Supporting Information

Highly Enantioselective Nitroaldol Reactions Catalyzed by Copper(II) Complexes Derived from Substituted 2-(Pyridine-2-yl)imidazolidine-4-one Ligands

Illia Panov[†], Pavel Drabina[†*], Zdeňka Padělková[§], Petr Šimůnek[†] and Miloš Sedlák[†]

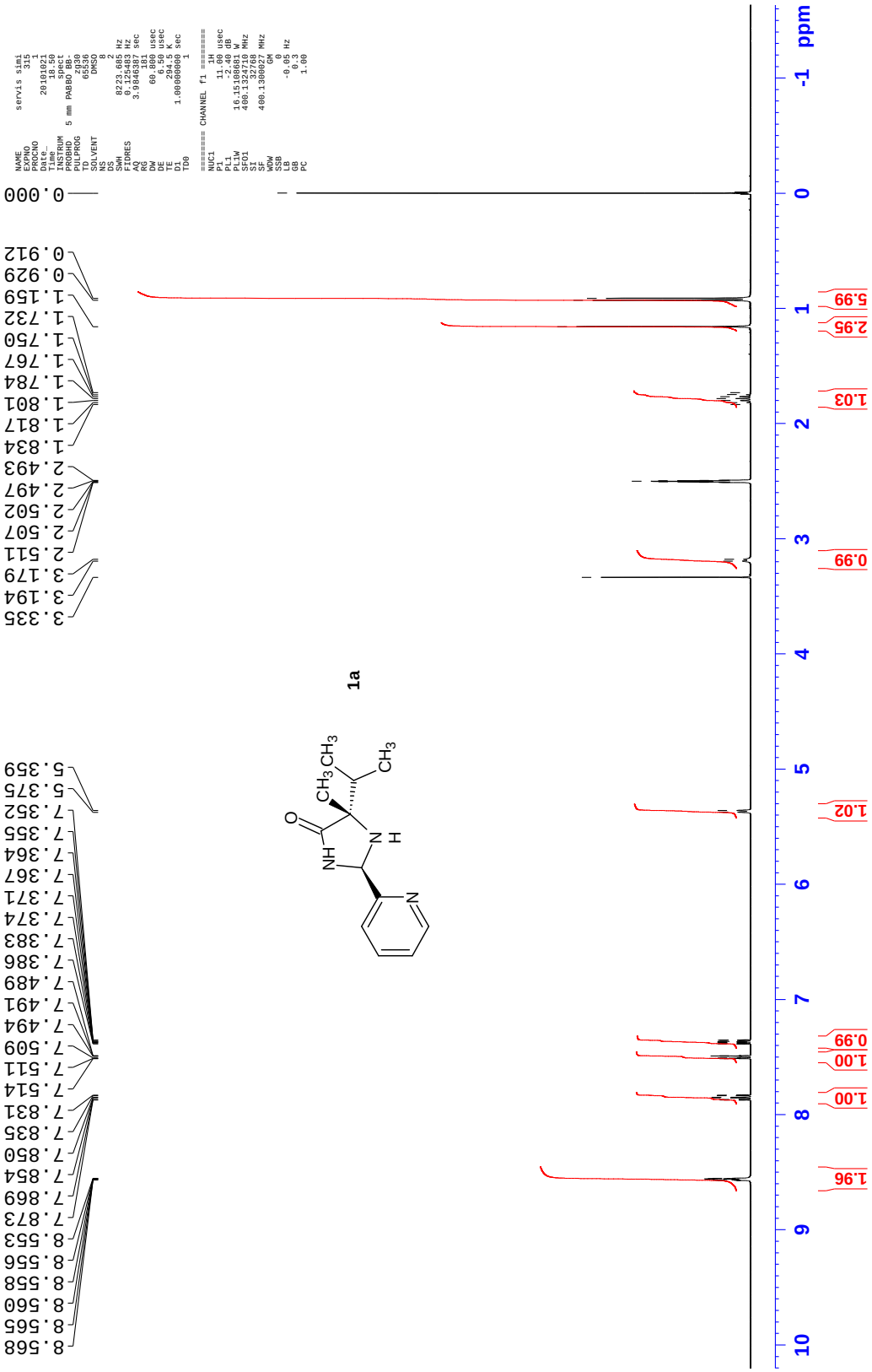
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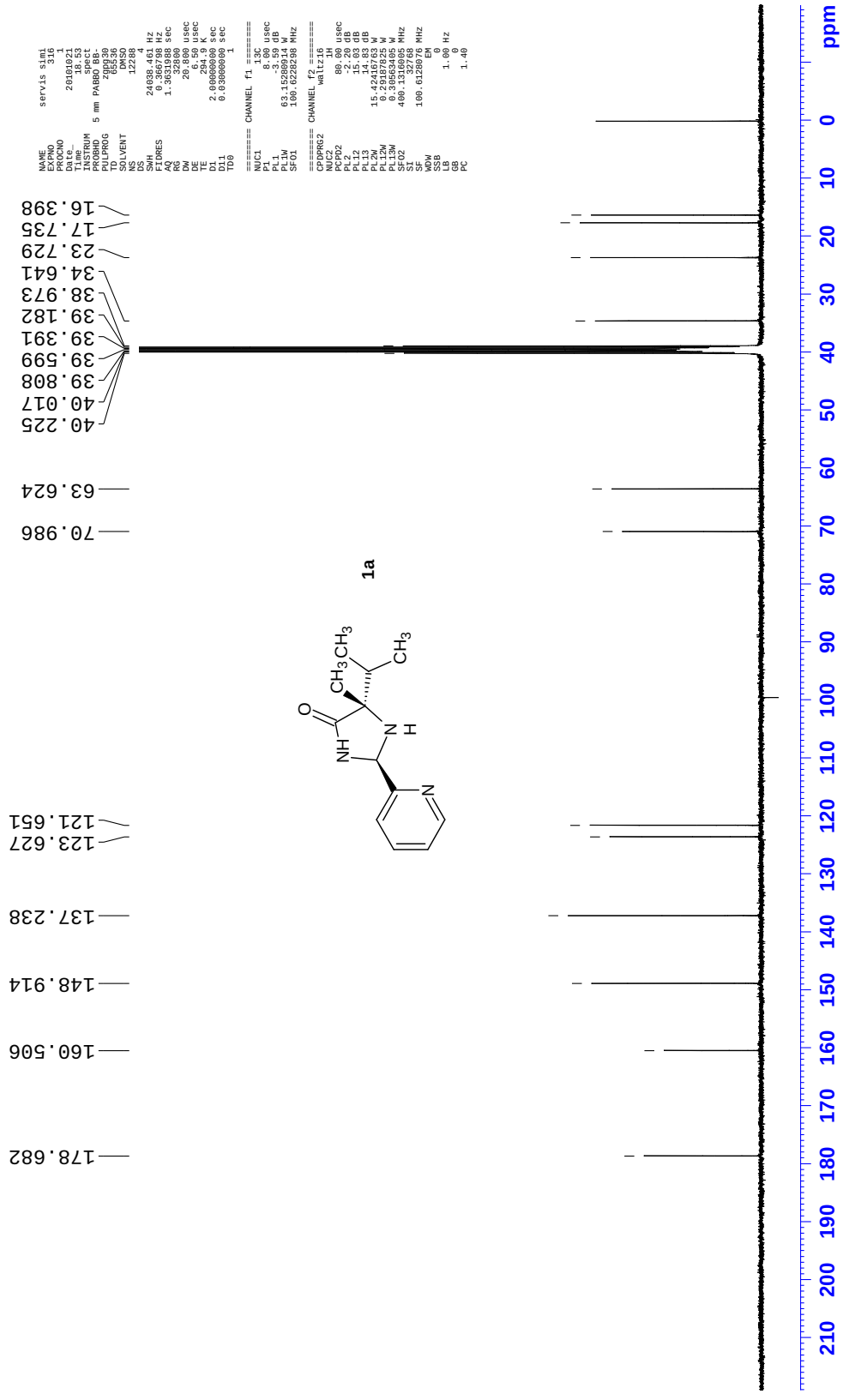
[§]*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

