Cover Page for Supporting Information

Title:

One-pot Synthesis and Unpredicted Hydrogen Bonds of the Guanidinium Triflates from Readily Available Amines, Carbodiimides and $Zn(OTf)_2$

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Affiliations:

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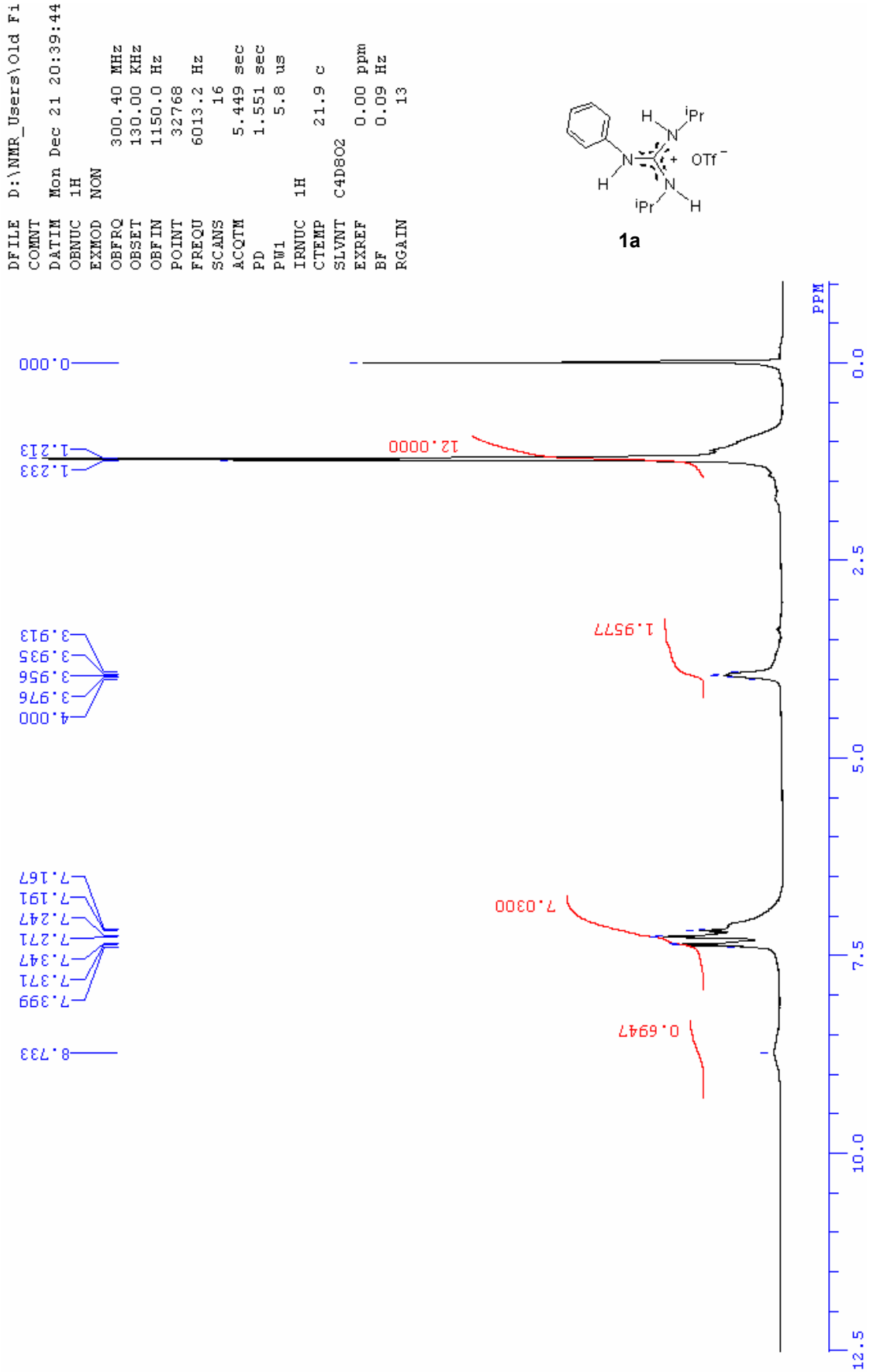
