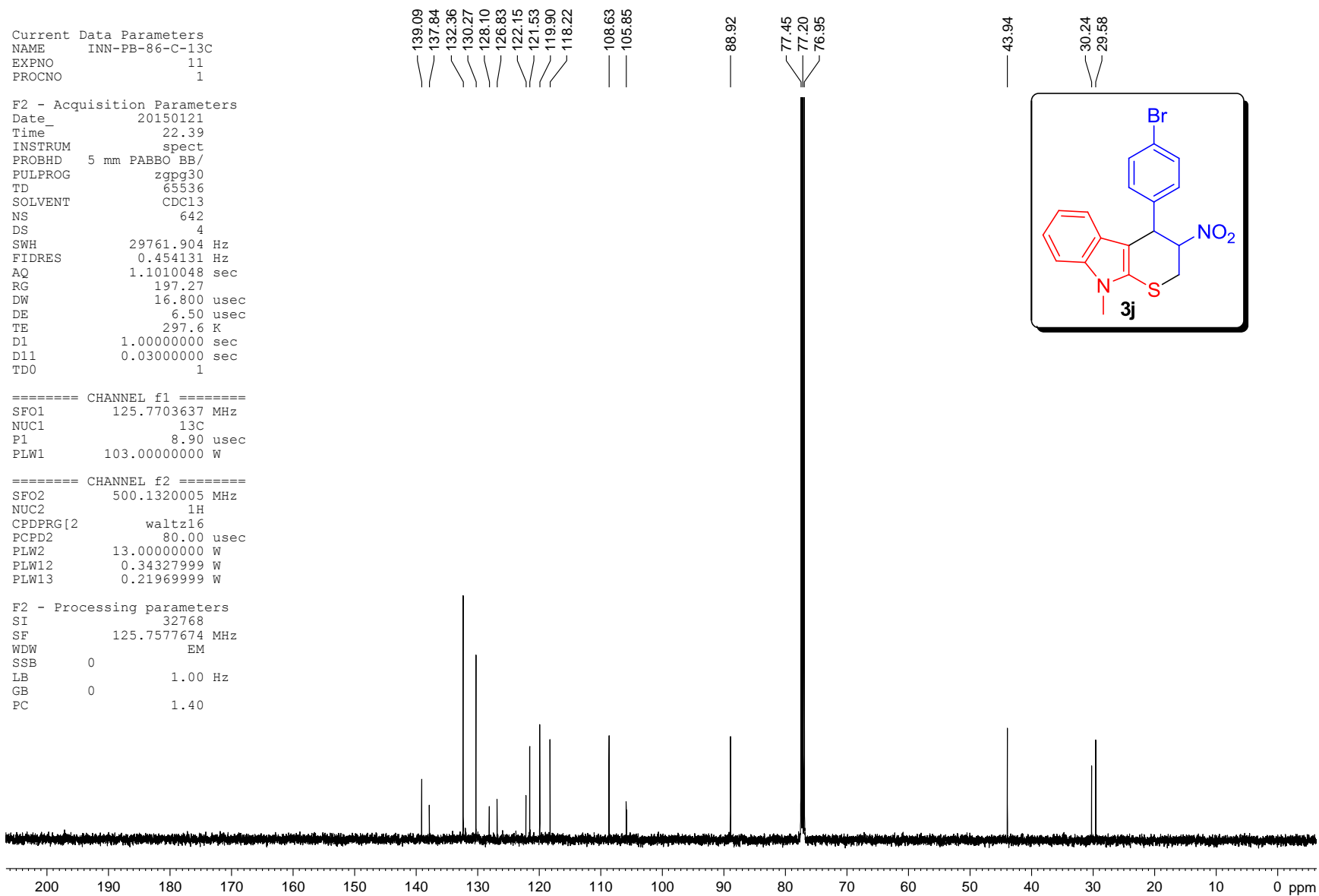


Figure S30. ¹H NMR Spectrum of 3j (Major isomer)



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 CDC13
 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

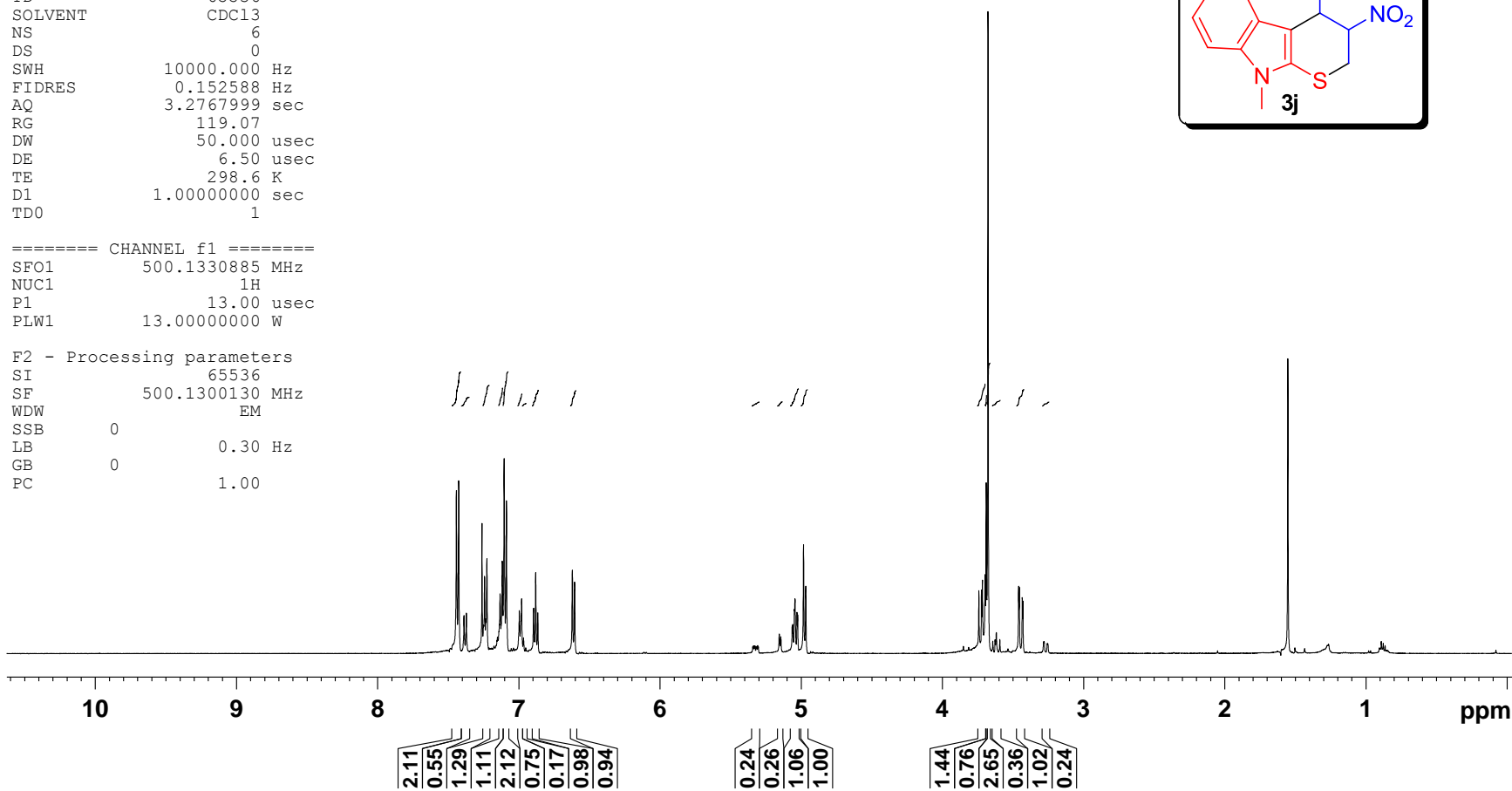
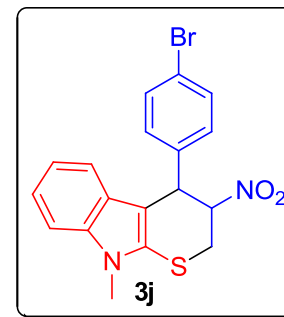
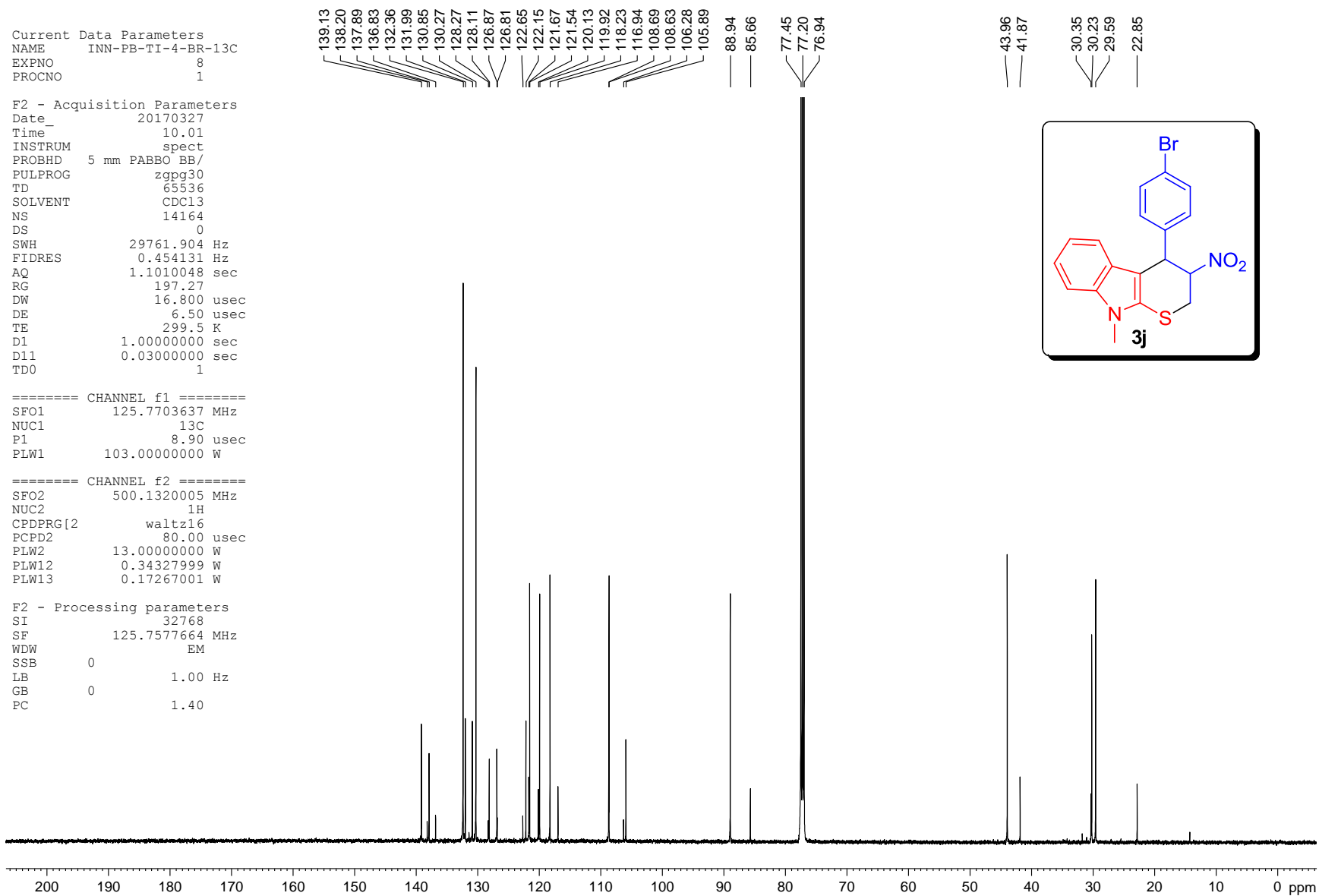
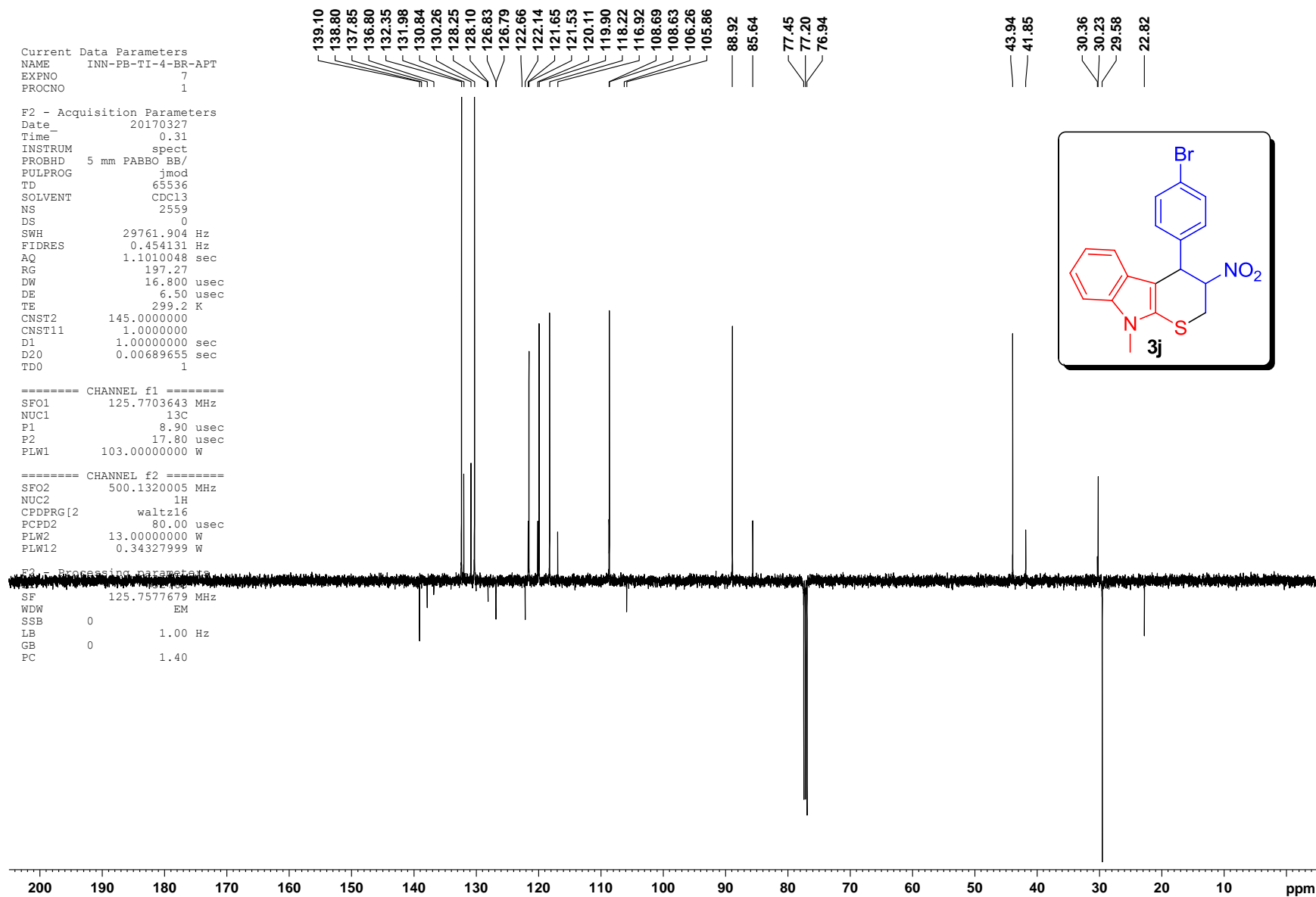


Figure S32. ^1H NMR Spectrum of 3j (major + minor, dr 87:13)

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

Figure S34. ¹³C-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 CDC13
 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

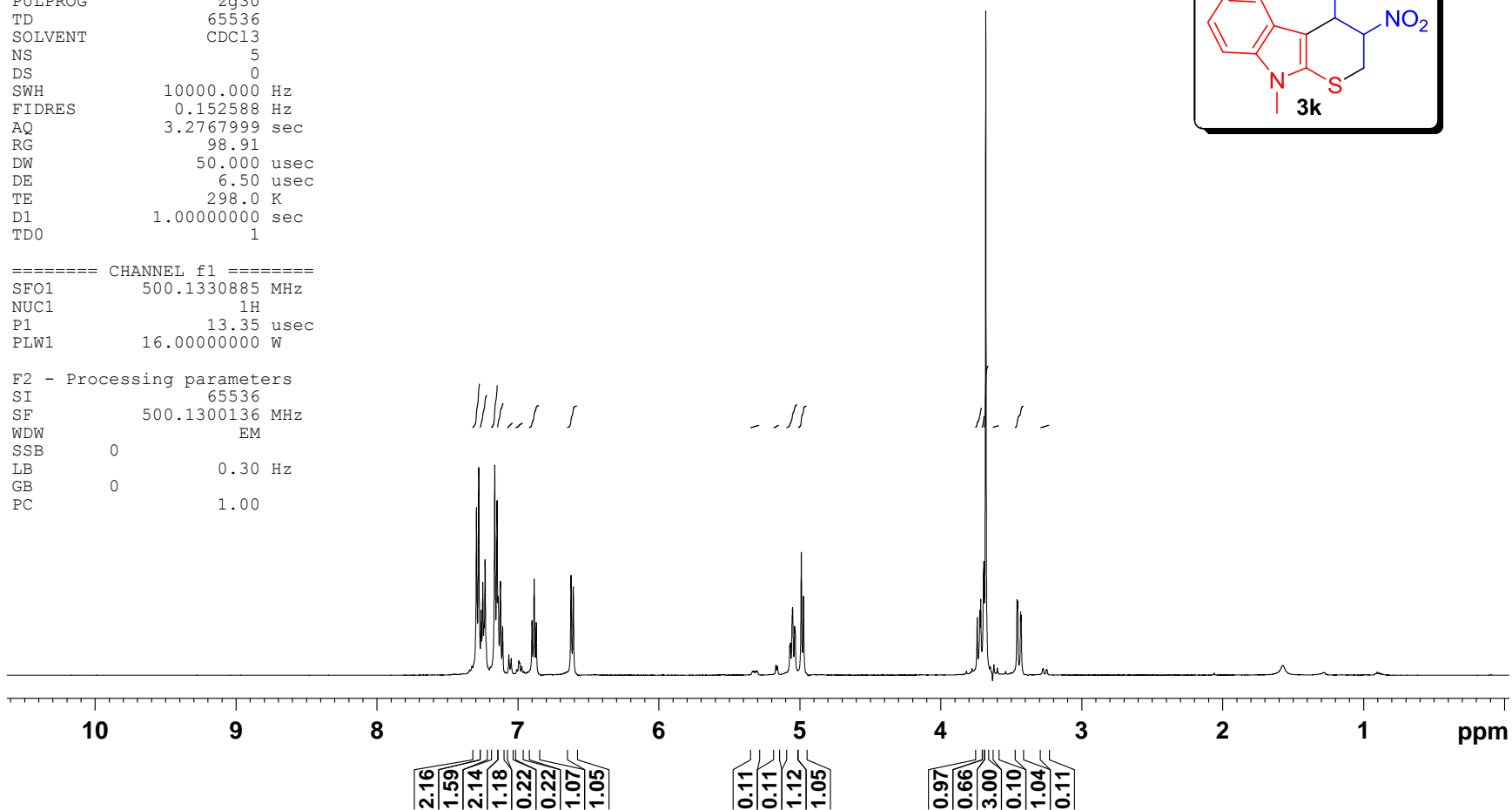


Figure S35. ¹H NMR Spectrum of 3k (major + minor, dr 90:10)