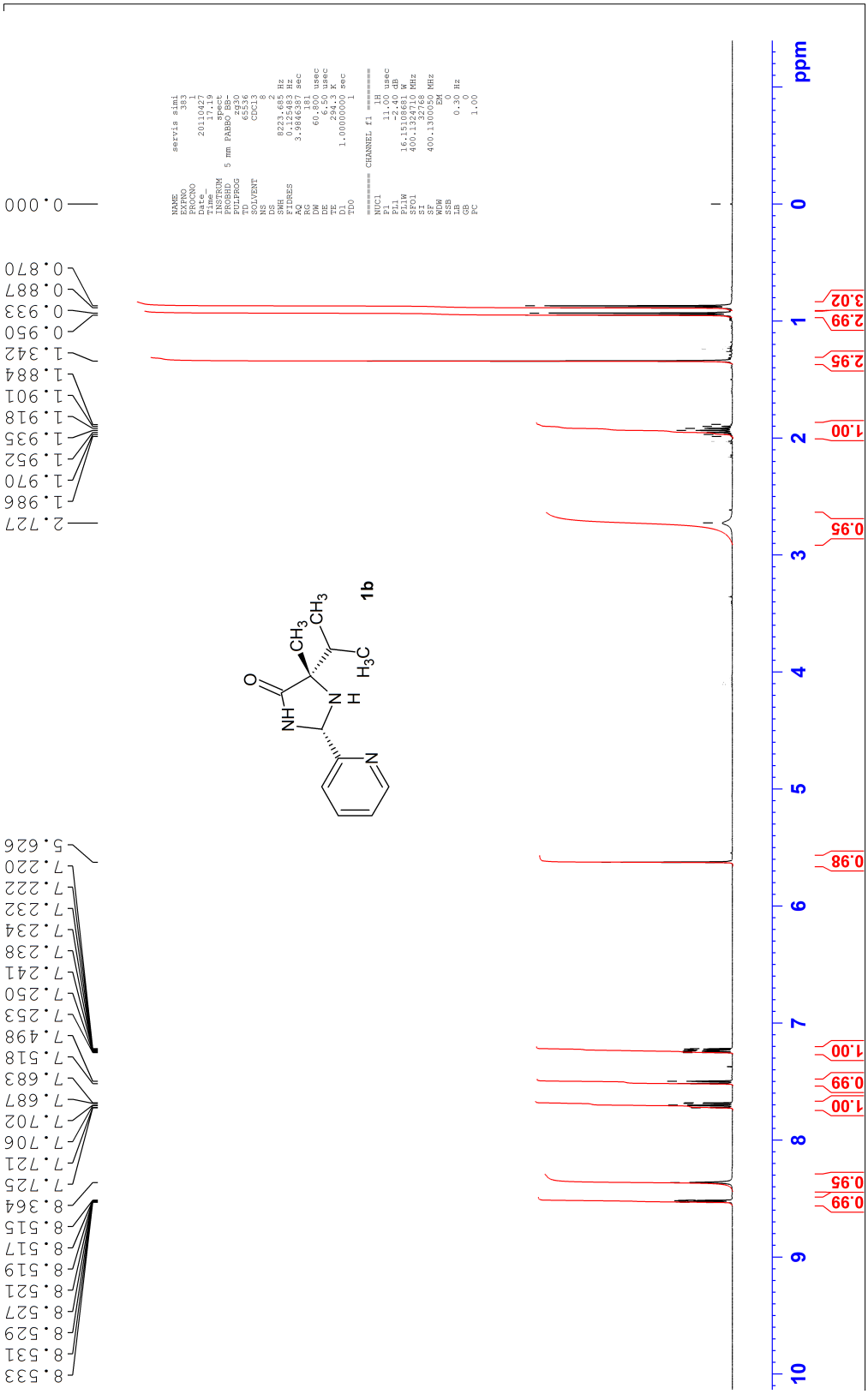
pavel.drabina@upce.cz

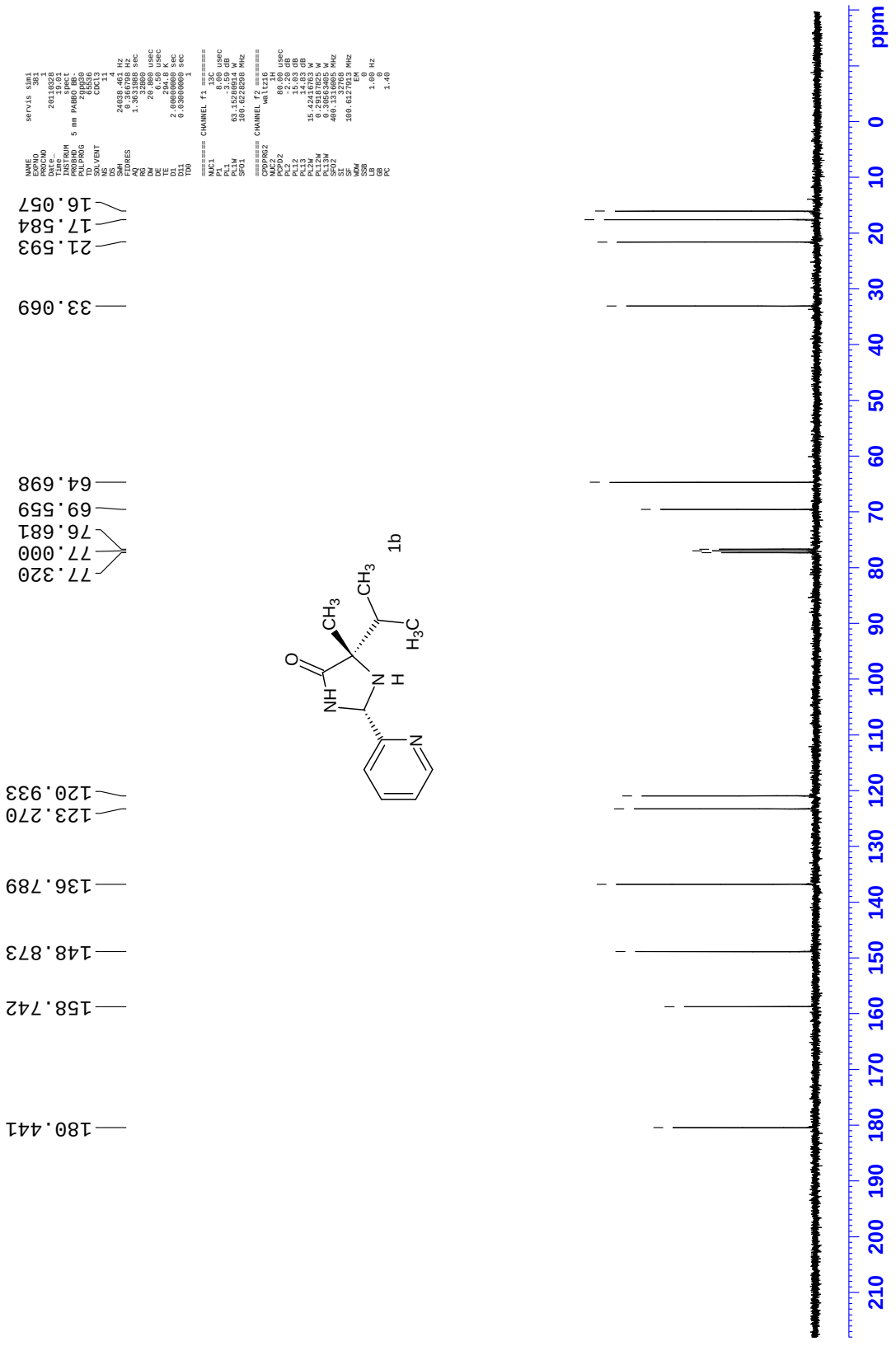
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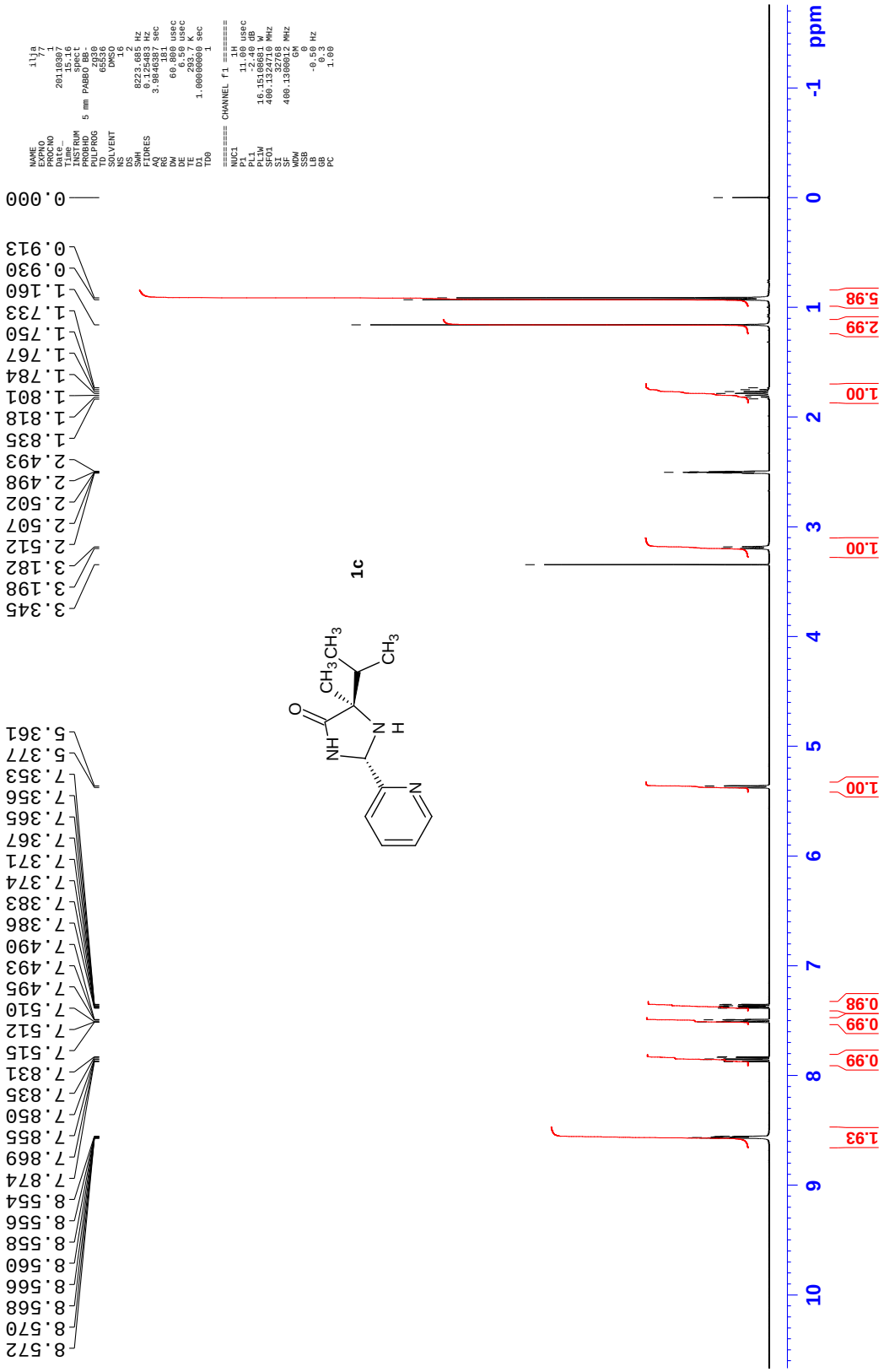
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^{1}H NMR 1D NOESY experiments (for **1b, 4a**, **4b**)…….....S22–S24
X-ray……..….. S25–S26
References……..….….S27