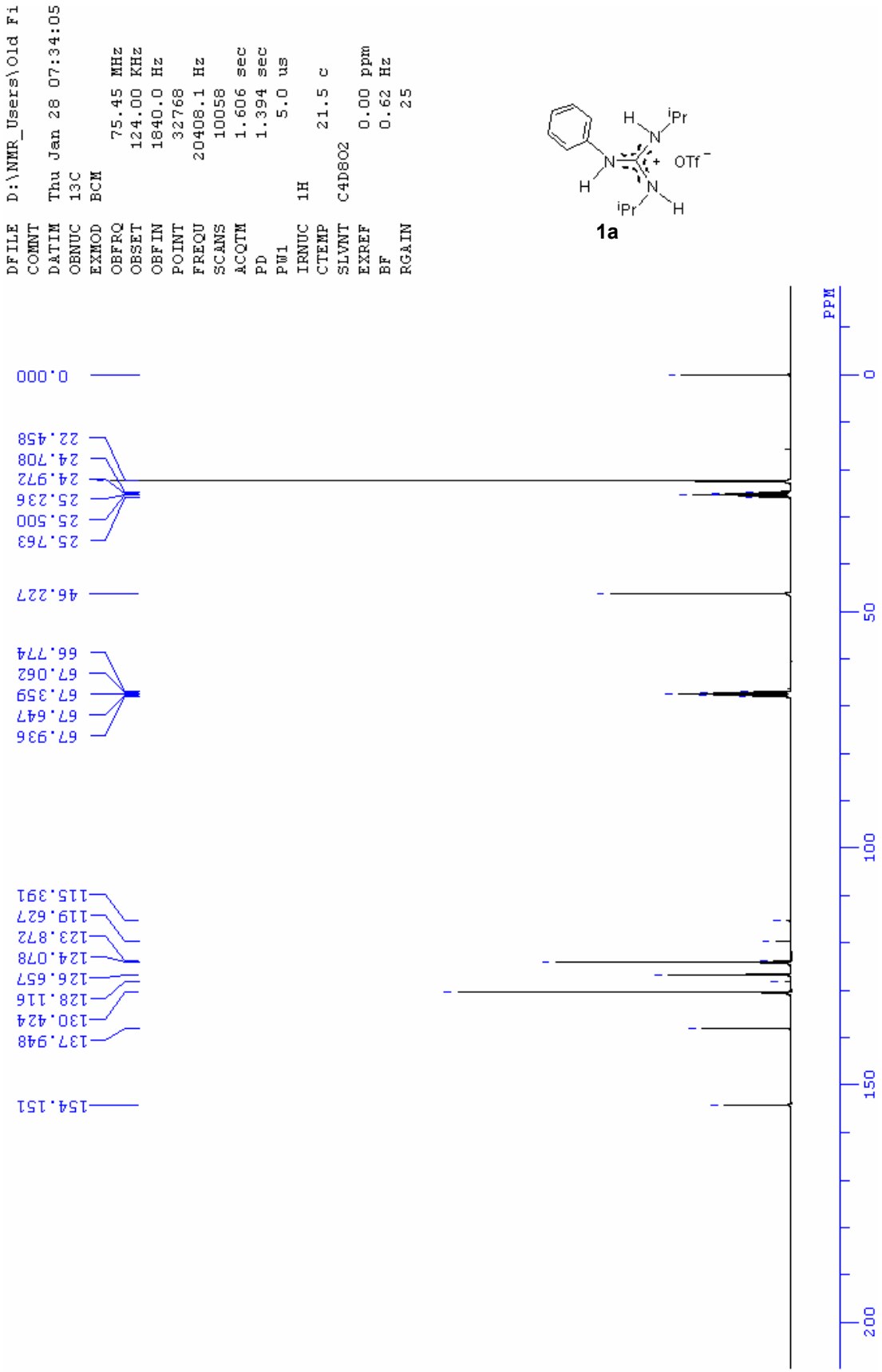
Contents:

1) Copies of ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

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H
N
iPr
N
H
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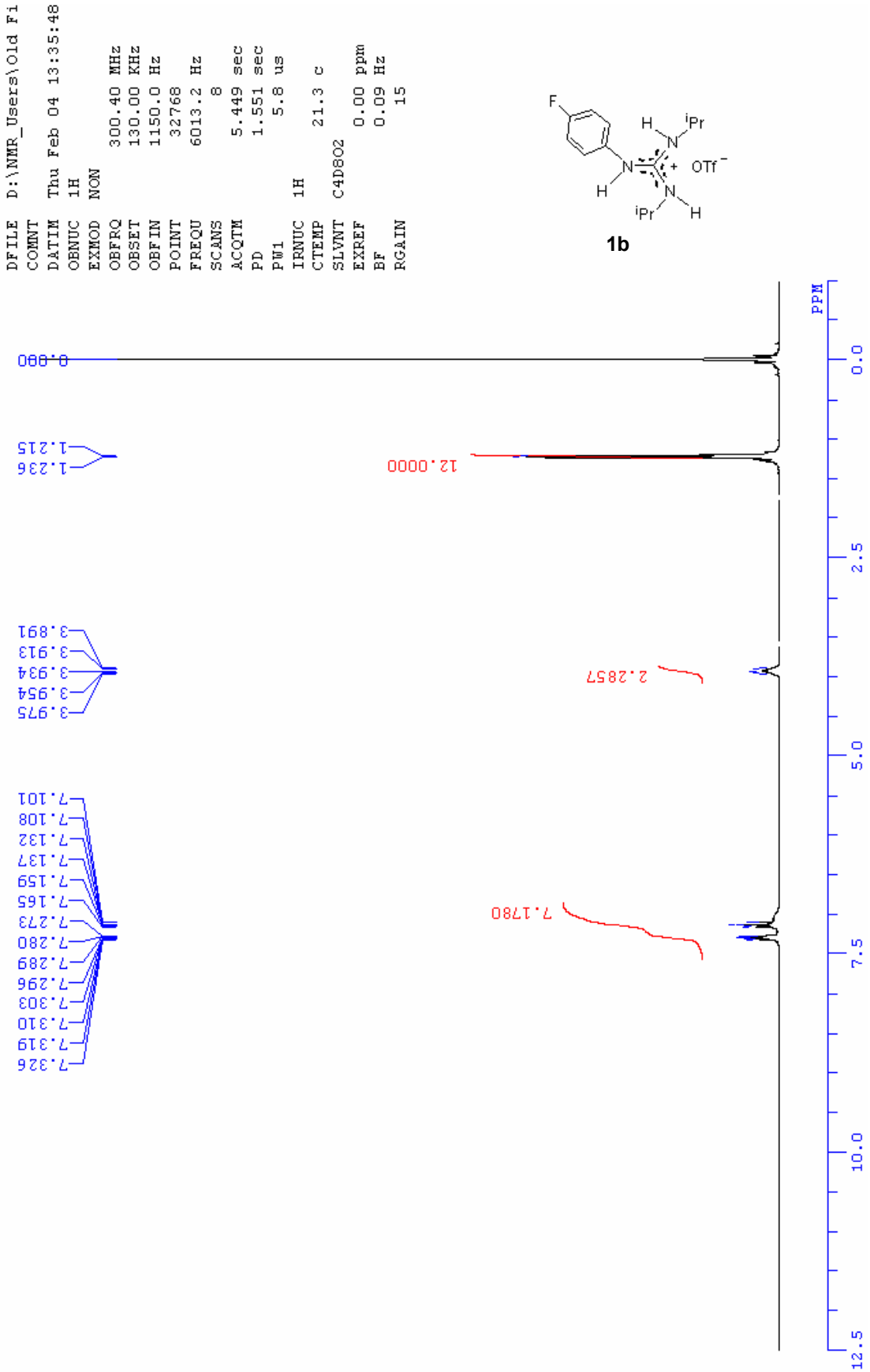
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N
+
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N