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 CDC13
 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

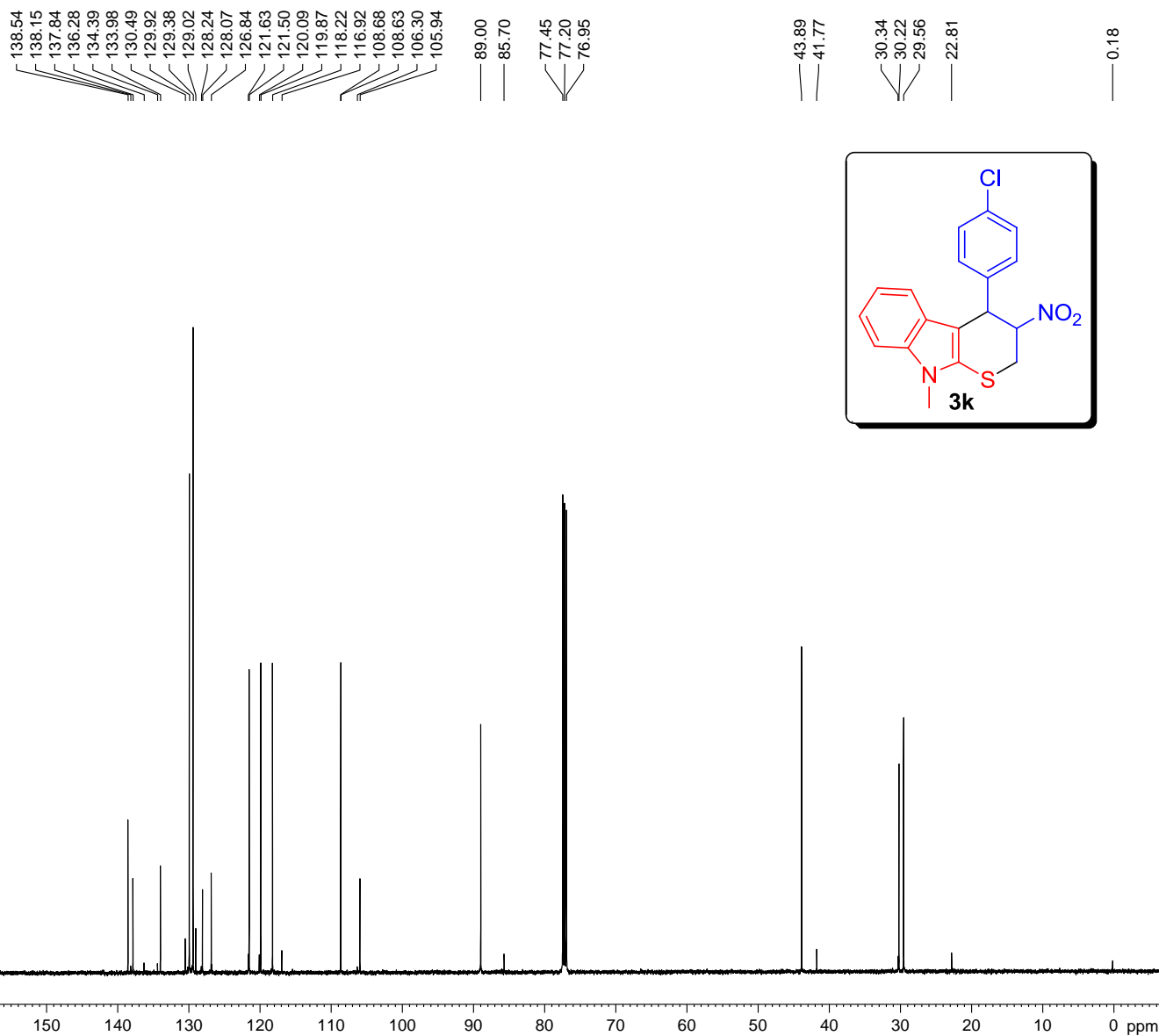
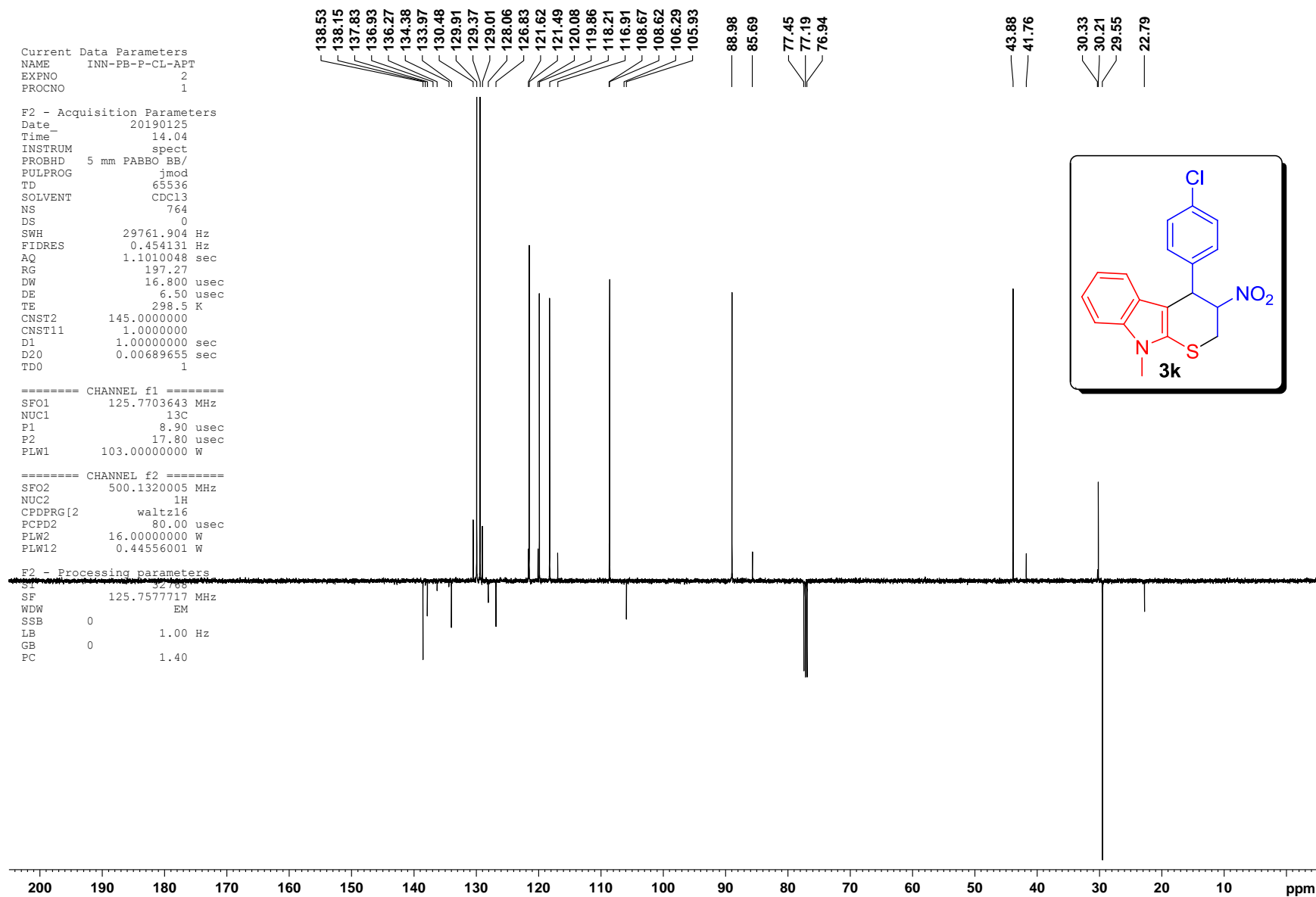


Figure S36. ^{13}C NMR Spectrum of 3k (major + minor, dr 90:10)

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

Current Data Parameters
 NAME INN-PB-CH-63-1H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20170215
 Time_ 17.24
 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 128
 DW 60.800 usec
 DE 6.50 usec
 TE 297.1 K
 D1 1.0000000 sec
 TD0 1

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

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

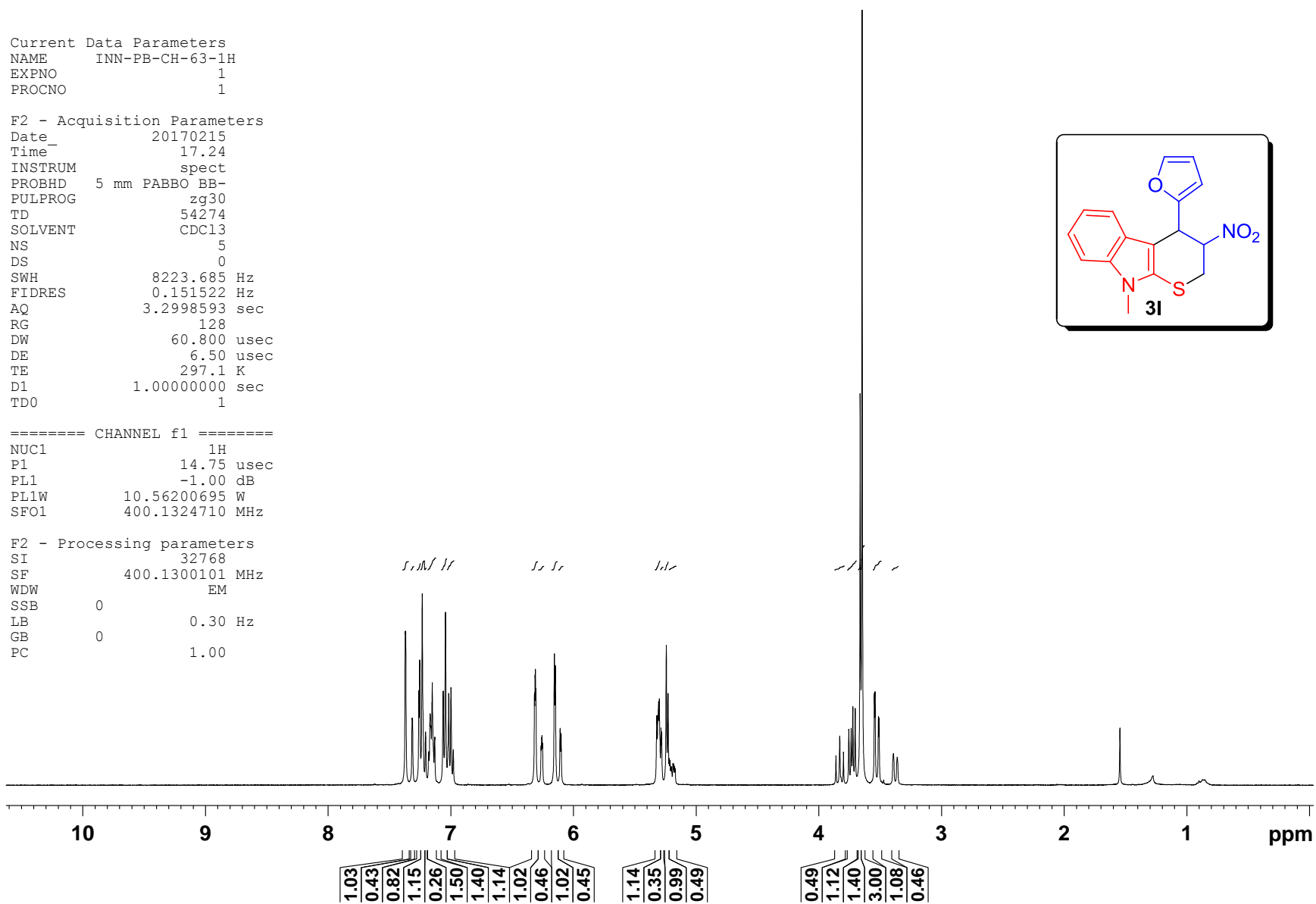
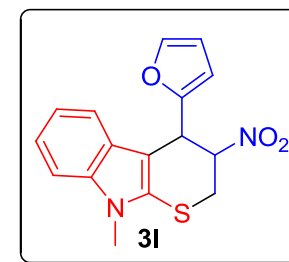


Figure S38. ¹H NMR Spectrum of 3l (major + minor, dr 70:30)

Current Data Parameters
 NAME INN-PB-CH-63-13C
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20170216
 Time_ 3.10
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 13396
 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 297.1 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 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 100.6127533 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

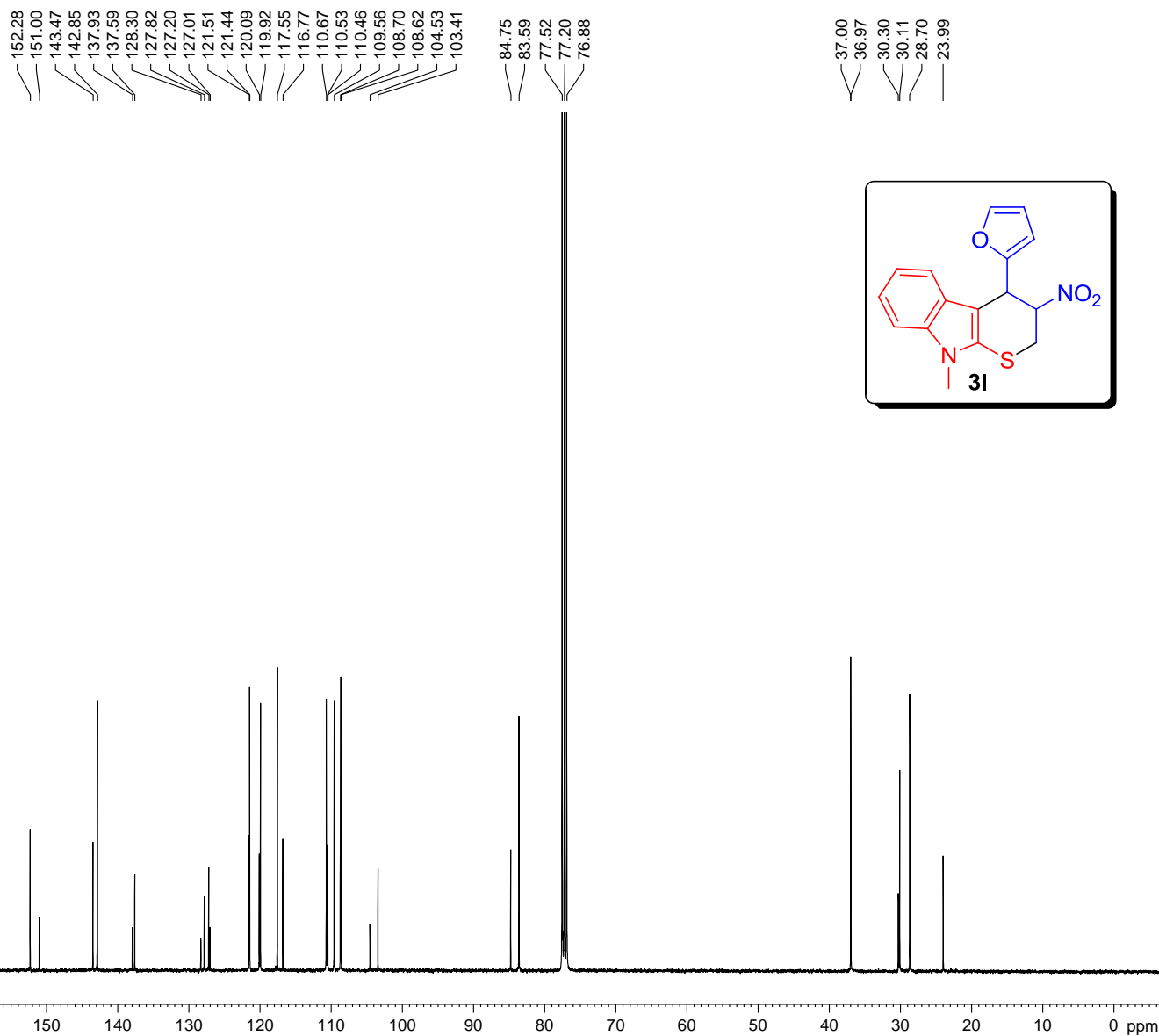
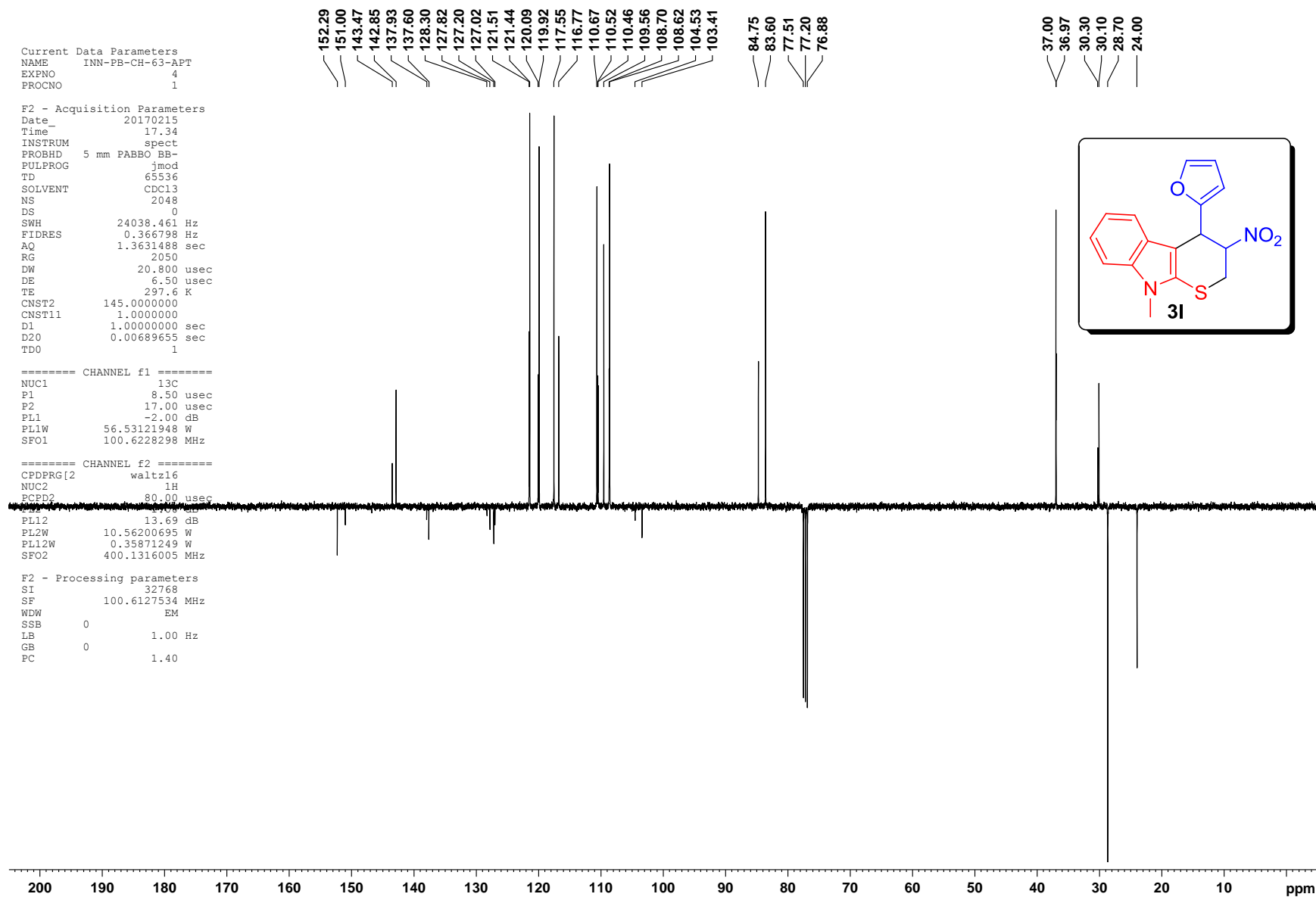