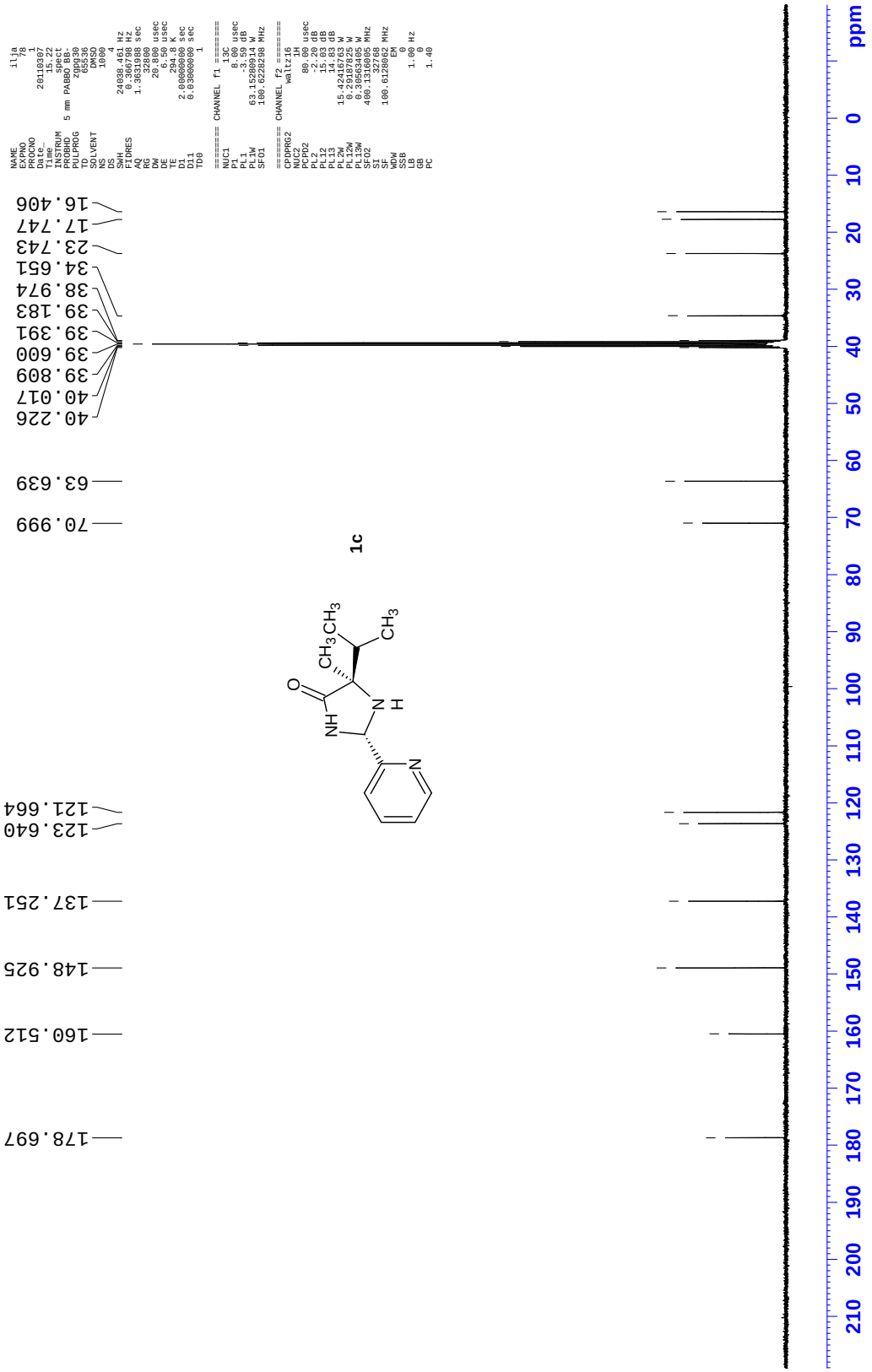

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6.50 usec
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32768
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0.3 Hz
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1a
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1.817
1.834
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2.497
2.502
2.507
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7.374
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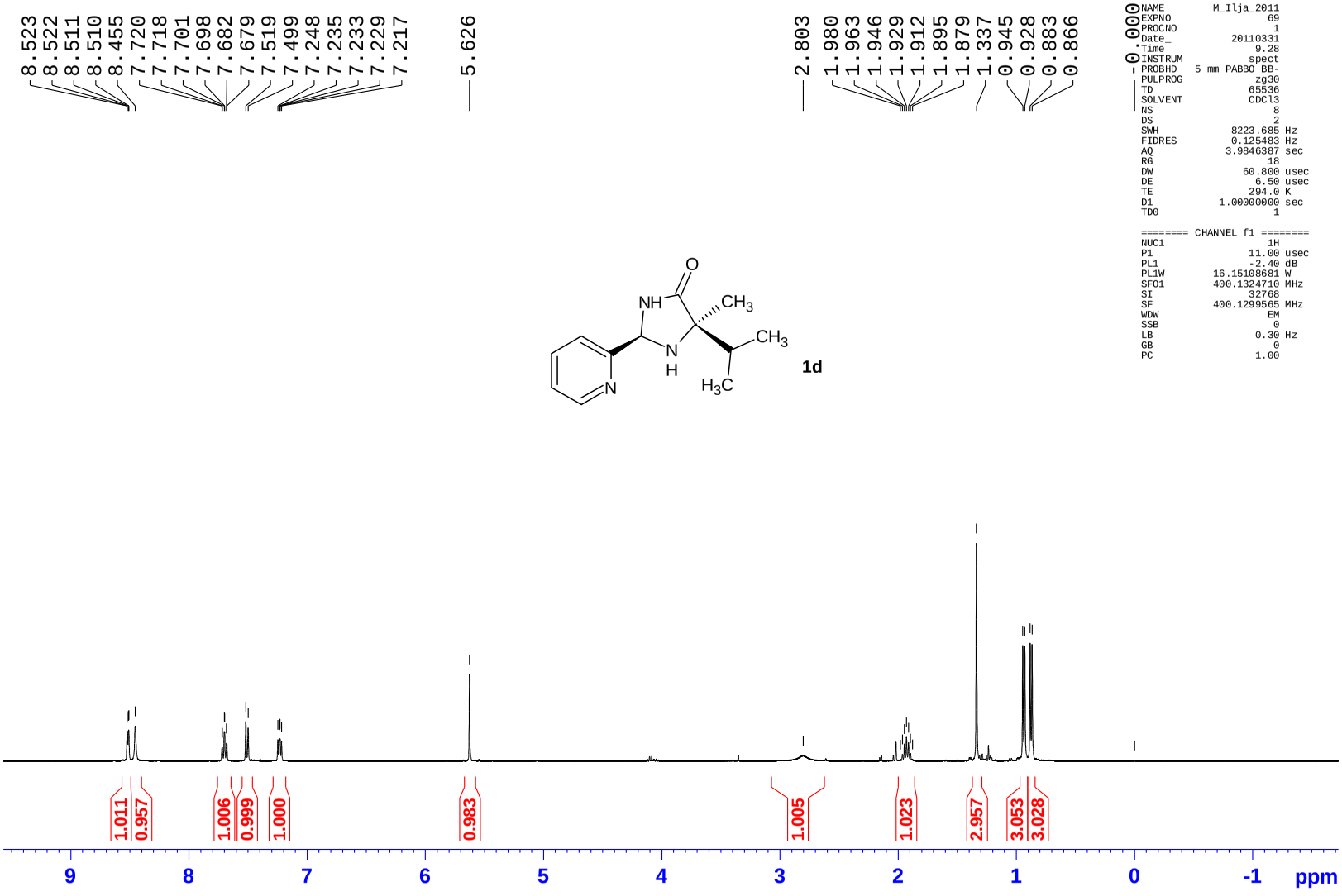

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NUC2 1H
PCPD2 80.00 usec
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PL12 15.60 dB
PL13 14.83 dB
PL2W 15.42416763 W
PL12W 0.29187825 W
PL13W 0.23654845 W
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LB 1.00 Hz
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PC 1.40
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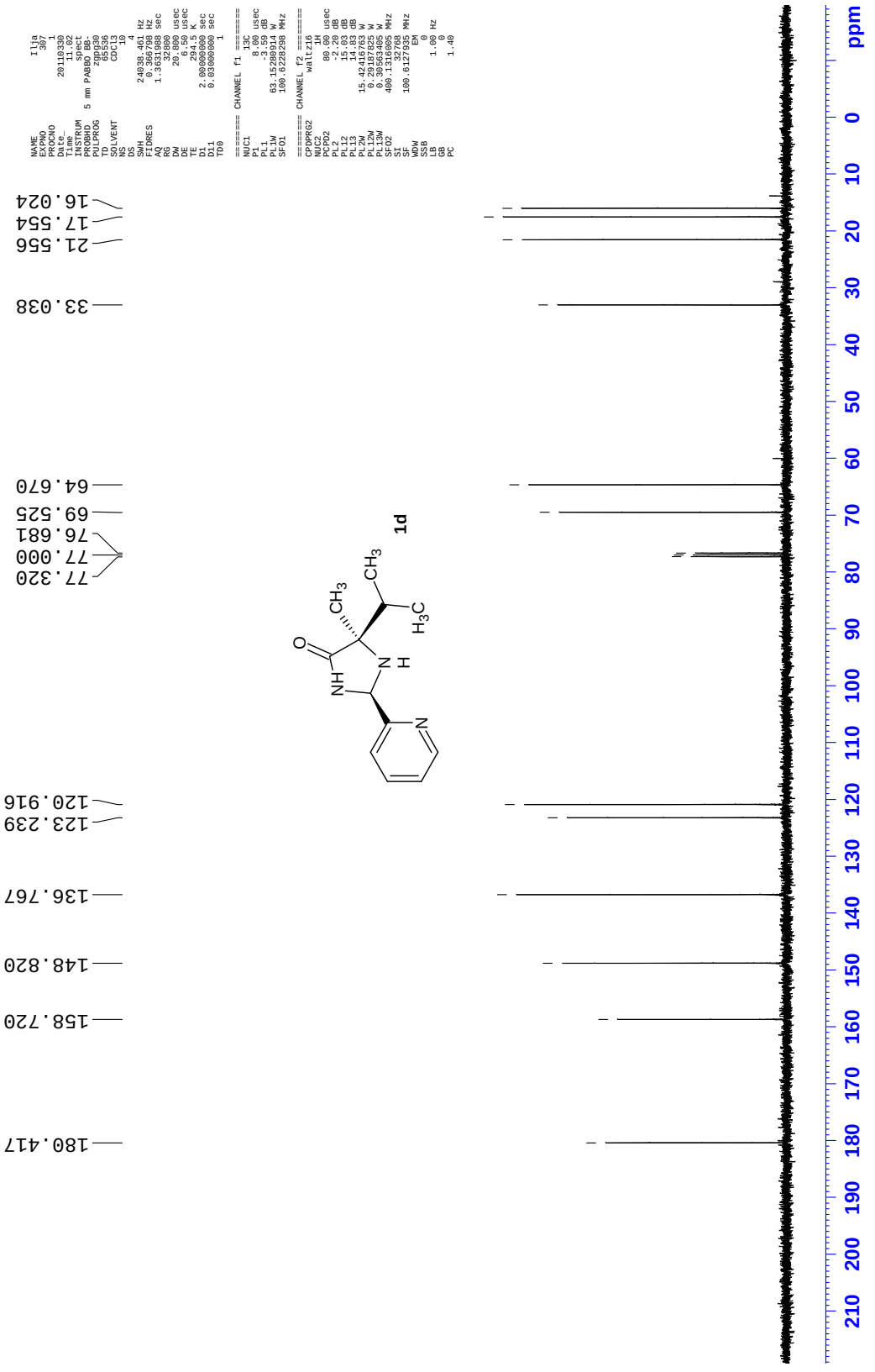

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7.222
7.232
7.234
7.238
7.241
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7.253
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7.683
7.687
7.702
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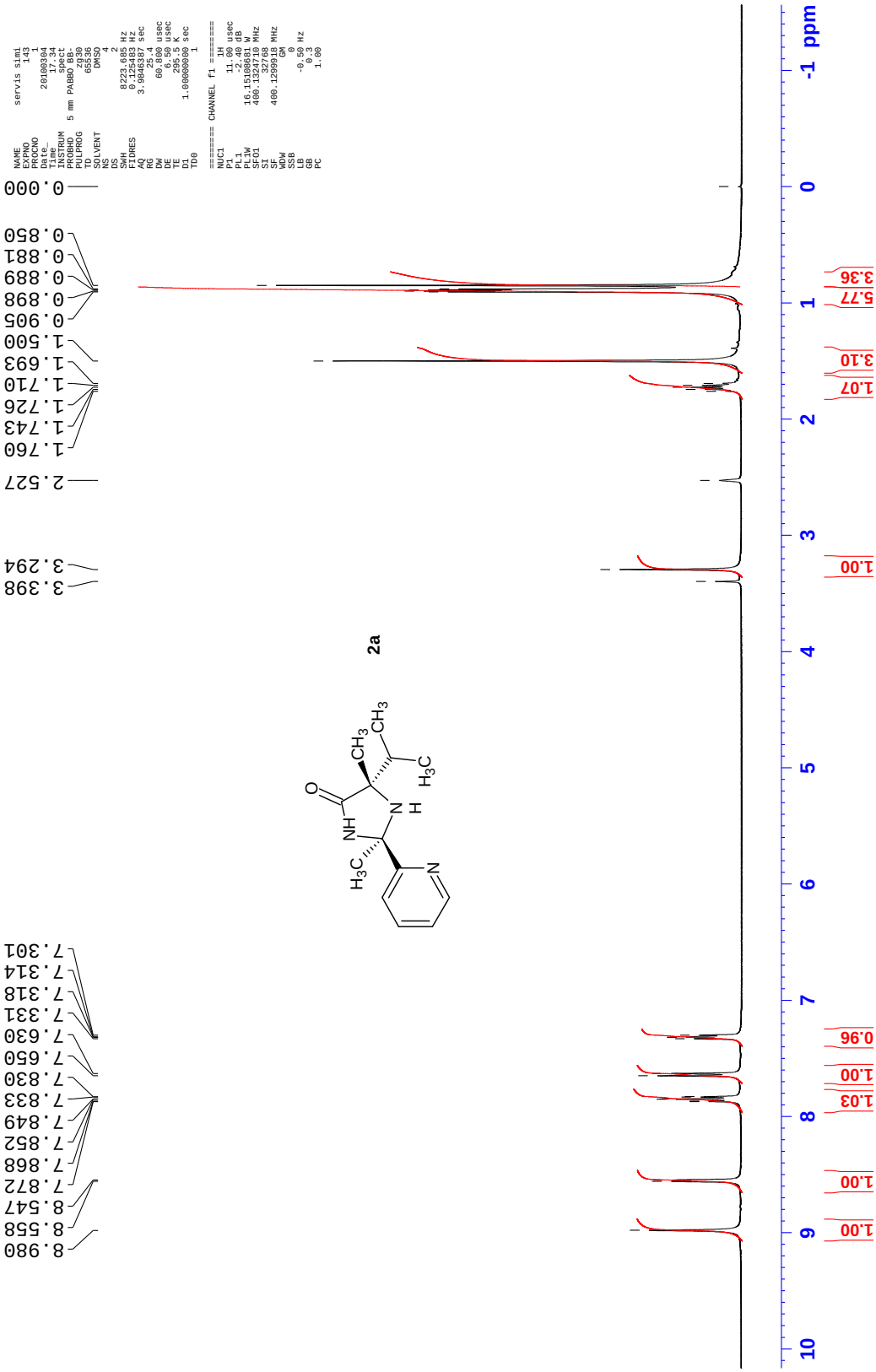

