Supplementary Material (ESI) for Chemical Communications

Supporting Information

Palladium-catalysed domino cyclisation of allenic bromoalkenes through zipper-mode cascade

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Table of Contents

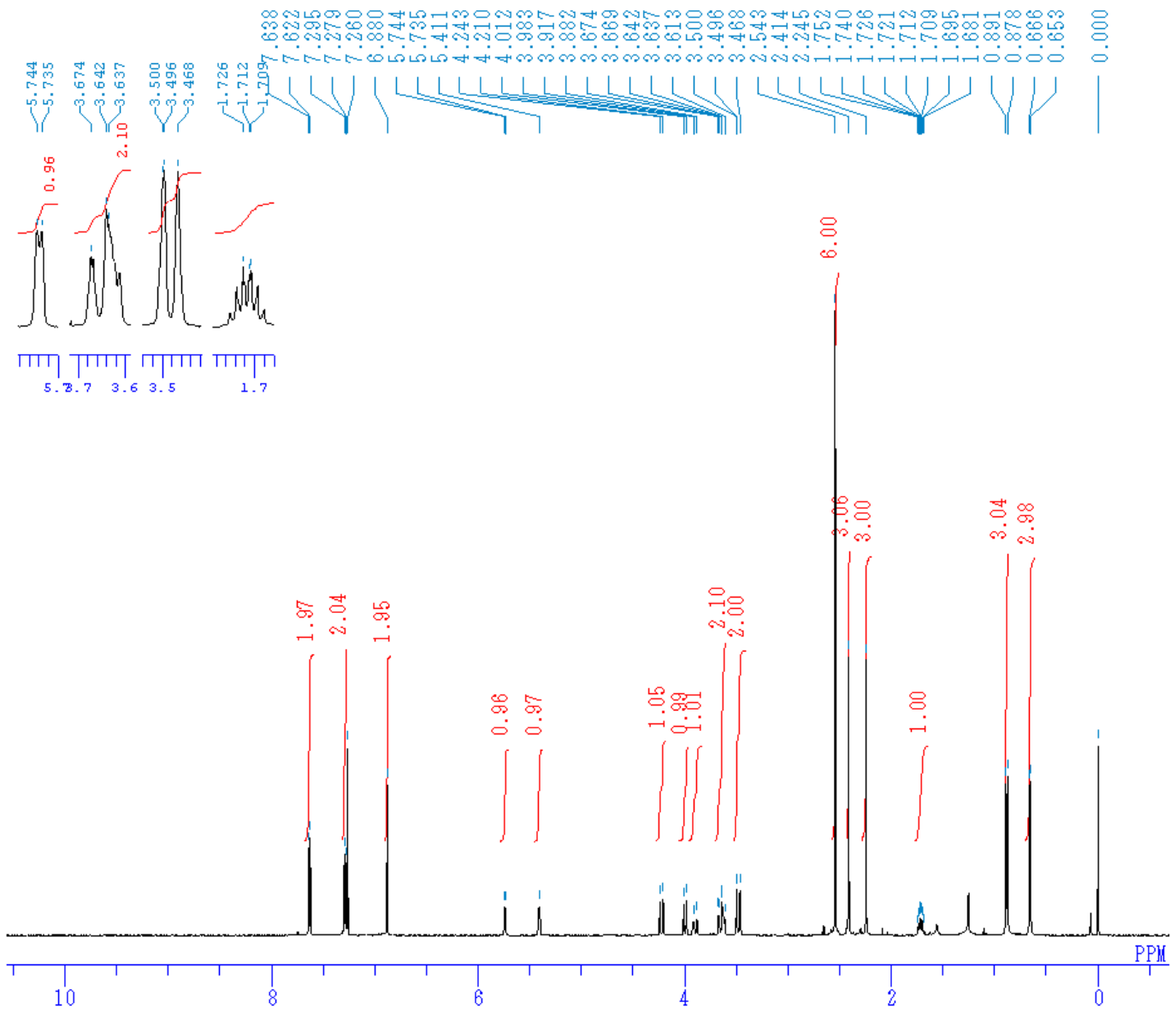
Experimental Section····· S2
NMR Spectra····· S3

Experimental Section

General Methods. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JMS-HX/HX 110A mass spectrometer. ^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz) were recorded using a JEOL ECA-500 spectrometer. Chemical shifts are reported in parts per million downfield from internal Me_4Si (s = singlet, d = doublet, m = multiplet). Analytical thin layer chromatography (TLC) was performed using Kieselgel 60 F254, and compounds were visualized with UV light, anisaldehyde solution, phosphomolybdic acid in EtOH and iodine. Optical rotations were measured with a JASCO sodium automatic polarimeter P-1020. Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 FT-IR spectrometer with JASCO ATR PRO410-S. For flash chromatography, Wakosil C-300E and silica gel 60 H (silica gel for thin-layer chromatography, Merck) were employed.

12a **13a**

General Procedure for Domino Cyclization of Allenic Bromoalkenes: (*S*)-3-Isopropyl-6-(4-methylphenylsulfonyl)-2-(2,4,6-trimethylphenylsulfonyl)-1,2,3,5,6,7-hexa-hydro-2,6-naphthyridine (13a) (Table 1, entry 8). To a stirred solution of allenic bromoalkene **12a** (40.0 mg, 0.0672 mmol) in MeCN (0.7 mL) were successively added $Pd_2(dba)_3{\cdot}CHCl_3$ (1.7 mg, 0.00168 mmol) and TBAF (168 μL, 0.168 mmol; 1.0 M solution in THF) at room temperature, and the resulting mixture was stirred for at 50 °C 3.5 h. Concentration under reduced pressure gave an oily residue, which was purified by column chromatography over silica gel with *n*-hexane/EtOAc (7:2) to give **13a** (31.6 mg, 91% yield) as a colorless oil: $[\alpha]^{23}_{D}$ +11.5 (*c* 1.60, $CHCl_3$); IR (ATR) cm^{-1}: 1561 (C=C), 1322 (NSO_2), 1154 (NSO_2); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.67 (d, *J* = 6.5 Hz, 3H, CMe), 0.88 (d, *J* = 6.5 Hz, 3H, CMe), 1.68–1.75 (m, 1H, C<u>H</u>Me_2), 2.25 (s, 3H, Ph<u>Me</u>), 2.41 (s, 3H, Ph<u>Me</u>), 2.54 (s, 6H, 2 × Ph<u>Me</u>), 3.46-3.50 (m, 2H, 7-C<u>H</u>H and 5-C<u>H</u>H), 3.61–3.67 (m, 2H, 1-C<u>H</u>H and 3-H), 3.90 (d, *J* = 17.5 Hz, 1H, 7-CH<u>H</u>), 4.00 (d, *J* = 14.5 Hz, 1H, 5-CH<u>H</u>), 4.23 (d, *J* = 11.5 Hz, 1H, 1-CH<u>H</u>), 5.41 (s, 1H, 8-H), 5.74 (d, *J* = 4.5 Hz, 1H, 4-H), 6.88 (s, 2H, Ph), 7.29 (d, *J* = 8.0 Hz, 2H, Ph), 7.63 (d, *J* = 8.0 Hz, 2H, Ph); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 19.6, 20.1, 20.8, 21.5, 23.1 (2C), 32.7, 42.7, 45.2, 47.6, 60.0, 118.1, 123.3, 127.7 (2C), 127.8 (2C), 129.6 (2C), 131.9 (2C), 133.1, 133.4, 139.8 (2C), 142.3, 143.7; MS (FAB) *m/z* (%) 515 (MH^+, 32), 73 (100); HRMS (FAB) calcd for $C_{27}H_{35}N_2O_4S_2$ (MH^+): 515.2038; found: 515.2041.

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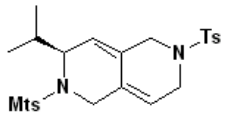
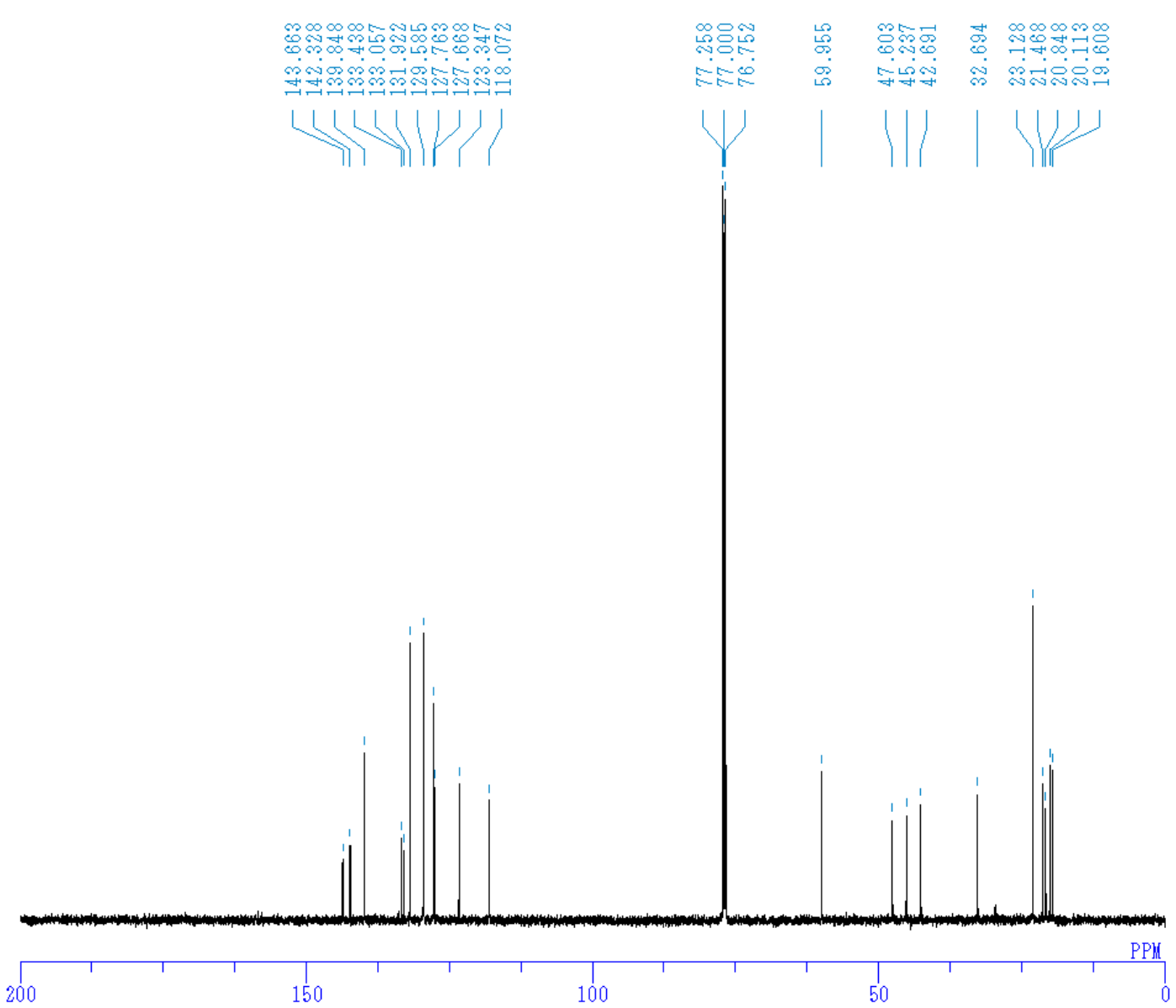