Figure S39. ^{13}C NMR Spectrum of 3I (major + minor, dr 70:30)

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 CDC13
 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

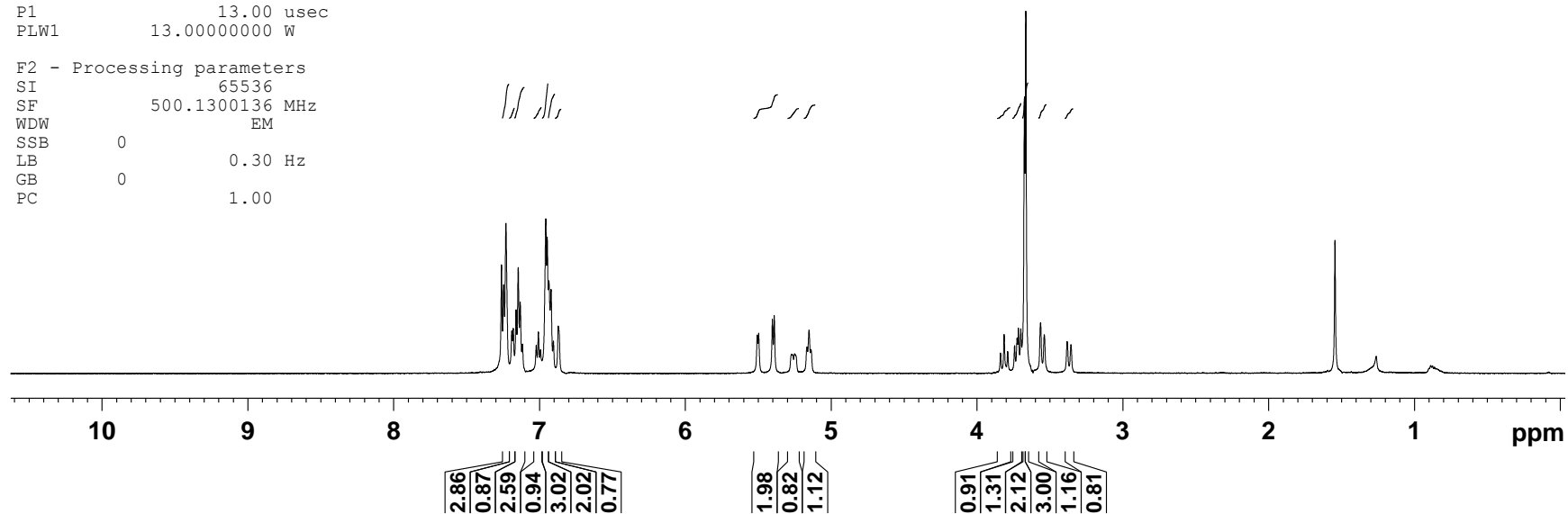
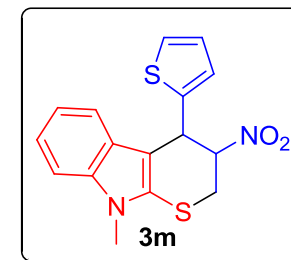


Figure S41. ¹H NMR Spectrum of 3m (major + minor, dr 60:40)

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

143.91
 141.48
 138.01
 137.66
 127.99
 127.65
 127.34
 127.15
 127.11
 127.03
 126.97
 126.38
 125.73
 121.58
 121.46
 120.14
 119.88
 117.98
 116.88
 108.67
 108.59
 107.33
 105.98
 87.84
 85.81
 77.45
 77.20
 76.94
 38.76
 37.87
 30.31
 30.14
 28.95
 23.13

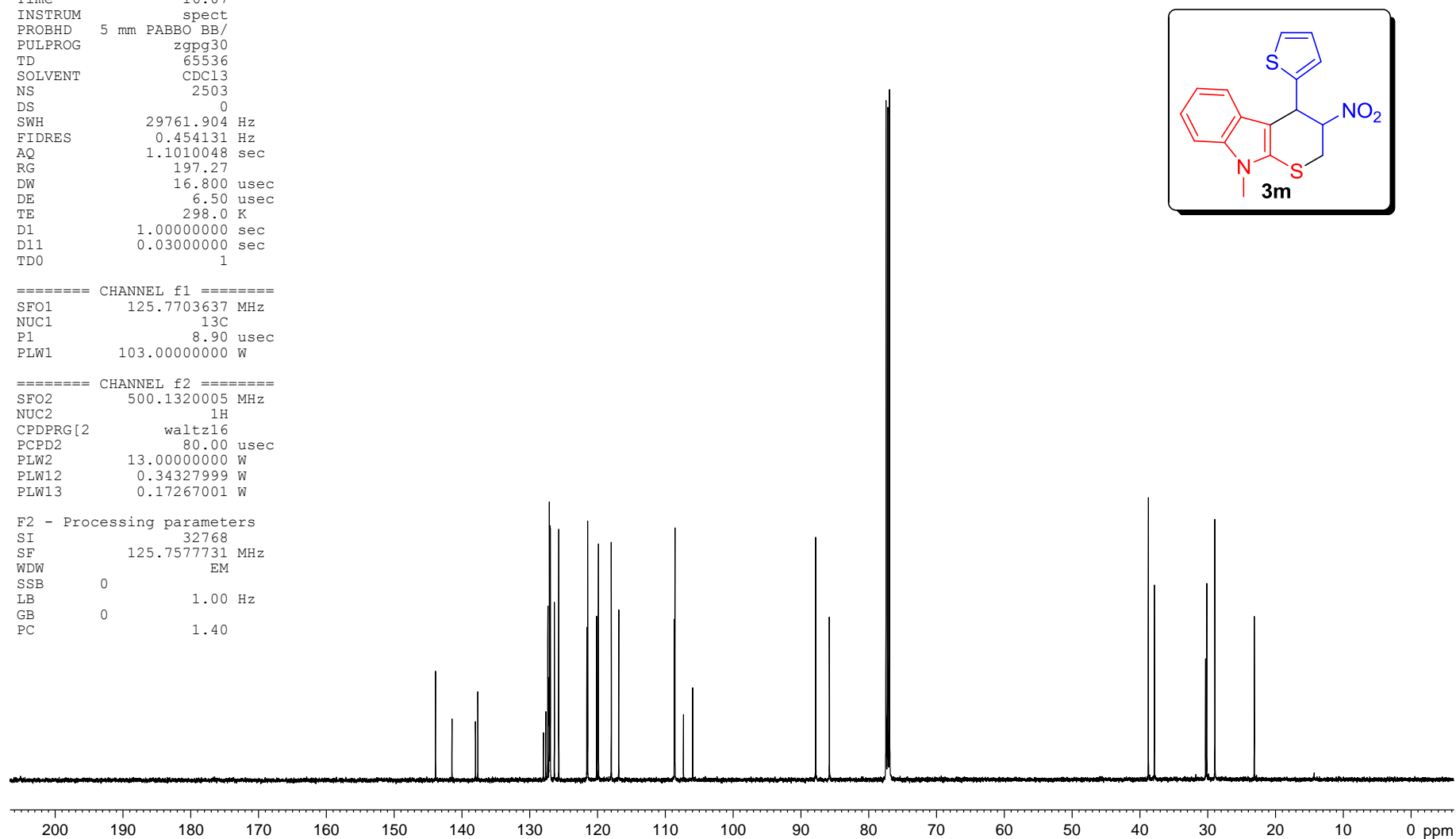


Figure S42. ¹³C NMR Spectrum of 3m (major + minor, dr 60:40)

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 CDC13
 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 1.0000000 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 125.7577729 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

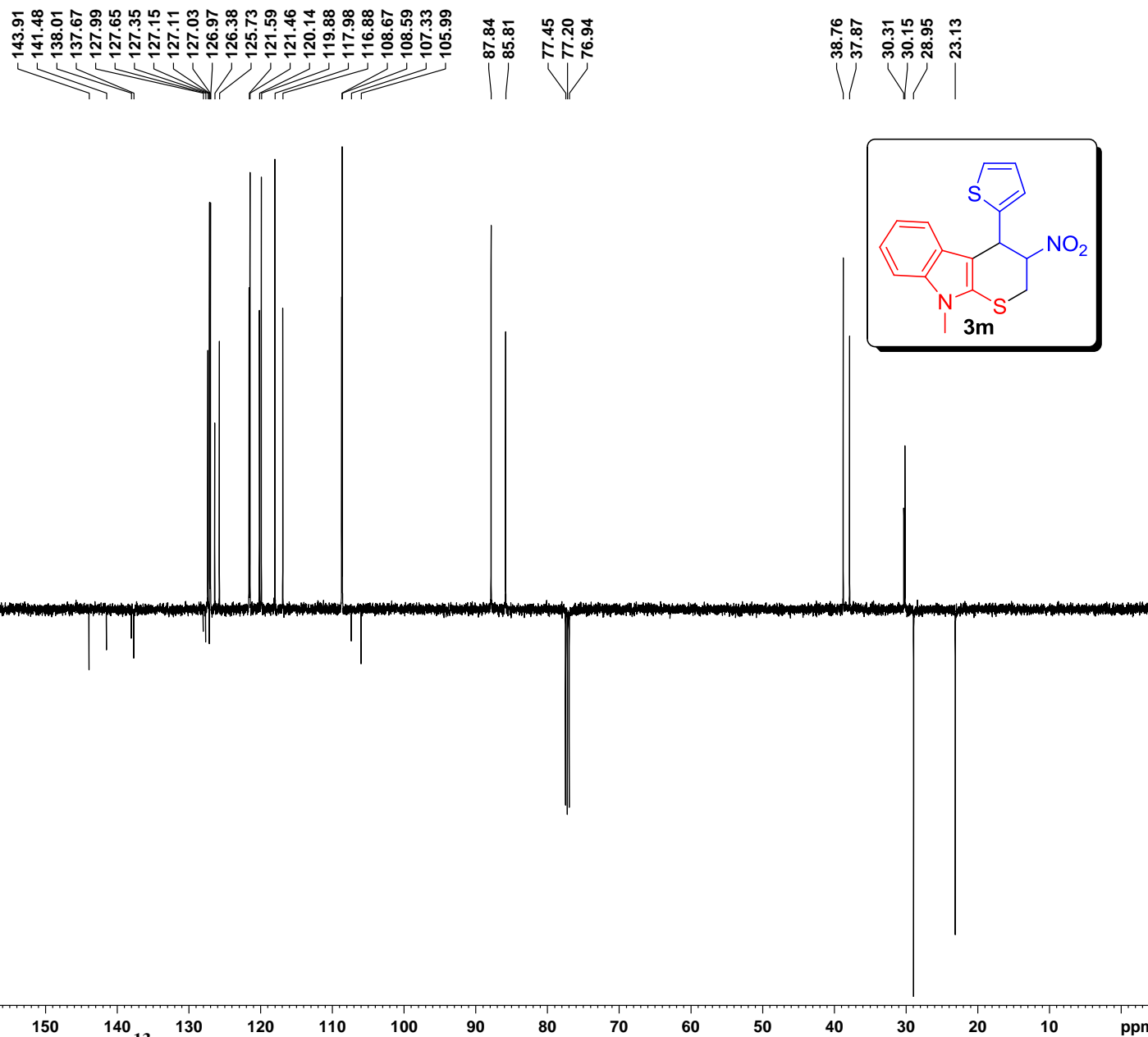


Figure S43. ¹³C-APT NMR Spectrum of 3m (major + minor, dr 60:40)