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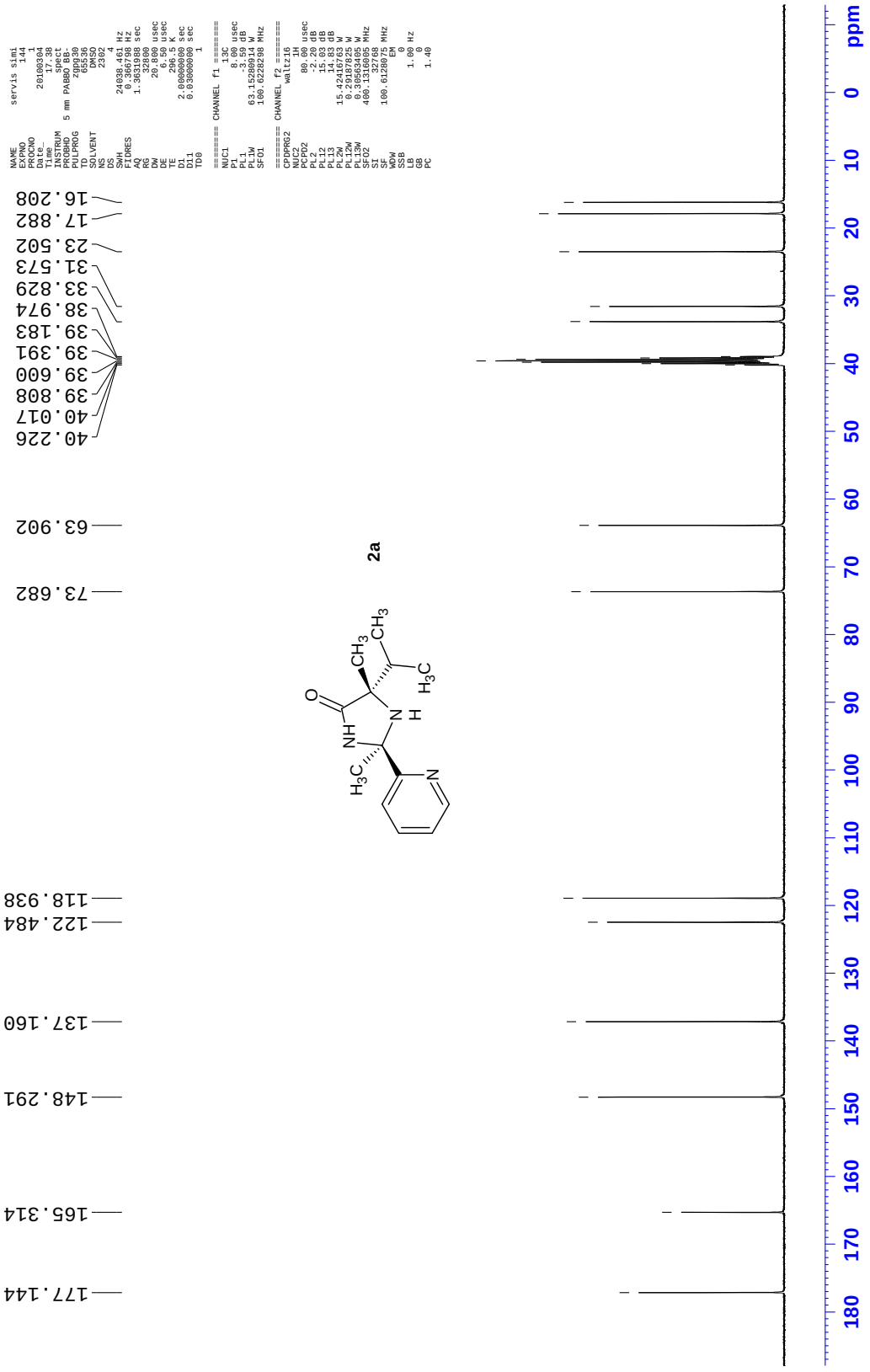

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2.498
2.502
2.507
2.512
3.182
3.198
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5.377
7.353
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7.374
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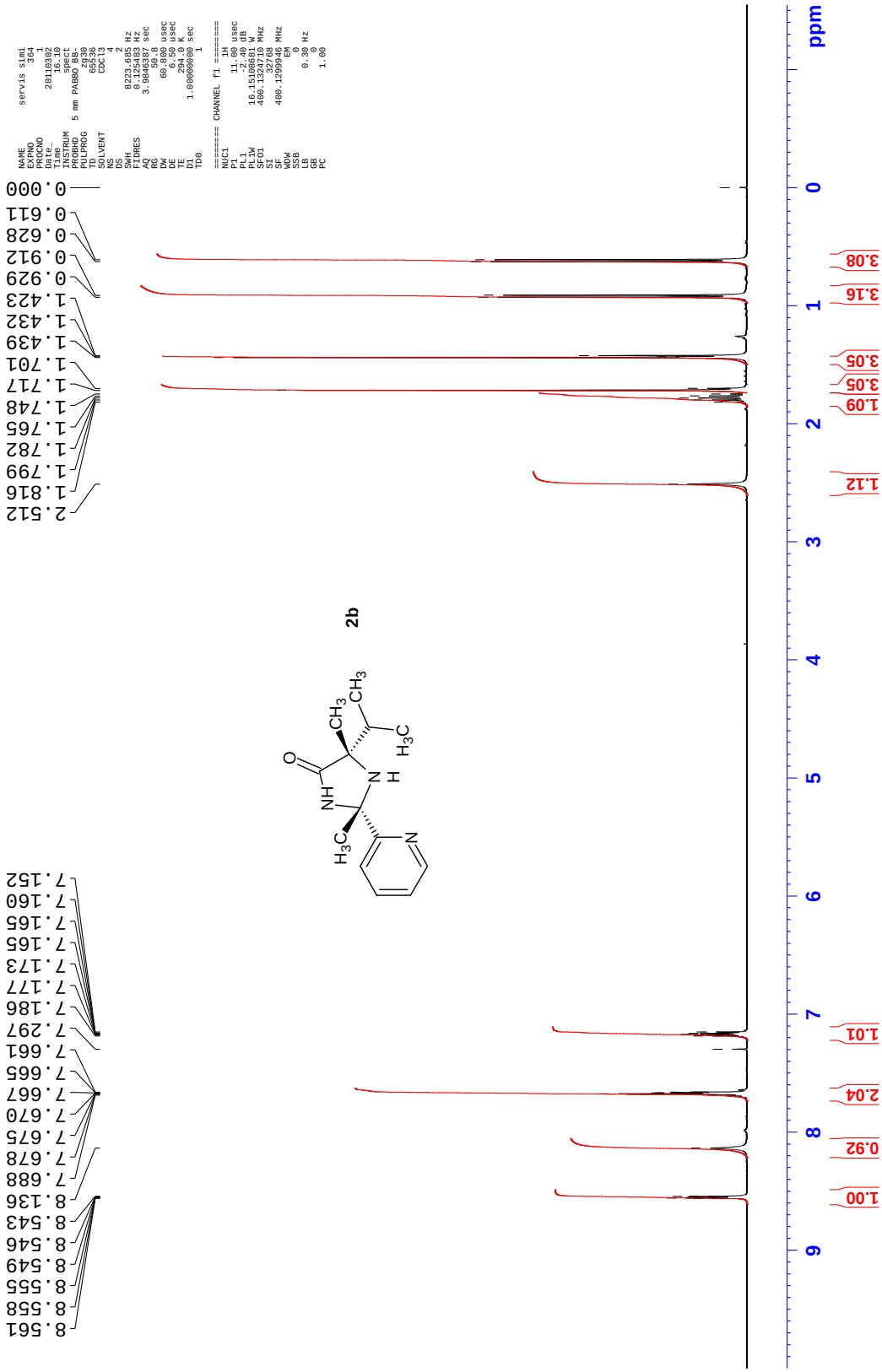

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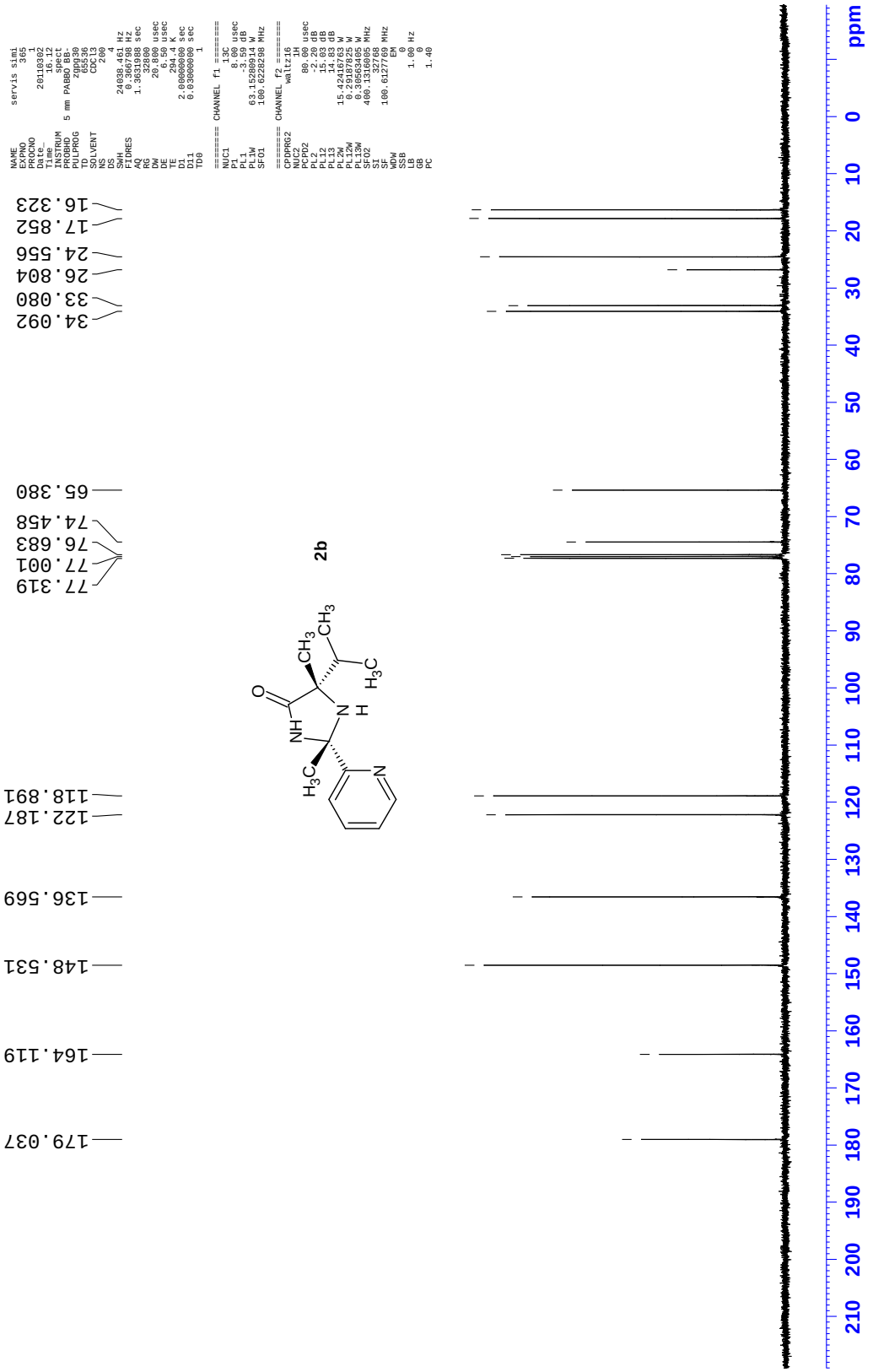