iPr
H
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12.0000
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3.954
3.934
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7.296
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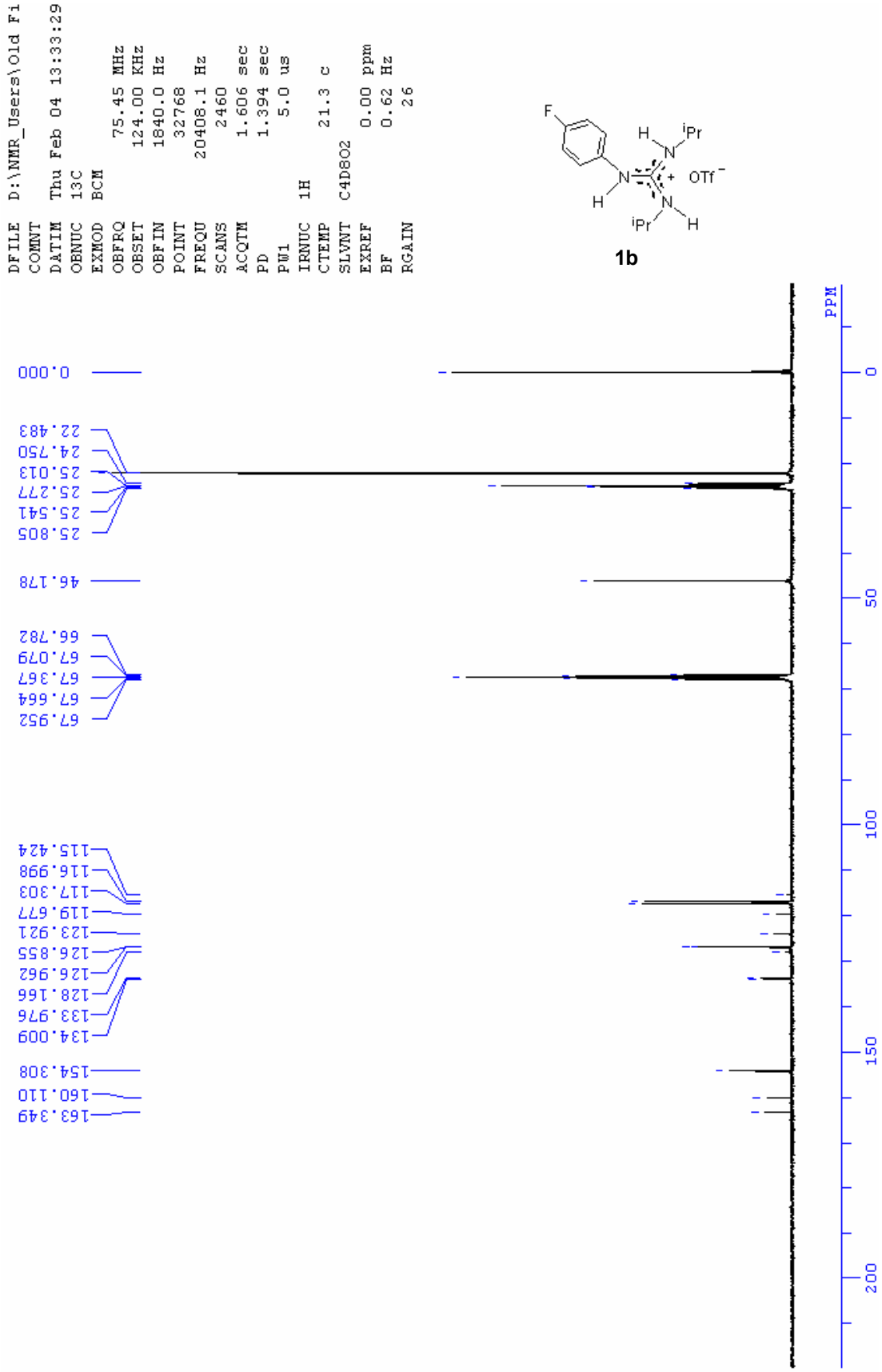
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iPr
N