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

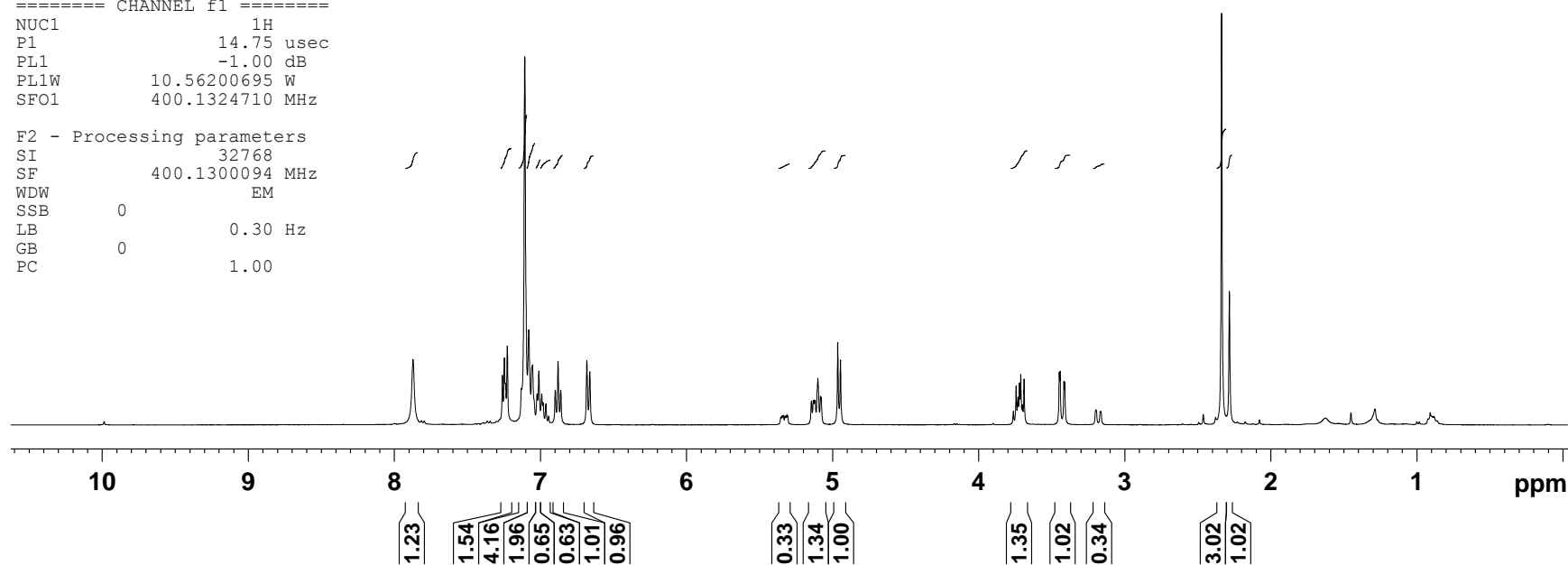
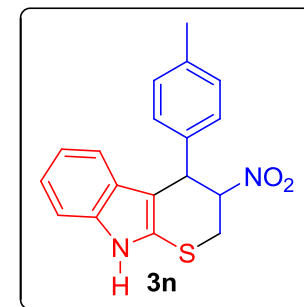
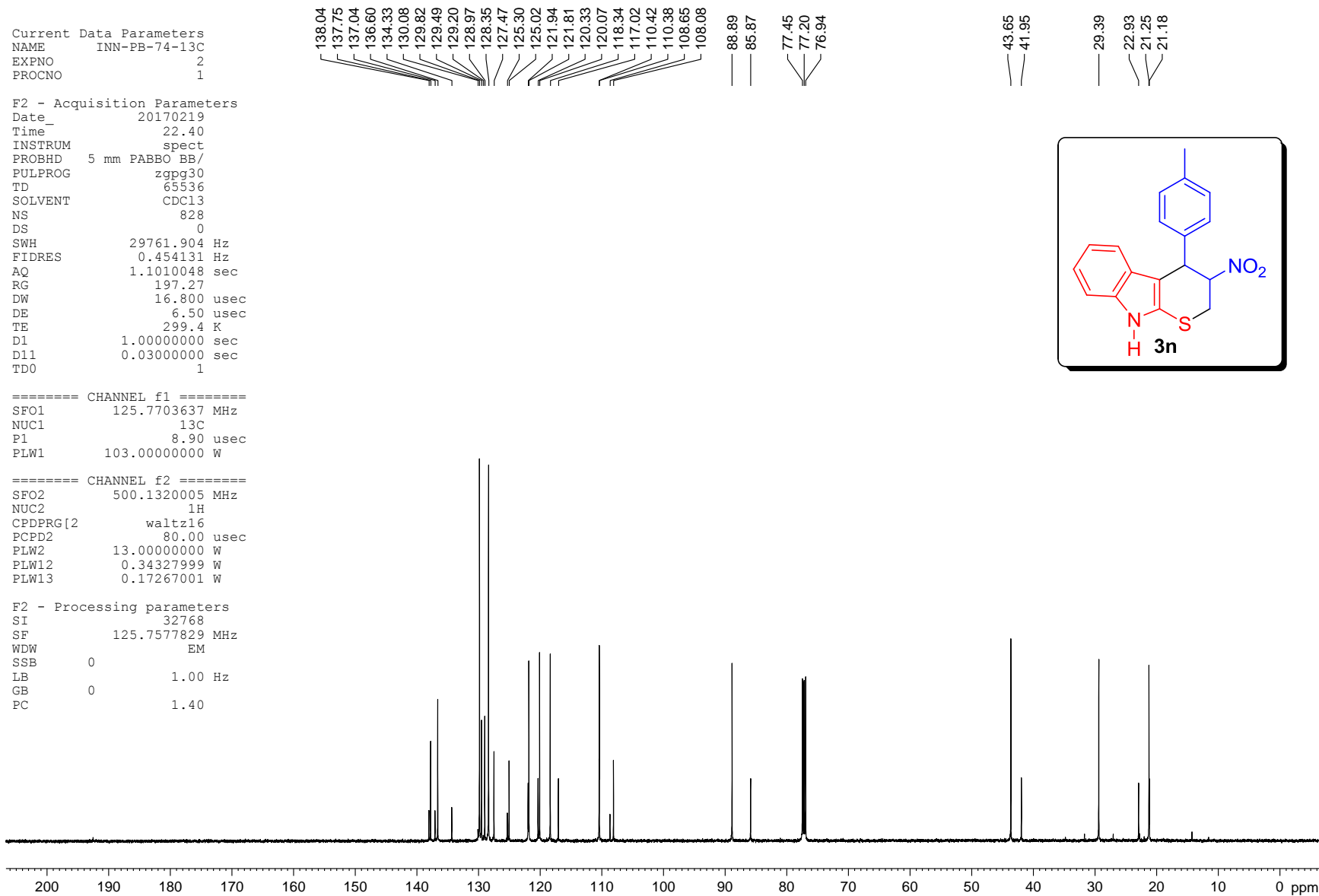
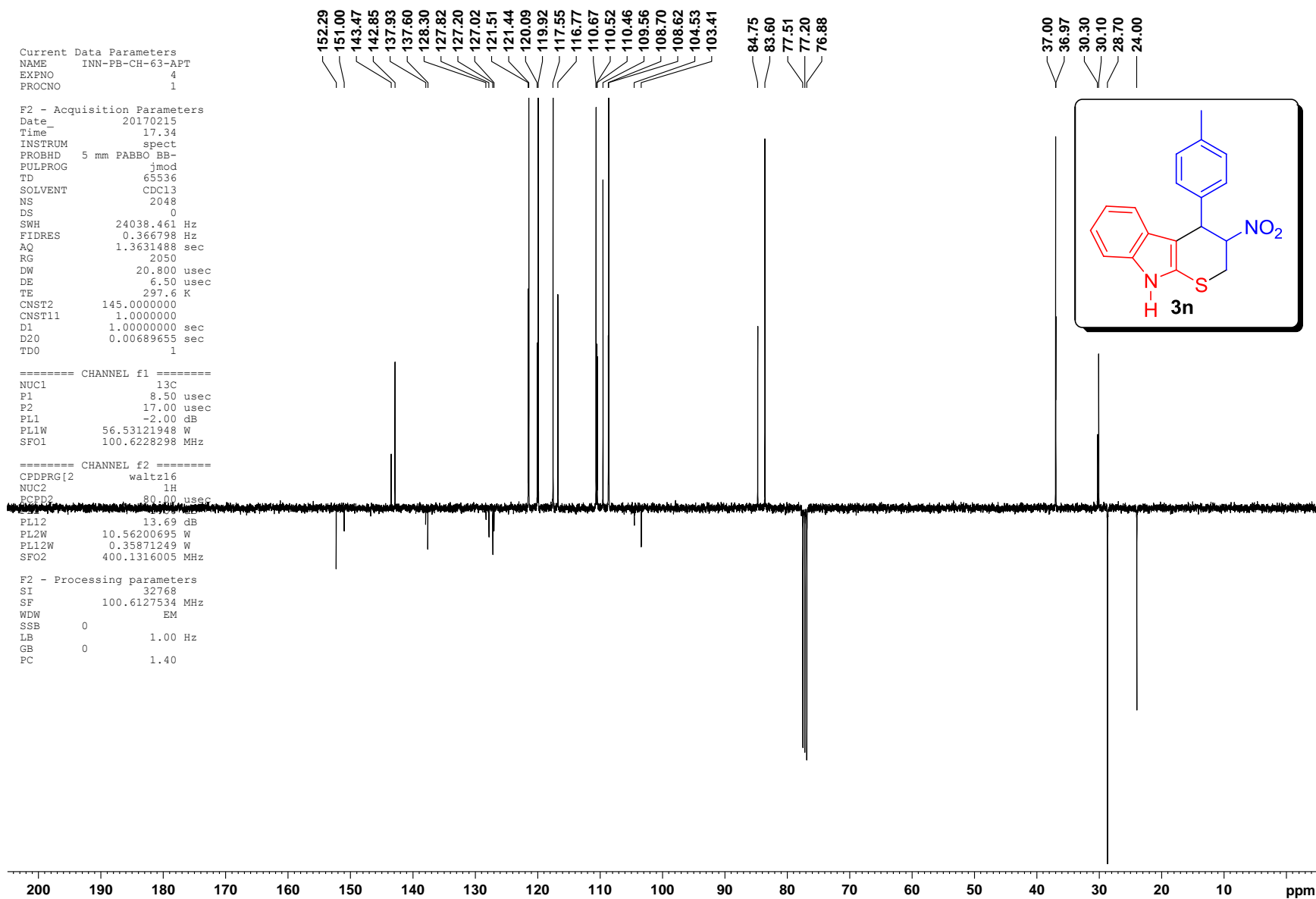


Figure S44. ¹H NMR Spectrum of 3n (major + minor, dr 77:23)



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 CDC13
 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

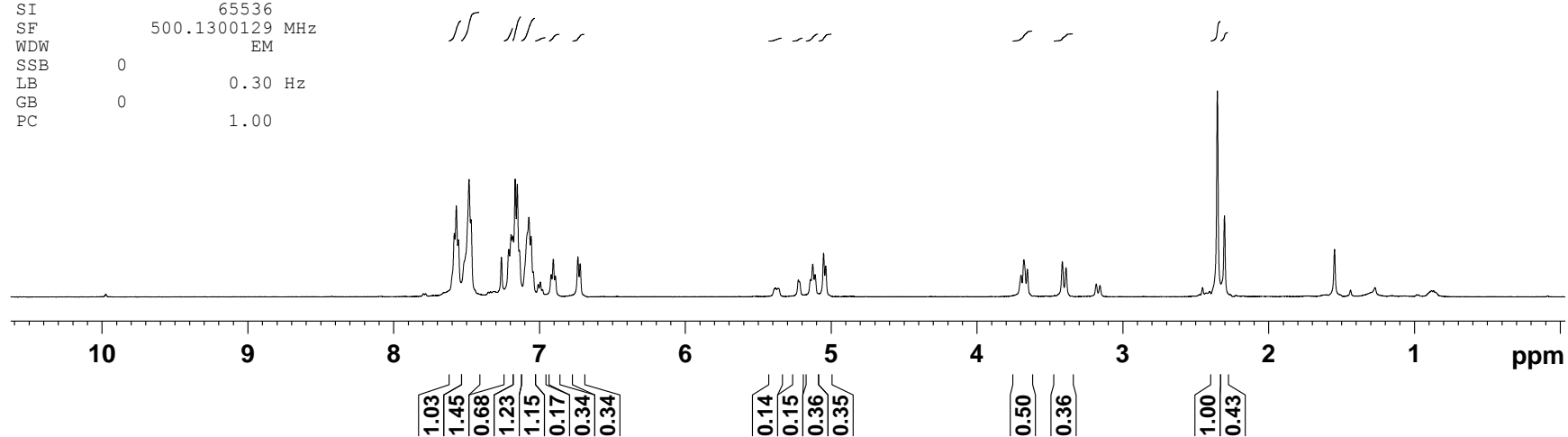
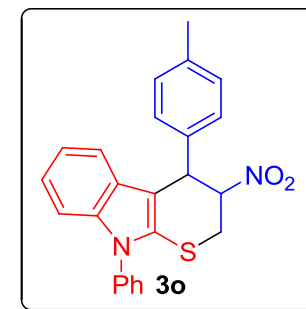
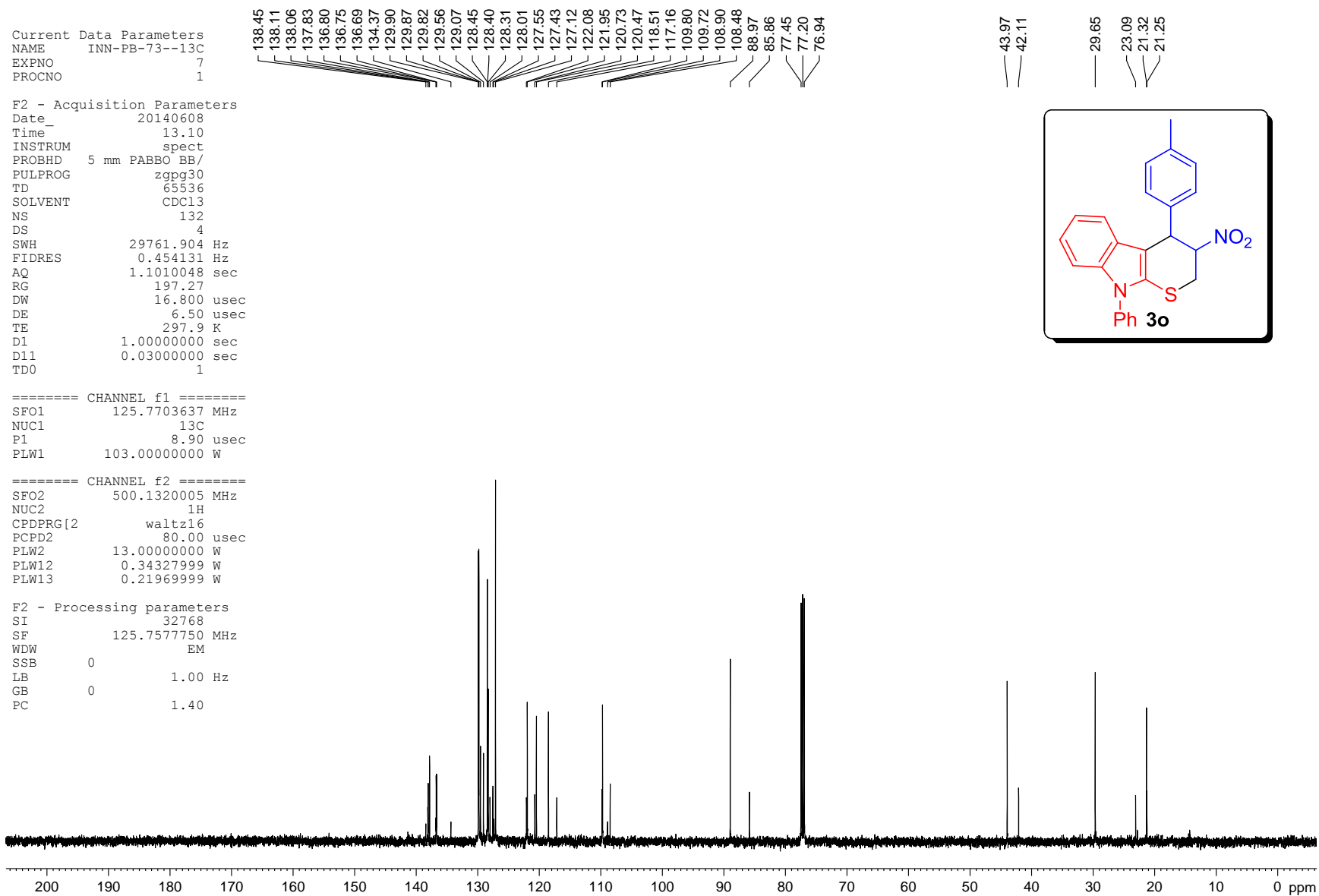
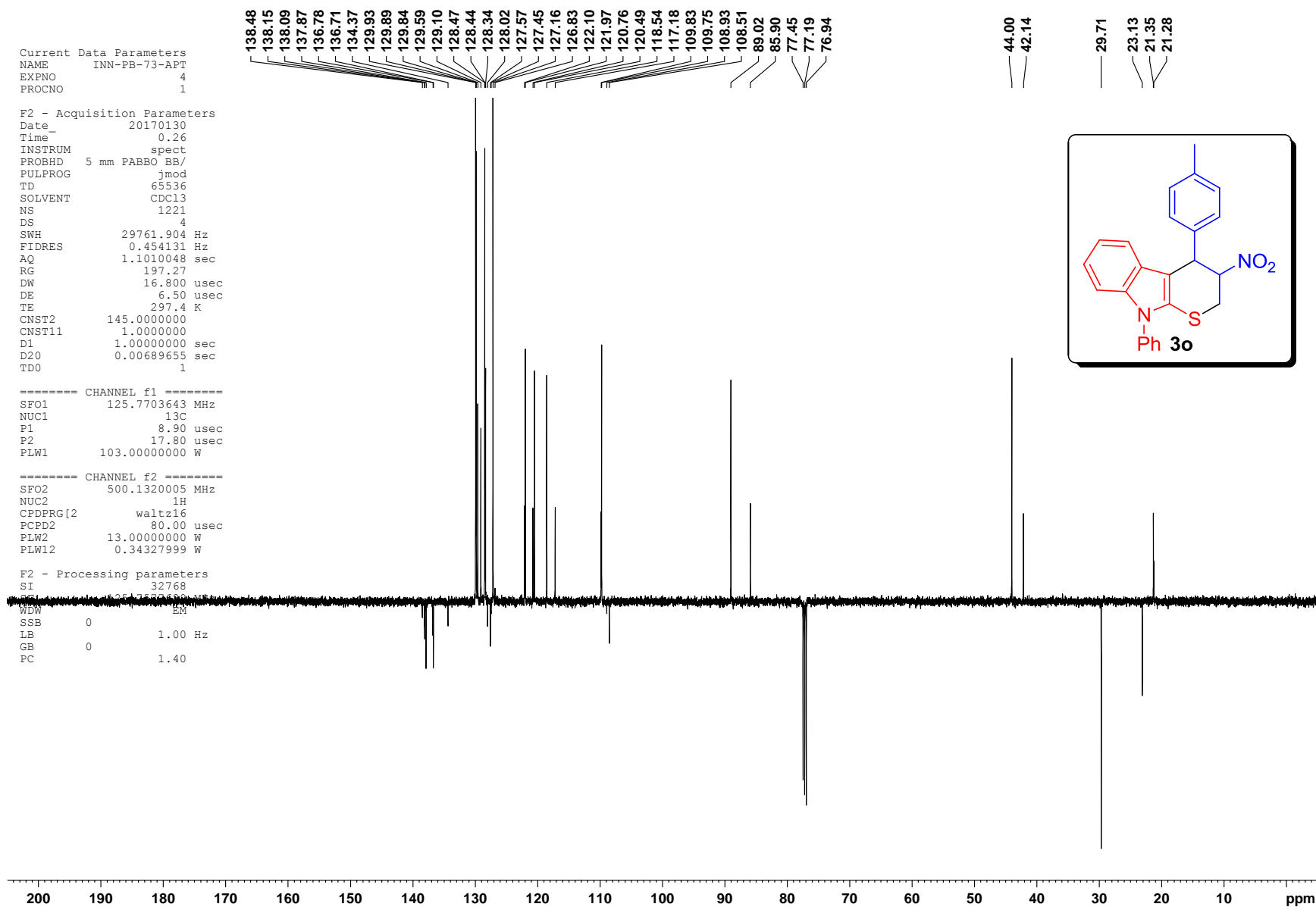


Figure S47. ¹H NMR Spectrum of 3o (major + minor, dr 75:25)

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

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

Current Data Parameters
 NAME INN-PB-359-
 EXPNO 8
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20190120
 Time_ 22.17
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 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 298.9 K
 D1 1.00000000 sec
 TD0 1

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

F2 - Processing parameters
 SI 65536
 SF 500.1300134 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