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7.248
7.235
7.233
7.229
7.217
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TE 294.0 K
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SI 32768
SF 400.1299565 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
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CH3
N
H
H3C
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1d
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0.999
1.000
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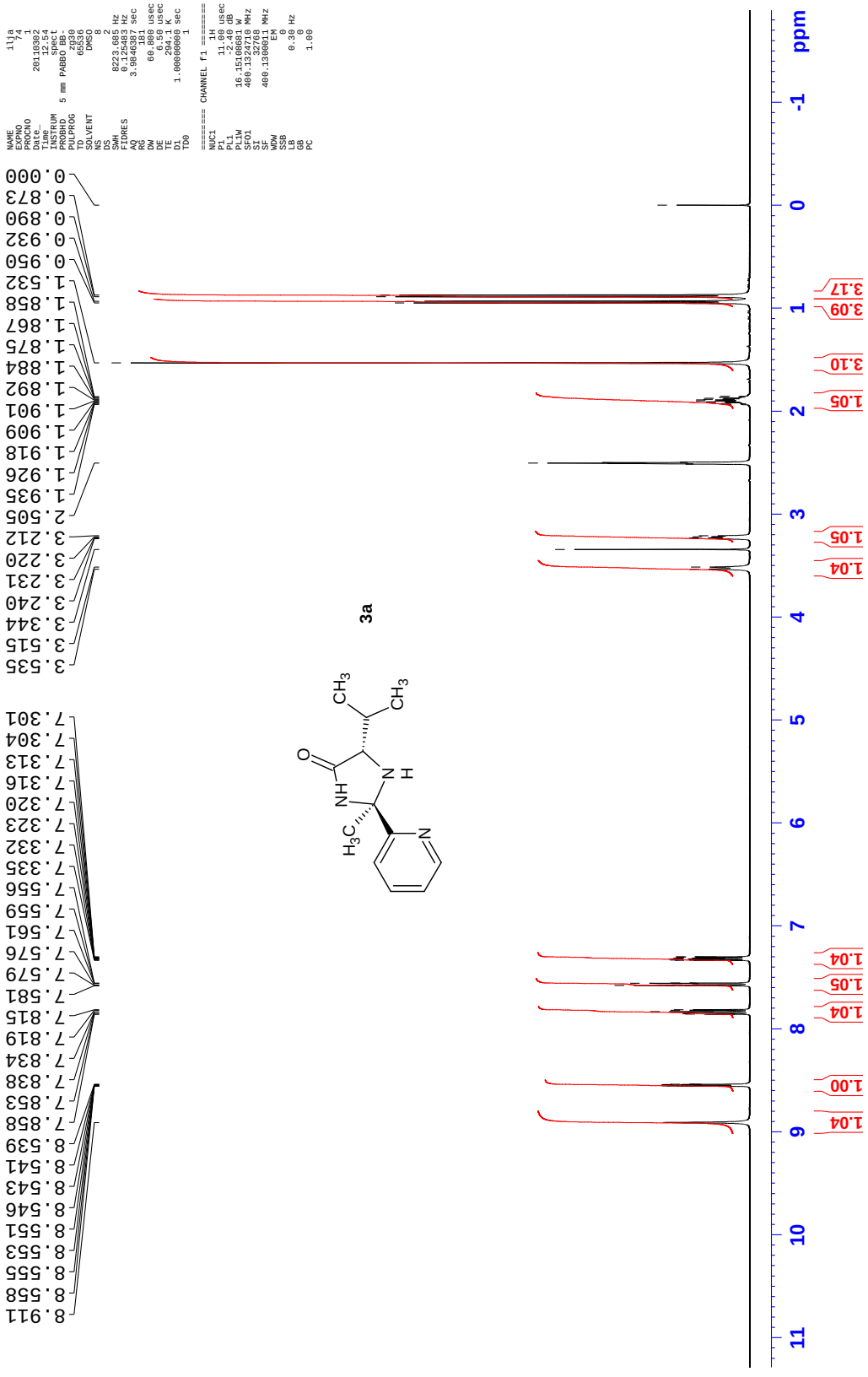

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AQ 1.3631988 sec
RG 228
DW 20.800 usec
DE 6.50 usec
TE 294.5 K
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D11 0.03000000 sec
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NUC1 13C
P1 8.00 usec
PL1 -3.59 dB
PL1W 62.15200514 W
SFO1 100.6228298 MHz
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NUC2 1H
PCPD2 80.00 usec
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PL12 15.03 dB
PL13 14.65 dB
PL2W 15.42416763 W
PL12W 0.29187825 W
PL13W 0.25514695 W
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SI 32768
SF 100.6127935 MHz
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SSB 0
LB 1.00 Hz
GB 0
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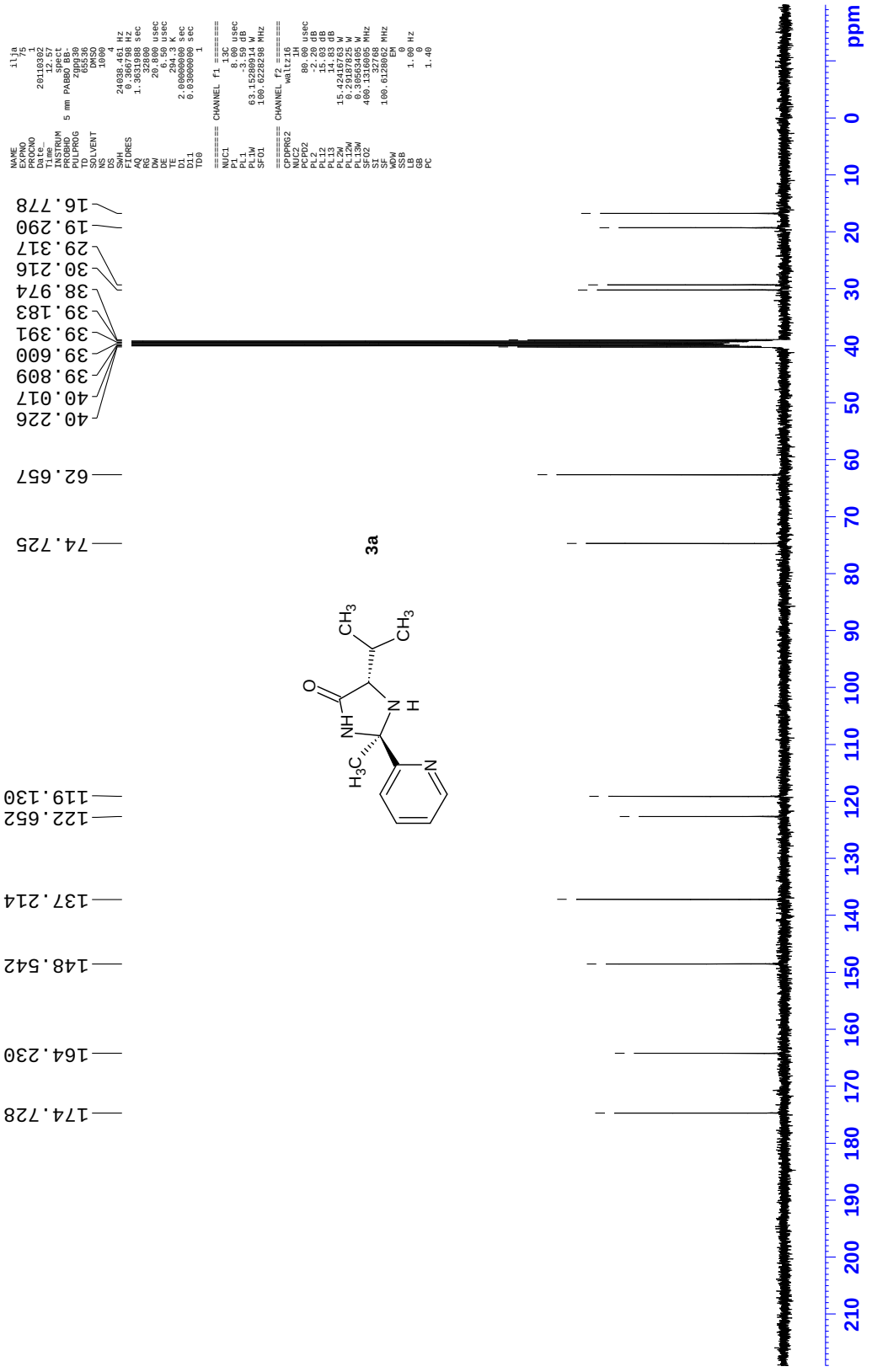

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3.398
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7.314
7.318
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7.830
7.833
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7.852
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1.00
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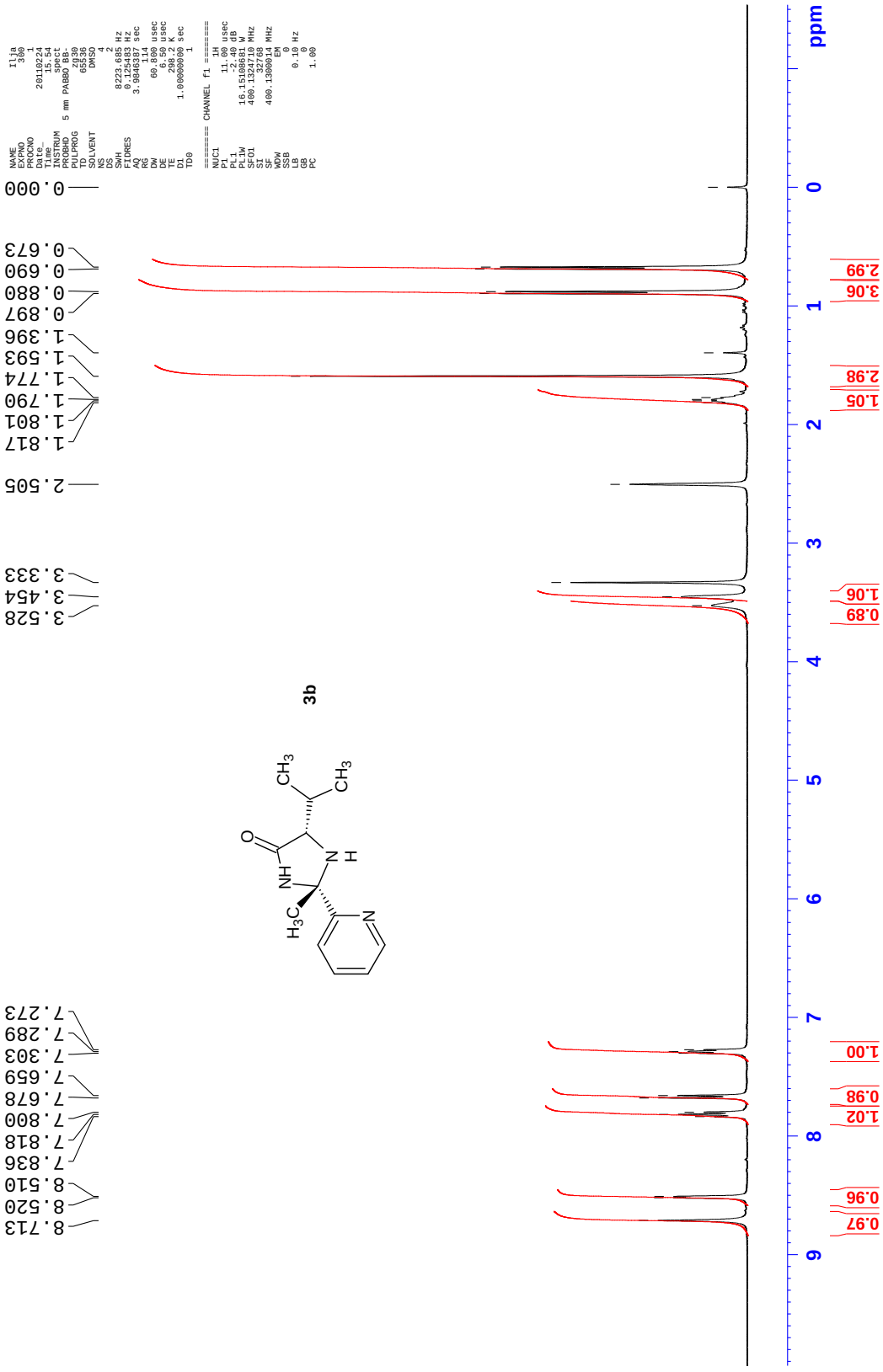

