Supporting Information

Stereoselective Synthesis of Chiral 2,3-*cis*-2-Ethynylaziridines by Base-mediated Intramolecular Amination of Bromoallenes

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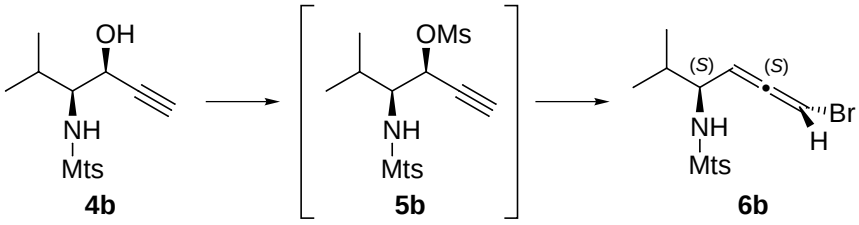
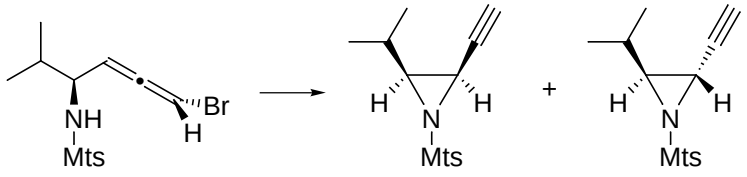
General Methods. Melting points are uncorrected. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$. Chemical shifts are reported in parts per million downfield from internal Me_4Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, q = quartet, m = multiplet). Optical rotations were measured in $CHCl_3$ with a JASCO DIP-360 digital polarimeter. For flash chromatography, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed.



(4*S*,a*S*)-1-Bromo-5-methyl-4-[*N*-(2,4,6-trimethylphenylsulfonyl)amino]-1,2-hexadiene (6b). To a stirred mixture of **4b**[1] (155 mg, 0.5 mmol) and Et_3N (0.35 mL, 2.5 mmol) in THF (3 mL) was added dropwise methanesulfonyl chloride (0.077 mL, 1.0 mmol) at –78 °C. The mixture was stirred for 30 min with warming to –40 °C. The mixture was made acidic with 1N HCl at –40 °C, and the whole was extracted with a mixed solvent of Et_2O–EtOAc (1:1). The extract was washed successively with water, saturated $NaHCO_3$, and water, and dried over $MgSO_4$. Usual workup followed by rapid filteration though a short pad of SiO_2 with Et_2O gave a crude mesylate **5b**, which was used without further purification. A mixture of CuBr·DMS (205 mg, 1.0 mmol) and LiBr (86.9 mg, 1.0 mmol) were dissolved in THF (2 mL) at room temperature under nitrogen. After stirring for 2 min, a solution of the above crude mesylate **5b** in THF (1 mL) was added to the black reagent at room temperature. The mixture was stirred for 12 h at this temperature, followed by quenching with saturated NH_4Cl (2 mL) and 28% NH_4OH (2 mL). The whole was extracted with Et_2O, and the extract was washed with water and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (10:1) to give the title compound **6b** (141 mg, 76% yield from **4b**, de = 90%).

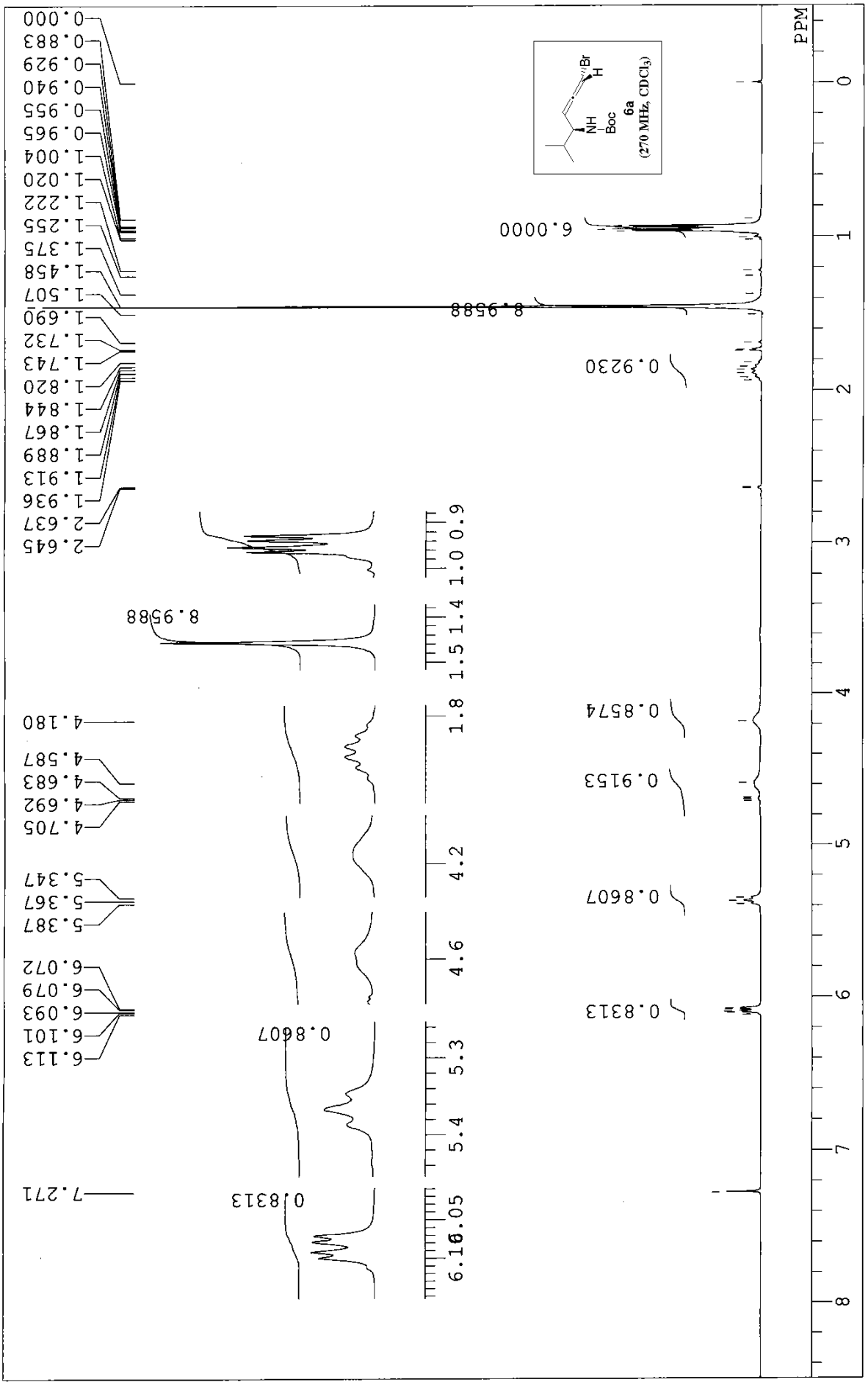
Recrystallization from *n*-hexane gave pure **6b** as colorless crystals: mp 64 °C; $[\alpha]^{24}_{D}$ +153 (*c* 1.25, $CHCl_3$); IR (KBr) cm^{-1}: 3280 ($NHSO_2$), 1959 (C=C=C), 1325 ($NHSO_2$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.86 (d, *J* = 6.8 Hz, 3H, CMe), 0.92 (d, *J* = 7.0 Hz, 3H, CMe), 1.82-1.94 (m, 1H, 5-H), 2.30 (s, 3H, Ph-Me), 2.63 (s, 6H, 2 × Ph-Me), 3.63-3.71 (m, 1H, 4-H), 4.73 (d, *J* = 8.4 Hz, 1H, NH), 5.11 (dd, *J* = 7.0, 5.7 Hz, 1H, 3-H), 5.86 (dd, *J* = 5.7, 1.6 Hz, 1H, 1-H), 6.94 (s, 2H, Ph); ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ: 18.2, 18.3, 21.0, 23.2 (2C), 33.0, 57.7, 74.1, 99.4, 131.9 (2C), 134.2, 138.8 (2C), 142.1, 201.2. *Anal.* Calcd for $C_{16}H_{22}BrNO_2S$: C, 51.61; H, 5.96; N, 3.76. Found: C, 51.48; H, 5.86; N, 3.75.