+
OTf⁻
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N
iPr
N
H
1b
PPM
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25.277
25.541
25.805
46.178
66.782
67.079
67.367
67.664
67.952
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116.998
117.303
119.677
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100
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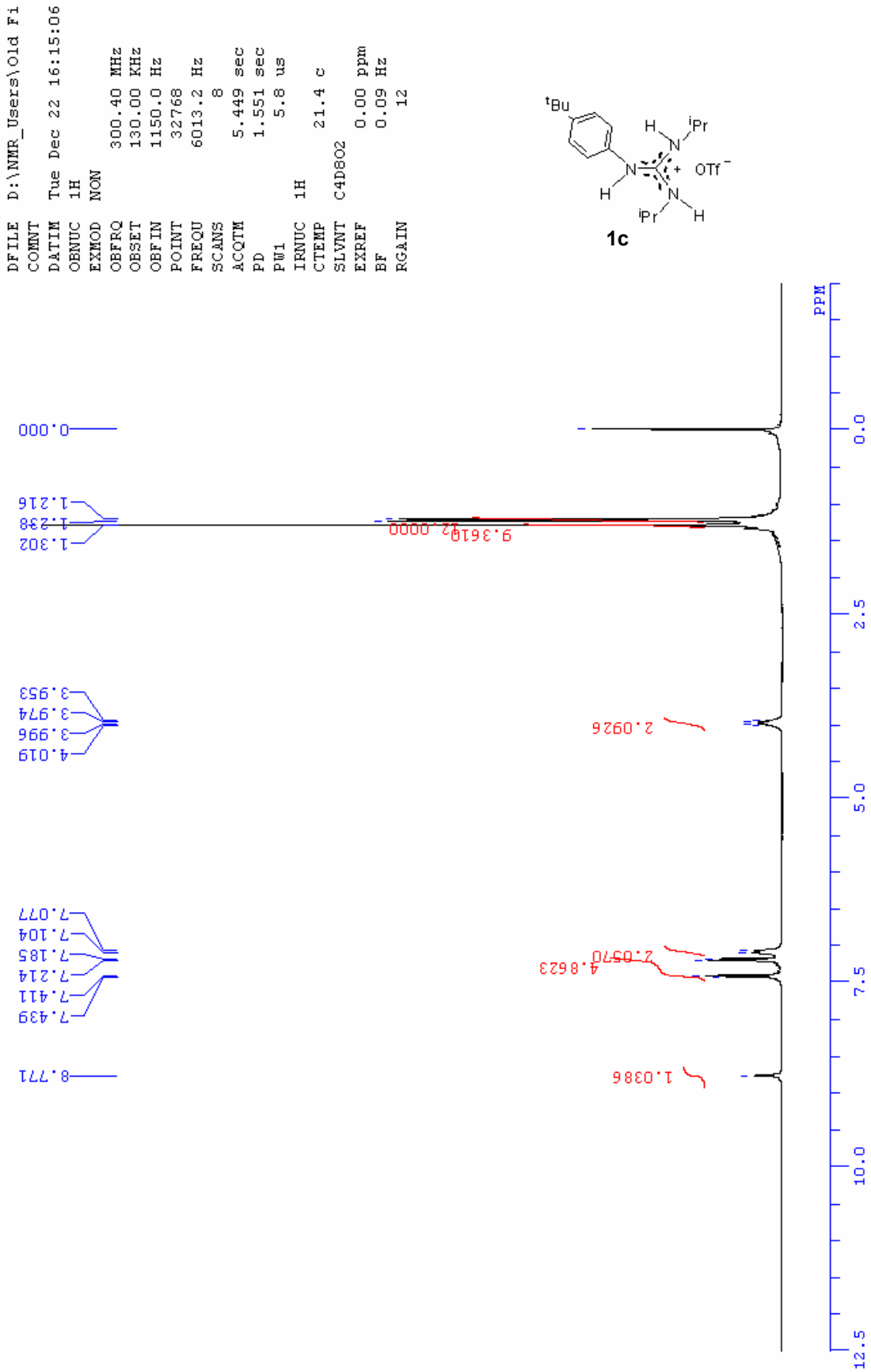
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H
iPr
N
N
+
OTf
H
N
iPr
H
1c
PPM
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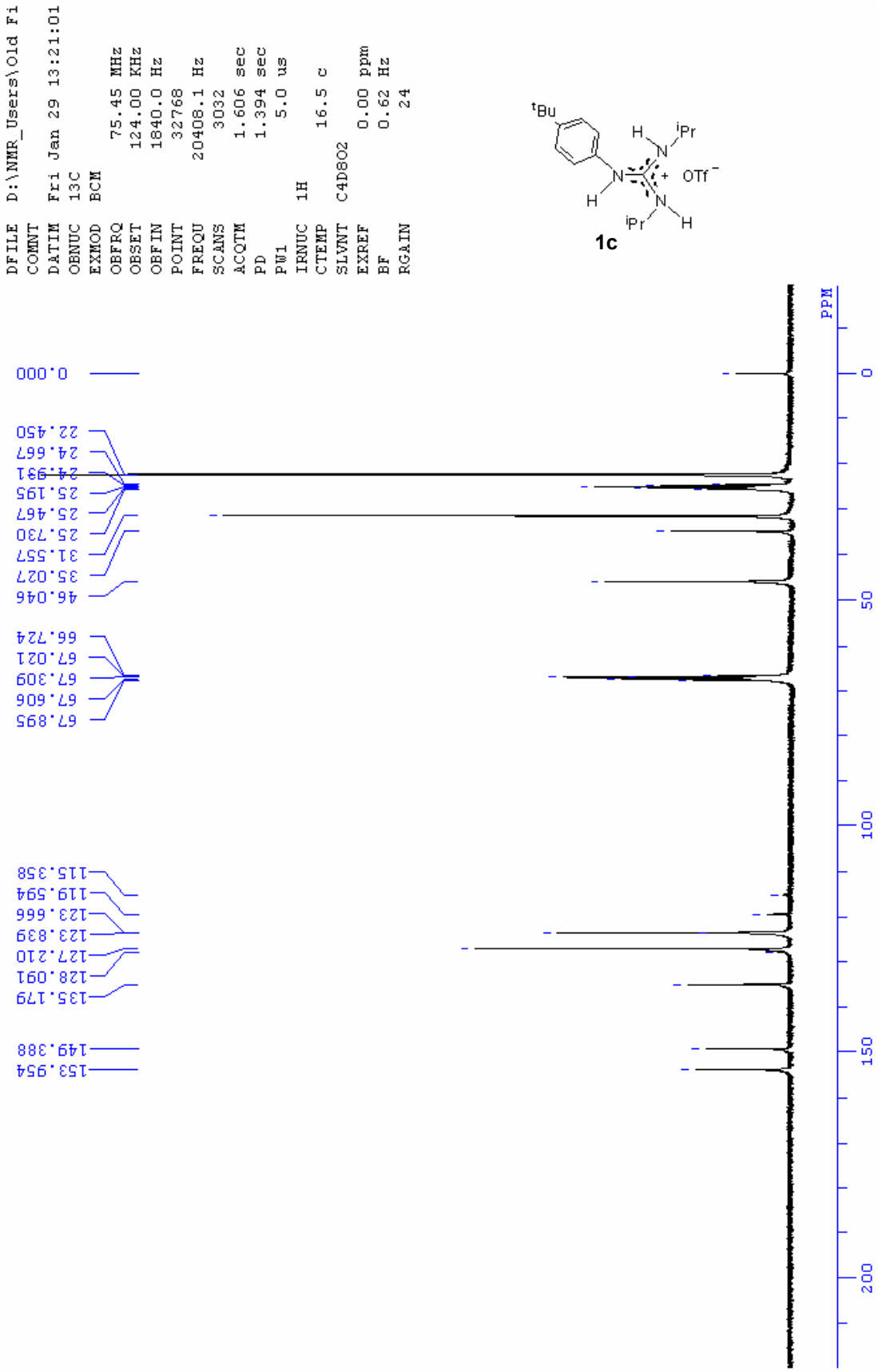
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BF 0.62 Hz
RGAIN 24
tBu
H
iPr
N
N
+
OTf⁻
H
N
iPr
H
1c
PPM
0.000
22.450