13a ^{1}H NMR (500 MHz)

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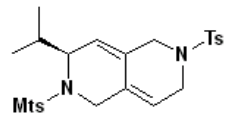

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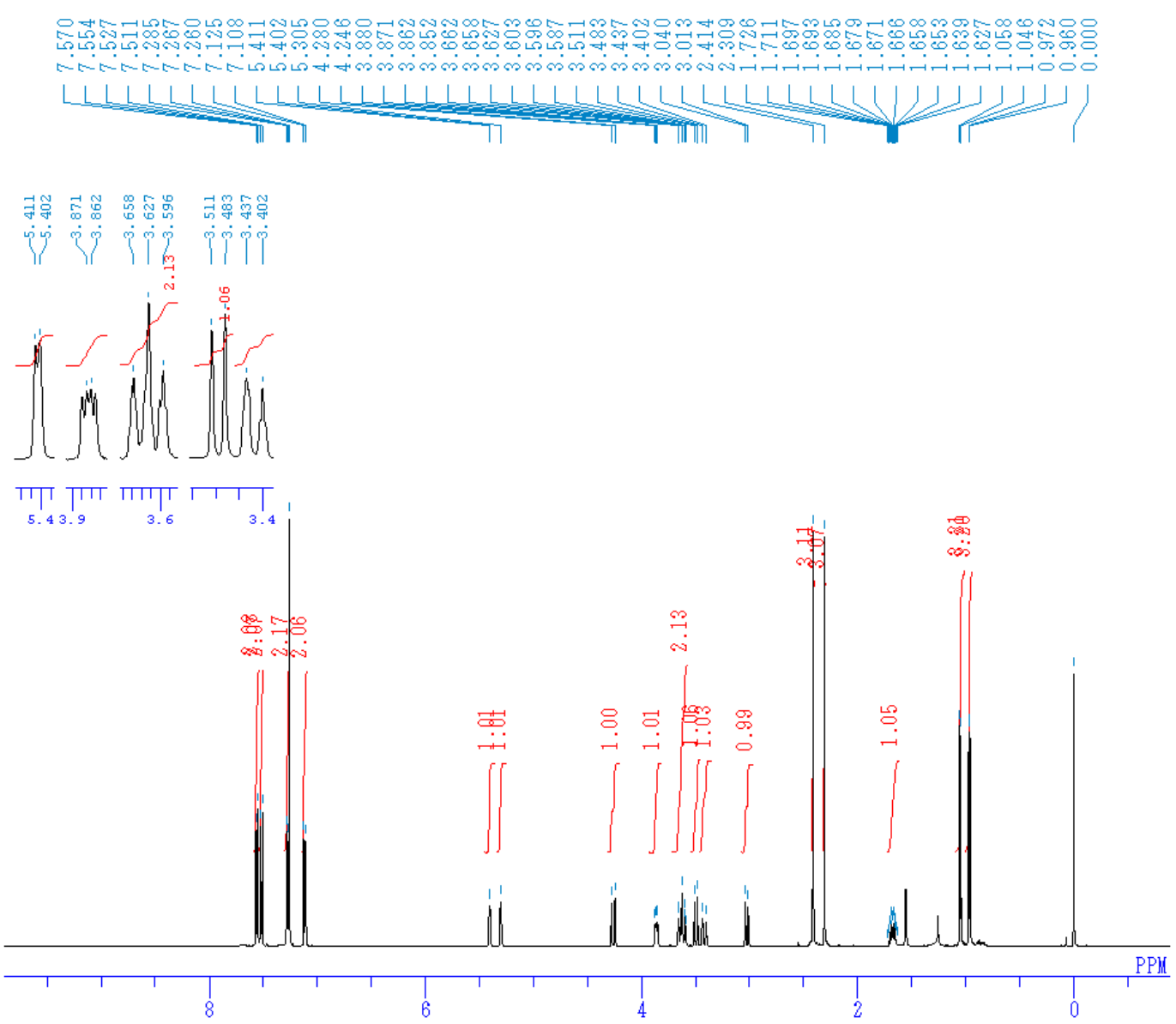

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FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
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IRNUC 1H
CTEMP 25.9 c
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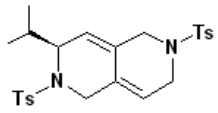
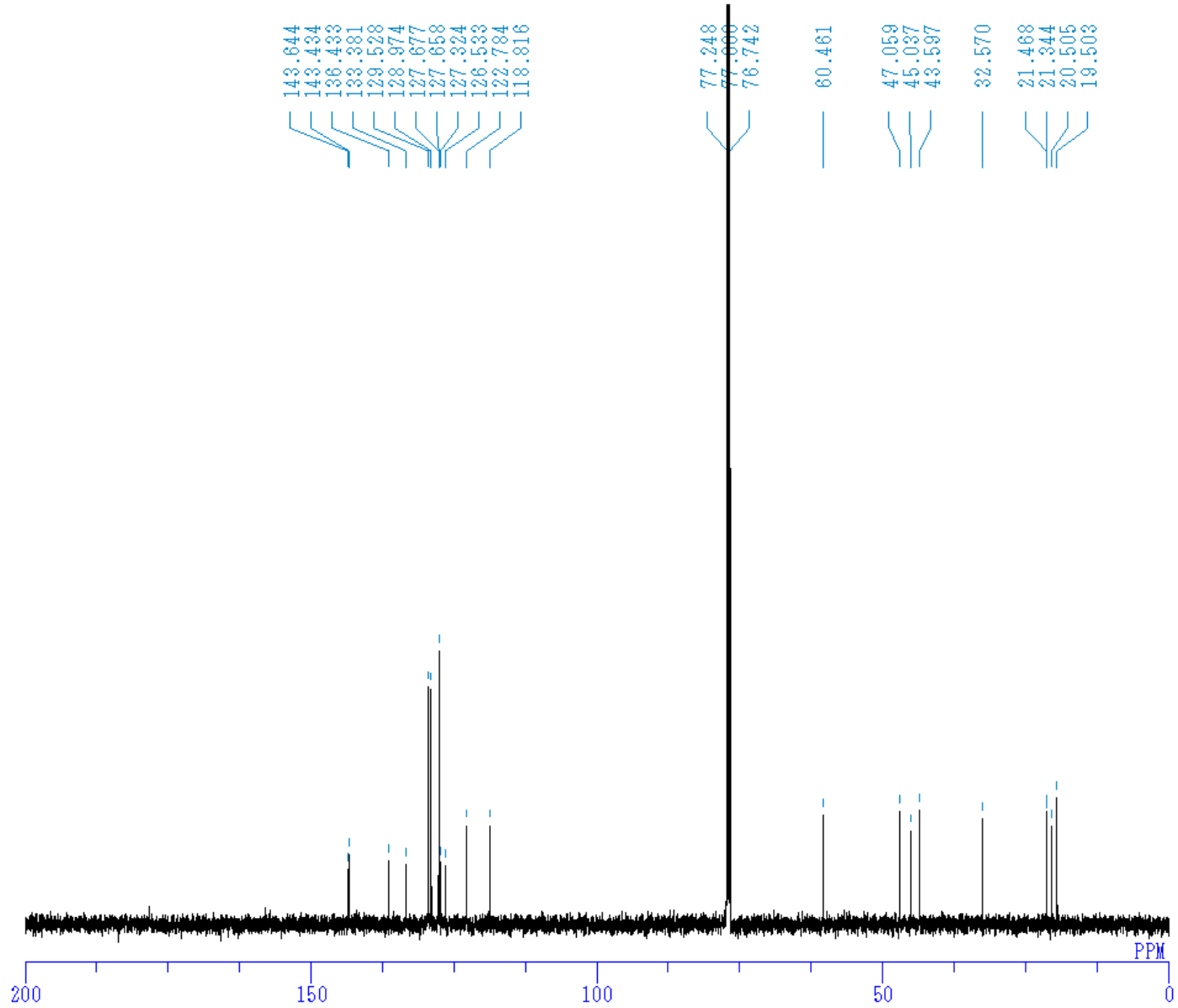
BF 0.12 Hz
RGAIN 44



13b ^{1}H NMR (500 MHz)



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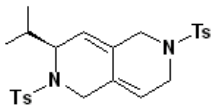