6b **10b** **11b**

(2*R*,3*S*)-2-Ethynyl-3-isopropyl-*N*-(2,4,6-trimethylphenylsulfonyl)aziridine (10b) and Its (2*S*,3*S*)-Isomer (11b). To a stirred suspension of NaH (9.6 mg, 0.24 mmol) in DMF (2 mL) under nitrogen was added a solution of the bromoallene **6b** (74.3 mg, 0.20 mmol) in DMF (1 mL) at 0 °C. After the mixture was stirred at room temperature for 1 h, the mixture was poured into ice–water (2 mL) saturated with NH_4Cl. The whole was extracted with Et_2O, and the extract was washed with water, and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane–EtOAc (10:1) gave, in order of elution, 2,3-*cis*-aziridine **10b** (44 mg, 76.2% yield) and its 2,3-*trans*-isomer **11b** (10 mg, 16.3% yield). All the spectroscopic data of both the aziridines were in good agreeement with those of the authetic samples.[1]

(1) Ohno, H.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2949.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3
4
5
6
7
8
6a
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Boc
Br
H
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0.9230
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0.8607
0.8313
8.9588
0.8607
0.8313
7.271
6.113
6.101
6.093
6.079
6.072
5.387
5.367
5.347
4.705
4.692
4.683
4.587
4.180
2.645
2.637
1.936
1.913
1.889
1.867
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1.820
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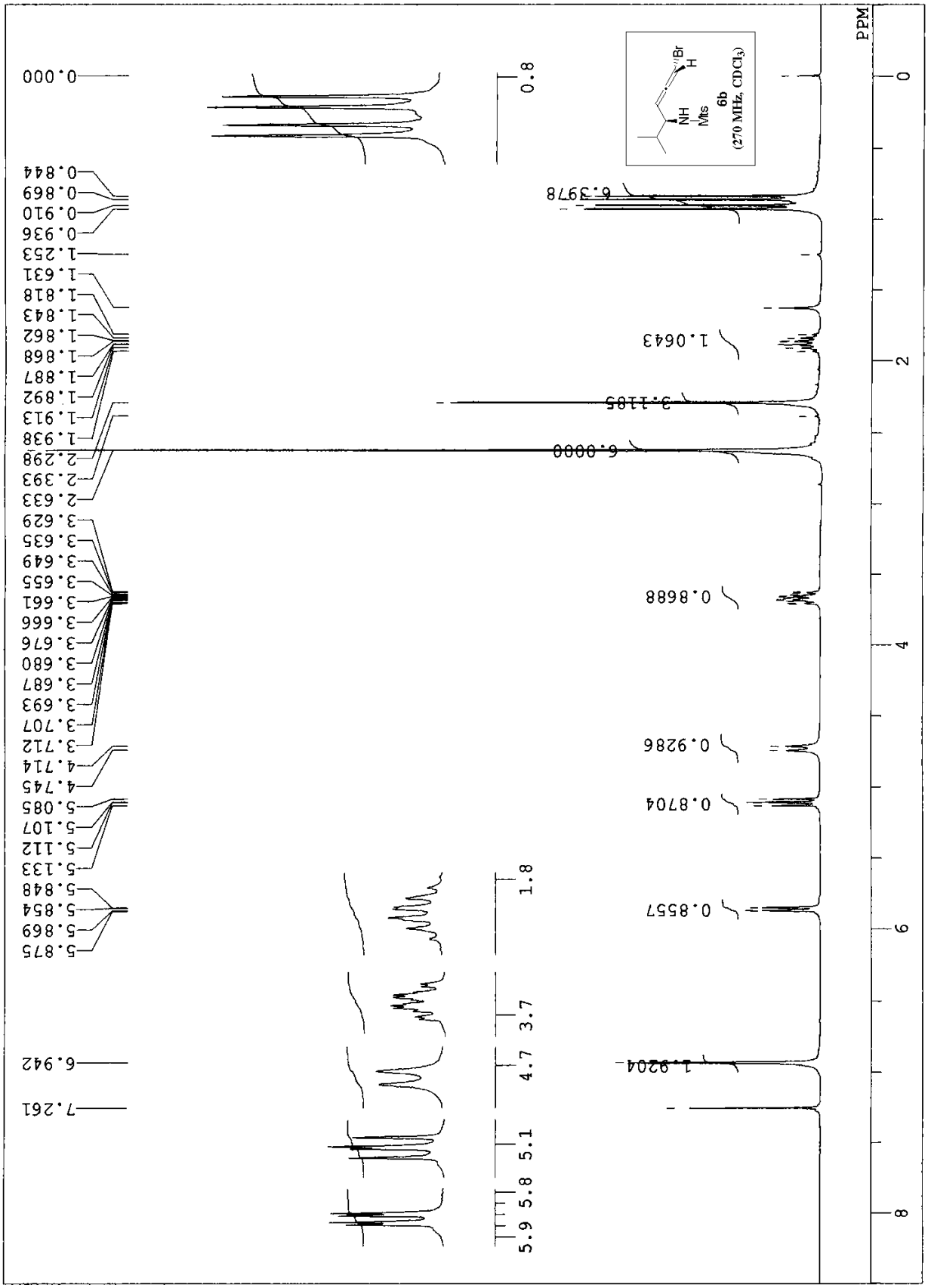
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5.1