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DE 6.50 usec
TE 296.5 K
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D11 0.03000000 sec
TD0 1
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NUC1 1H
P1 8.00 usec
PL1 -3.59 dB
PL1W 63.15280914 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.20 dB
PL12 15.03 dB
PL13 14.03 dB
PL2W 15.42416763 W
PL12W 0.29187825 W
PL13W 0.30563485 W
SFO2 400.1324768 MHz
SI 32768
SF 100.6128275 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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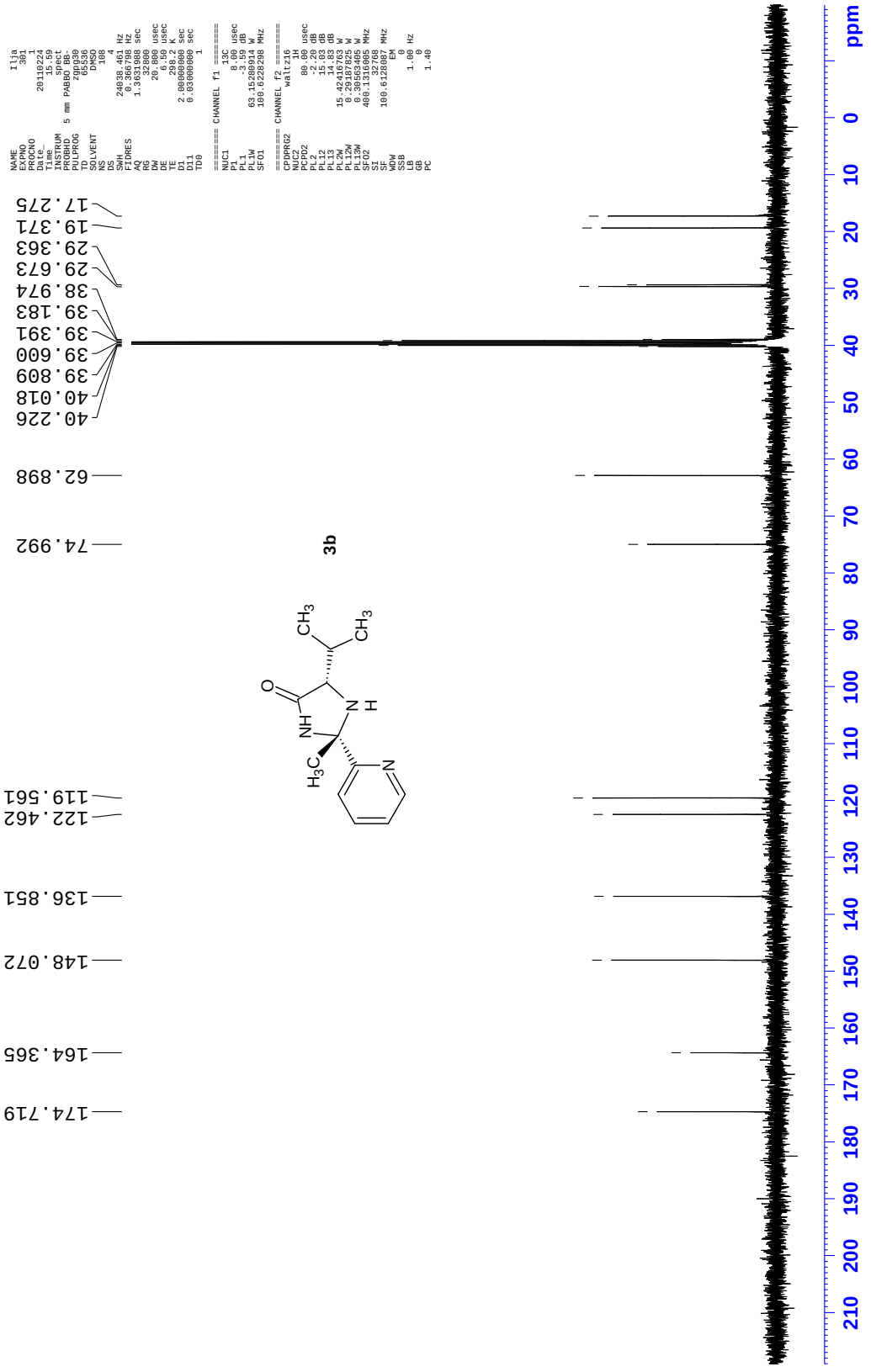

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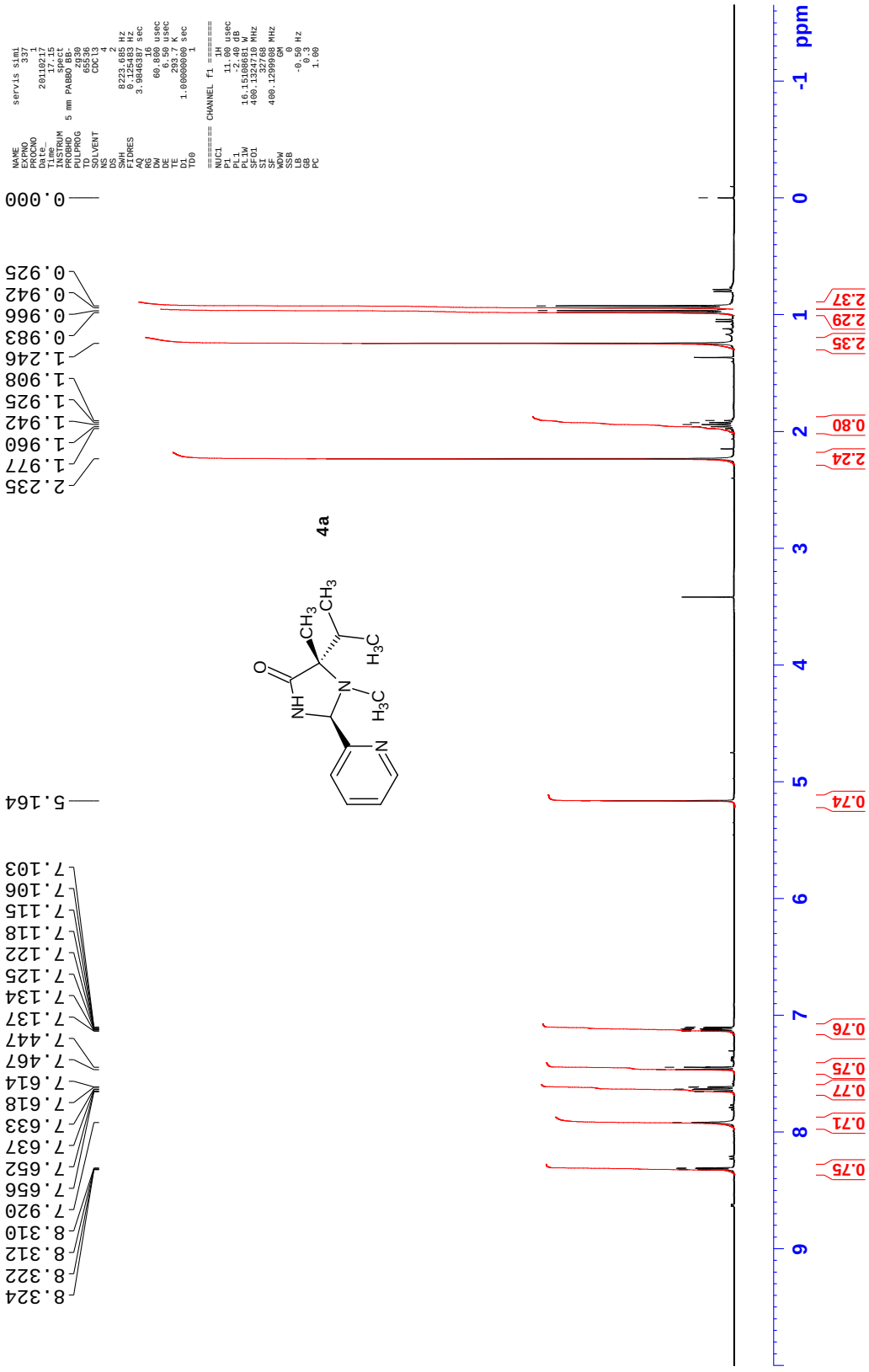

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DE 6.50 usec
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D11 0.03000000 sec
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NUC2 1H
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PL12 15.03 dB
PL13 14.03 dB
PL2W 15.42416763 W
PL12W 0.29187825 W
PL13W 0.30563405 W
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SI 32768
SF 100.6127769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
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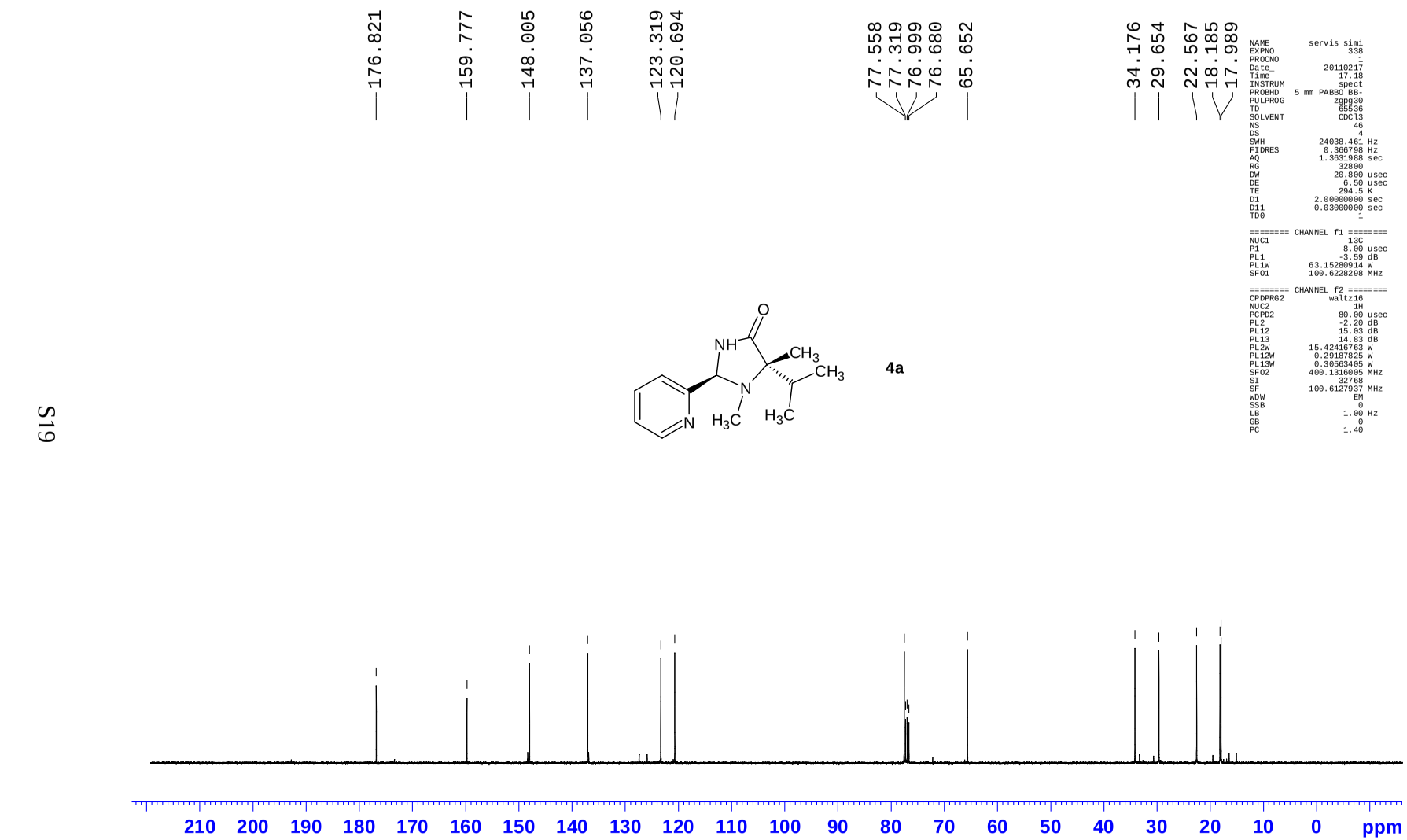