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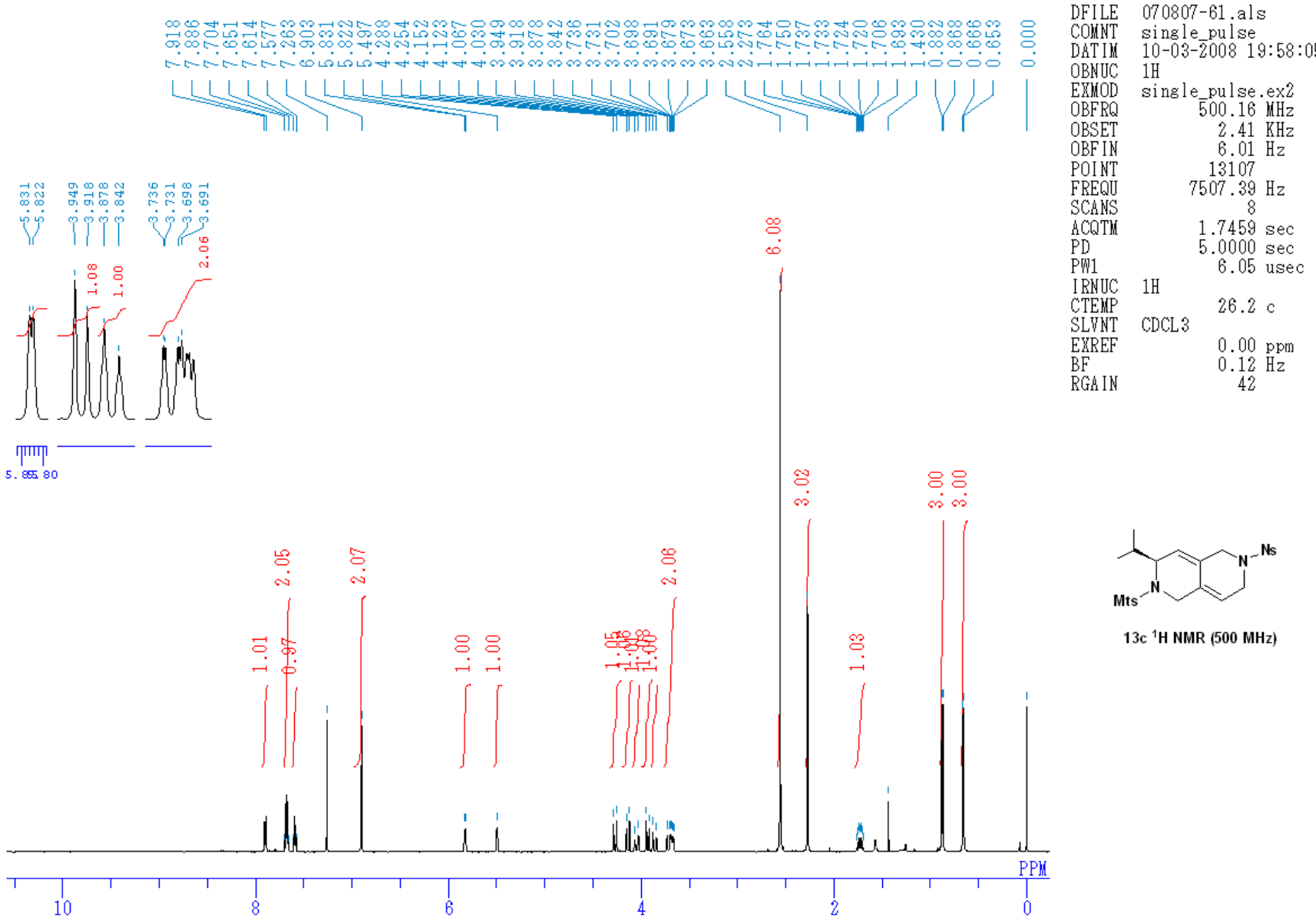
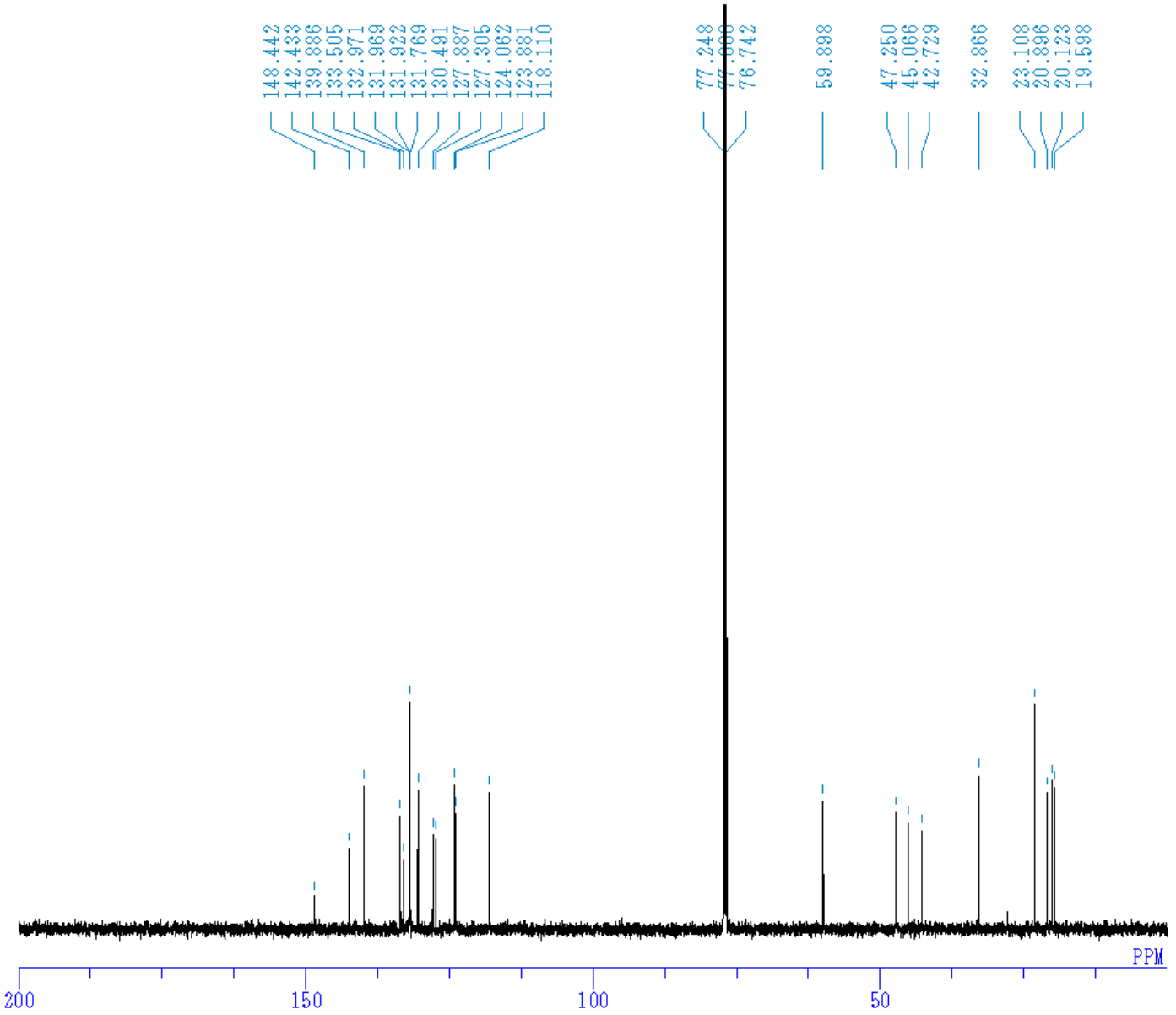


13c ^{1}H NMR (500 MHz)

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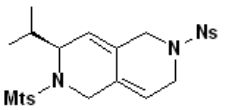
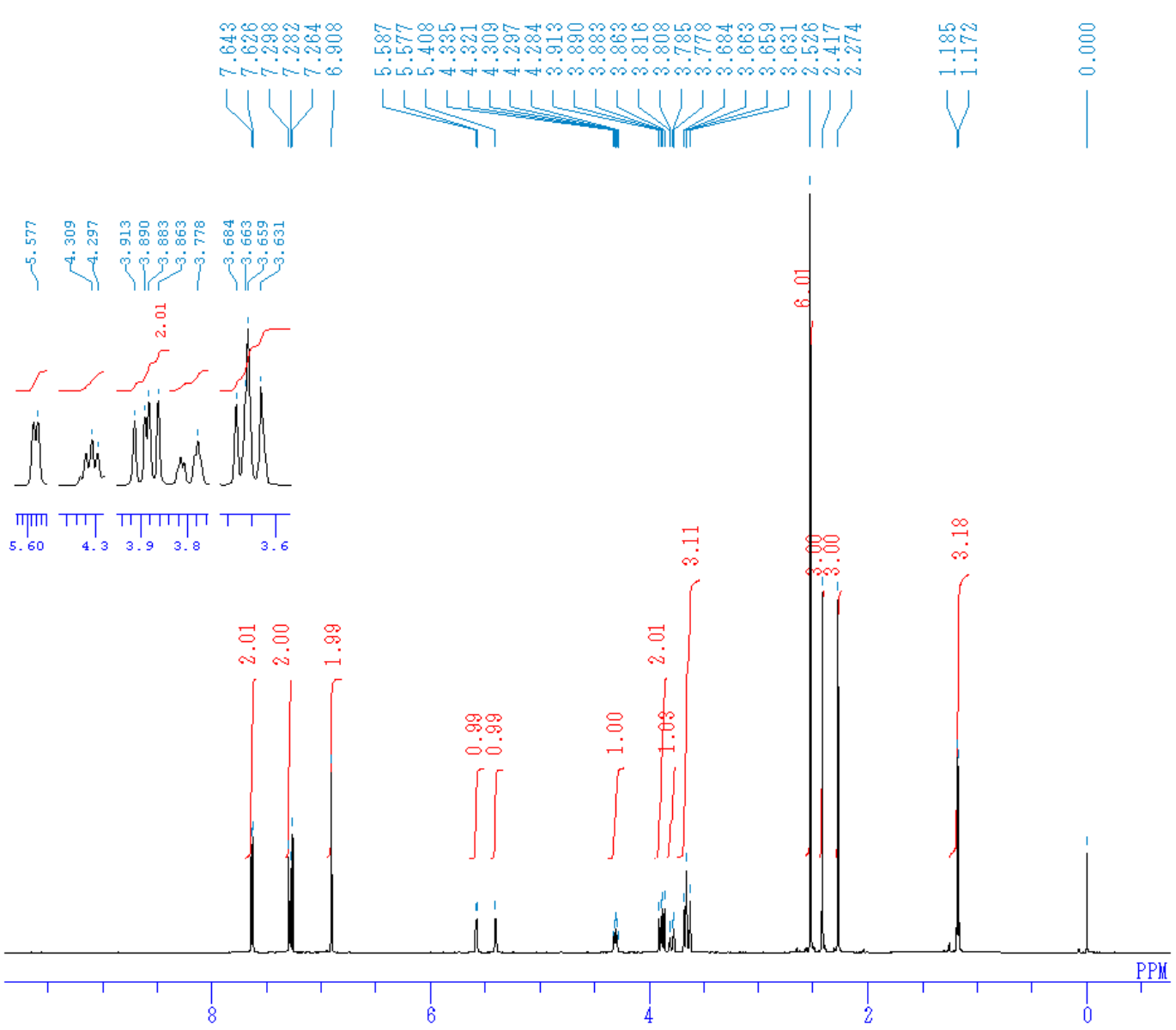


13c ^{13}C NMR (125MHz)