5.8
5.9
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2.633
3.629
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3.649
3.655
3.661
3.666
3.676
3.680
3.687
3.693
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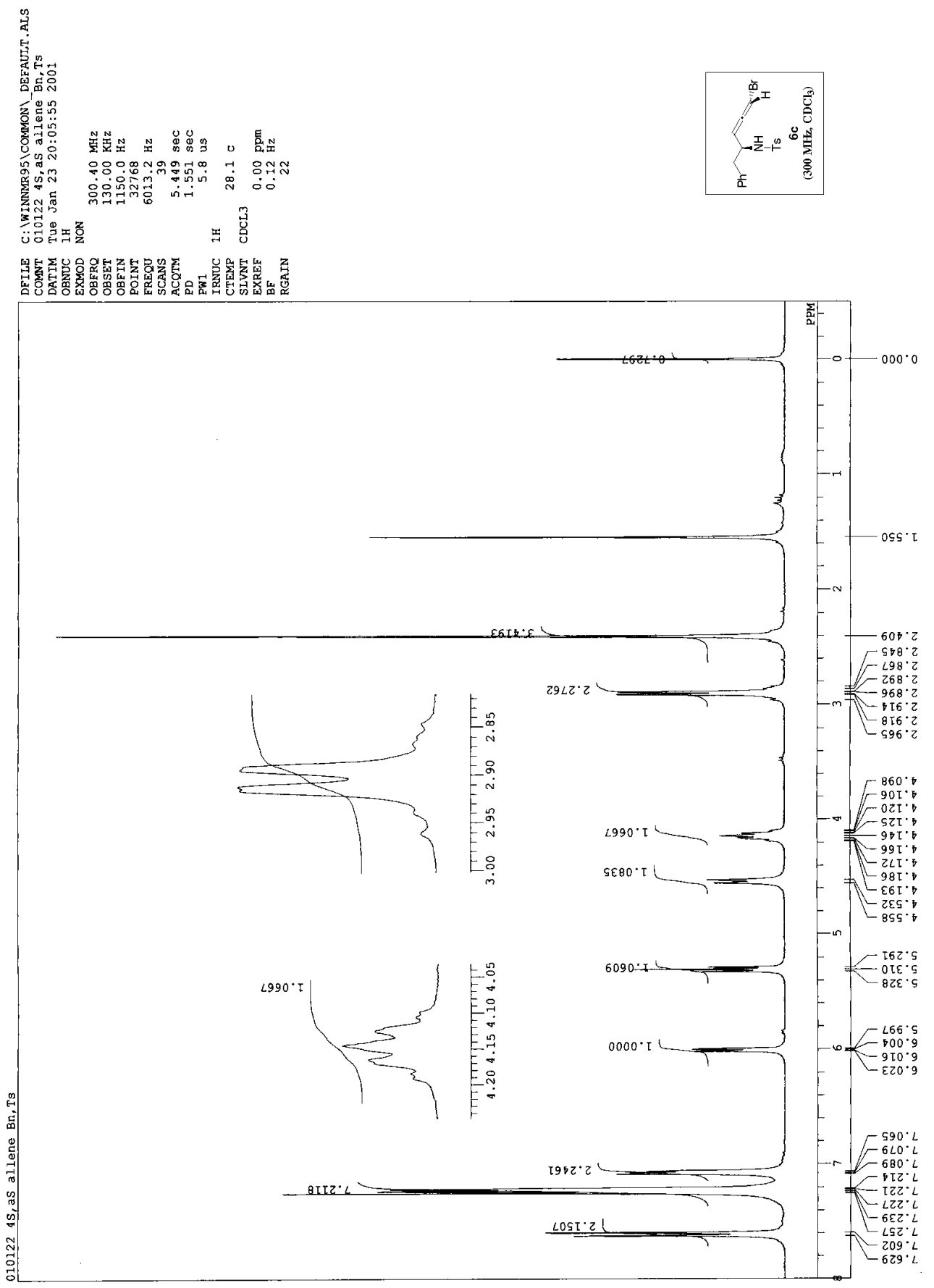
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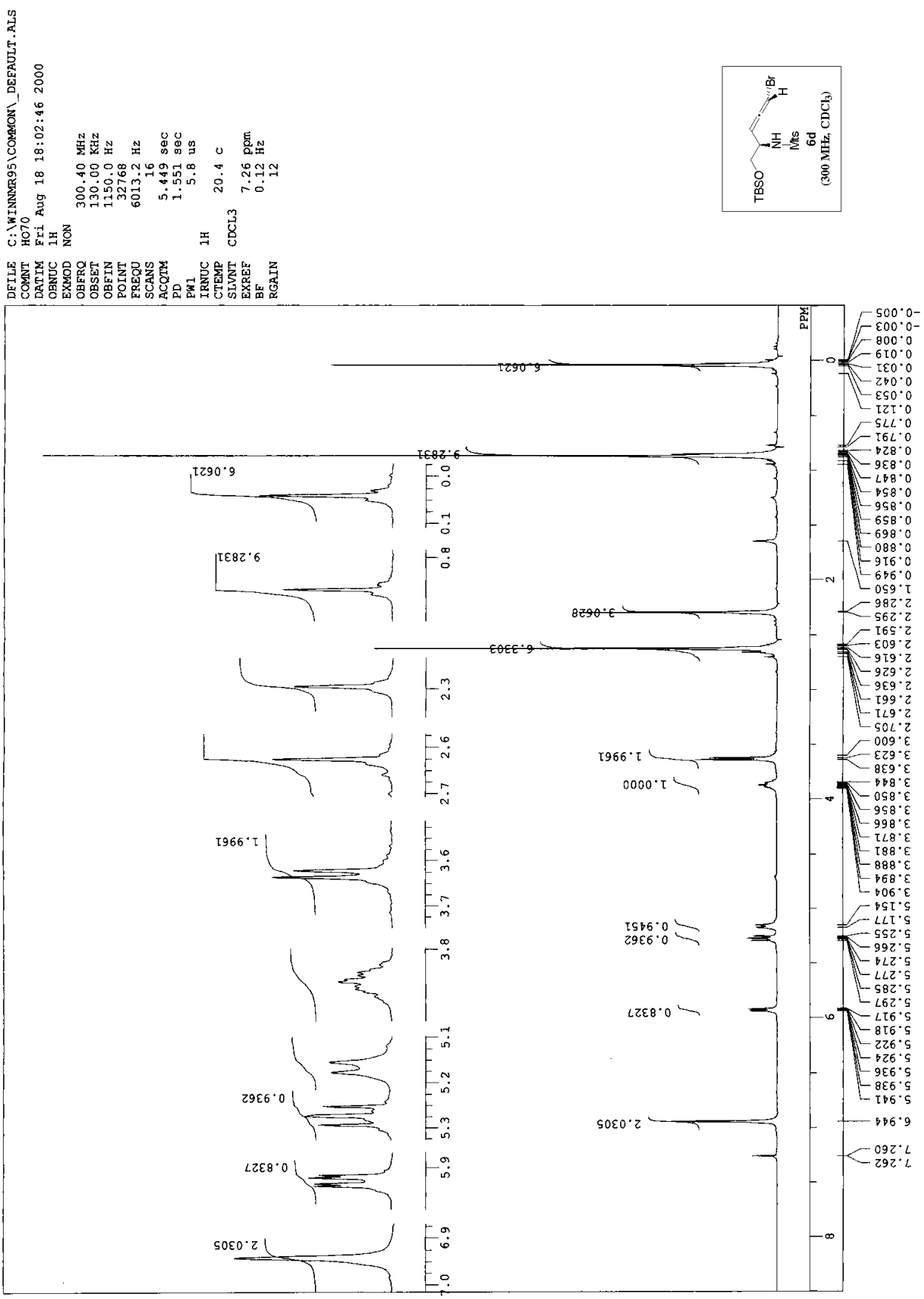
(300 MHz, CDCl3)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NH
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Br
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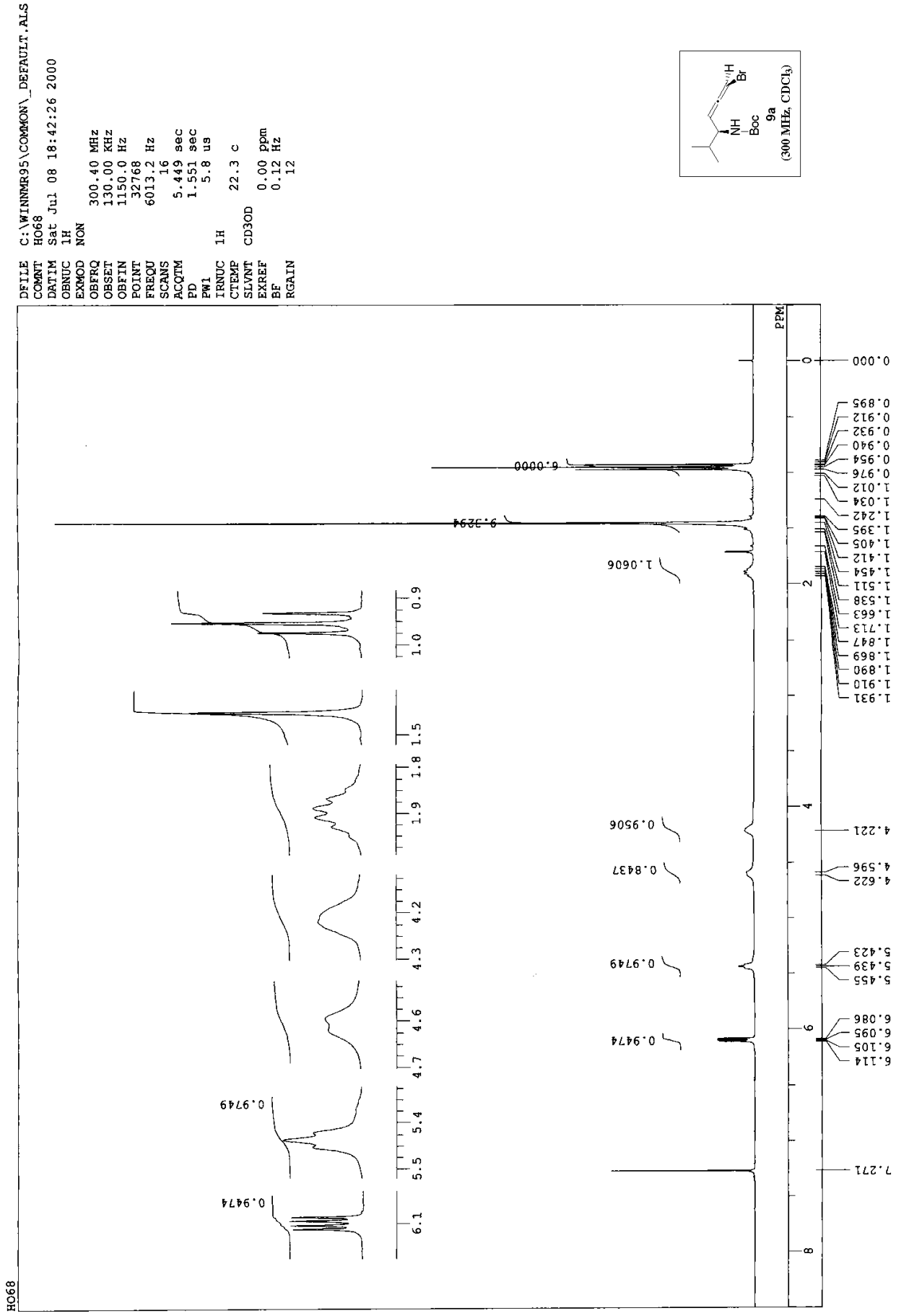
6d
(300 MHz, CDCl3)
PPM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NH
Boc
Br
9a
(300 MHz, CDCl3)