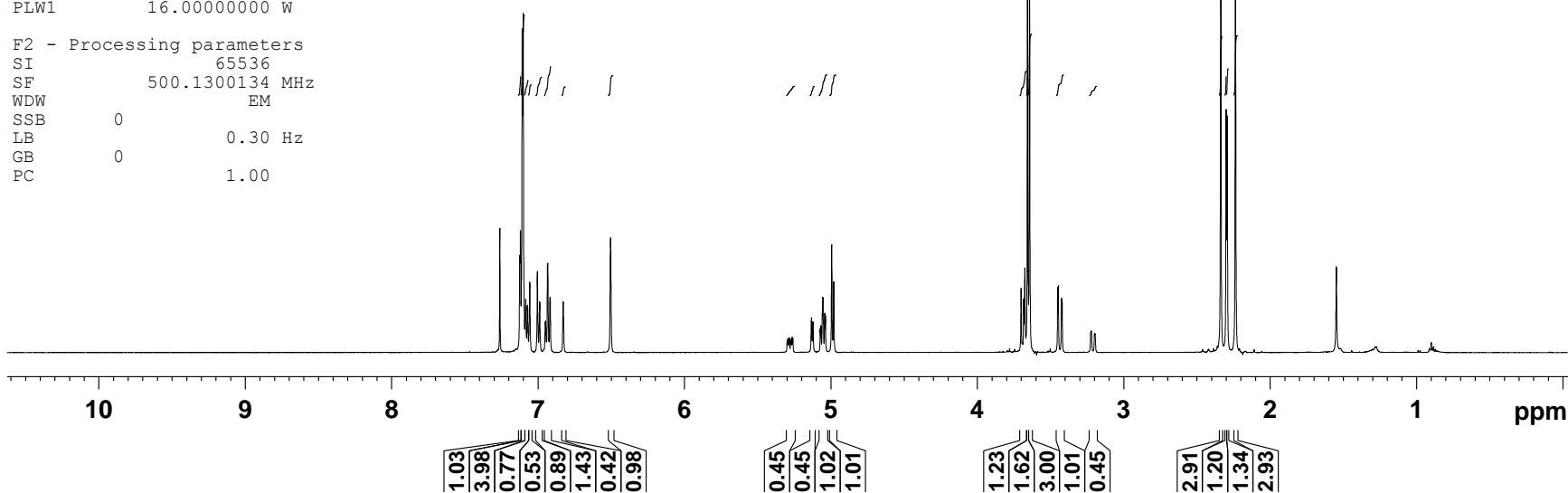
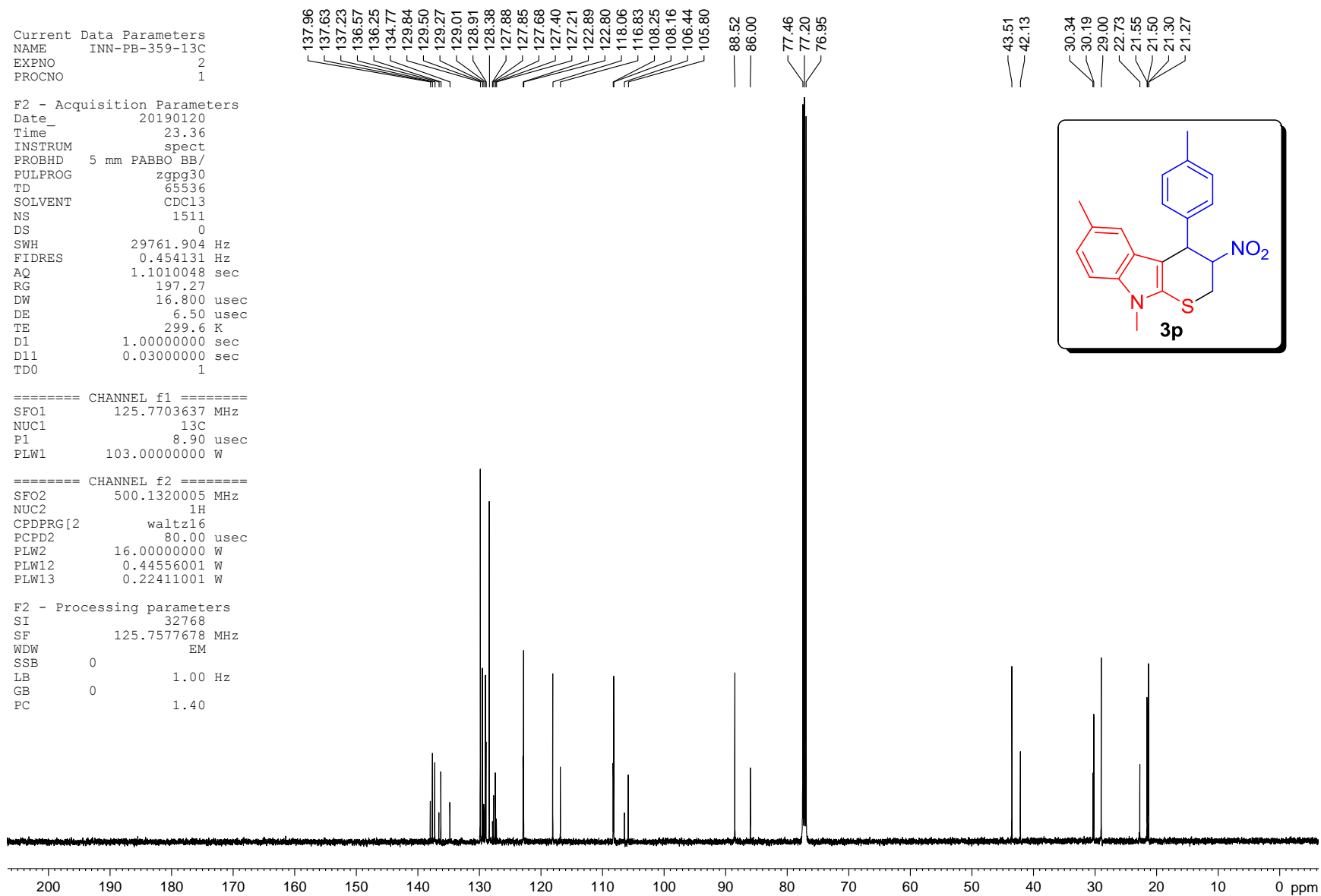
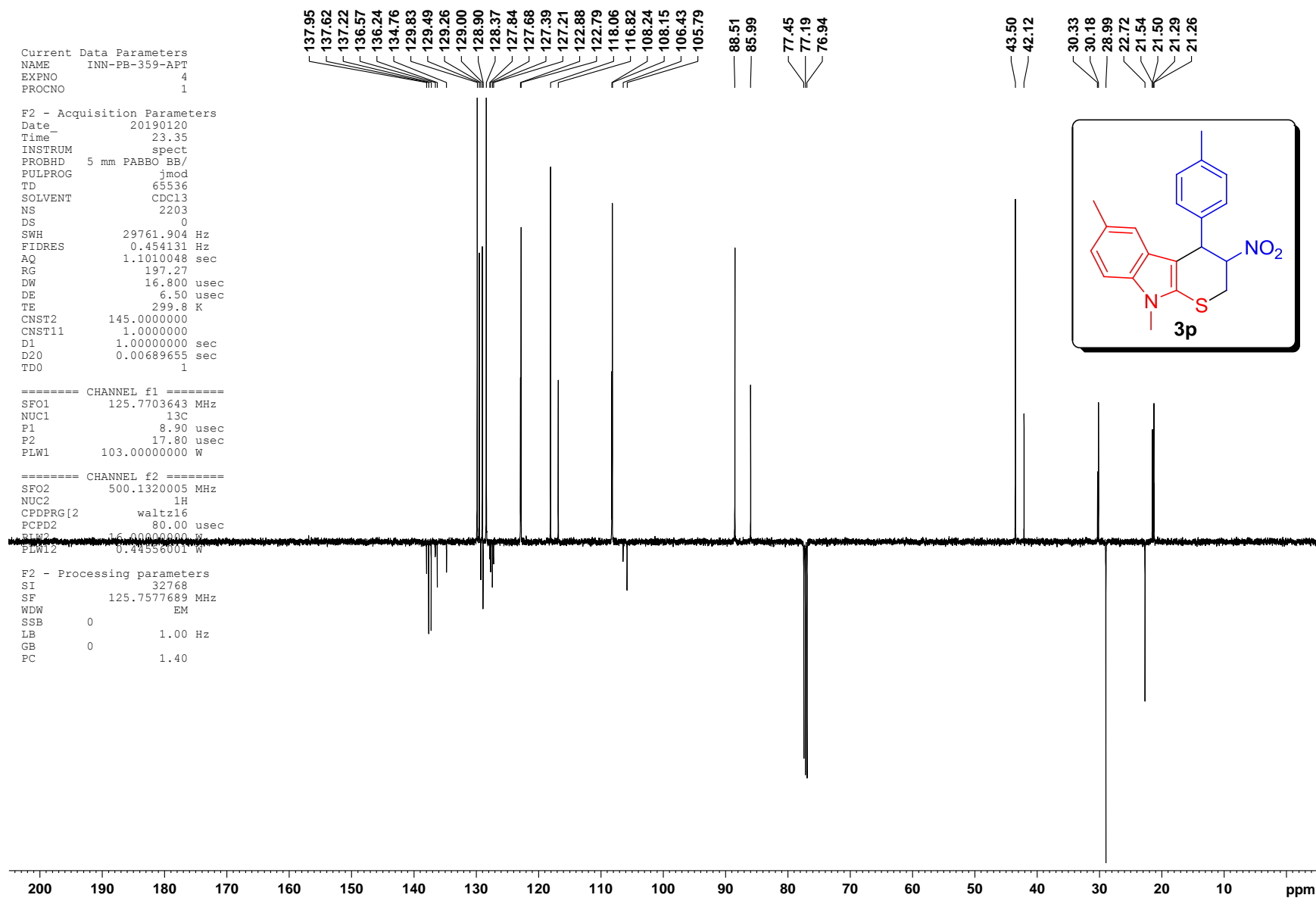


Figure S50. ¹H NMR Spectrum of 3p (major + minor, dr 69:31)

Figure S51. ¹³C NMR Spectrum of 3o (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

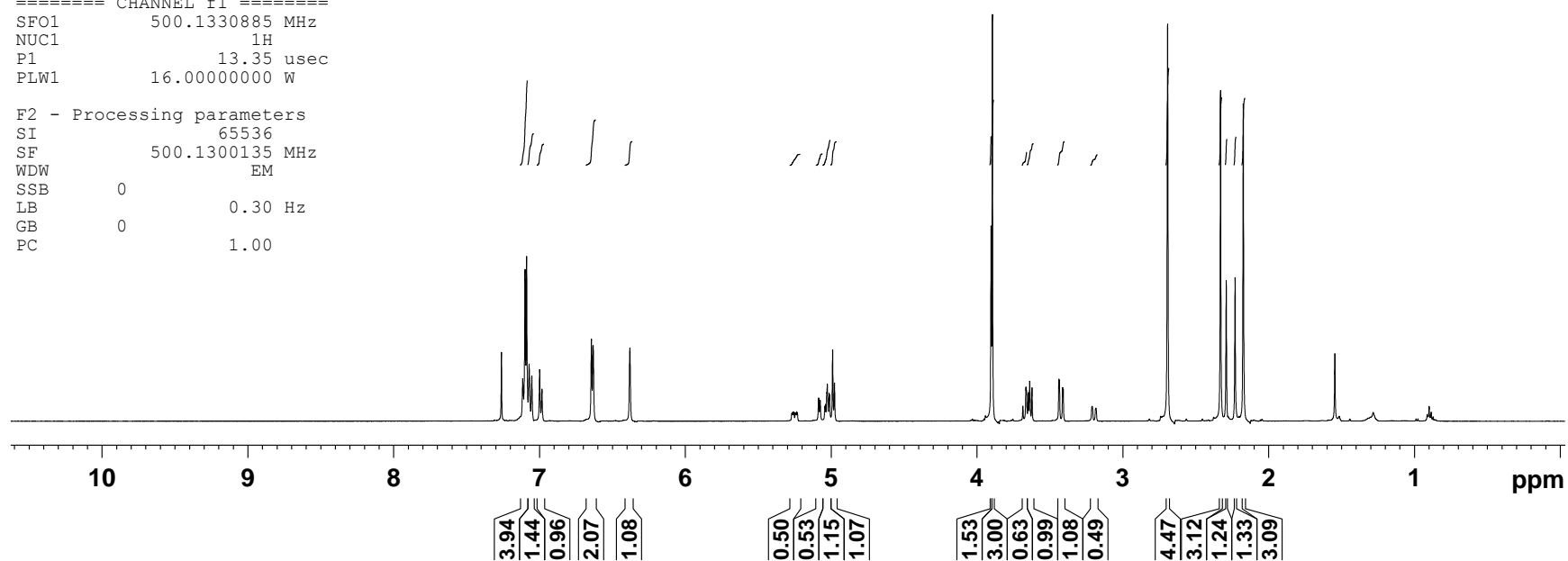
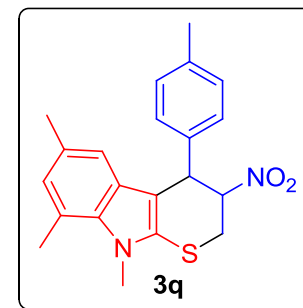
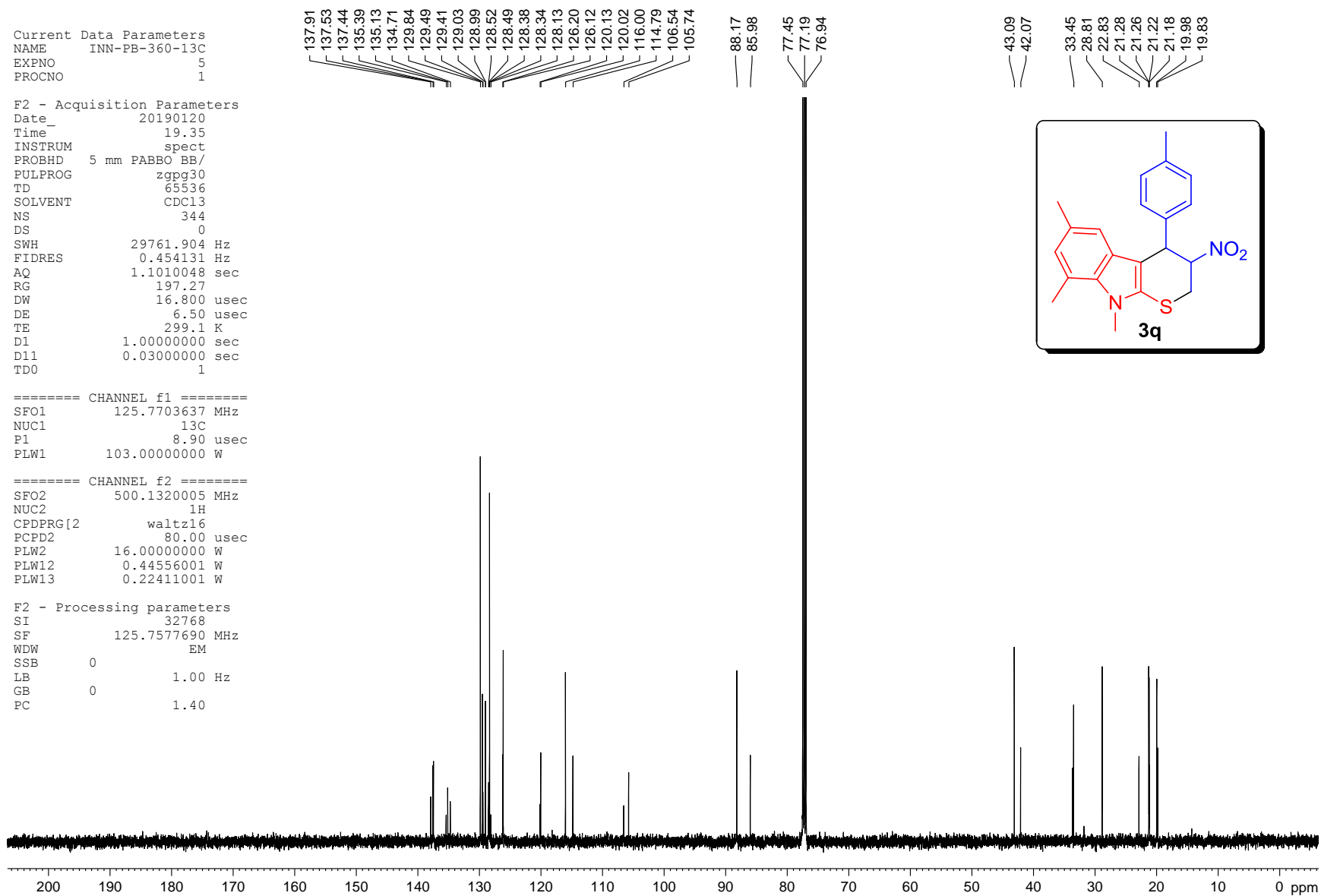
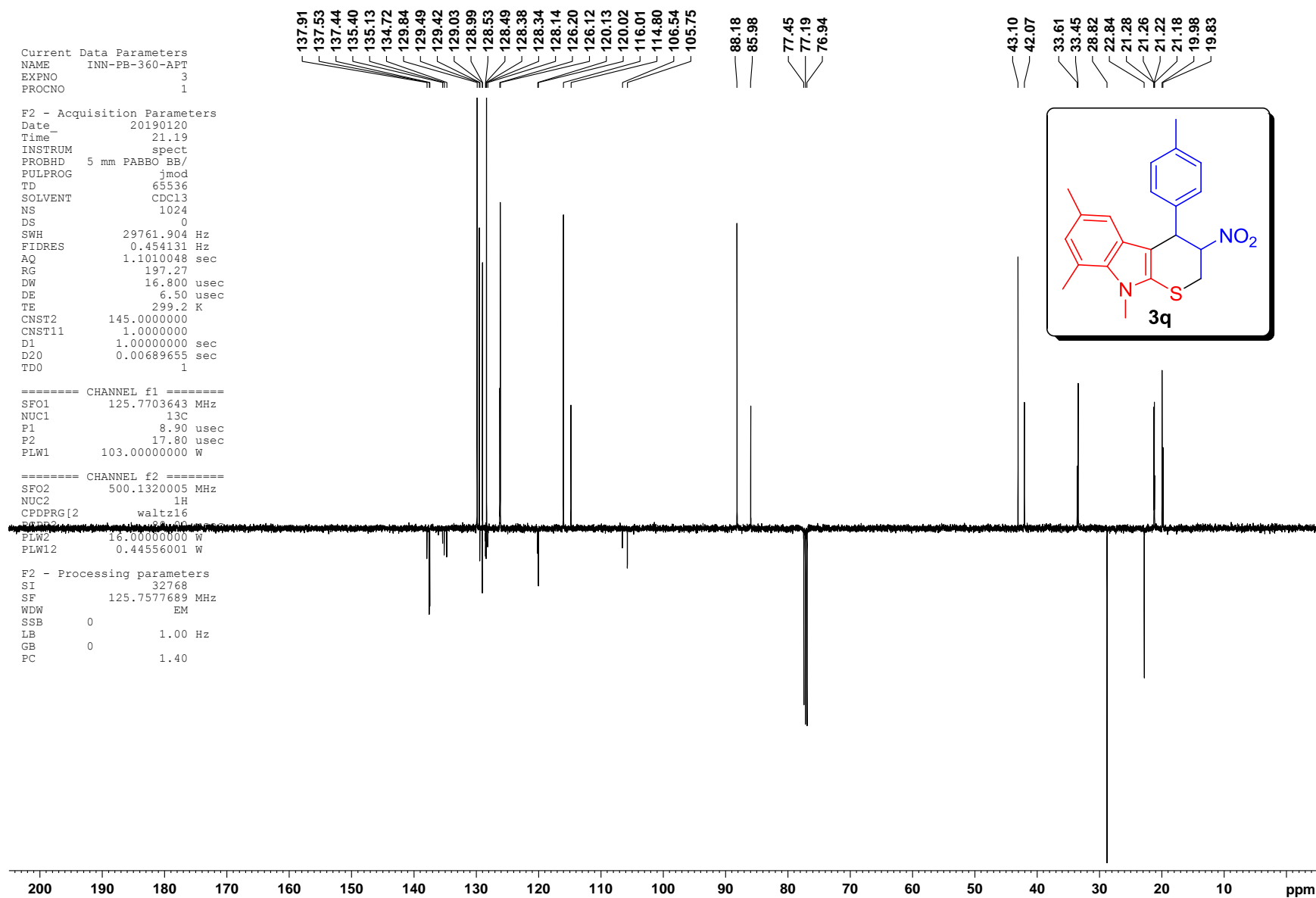