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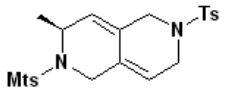
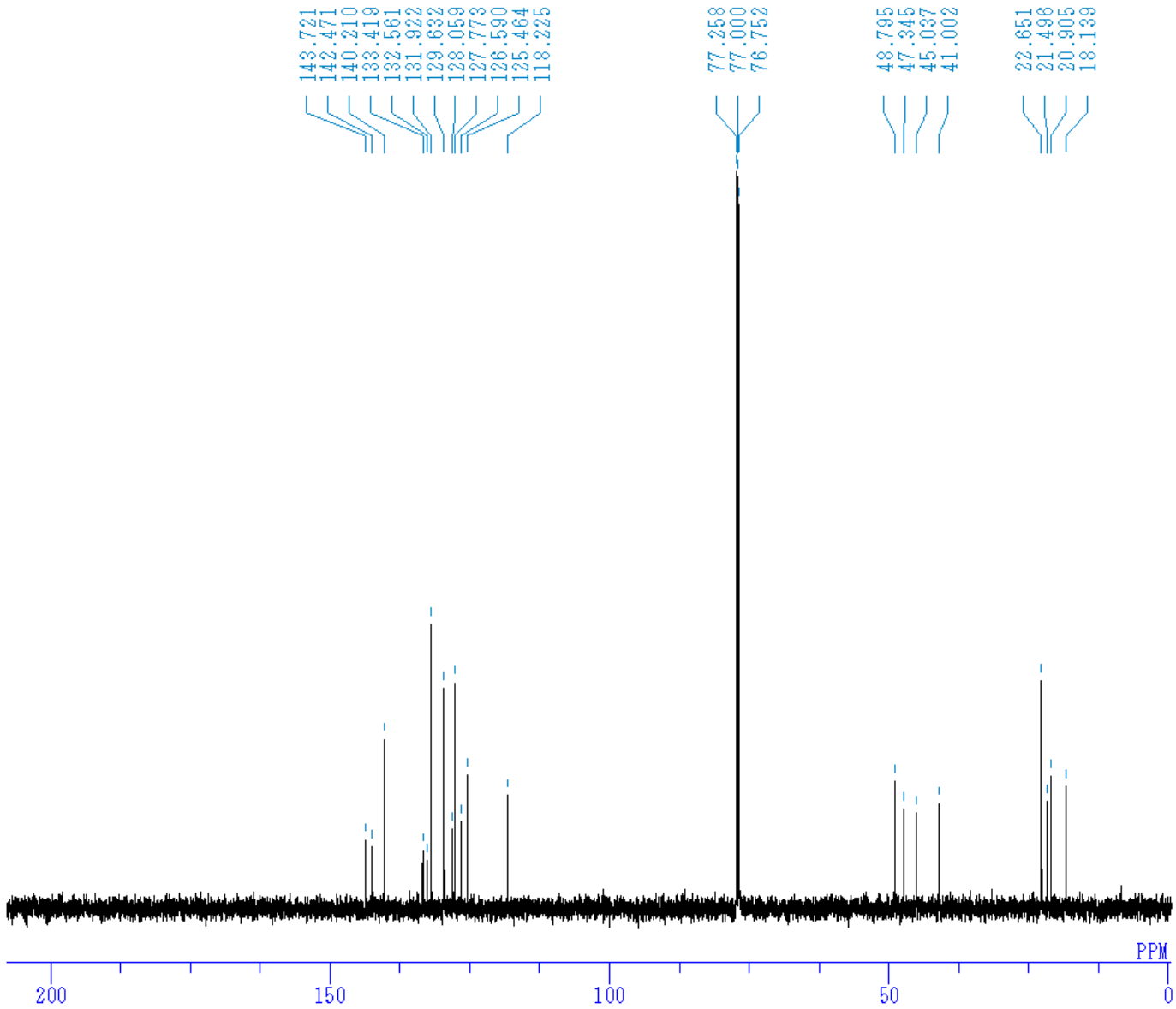
RGAIN 38



13d ^{1}H NMR (500 MHz)



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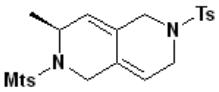
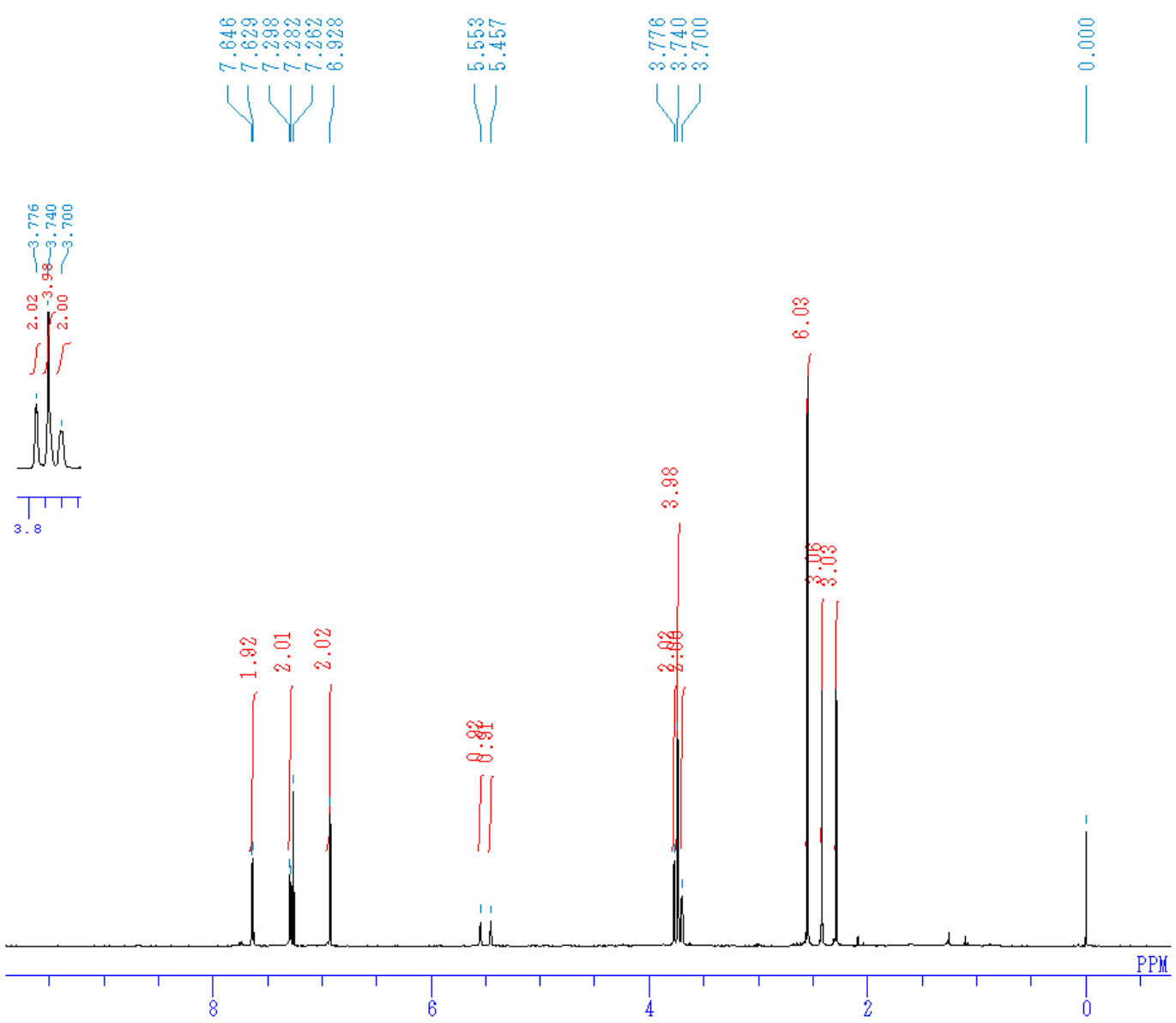
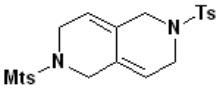
RGAIN	60

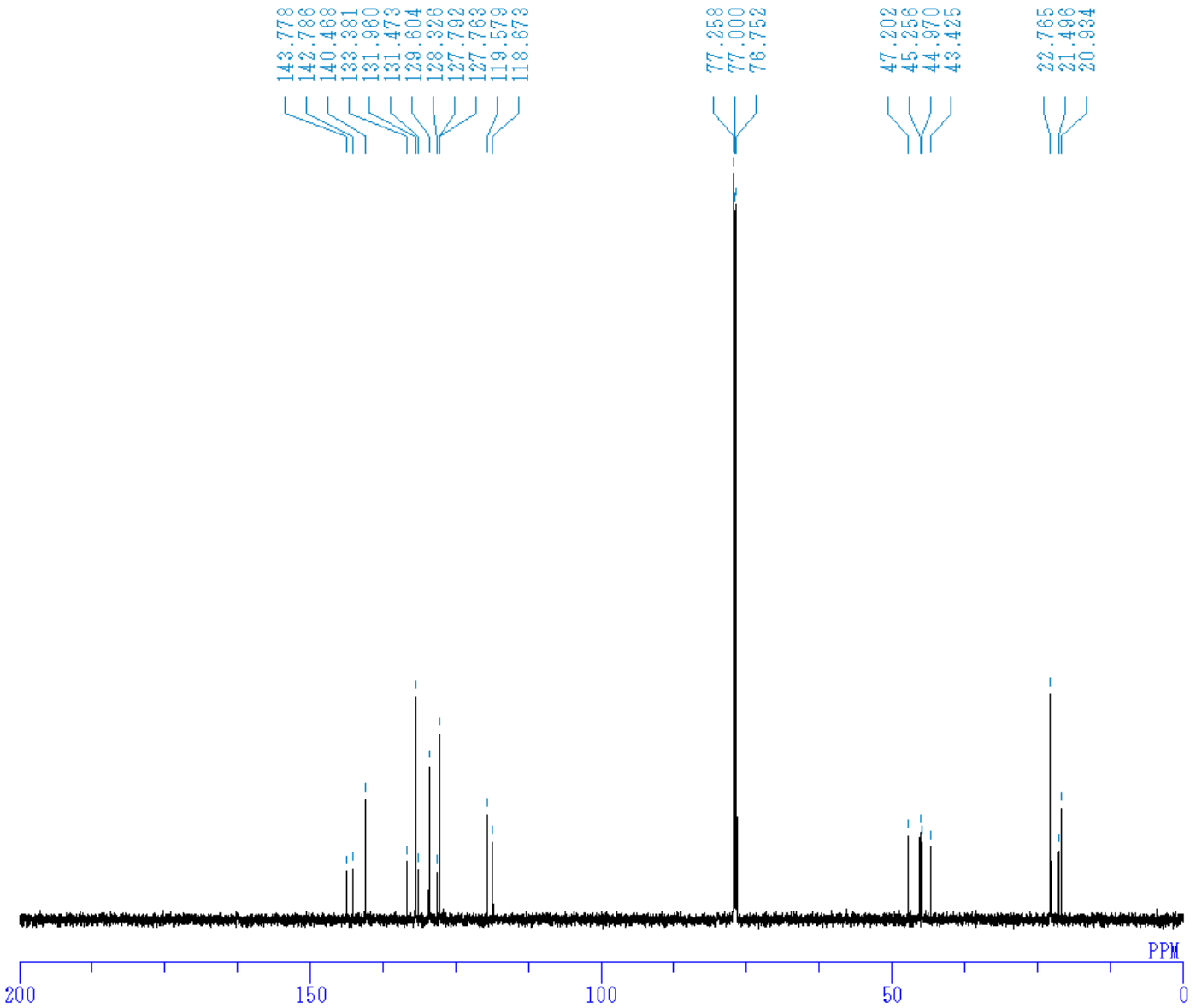


13d ^{13}C NMR (125MHz)