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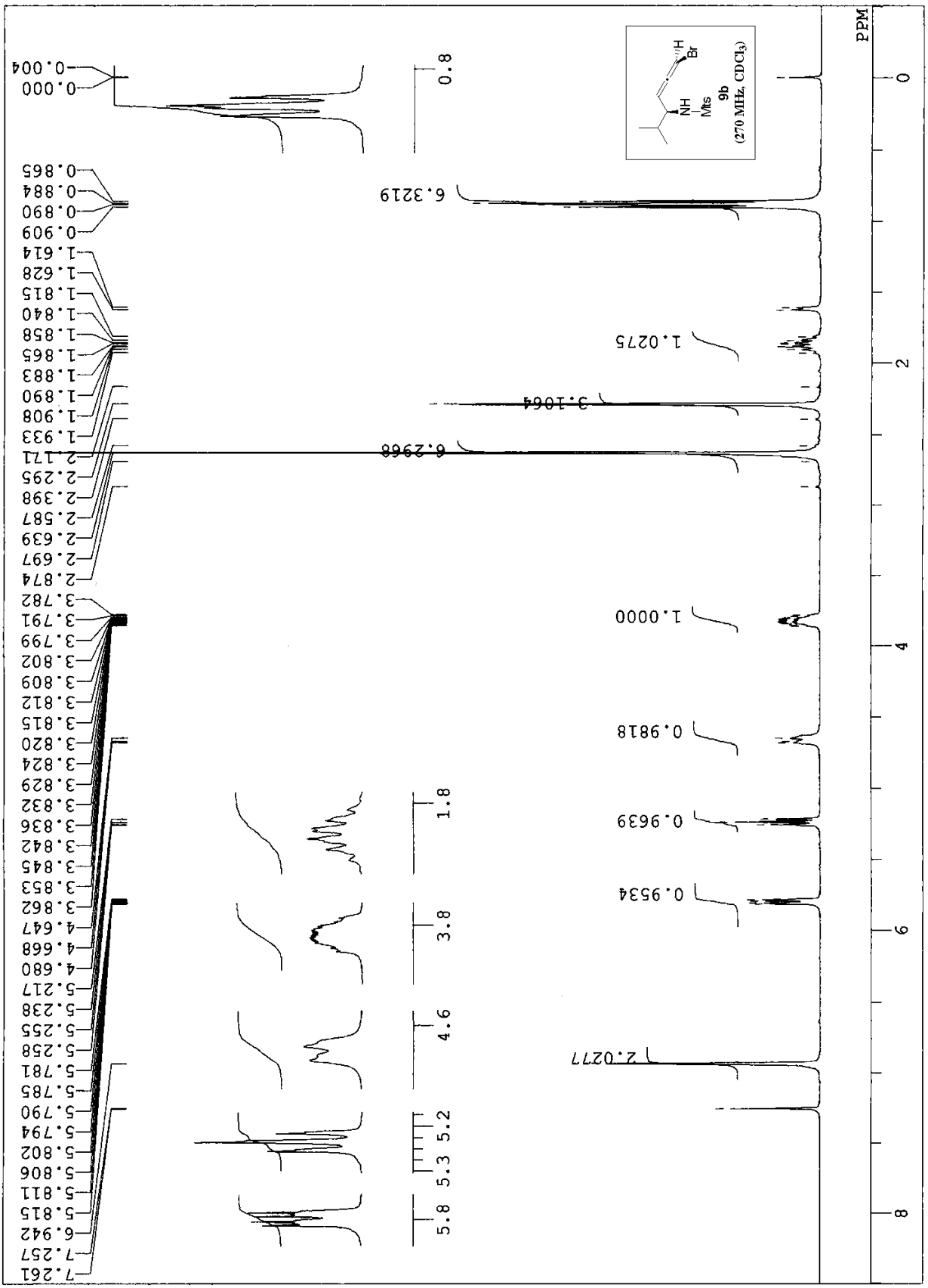
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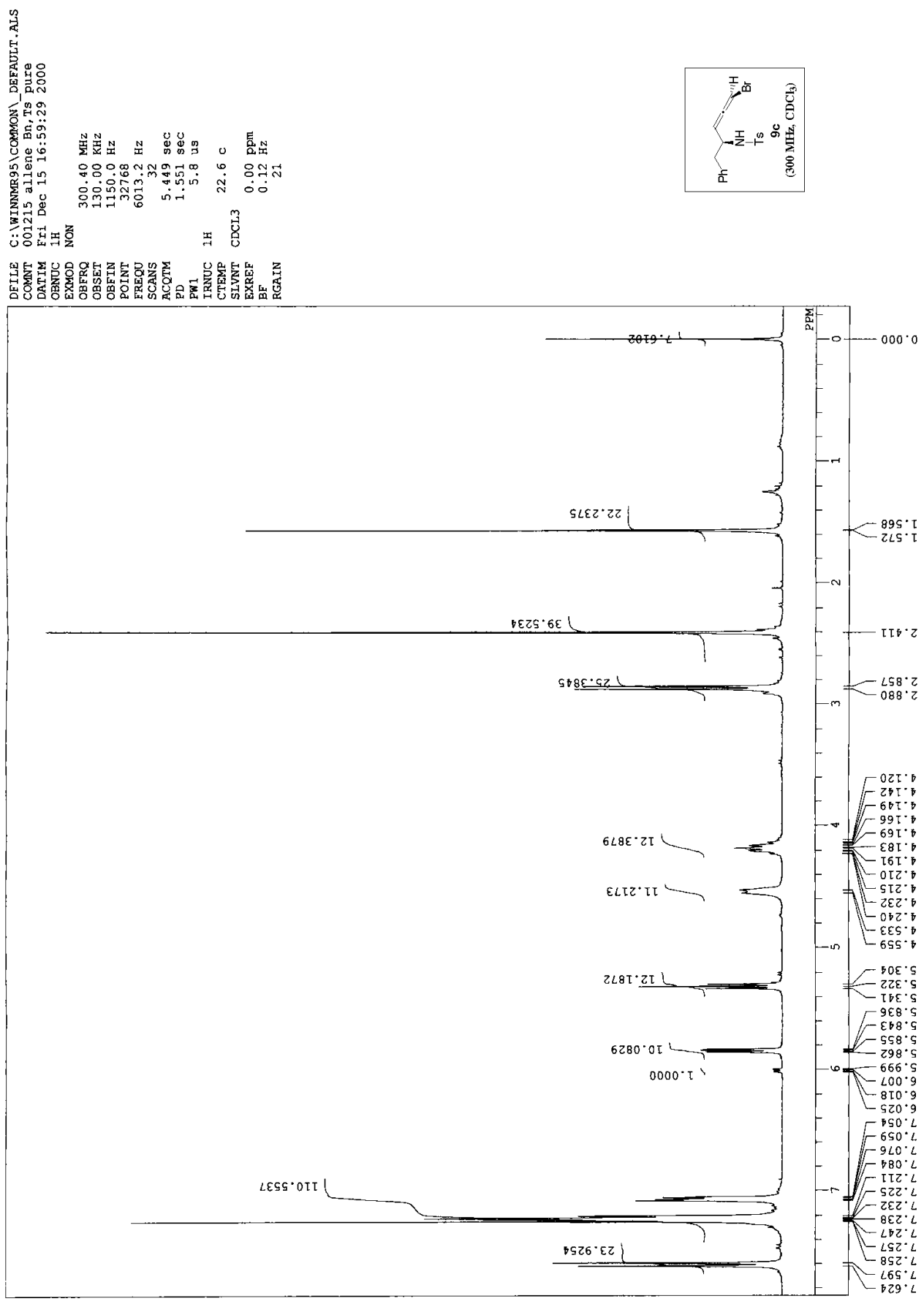
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BF 0.12 Hz
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Ph
NH
Ts
Br
9c
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4.169
4.183
4.191
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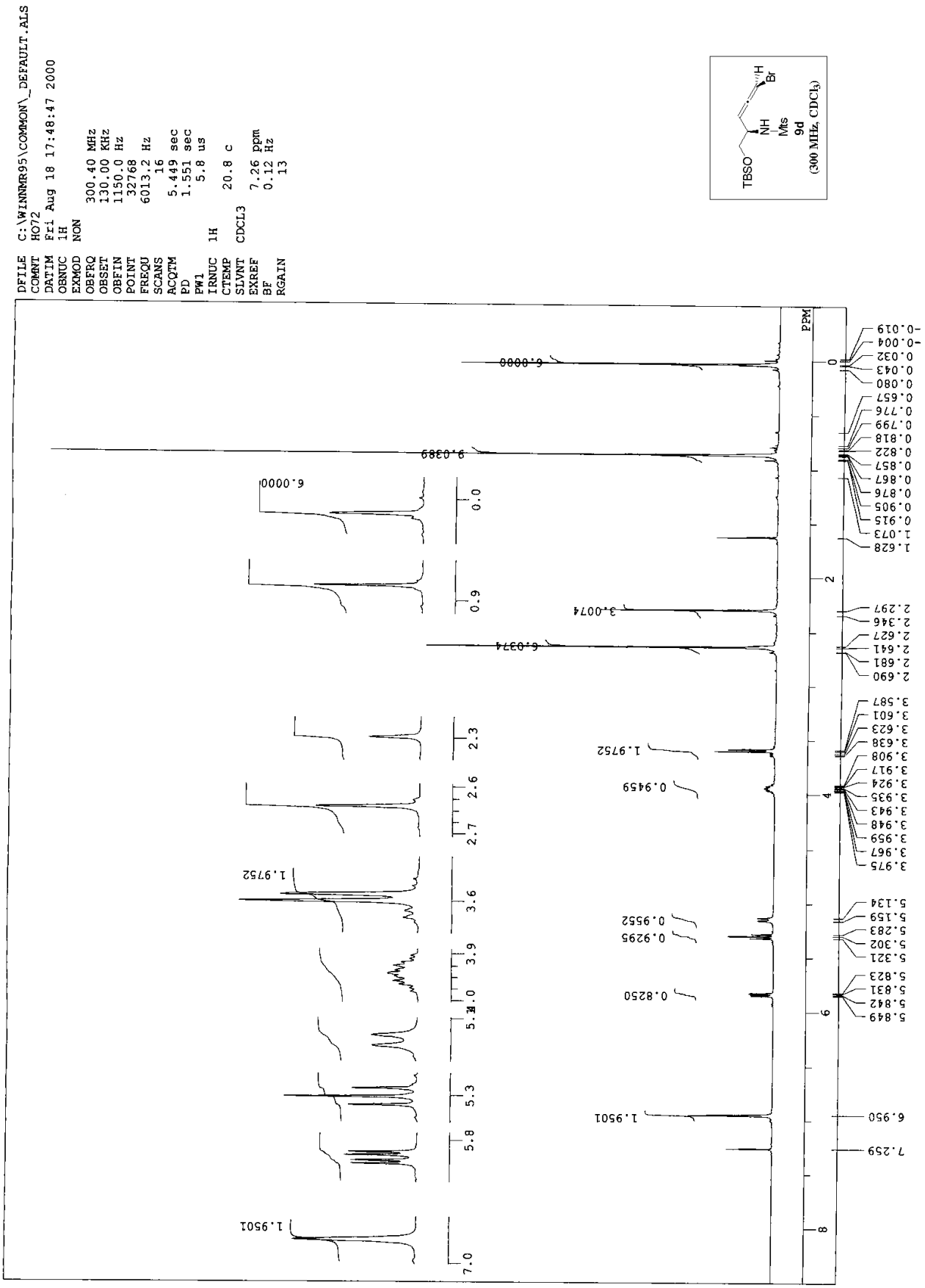
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CTEMP 20.8 c
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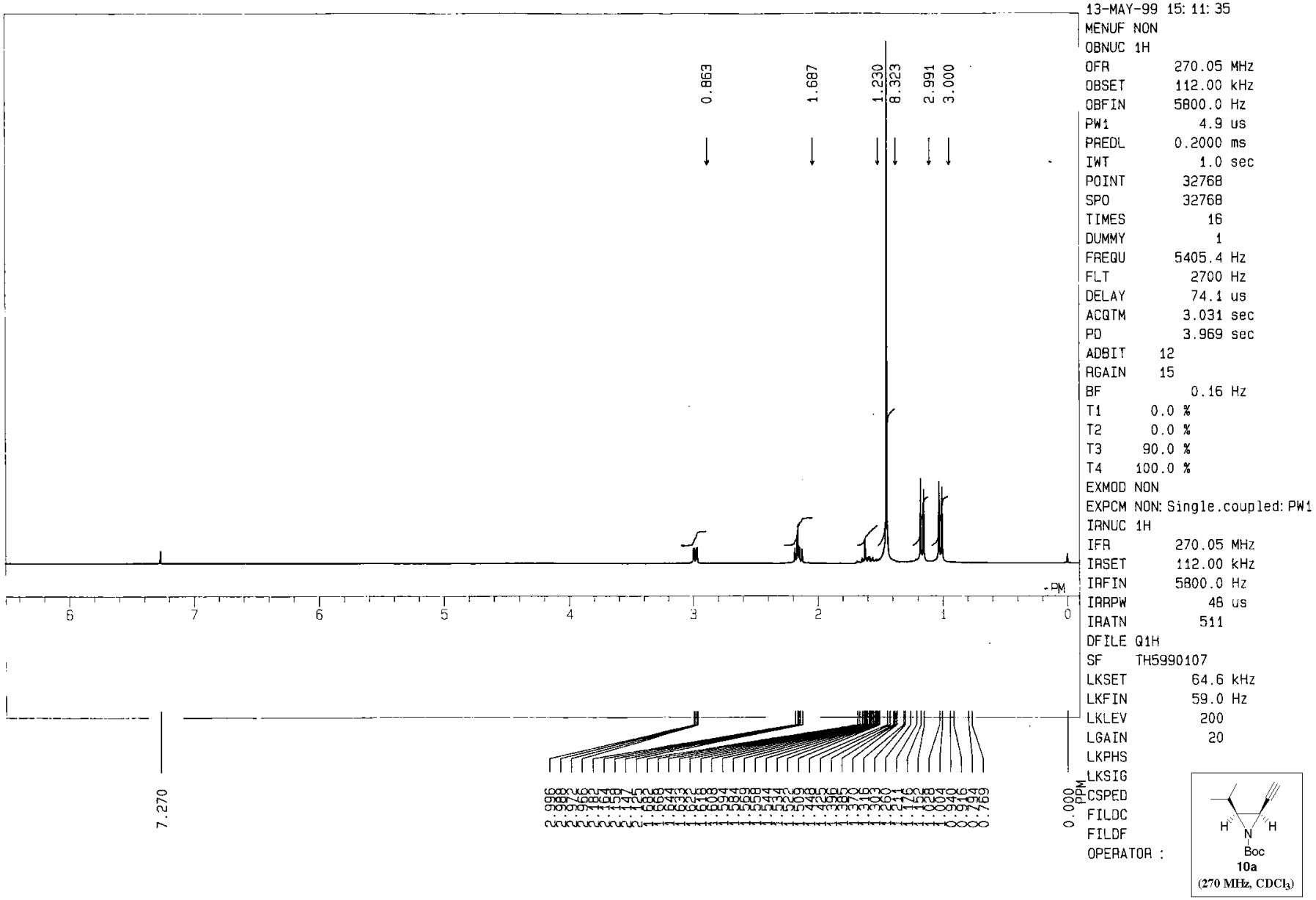
Ms
Br
9d
(300 MHz, CDCl3)
PPM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3
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1