Figure S53. ¹H NMR Spectrum of 3q (major + minor, dr 66:34)

Figure S54. ¹³C 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 CDC13
 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

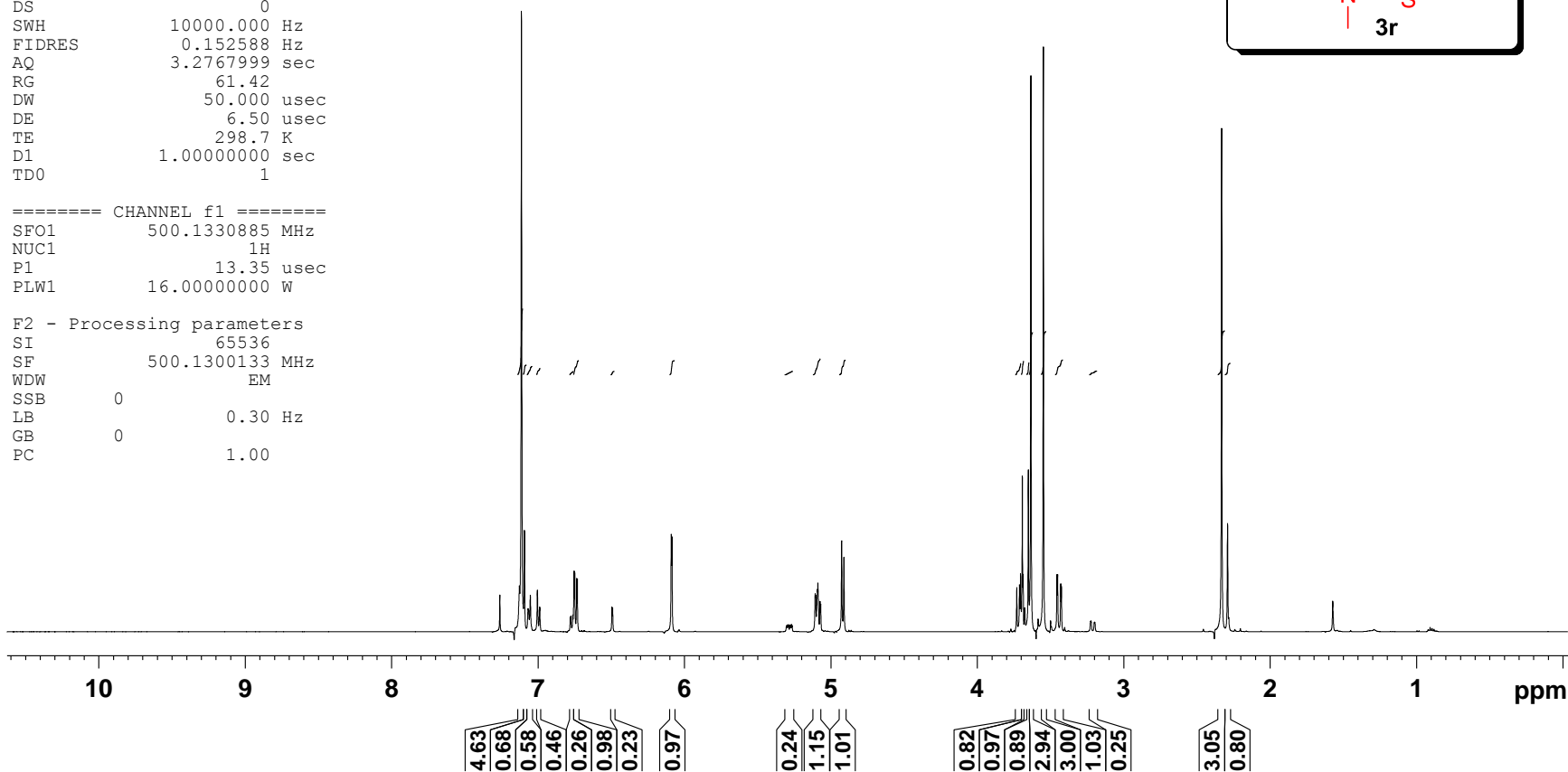
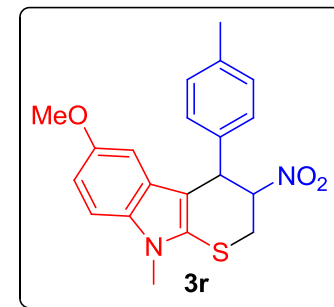
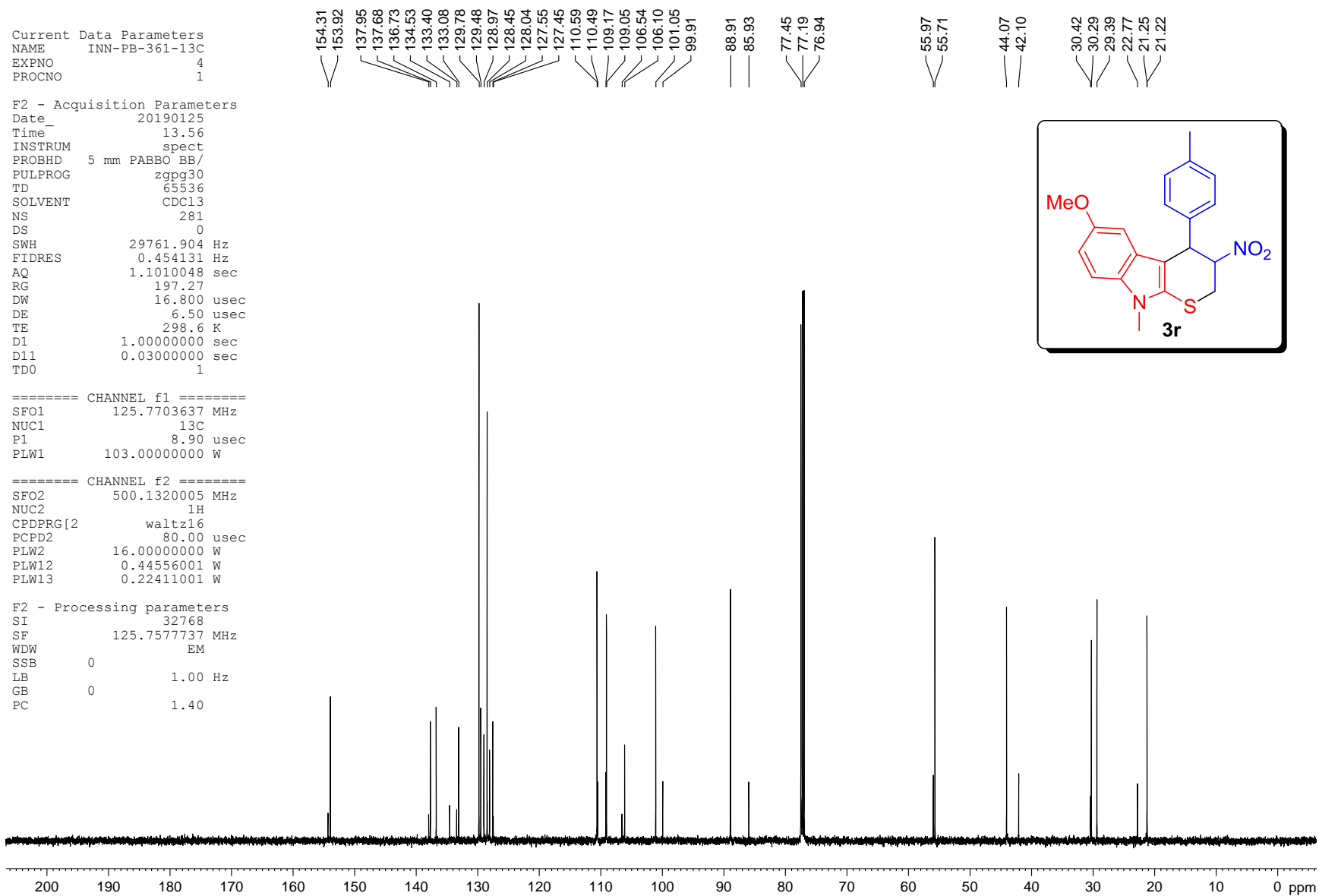
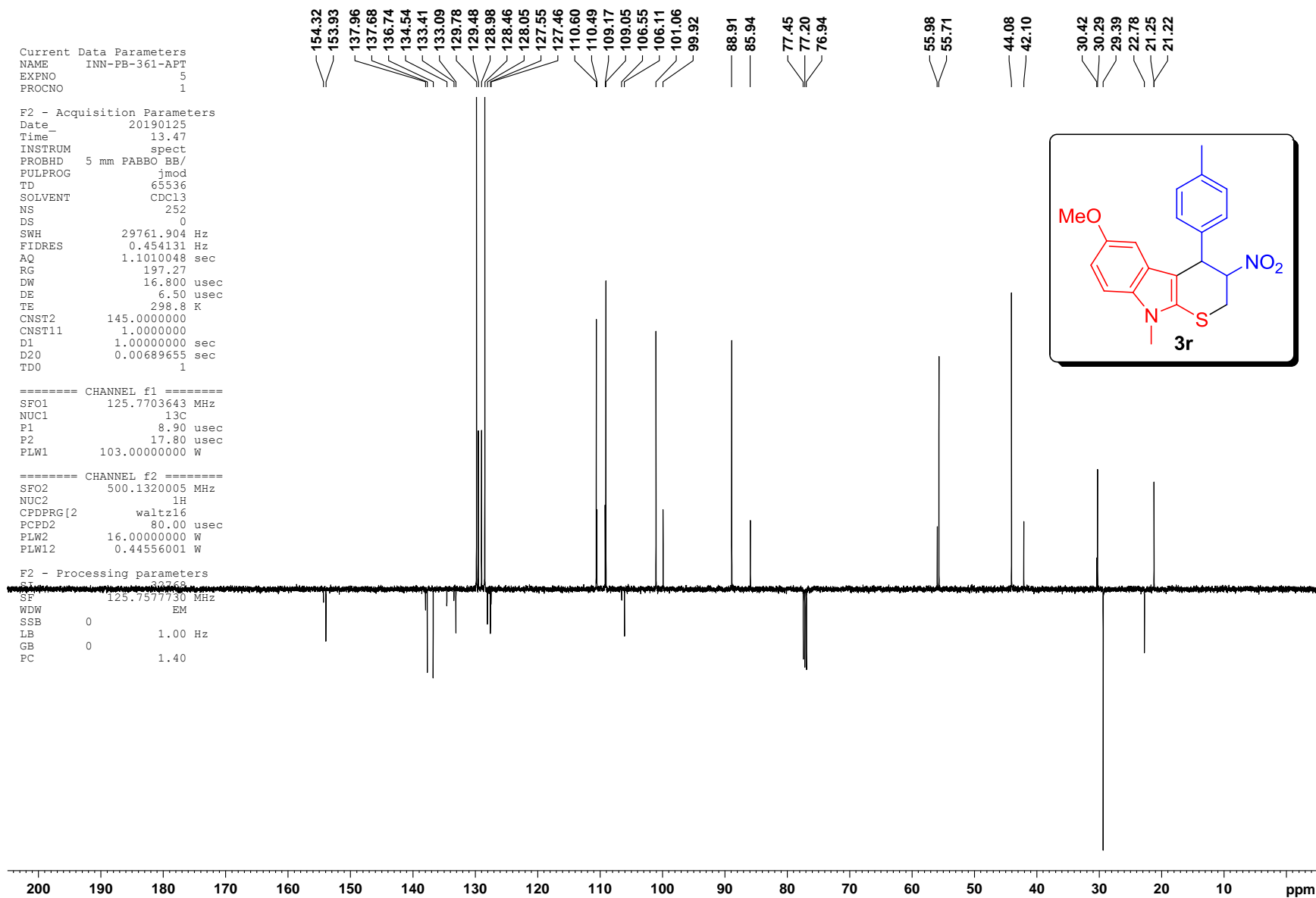


Figure S56. ¹H NMR Spectrum of 3r (major + minor, dr 79:21)

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

Figure S58. ¹³C-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

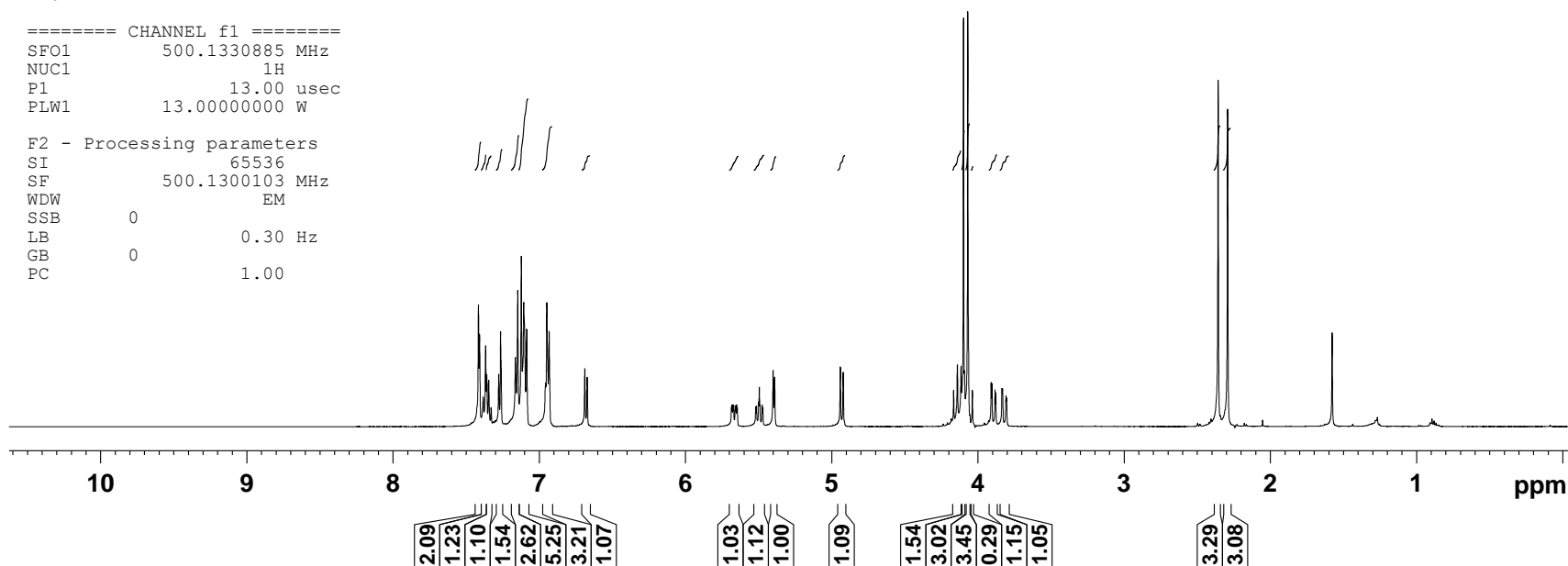
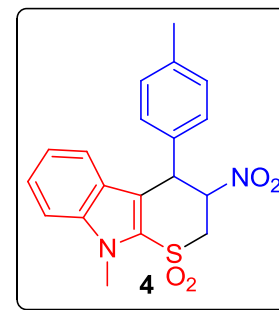
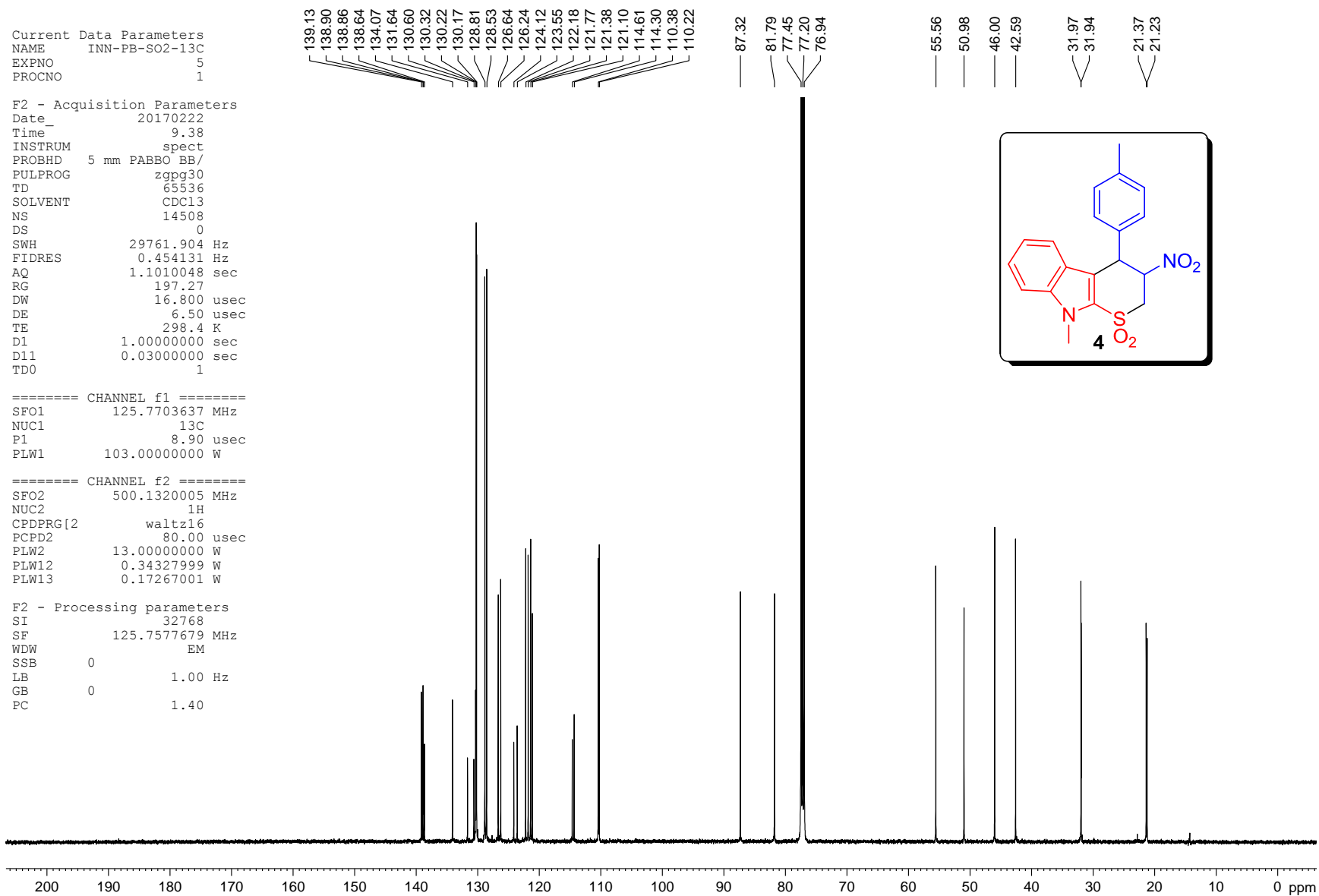
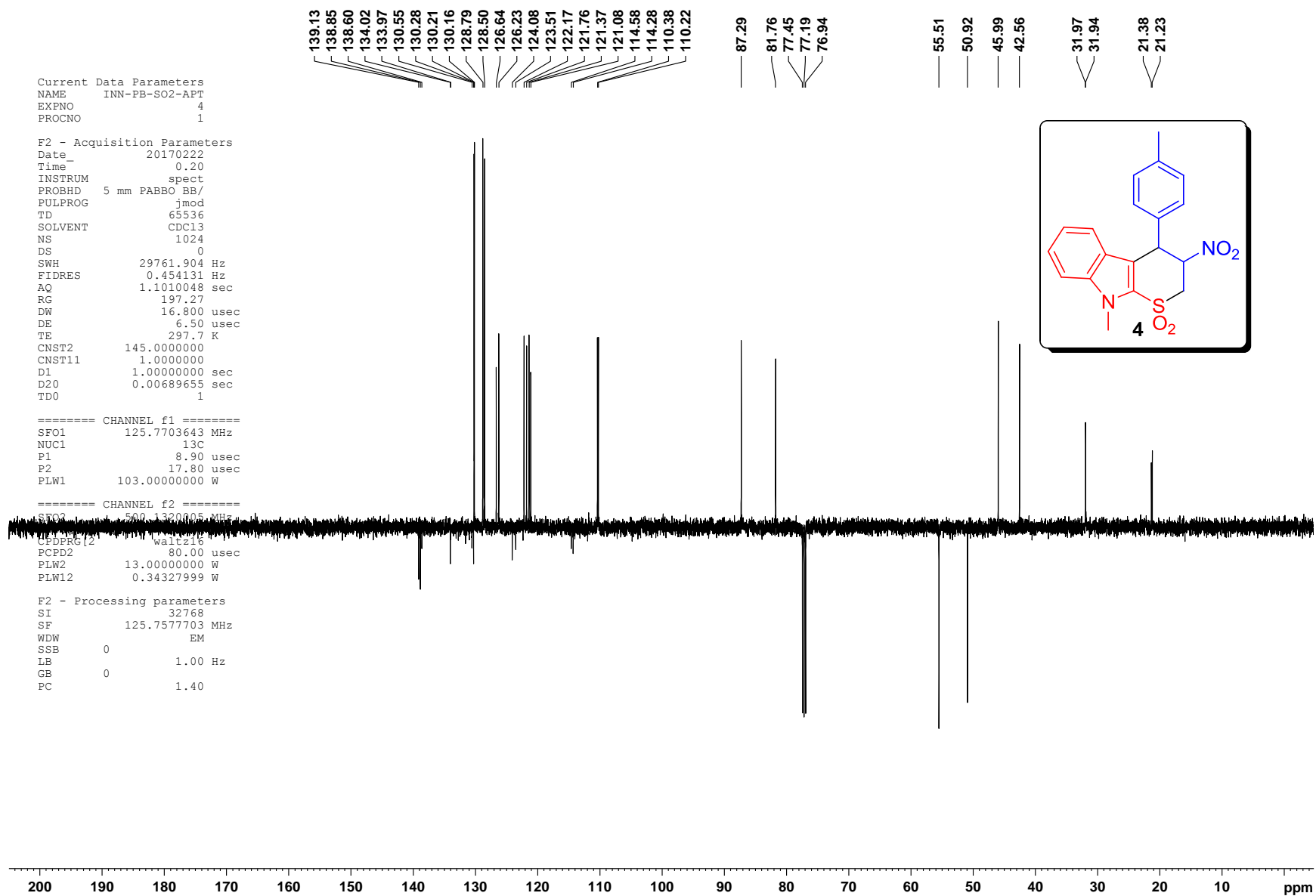