13e ^{1}H NMR (500 MHz)

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PD            2.0000 sec
PW1             3.83 usec
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RGAIN             60
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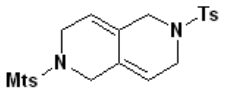
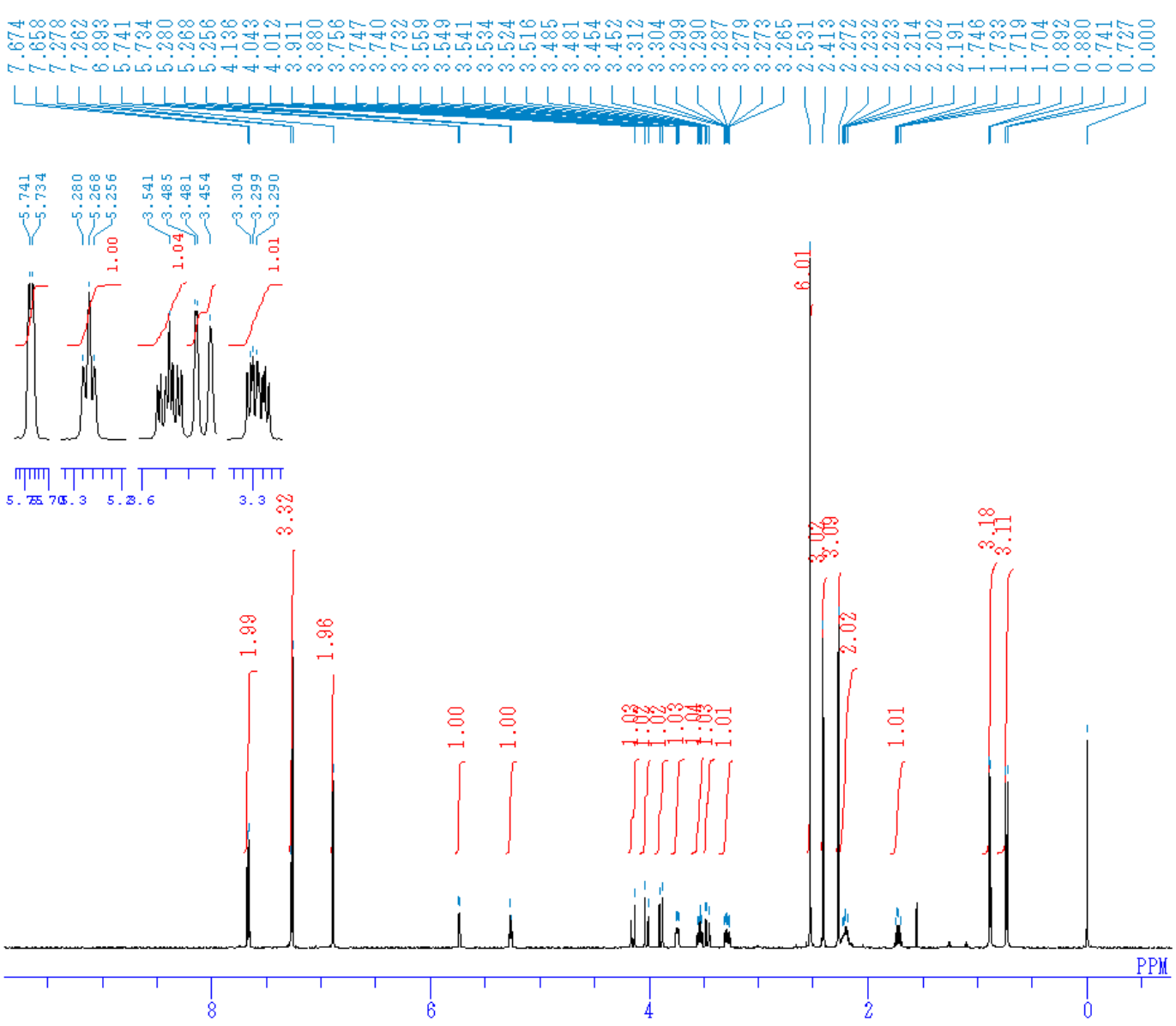


13e ^{13}C NMR (125MHz)



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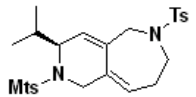
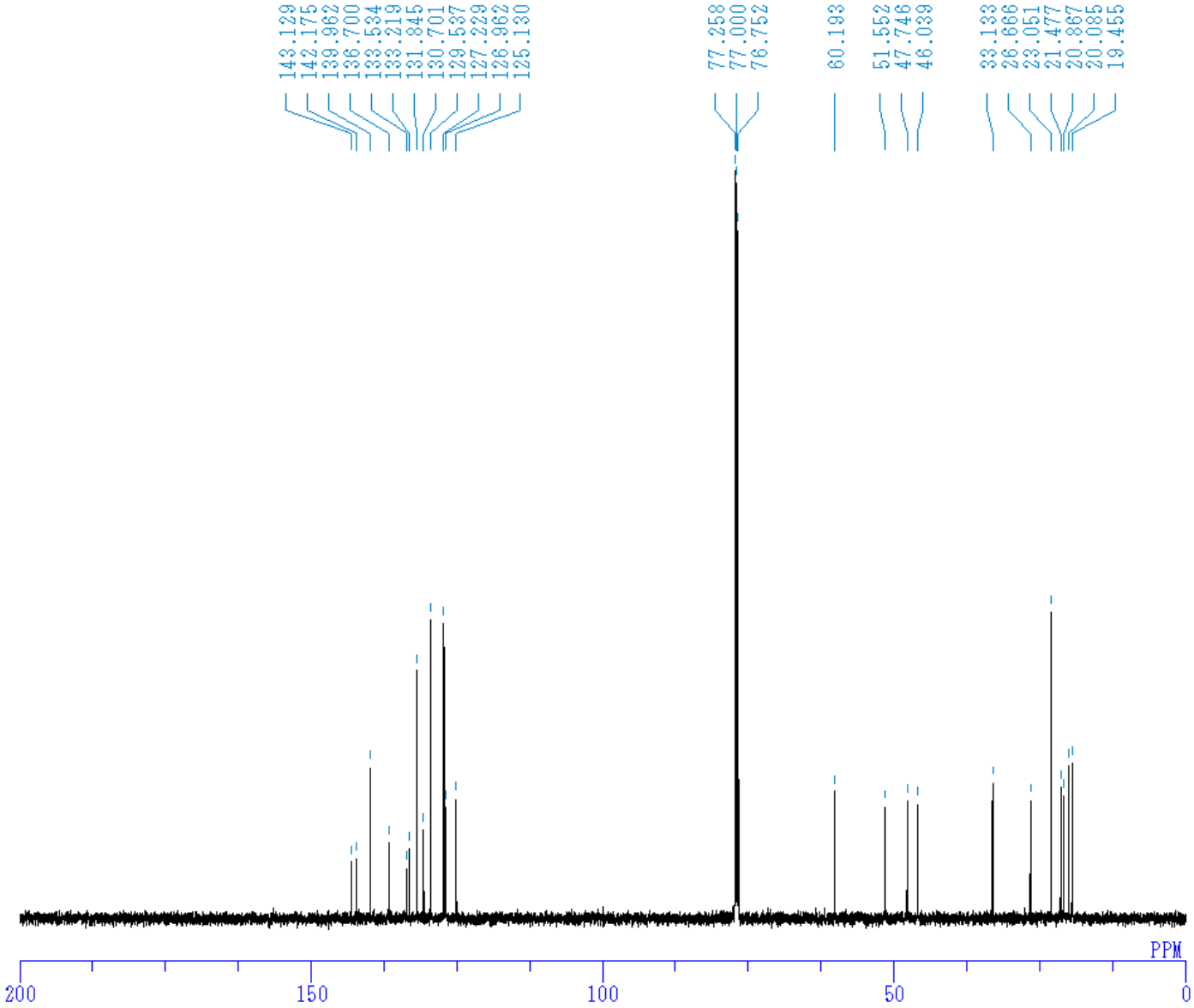
PW1 6.05 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44



15 ^{1}H NMR (500 MHz)