0
7.270
0.000
PPM
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SPO 32768
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T3 90.0 %
T4 100.0 %
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LKFIN 59.0 Hz
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CSPED
FILDC
FILDF
OPERATOR :
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N
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Boc
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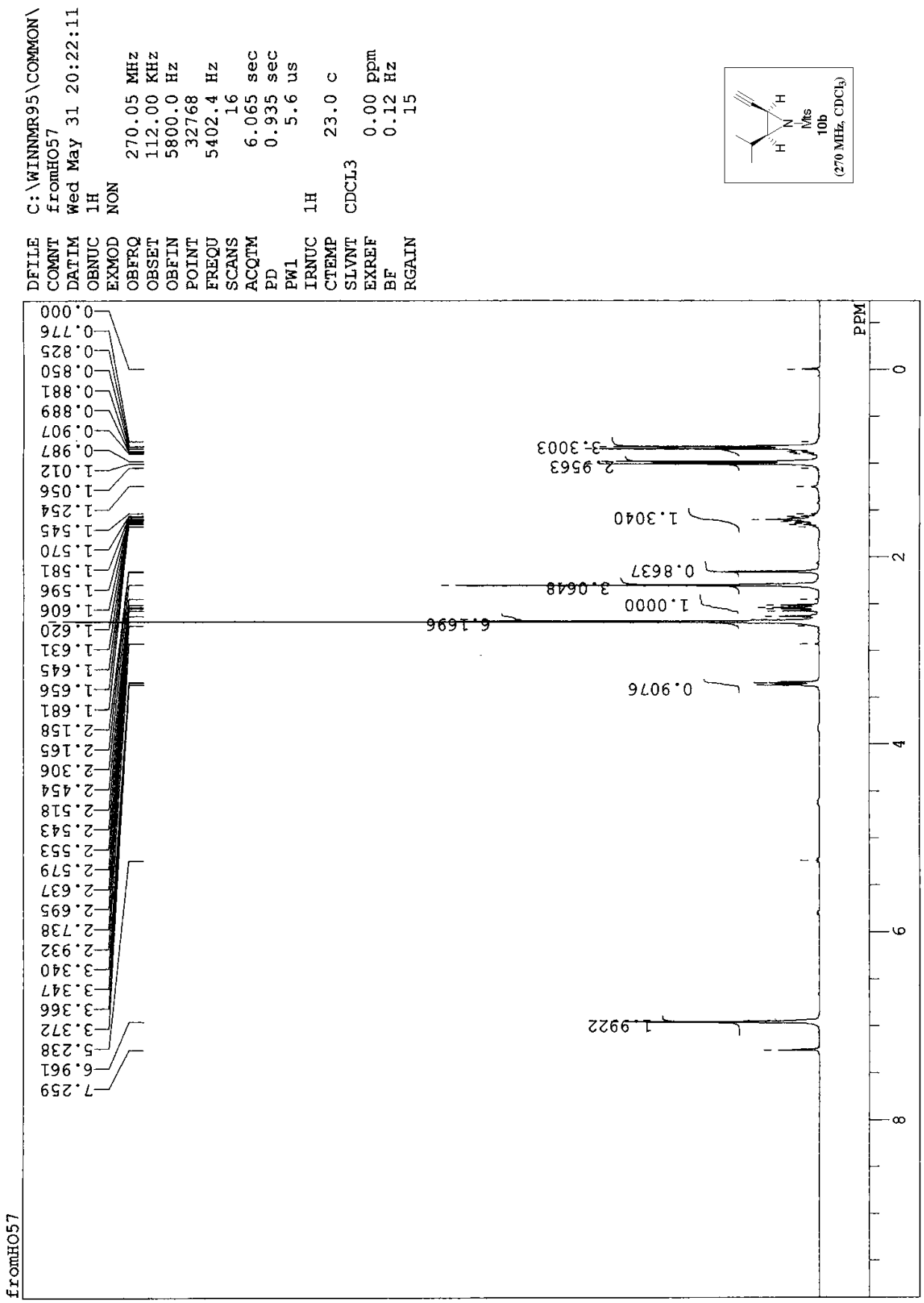
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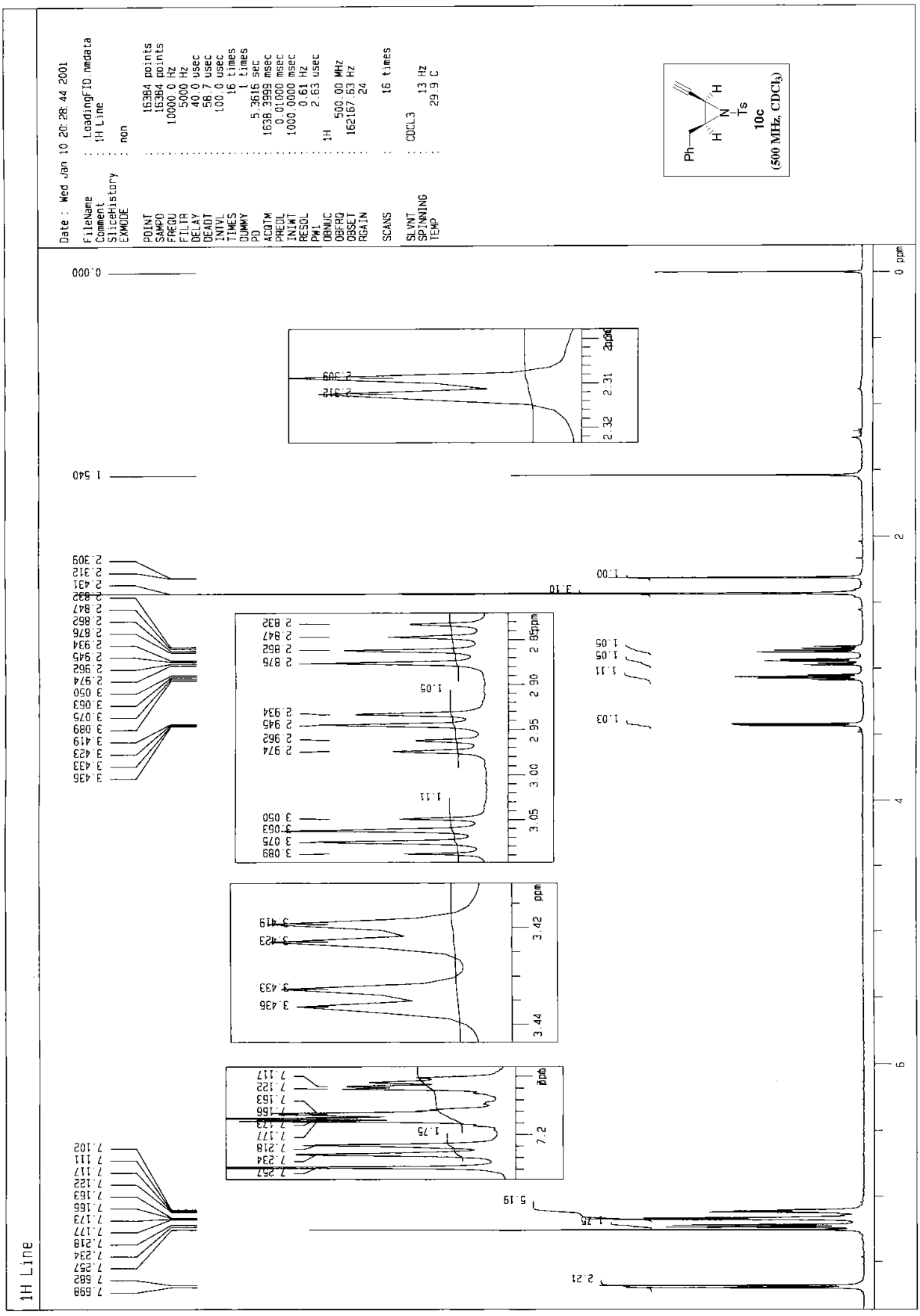
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DUMMY 1 times
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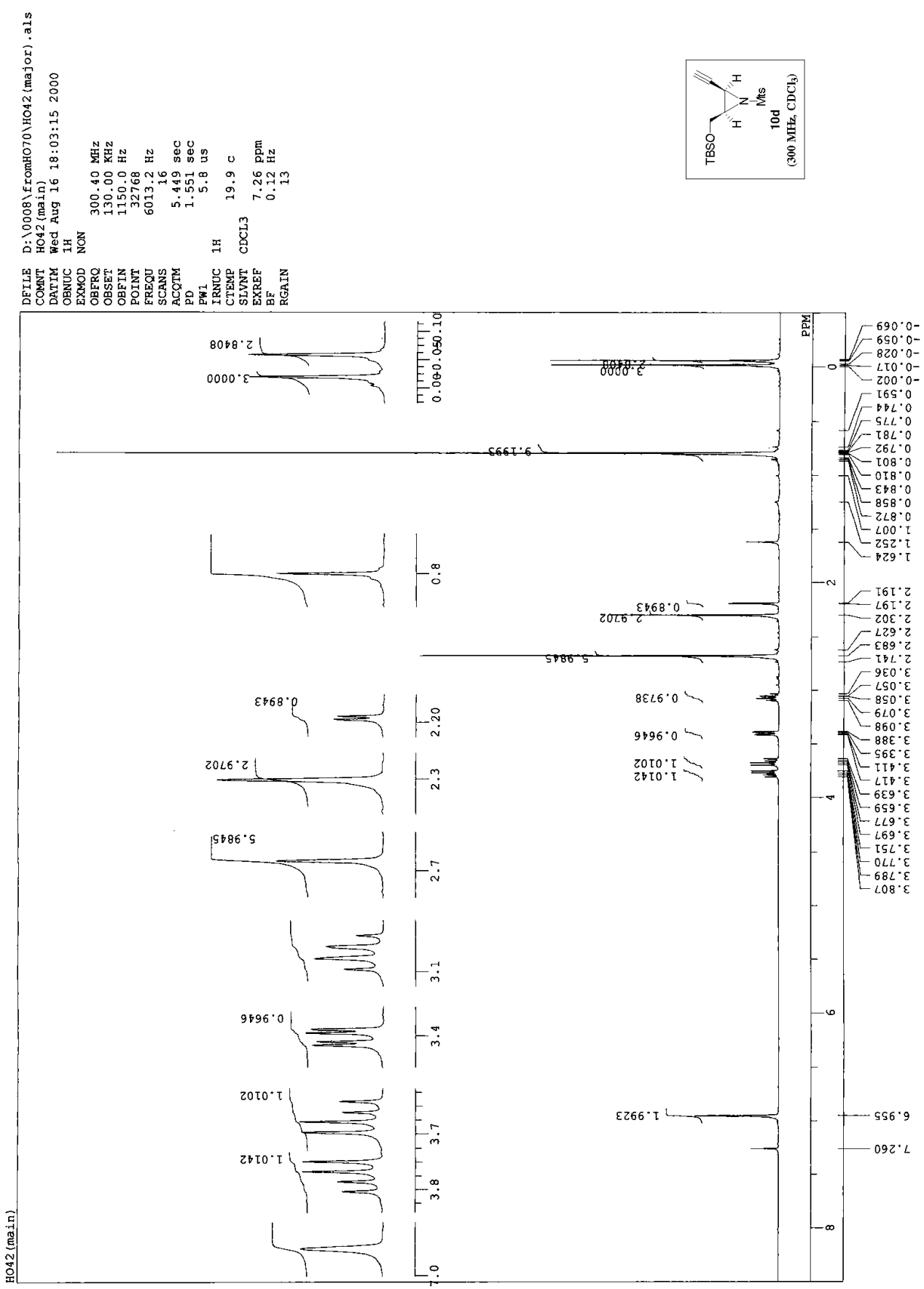