24.667
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25.195
25.467
25.730
31.557
35.027
46.046
66.724
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67.606
67.895
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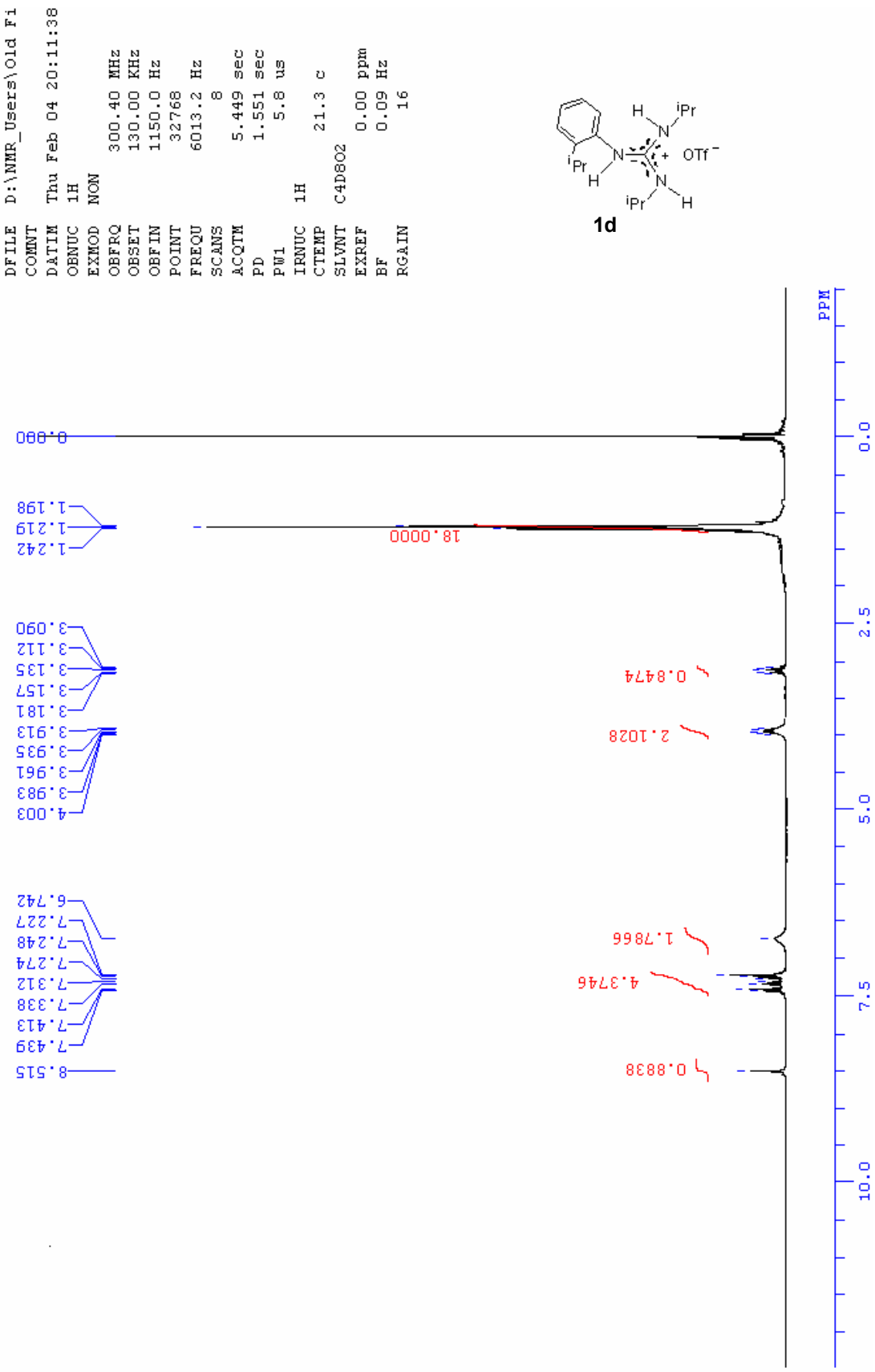
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PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 21.3 c