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SCANS            577
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PD            2.0000 sec
PW1             3.83 usec
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BF              1.20 Hz
RGAIN             60
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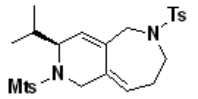
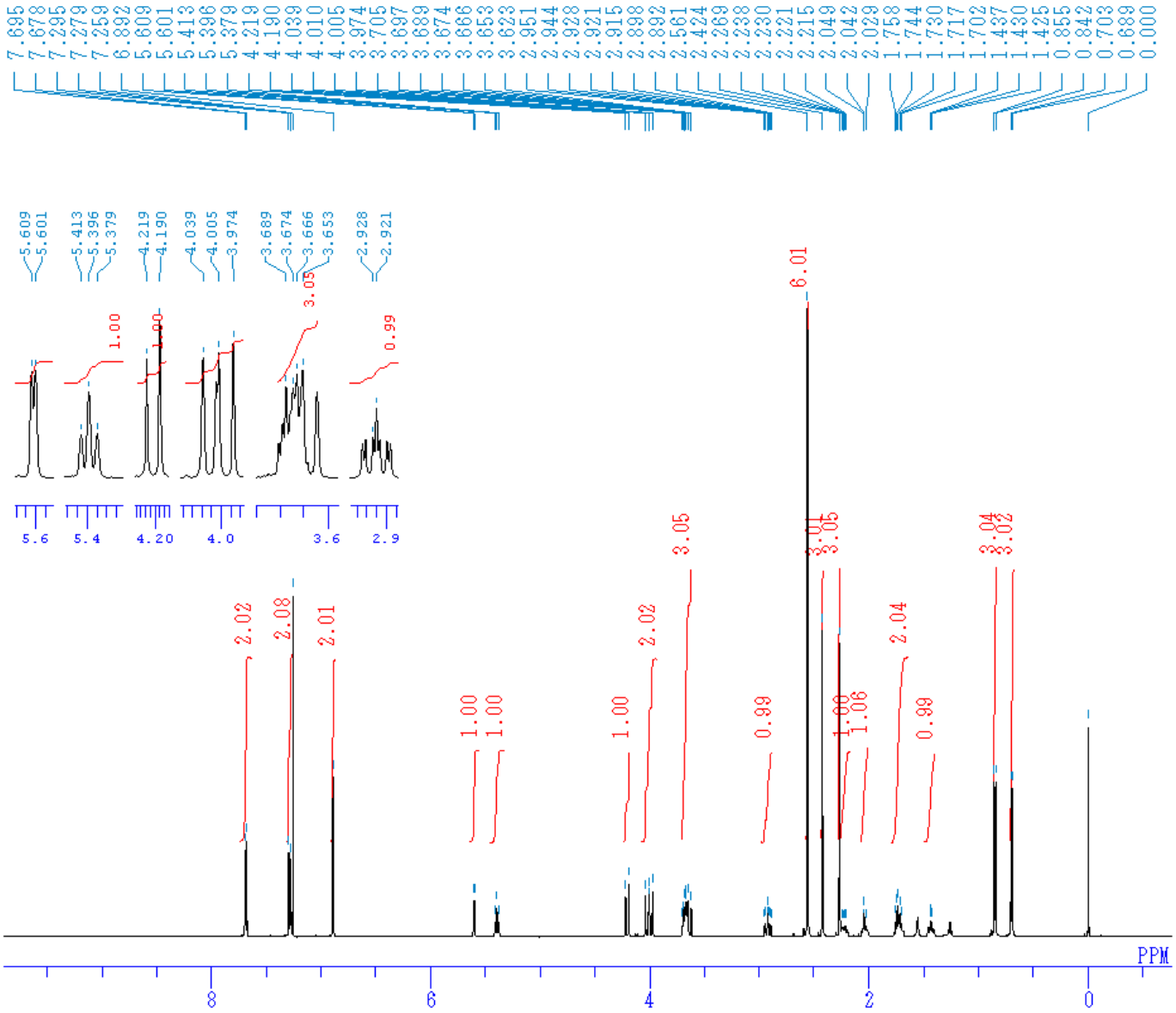


15 ^{13}C NMR (125MHz)



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ACQTM 1.7459 sec
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IRNUC 1H
CTEMP 25.6 c
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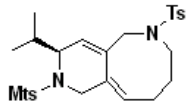
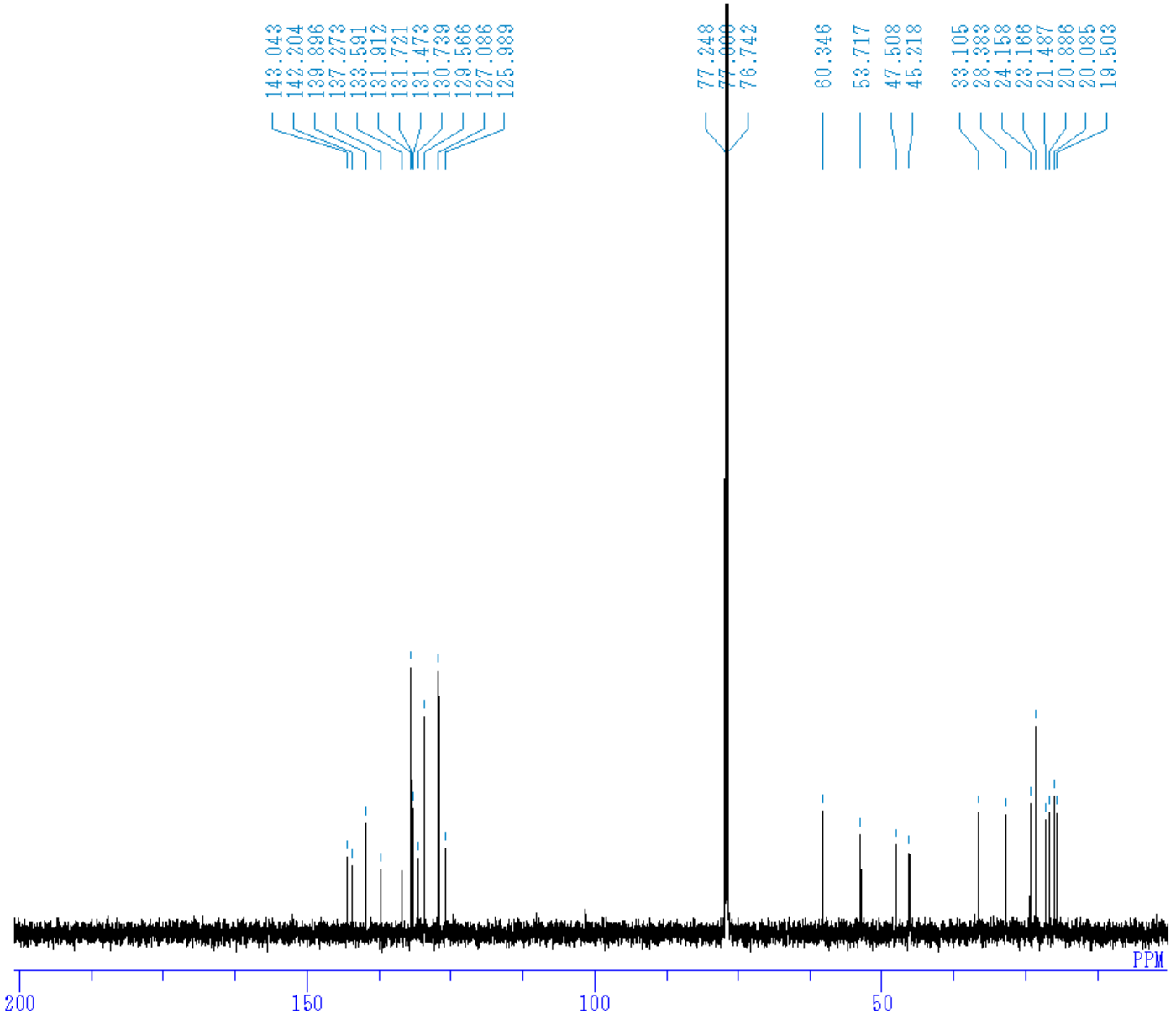
RGAIN 44



17 ^{1}H NMR (500 MHz)



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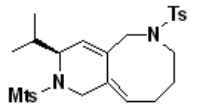
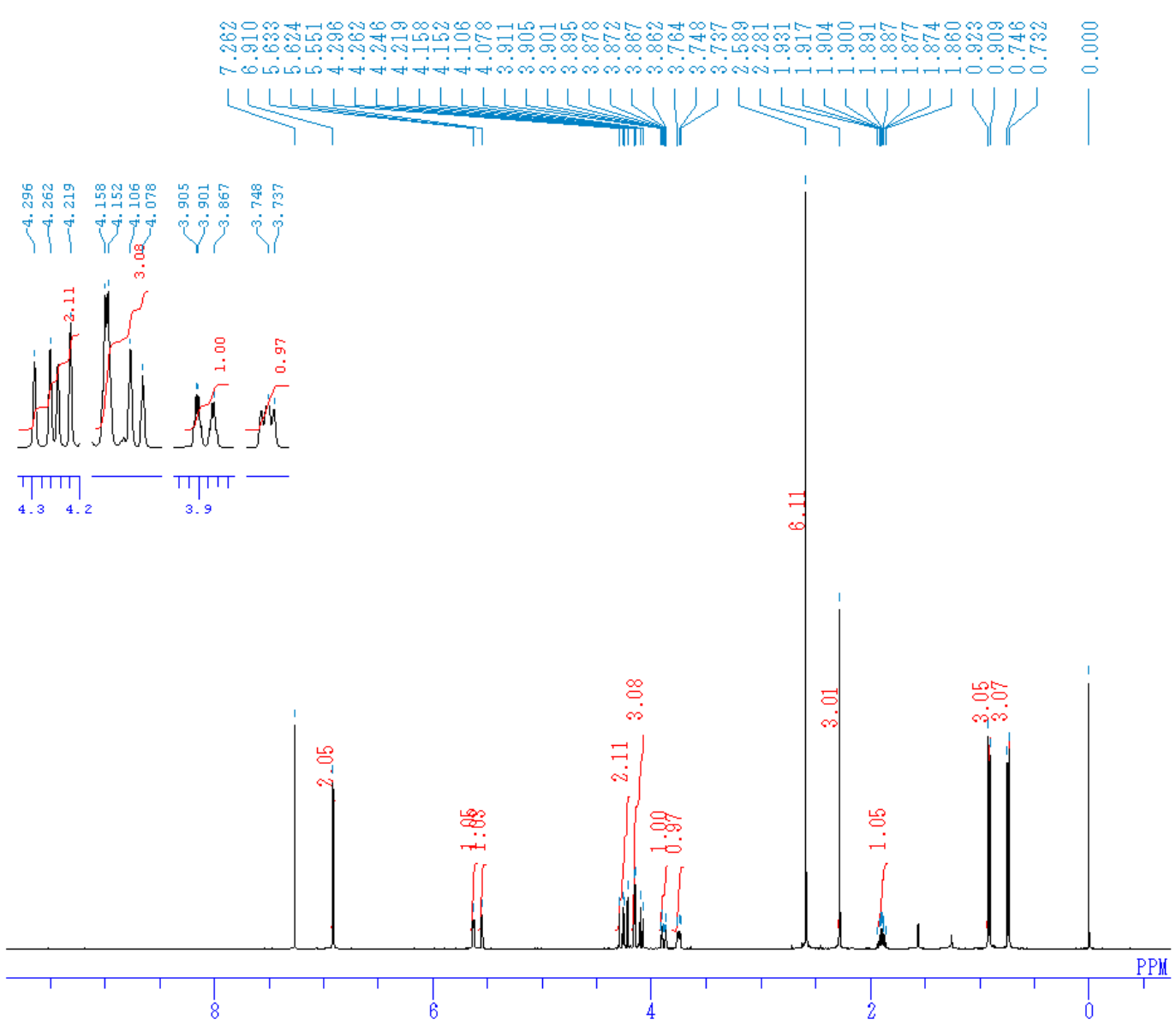
RGAIN	58



17 ^{13}C NMR (125 MHz)