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3.535
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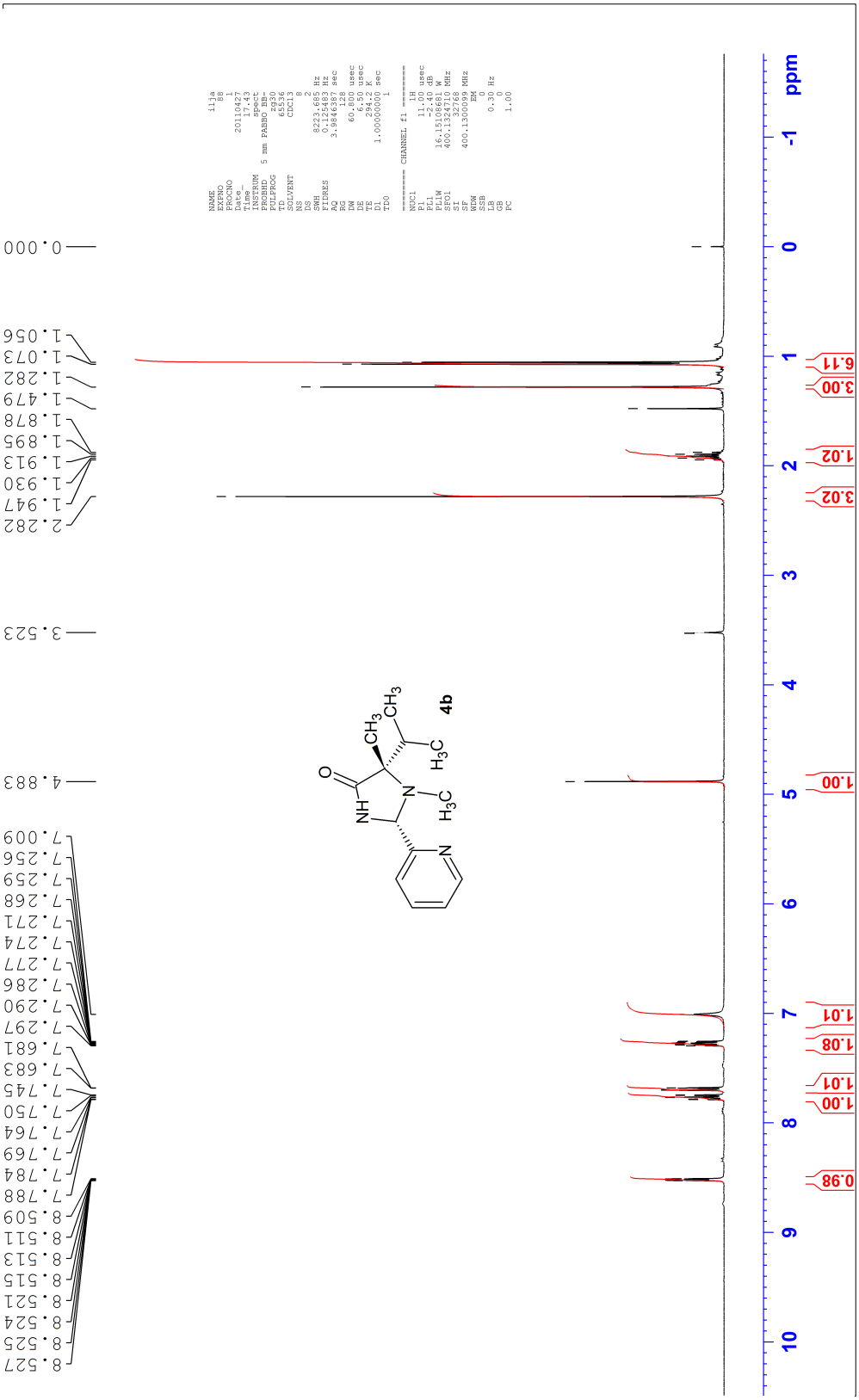

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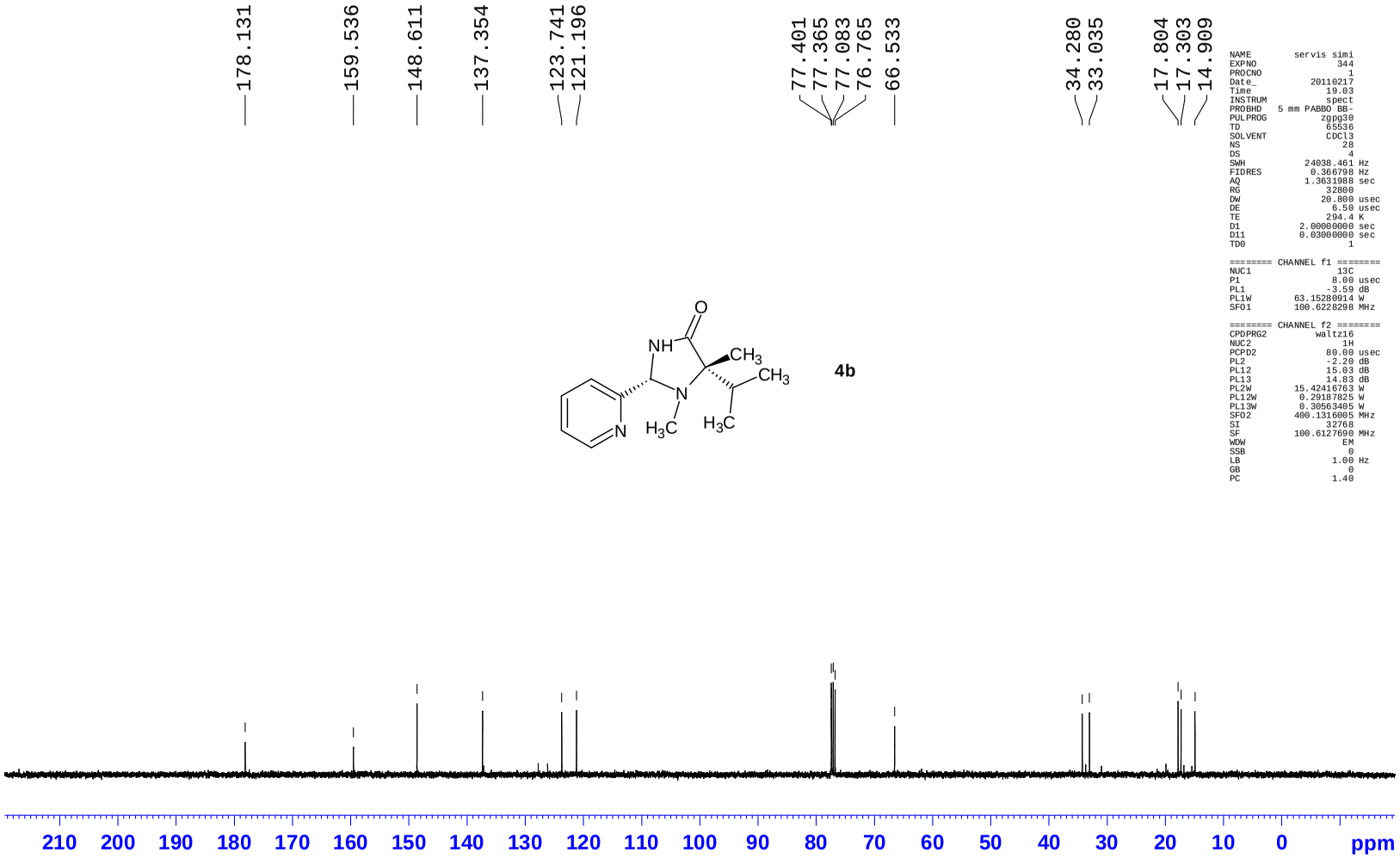

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7.289
7.303
7.659
7.678
7.800
7.818
7.836
8.510
8.520
8.713
2.99
3.06
2.98
1.05
1.06
0.89
1.00
1.02
0.98
0.97
0.96


17.275
19.371
29.363
29.673
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39.183
39.391
39.600
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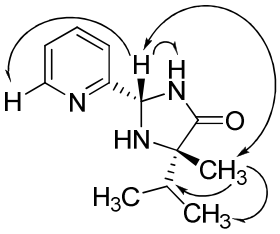

4a
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77.319
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22.567
18.185
17.989
NAME servis simi
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PROCNO 1
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FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 32800
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DE 6.50 usec
TE 294.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 -3.59 dB
PL1W 63.15280914 W
SFO1 100.6228298 MHz
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CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.20 dB
PL12 15.03 dB
PL13 14.83 dB
PL2W 15.42416763 W
PL12W 0.29187825 W
PL13W 0.30563405 W
SFO2 400.1316005 MHz
SI 32768
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WDW EM
SSB 0
LB 1.00 Hz
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PC 1.40
O
NH
CH3
CH3
N
H3C
H3C
N
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

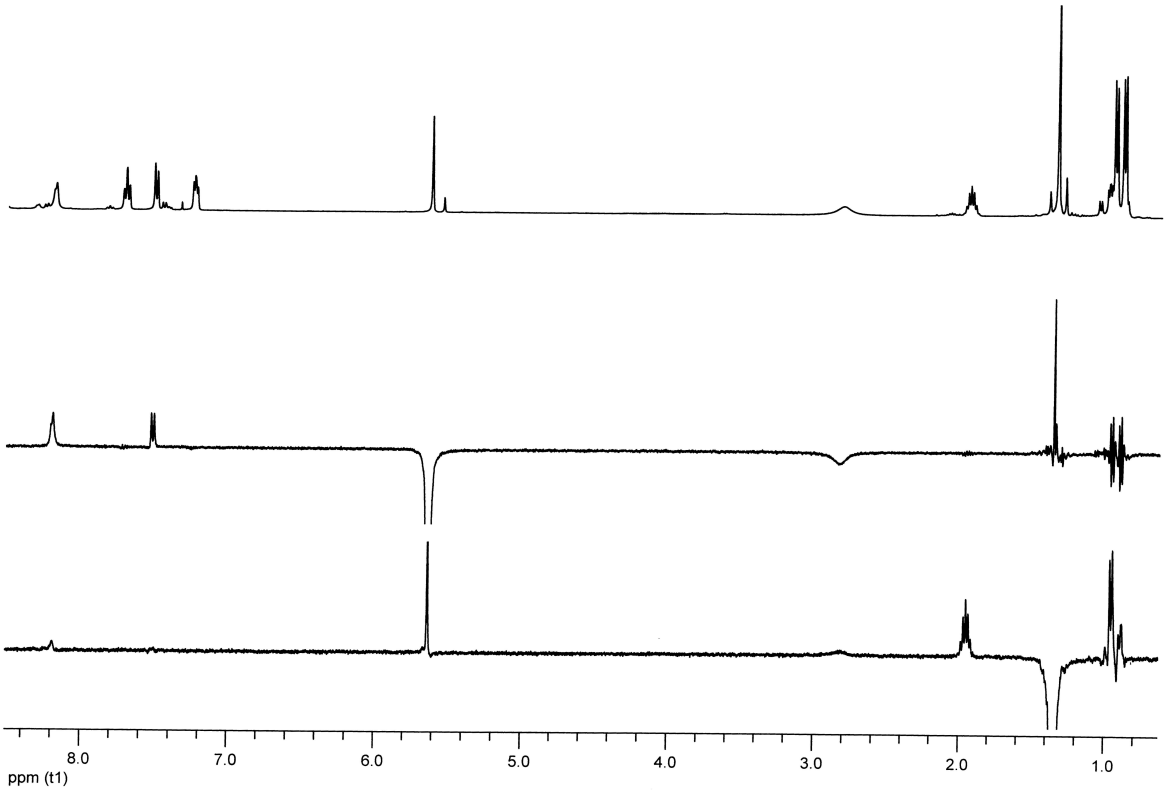

4b
NH
O
N
N
CH3
CH3
H3C
H3C
ppm
10
9
8
7
6
5
4
3
2
1
0
-1
6.11
3.00
1.02
3.02
1.00
1.01
1.08
1.01
1.00
0.98
0.000
1.056
1.073
1.282
1.479
1.878
1.895
1.913
1.930
1.947
2.282
3.523
4.883
7.009
7.256
7.259
7.268
7.271
7.274
7.277
7.286
7.290
7.297
7.681
7.683
7.745
7.750
7.764
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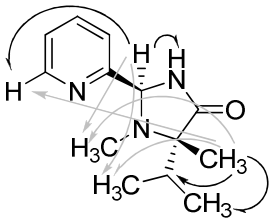