Figure S59. ¹H NMR Spectrum of 4 (major + minor, dr 50:50)

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

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

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

F2 - Acquisition Parameters
 Date_ 20141222
 Time 16.14
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 54274
 SOLVENT CDC13
 NS 16
 DS 0
 SWH 8223.685 Hz
 FIDRES 0.151522 Hz
 AQ 3.2998593 sec
 RG 32
 DW 60.800 usec
 DE 6.50 usec
 TE 295.3 K
 D1 1.00000000 sec
 TD0 1

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

F2 - Processing parameters
 SI 32768
 SF 400.1300098 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

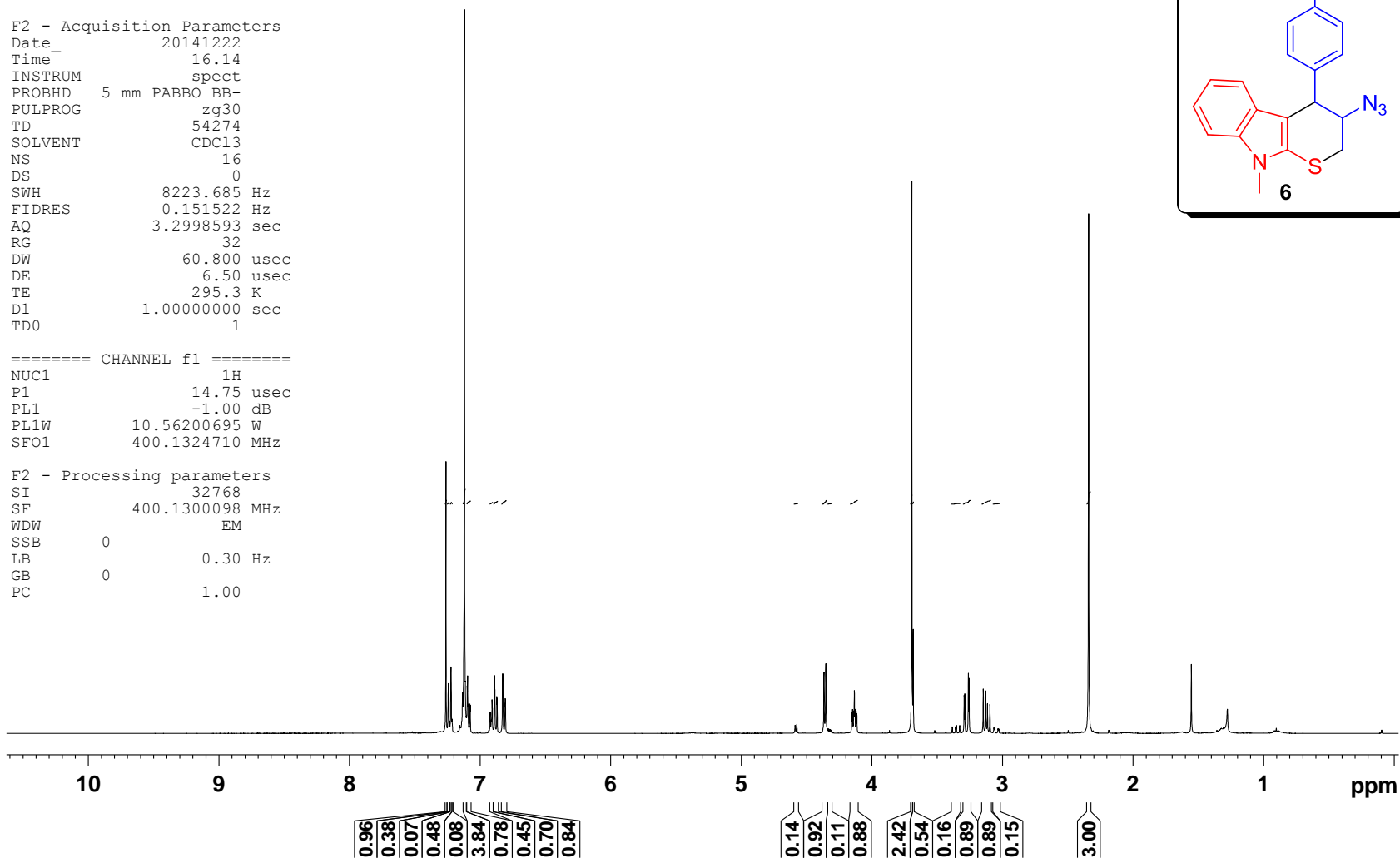
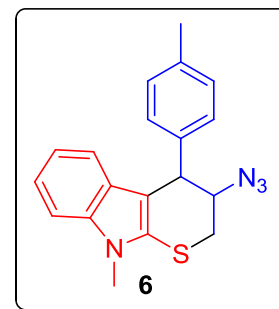


Figure S62. ^1H NMR Spectrum of 6 (major + minor, dr 85:15)

Current Data Parameters
 NAME INN-PB-AZIDE-13C
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20141222
 Time_ 16.14
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 366
 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 295.3 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 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 100.6127545 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

139.18
137.76
137.15
137.02
136.56
129.94
129.57
129.05
128.71
128.67
128.46
127.67
127.37
120.89
119.46
119.41
117.86
117.57
108.30
107.32
106.17

77.52
77.40
77.20
76.88

62.96
61.44

44.50
42.59

30.15
30.08
28.97
27.16
21.27

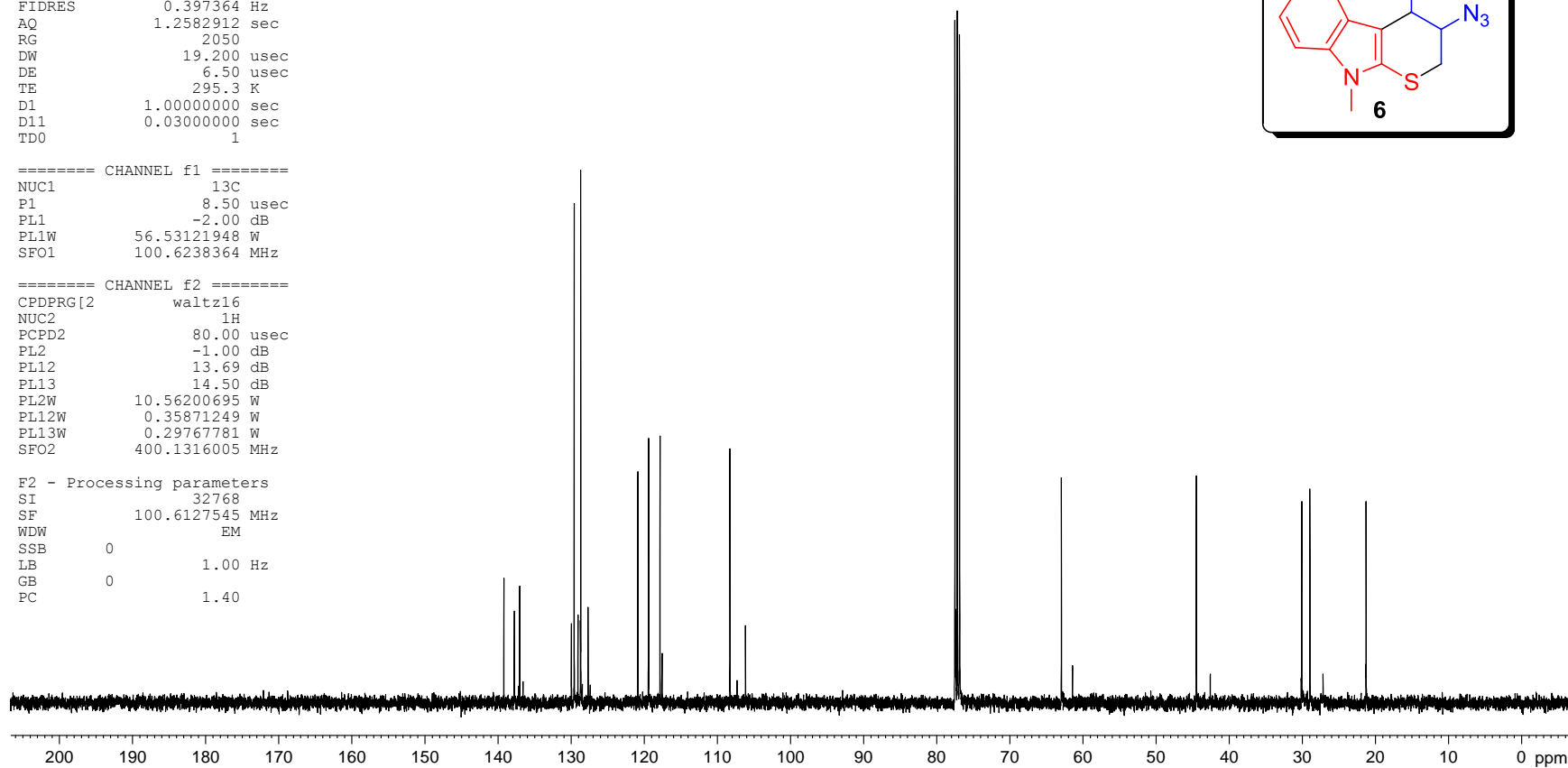
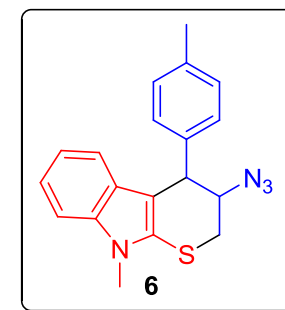


Figure S63. ^{13}C NMR Spectrum of 6 (major + minor, dr 85:15)

Current Data Parameters
 NAME inn-pb-triazazole-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 CDC13
 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