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FREQU        9384.38 Hz
SCANS              8
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PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP          25.9 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            44
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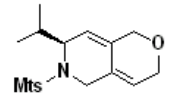
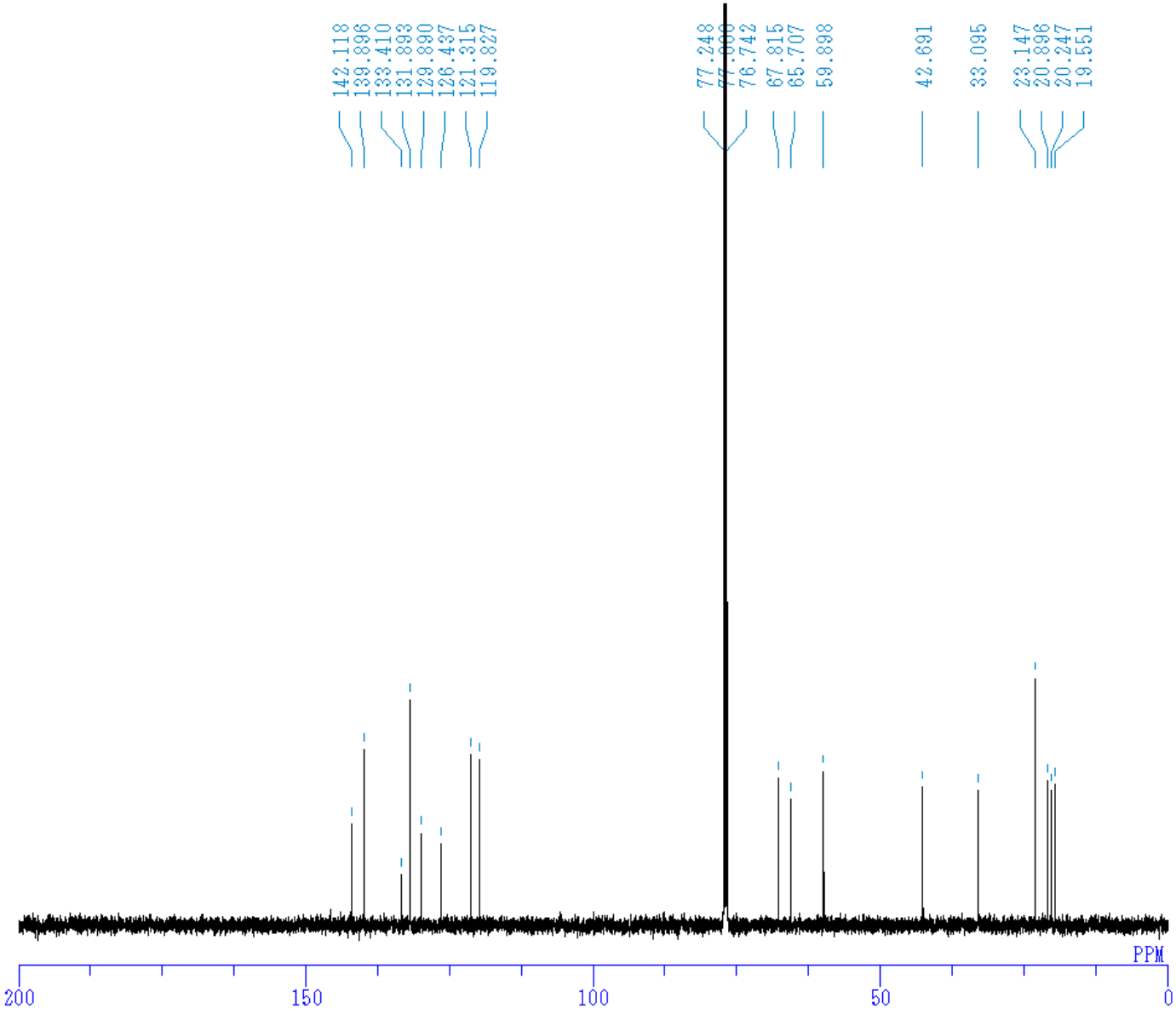


19 ^{1}H NMR (500 MHz)

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OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            758
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.83 usec
IRNUC   1H
CTEMP           26.0 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              1.20 Hz
RGAIN             60
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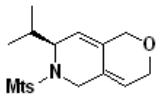
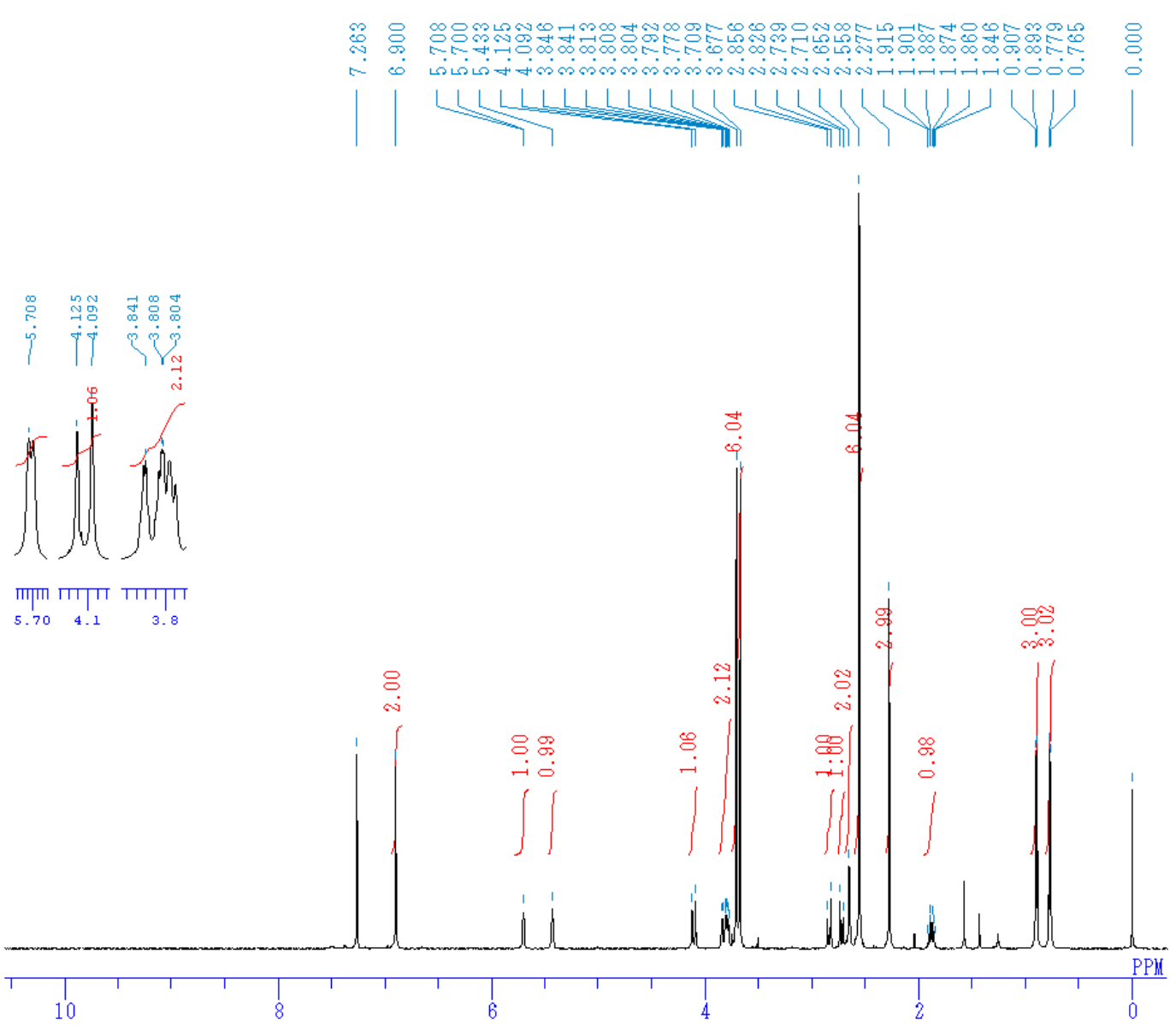
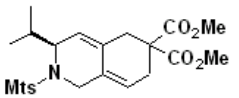


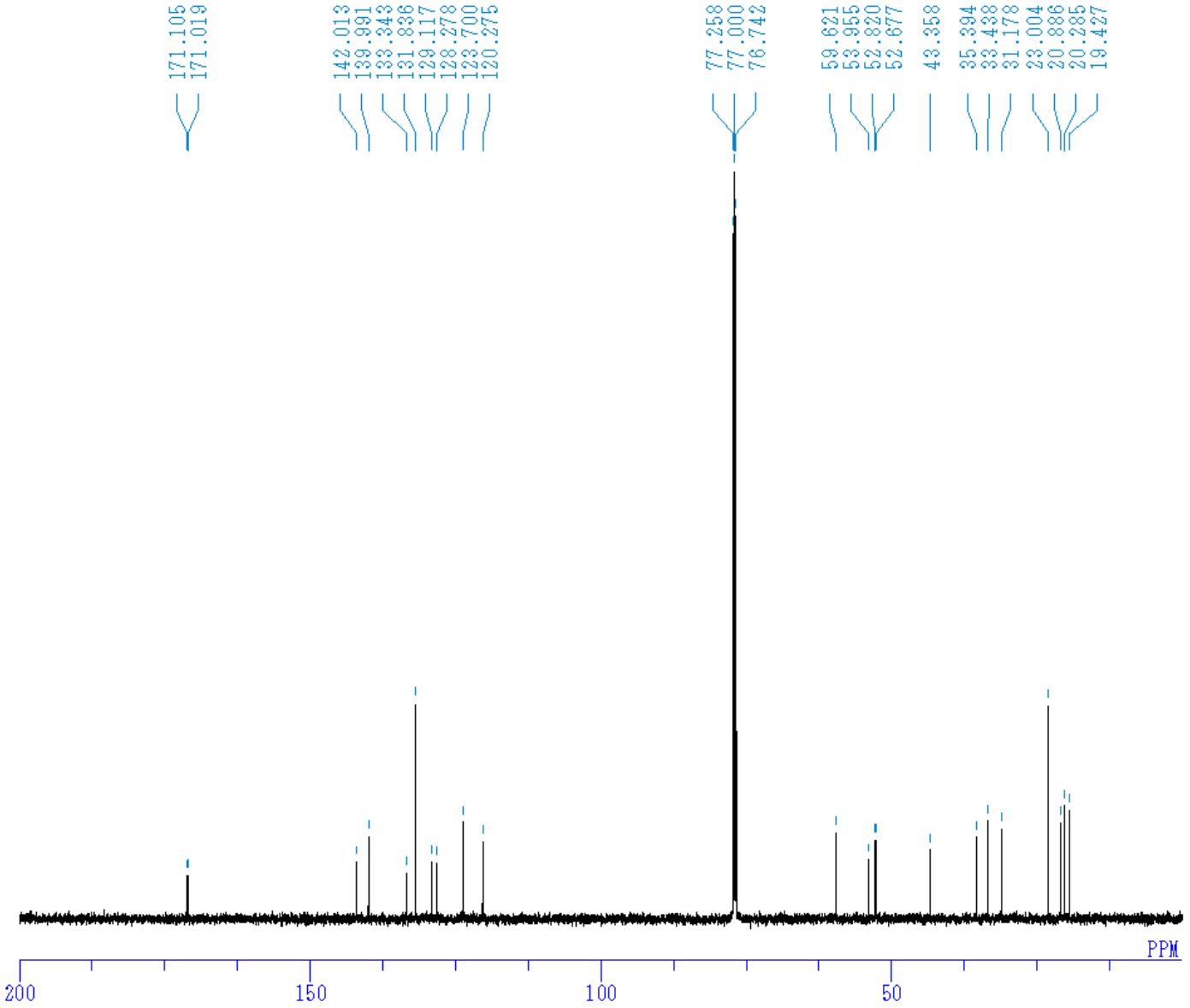
19 ^{13}C NMR (125 MHz)