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PD 1.551 sec
PW1 5.8 us
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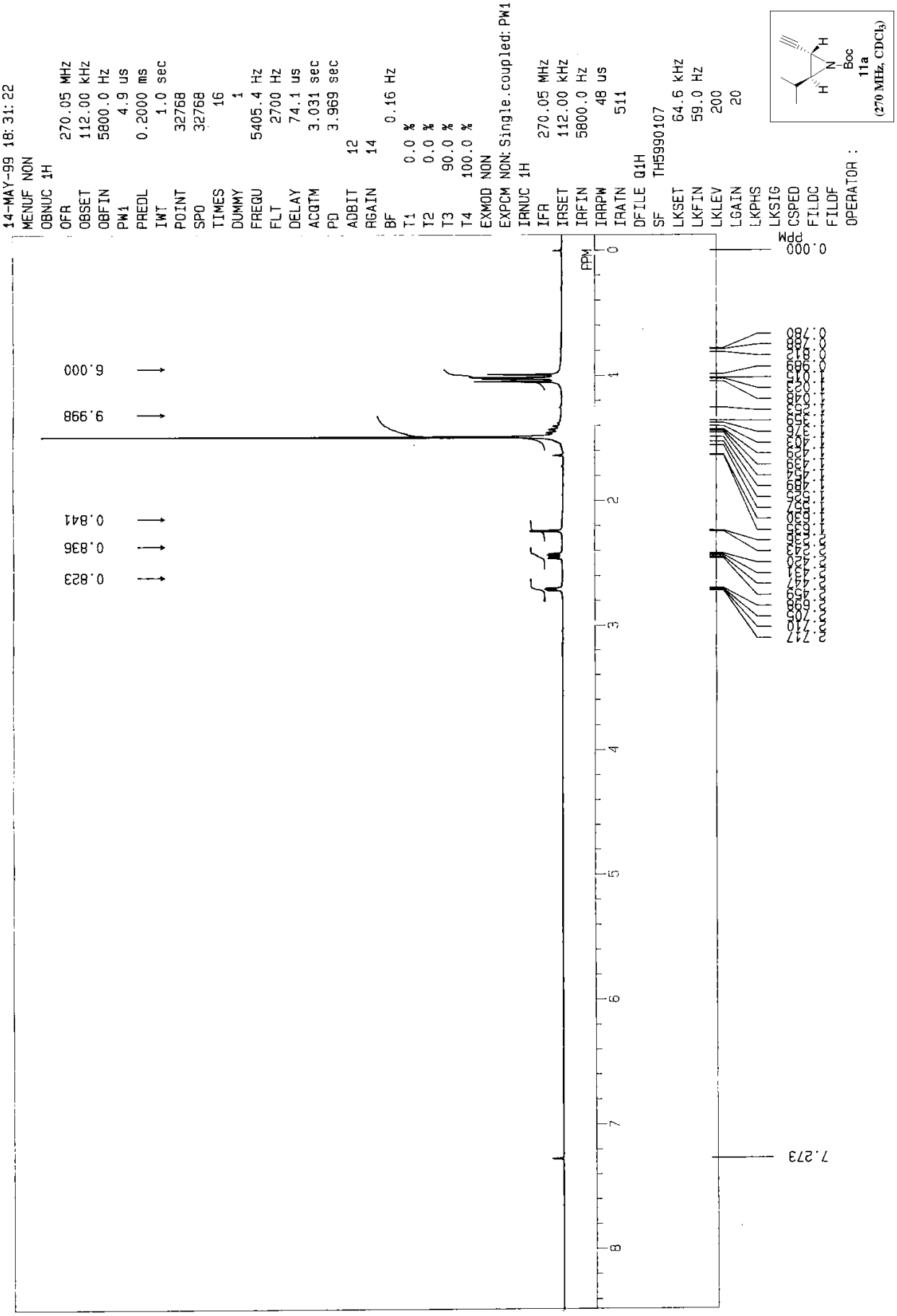
TBSO
Ms
10d
(300 MHz, CDCl3)
HO42(main)
PPM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T2 0.0 %
T3 90.0 %
T4 100.0 %
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FILDC
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ppm
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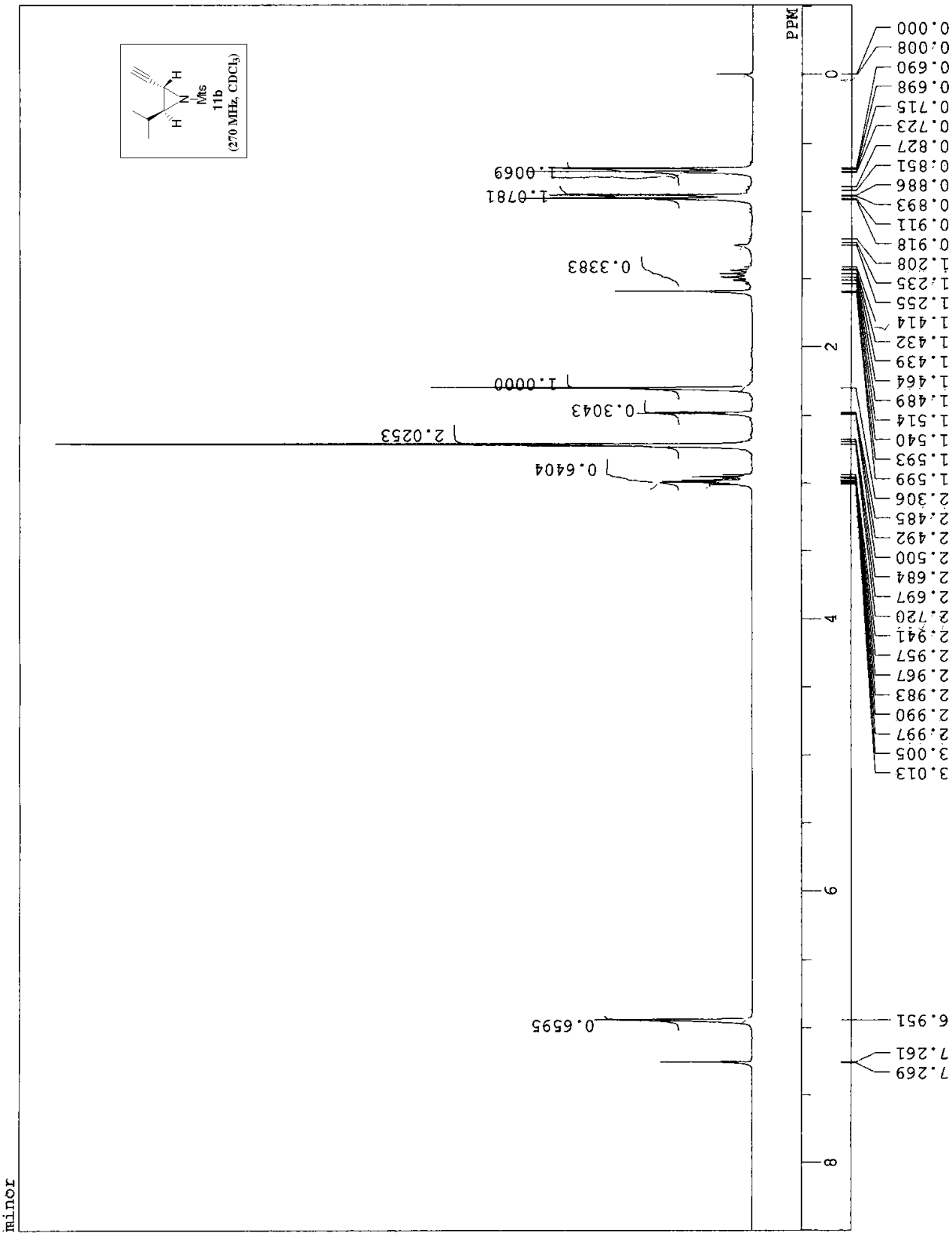
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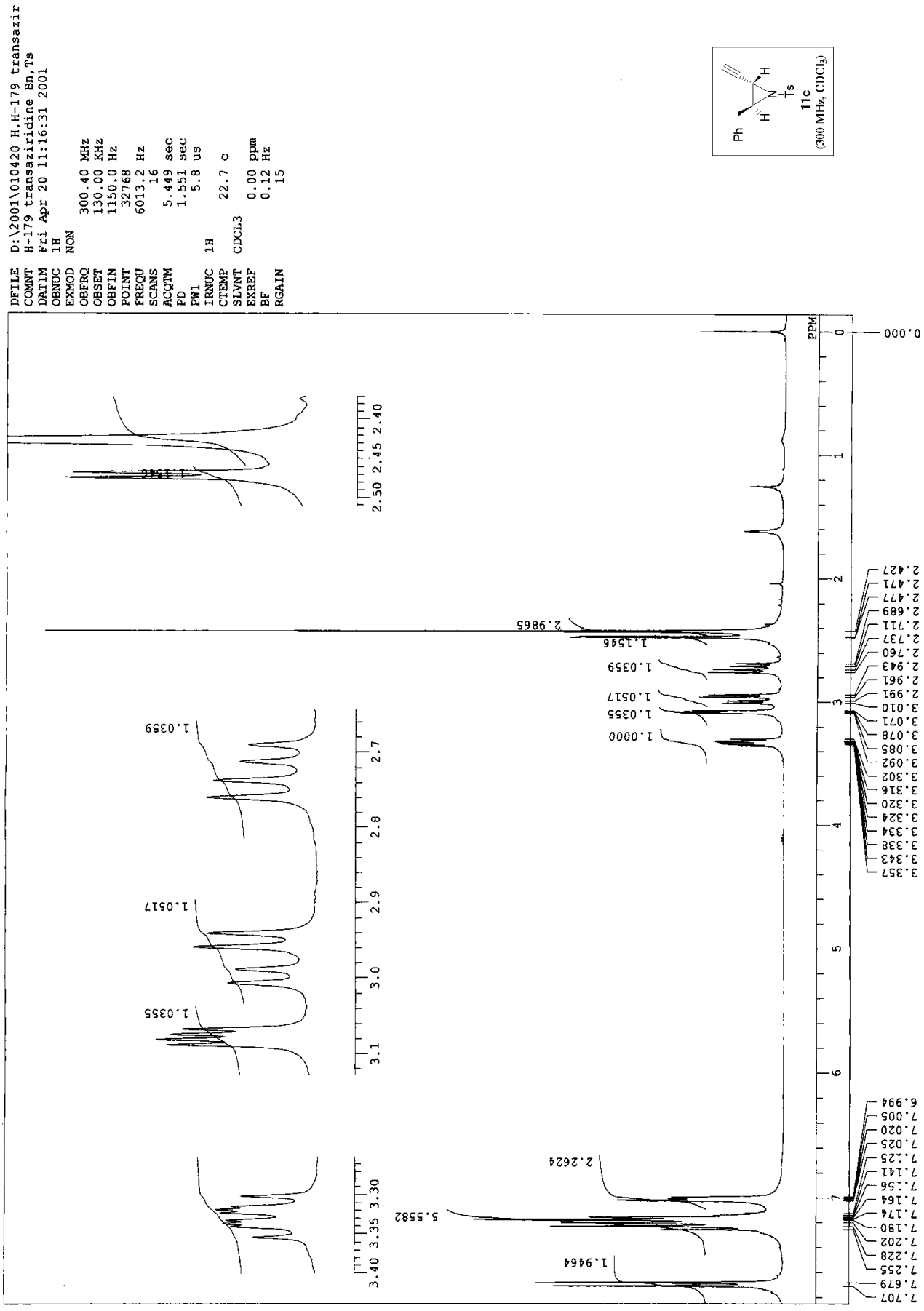
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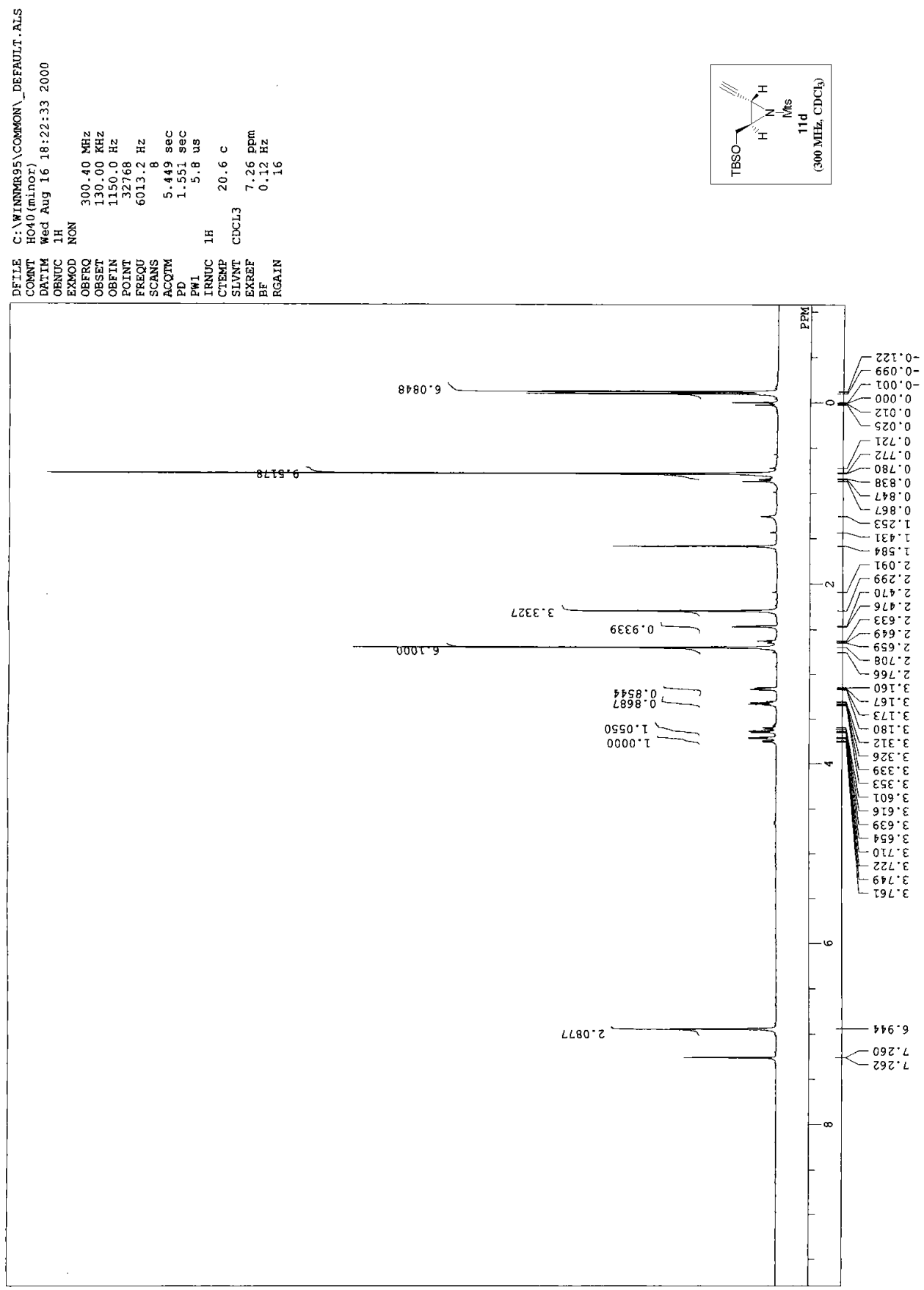
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
Ph
H
N
Ts
H
11c
(300 MHz, CDCl3)
PPM
0.000
2.9865
1.1546
1.0359
1.0517
1.0355
1.0000
5.5582
2.2624
1.9464


DFILE C:\WINNMR95\COMMON_DEFAULT.ALS
COMNT HO40(minor)
DATIM Wed Aug 16 18:22:33 2000
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6013.2 Hz
SCANS 8
ACQTM 5.449 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 16
TBSO
H
N
H
Ms
11d
(300 MHz, CDCl3)
PPM
6.0848
9.5178
3.3327
0.9339
6.1000
0.8687
0.8544
1.0550
1.0000
2.0877
7.262
7.260
6.944
3.761
3.749
3.722
3.710
3.654
3.639
3.616
3.601
3.539
3.353
3.339
3.326
3.312
3.180
3.173
3.167
3.160
2.766
2.708
2.659
2.649
2.633
2.476
2.470
2.299
2.091
1.584
1.431
1.253
0.867
0.847
0.838
0.780
0.772
0.721
0.025
0.012
0.000
-0.001
-0.099
-0.122