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33.035
17.804
17.303
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NAME servis simi
EXPNO 344
PROCNO 1
Date_ 20110217
Time 19.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
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DS 4
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FIDRES 0.366798 Hz
AQ 1.3631988 sec
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DE 6.50 usec
TE 294.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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P1 8.00 usec
PL1 -3.59 dB
PL1W 63.15280914 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
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PCPD2 80.00 usec
PL2 -2.20 dB
PL12 15.03 dB
PL13 14.83 dB
PL2W 15.42416763 W
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PL13W 0.30563405 W
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SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
NH
CH3
CH3
N
H3C
H3C
N
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H NMR 1D NOESY experiments

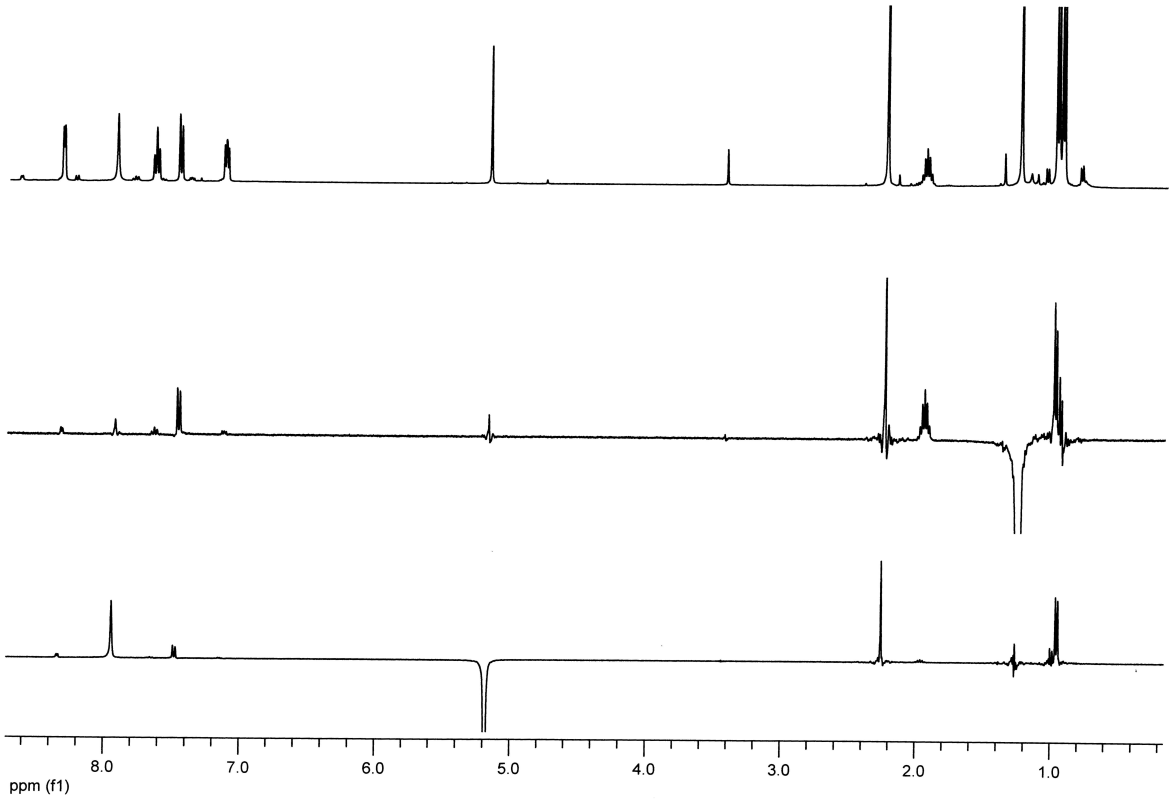


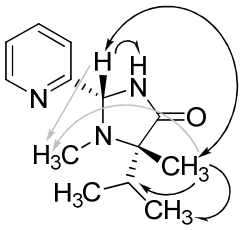
1b(2*S*,5*S*)



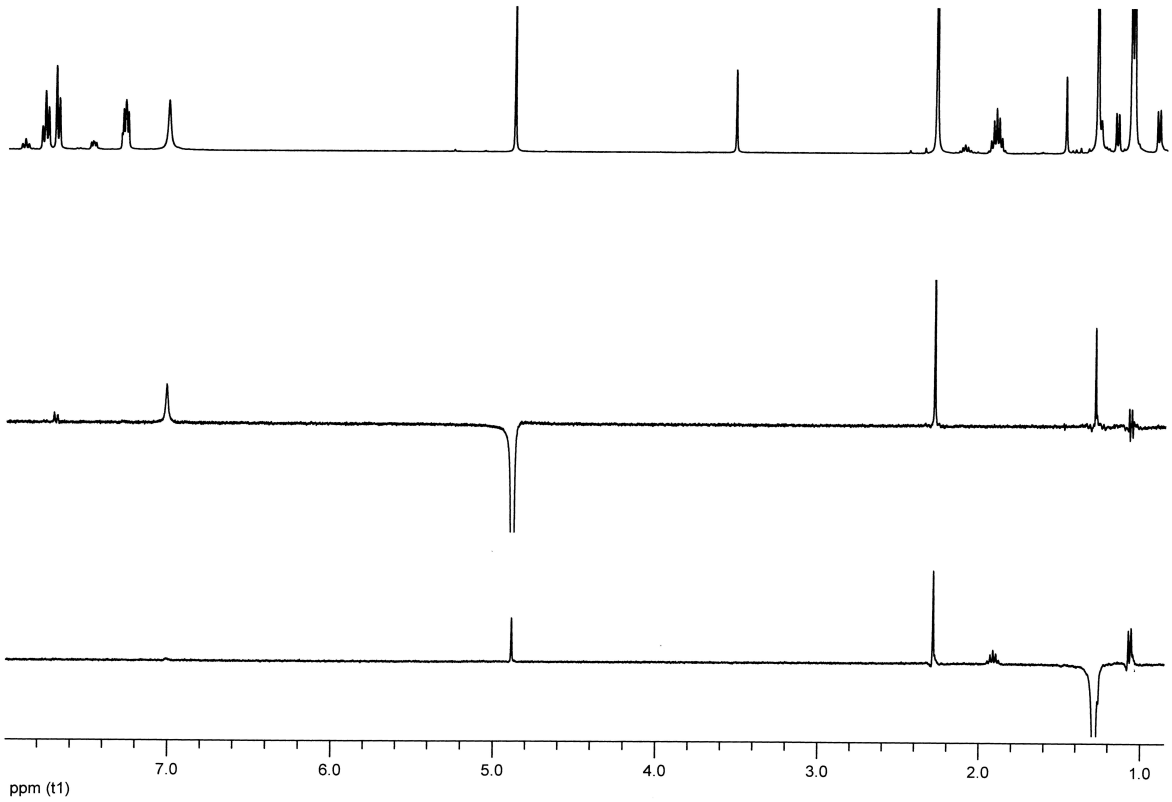


4a(2*S*,5*S*)





4b(2*R*,5*S*)



X-ray

The X-ray data (Table) for crystals of all compounds were obtained at 150K with MoK_α radiation (λ = 0.71073 Å) by the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[1] The absorption was corrected by integration methods.[2] Structures were solved by direct methods (Sir92)[3] and refined by full matrix least-square based on F^2 (SHELXL97).[4] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C–H = 0.96, 0.97, 0.93, 0.86 and 0.82 Å for methyl, methylene, hydrogen atoms in aromatic rings, N–H and O–H groups, respectively. Hydrogen atoms in coordinated water molecule were placed according to a difference Fourier map maxima location.

There are disordered non-coordinated solvents (toluene and water) in small, porous and weakly diffracting crystal of **5a**. Attempts were made to model this disorder or split maxima into two or three positions, but were unsuccessful. PLATON/SQUEZZE[5] program was used to correct the data for the presence of disordered solvent. A potential solvent volume of 886 $Å^3$ was found. 251 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be four additional molecules of toluene and four molecules of water per unit cell which results in 240 electrons per unit cell.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail:

deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk). CCDC deposition numbers: 813559; 813560; 813561.

Table

Compound	**1a**	**5a**	**6a**	**7a**
Formula	$C_{12}H_{17}N_3O$	$C_{30}H_{43}Cu_2N_6O_9$	$C_{17}H_{29}CuN_3O_7$	$C_{16}H_{25}CuN_3O_6$
Formula weight	219.29	868.95	450.97	418.93
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
Colour	colourless	blue	blue	blue
Space group	P 21 21 2	P 21	P 21	P 1
a/Å	11.2140(5)	13.683(1)	7.3920(3)	6.9140(3)
b/Å	11.4761(6)	13.855(1)	17.8921(13)	7.7171(5)
c/Å	9.3960(5)	21.7621(9)	8.0290(8)	9.6160(3)
α/°	90	90	90	89.630(4)
β/°	90	102.485(6)	101.047(5)	71.921(3)
γ/°	90	90	90	87.634(4)
V/Å^3	1209.20(11)	4028.0(6)	1042.22(14)	487.31(4)
D/g·cm^{-3}	1.205	1.433	1.437	1.428
Z	4	4	2	1
F(000)	472	2004	474	219
Θ range (°)	1–26.5	1.62–26	1–27.3	3.45–27.5
Reflections measured	8538	35423	13235	8921
Unique reflections	1542	13017	4461	2222
No. of data/restraint/param.	1542/0/147	13017/1/847	4461/1/258	4172/3/235
Goodness of fit, F	1.142	1.090	1.051	1.086
R_1, wR_2 [$I > 2\sigma(I)$]	0.0959, 0.1798	0.0549, 0.1225	0.0536, 0.1321	0.0279, 0.0706
R_1, wR_2 (all data)	0.1099, 0.1896	0.0702, 0.1322	0.0624, 0.1415	0.0282, 0.0710
Larges diff. peak (e Å^{-3})	–0.275 to 0.283	–0.586 to 0.510	–1.083 to 0.735	–0.661 to 0.338

References

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(2) Coppens, P.; In: Ahmed, F. R.; Hall, S. R.; Huber, C. P. Eds.; *Crystallographic Computing*; Munksgaard: Copenhagen, 1970, 255–270.

(3) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(4) Sheldrick, G. M.; SHELXL-97; University of Göttingen: Göttingen, 1997.

(5) Spek, A. L. *Acta Crystalllogr., Sect. A* **1990**, *46*, C34.