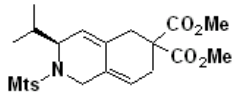
DFILE 070807-73.als
COMNT single_pulse
DATIM 17-03-2008 02:11:45
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



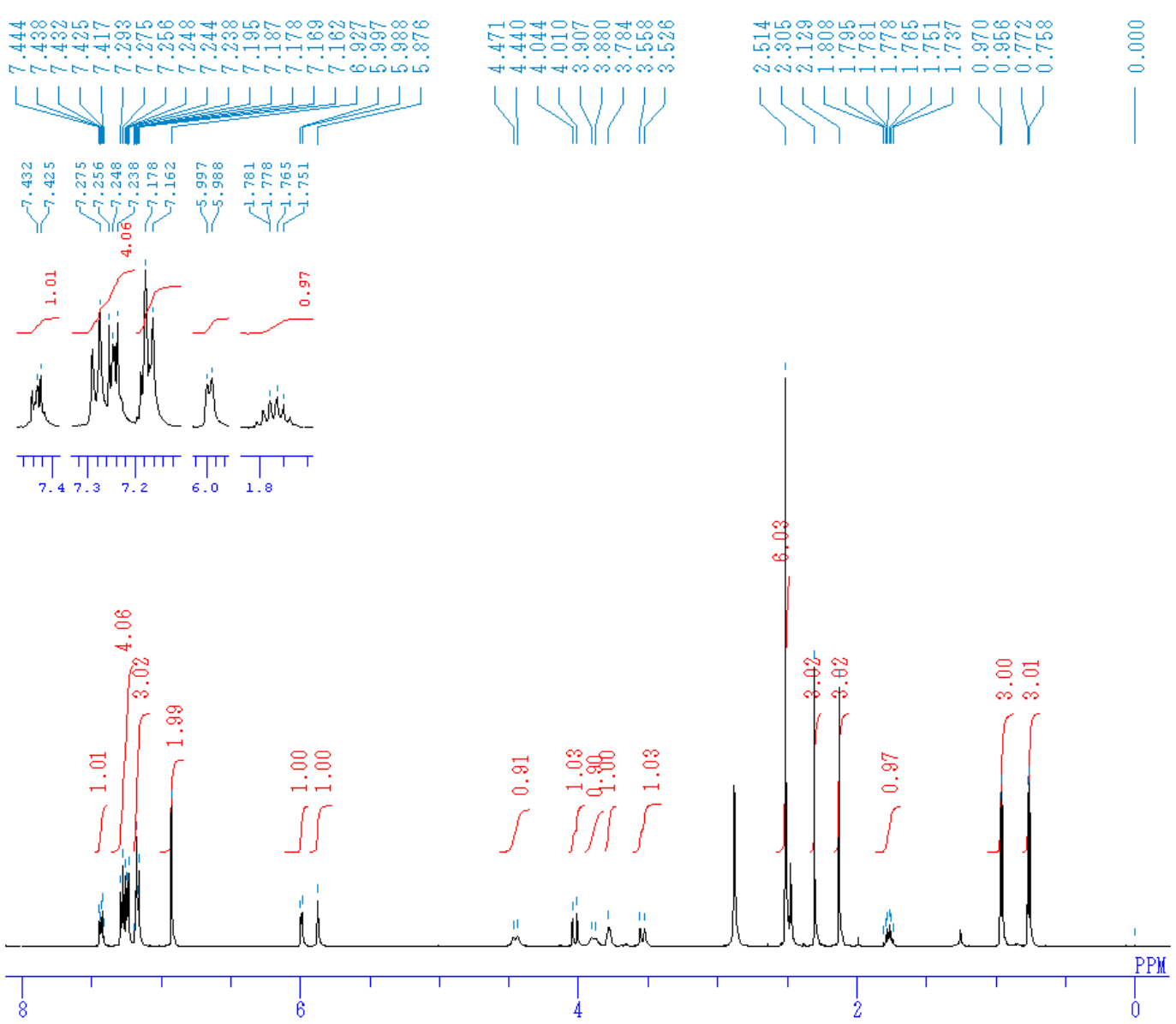
21 ^{1}H NMR (500 MHz)



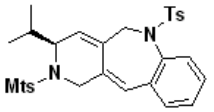

```
DFILE   070808-22.als
COMNT   single pulse decoupled gat
DATIM   17-03-2008 02:57:47
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          26214
FREQU       31446.06 Hz
SCANS            937
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.83 usec
IRNUC   1H
CTEMP           26.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             60
```



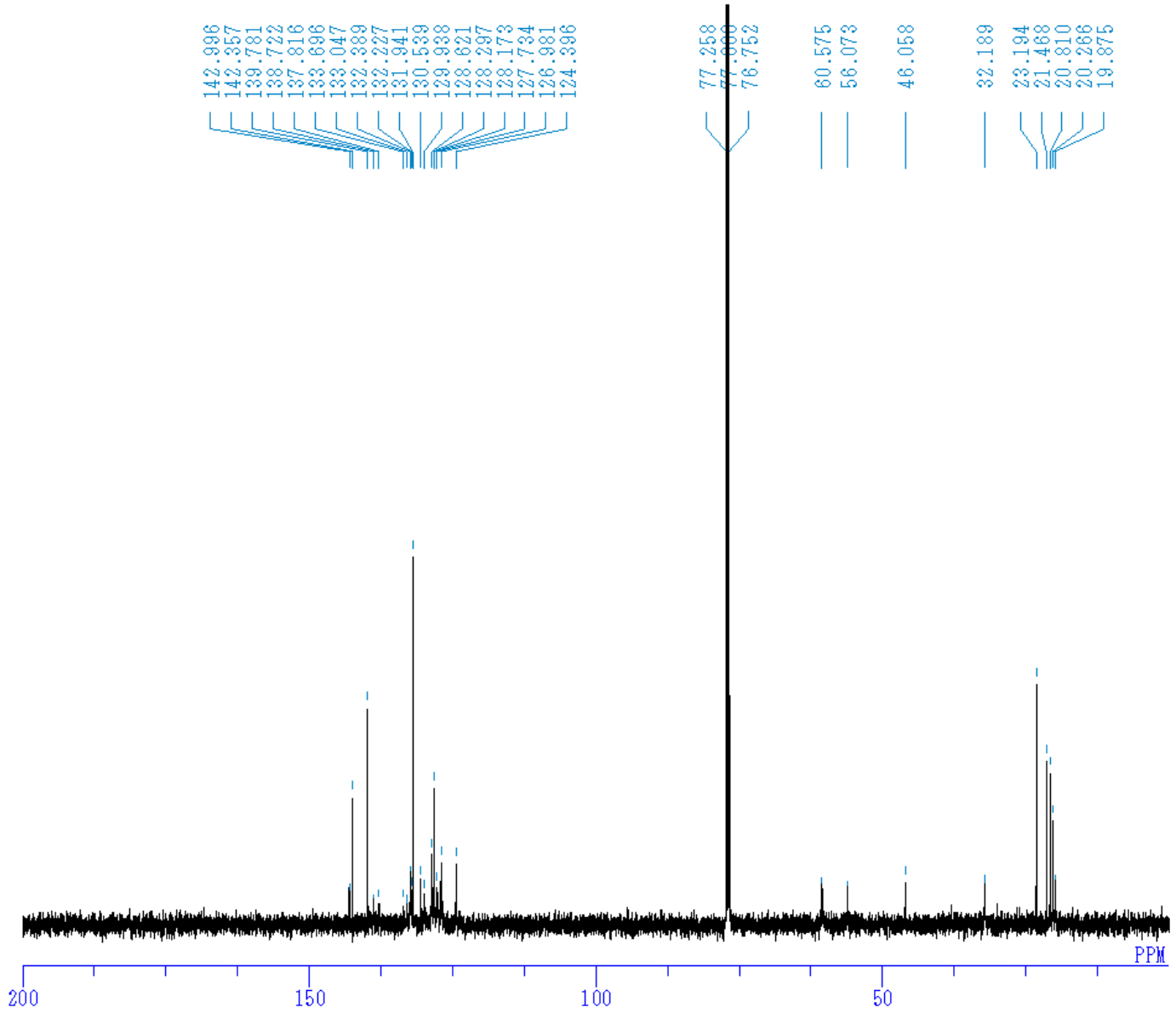
21 ^{13}C NMR (125 MHz)



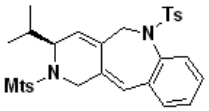

```
DFILE   070807-100.jdf
COMNT   single_pulse
DATIM   04-04-2008 20:23:02
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ         500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT          16384
FREQU        9384.38 Hz
SCANS             8
ACQTM         1.7459 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP          120.0 c
SLVNT   DMSO
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             48
```



23 ^{1}**H NMR (500 MHz)**




```
DFILE   070808-26.jdf
COMNT   single pulse decoupled gat
DATIM   02-04-2008 20:14:35
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ         125.77 MHz
OBSET           7.87 KHz
OBFIN           4.21 Hz
POINT          32768
FREQU       39308.18 Hz
SCANS            406
ACQTM         0.8336 sec
PD            2.0000 sec
PW1             3.83 usec
IRNUC   1H
CTEMP           26.4 c
SLVNT   CDCL3
EXREF           77.00 ppm
BF              1.20 Hz
RGAIN             60
```



23 ^{13}C NMR (125MHz)