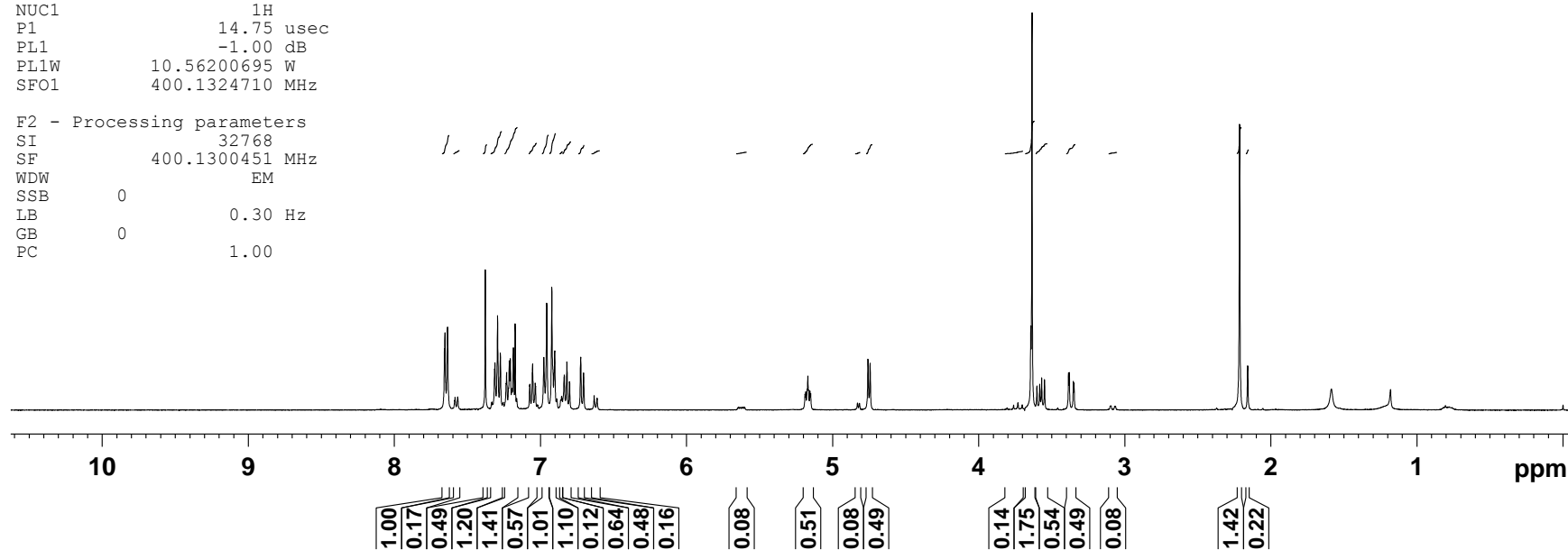
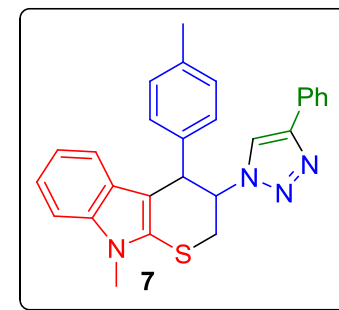
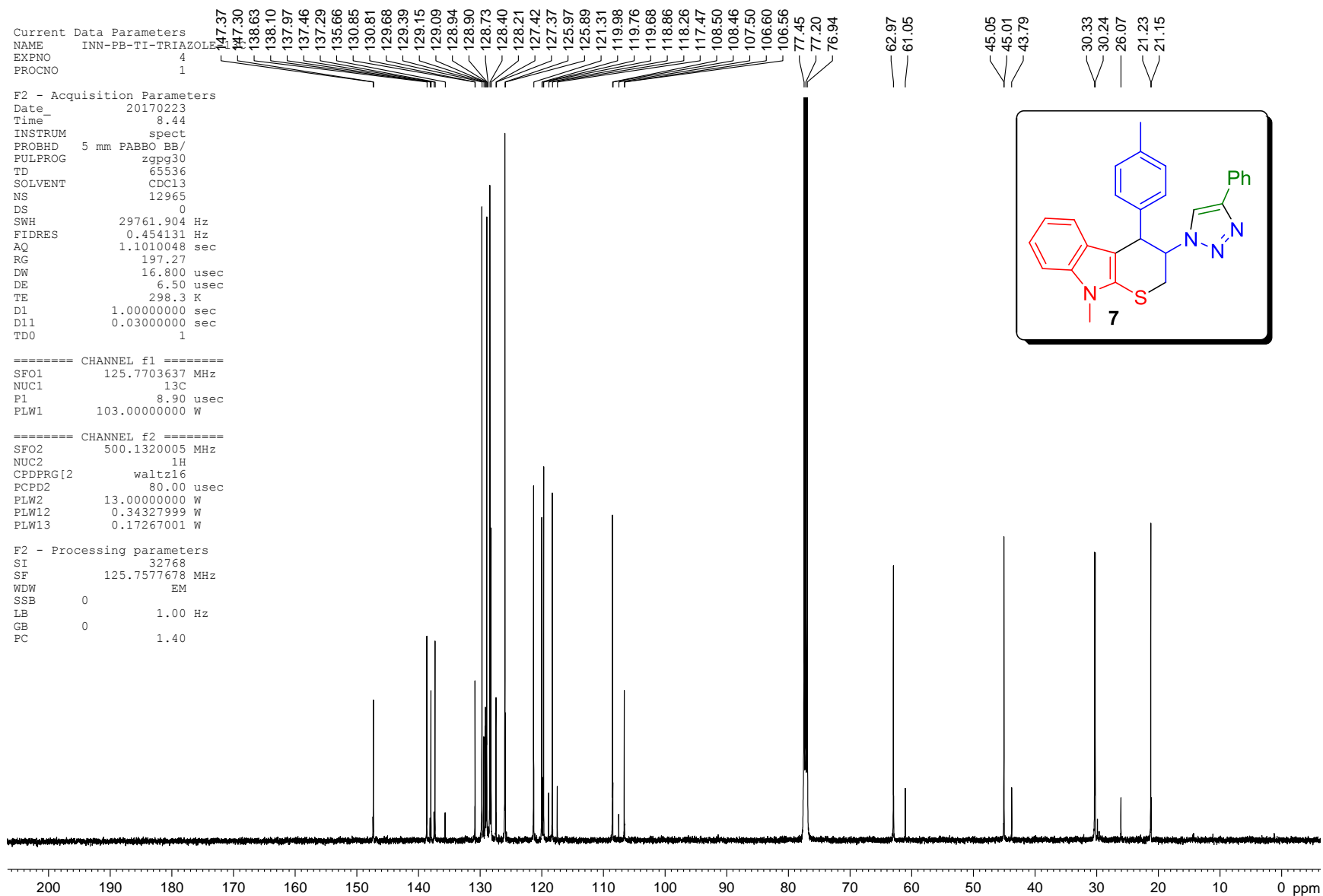
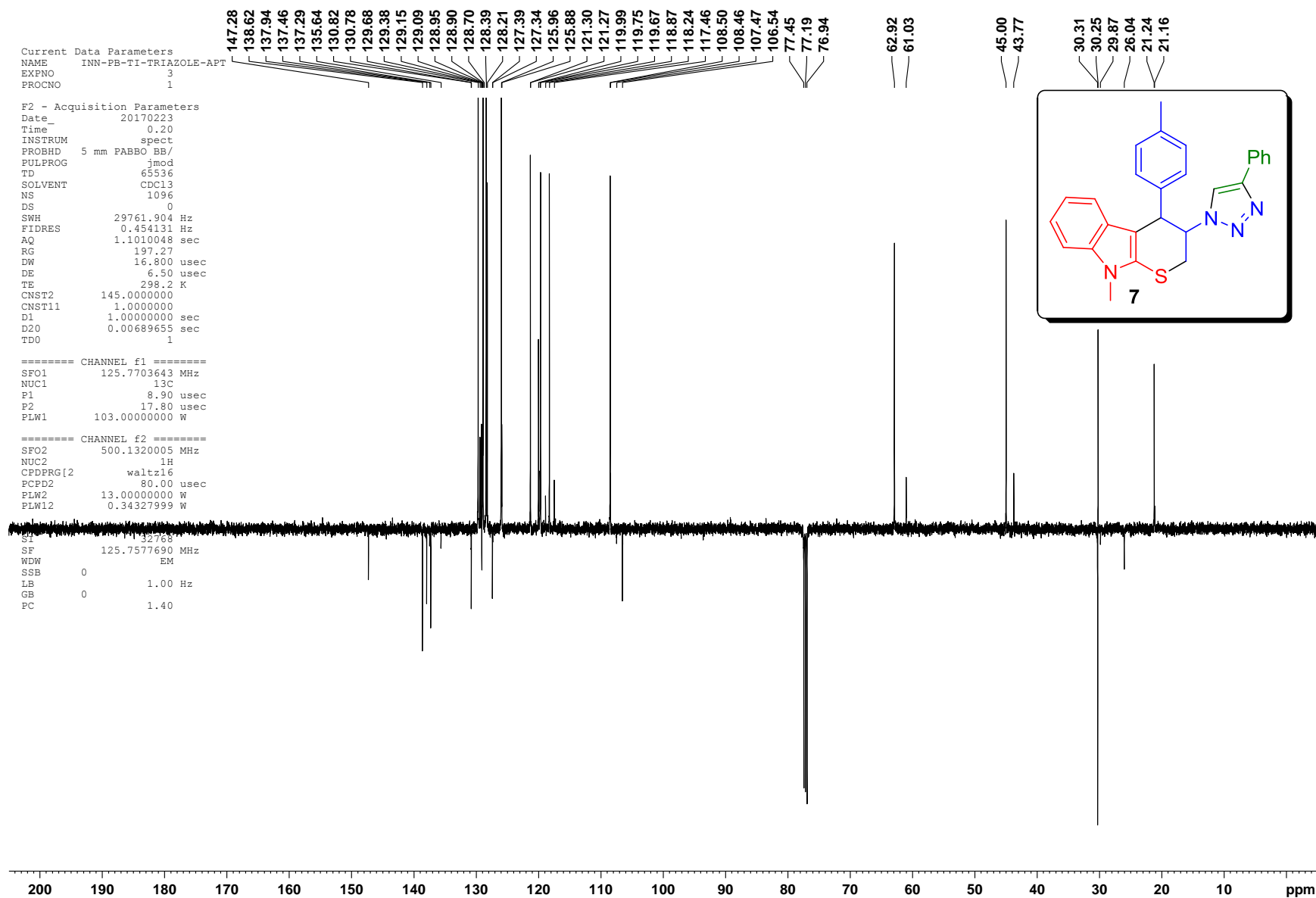


Figure S64. ¹H NMR Spectrum of 7 (major + minor, dr 86:14)

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

Figure S66. ¹³C-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

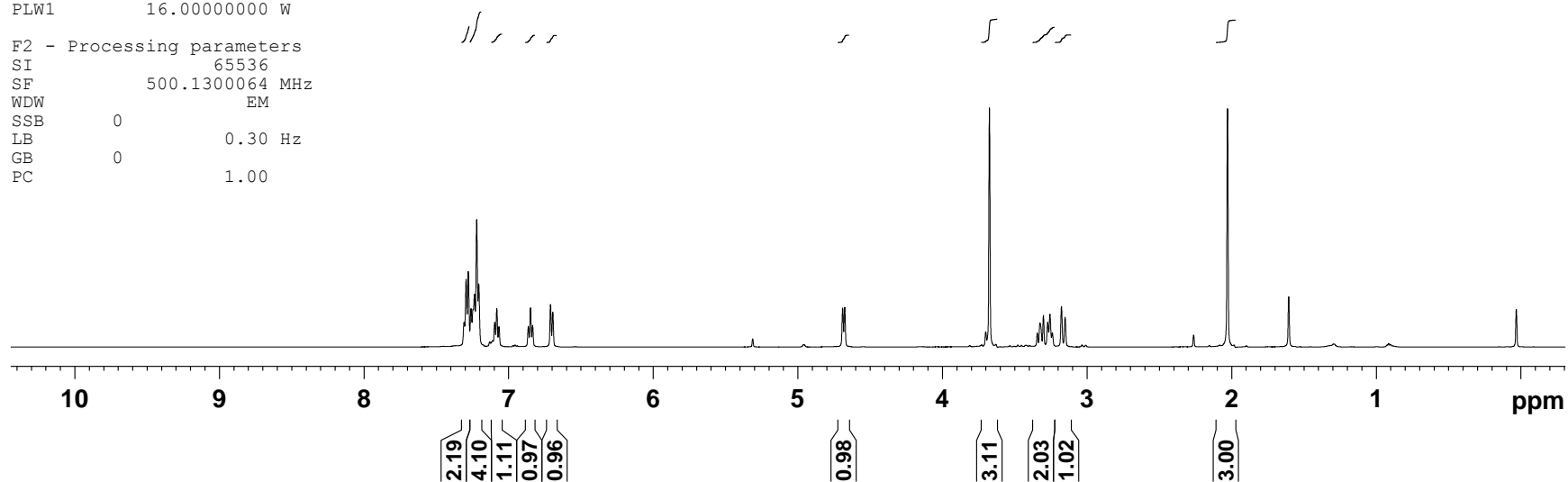
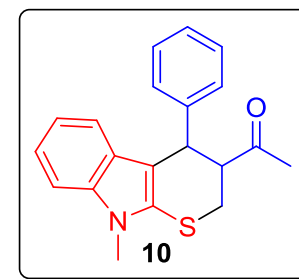


Figure S67. ¹H NMR Spectrum of 10 (major + minor, dr > 95:05)

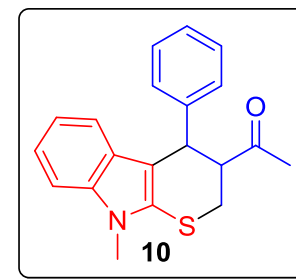
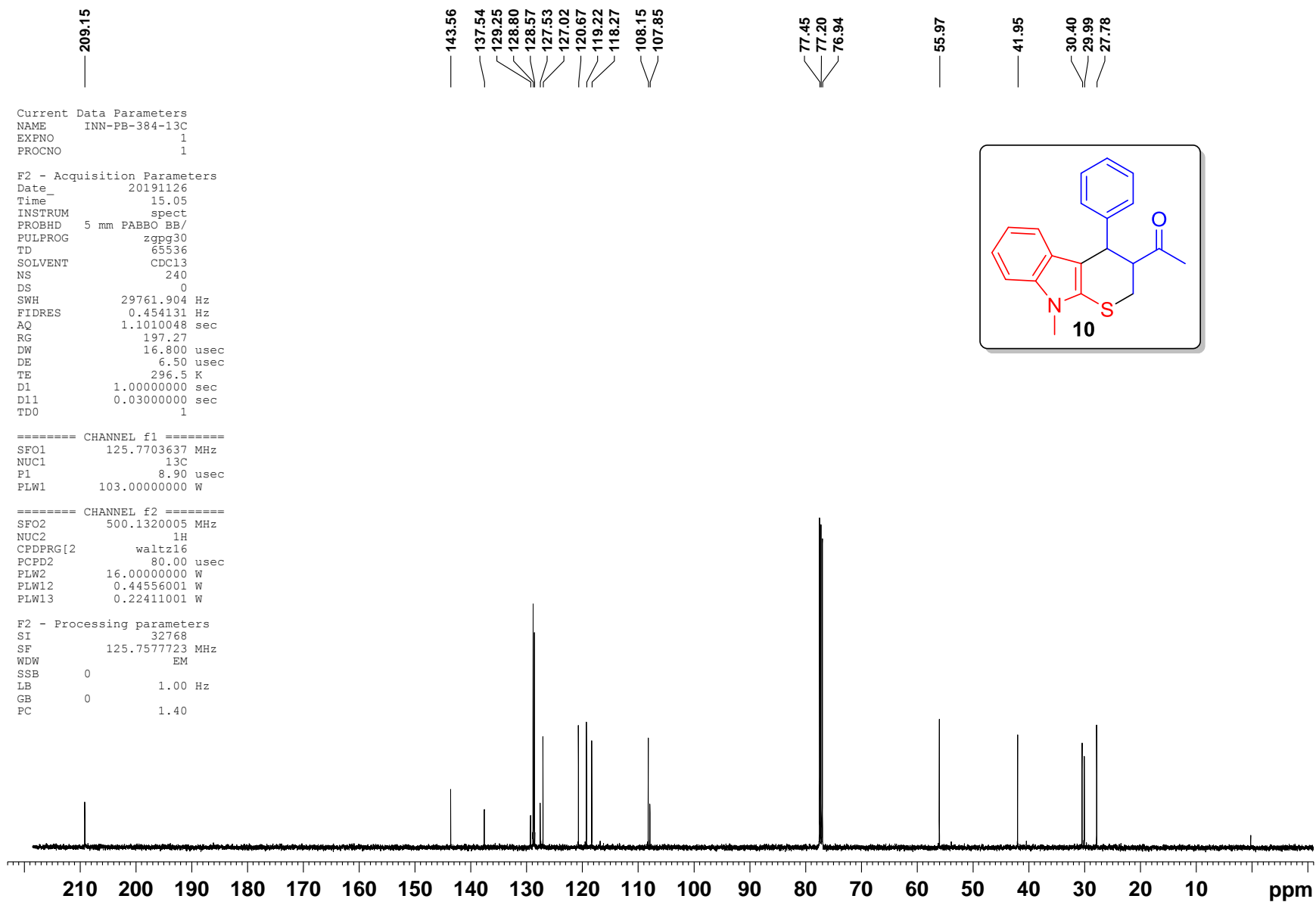


Figure S68. ¹³C NMR Spectrum of 10 (major + minor, > dr 95:05)

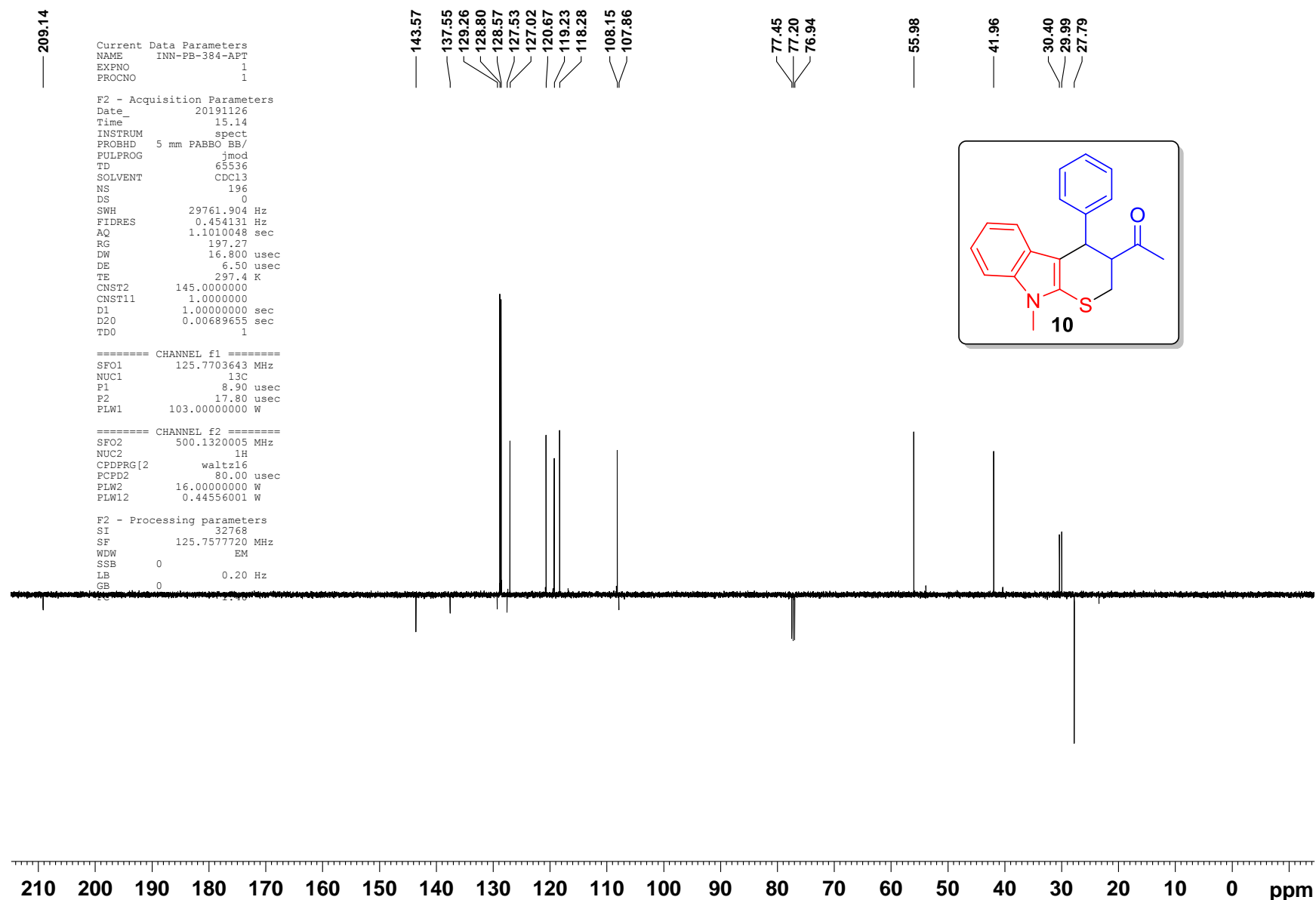
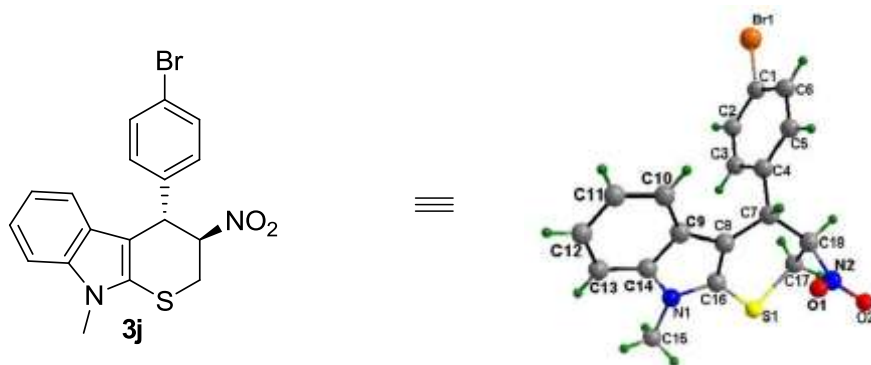
Figure S69. ¹³C-APT NMR Spectrum of 10 (major + minor, dr 95:05)

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	$\alpha = 90^\circ$.
	$b = 29.728(9)$ Å	$\beta = 90^\circ$.
	$c = 9.928(3)$ Å	$\gamma = 120^\circ$.
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 [$I > 2\sigma(I)$]	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. \AA^{-3}