SLVNT C4D8O2
EXREF 0.00 ppm
BF 0.09 Hz
RGAIN 16
OTf⁻
1d
PPM
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2.5
5.0
7.5
10.0
0.000
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1.219
1.242
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3.112
3.135
3.157
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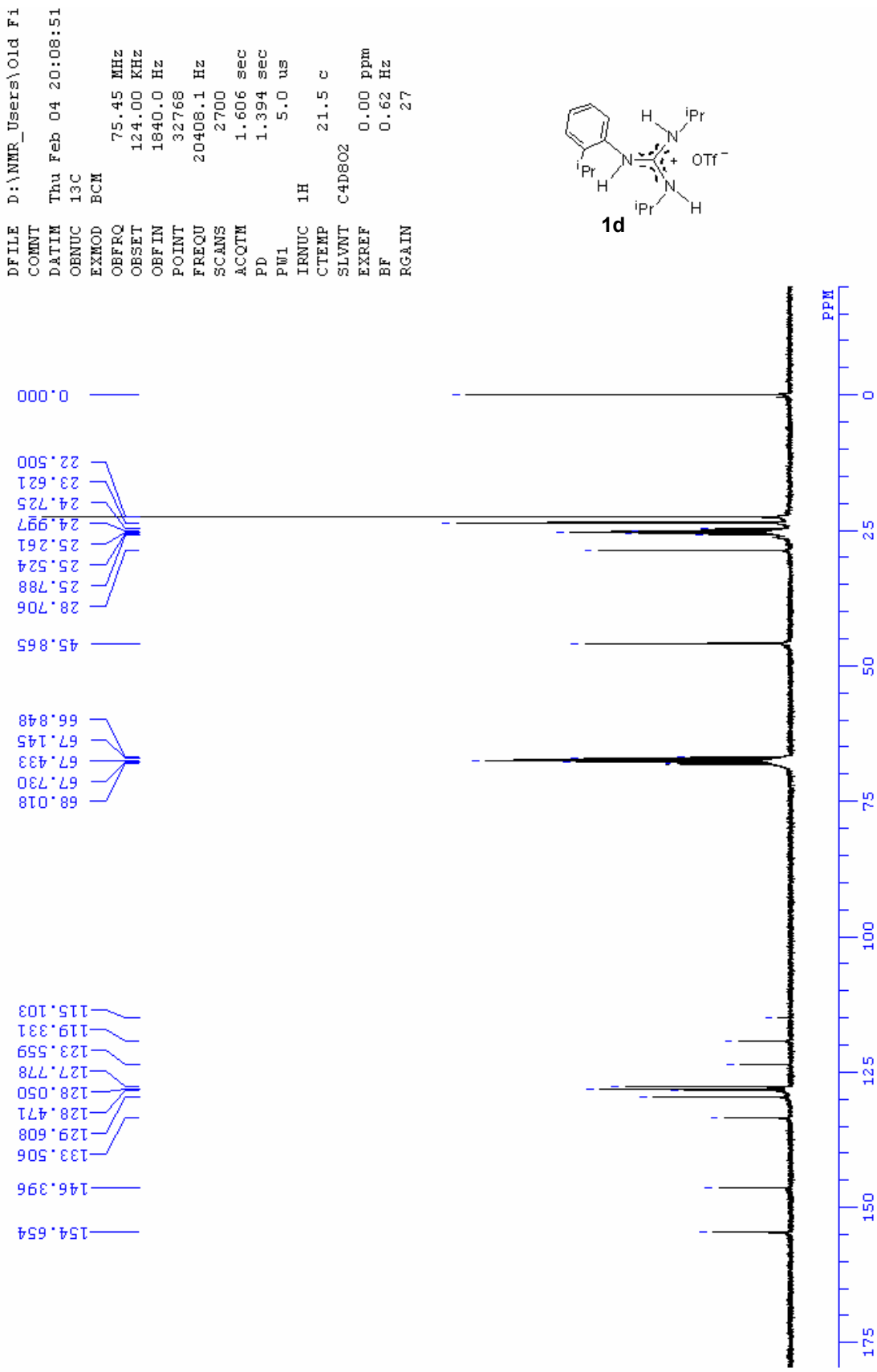
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PW1 5.0 us
IRNUC 1H
CTEMP 21.5 c
SLVNT C4D8O2
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BF 0.62 Hz
RGAIN 27
1d
OTf⁻
PPM
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24.725
24.997
25.261
25.524
25.788
28.706
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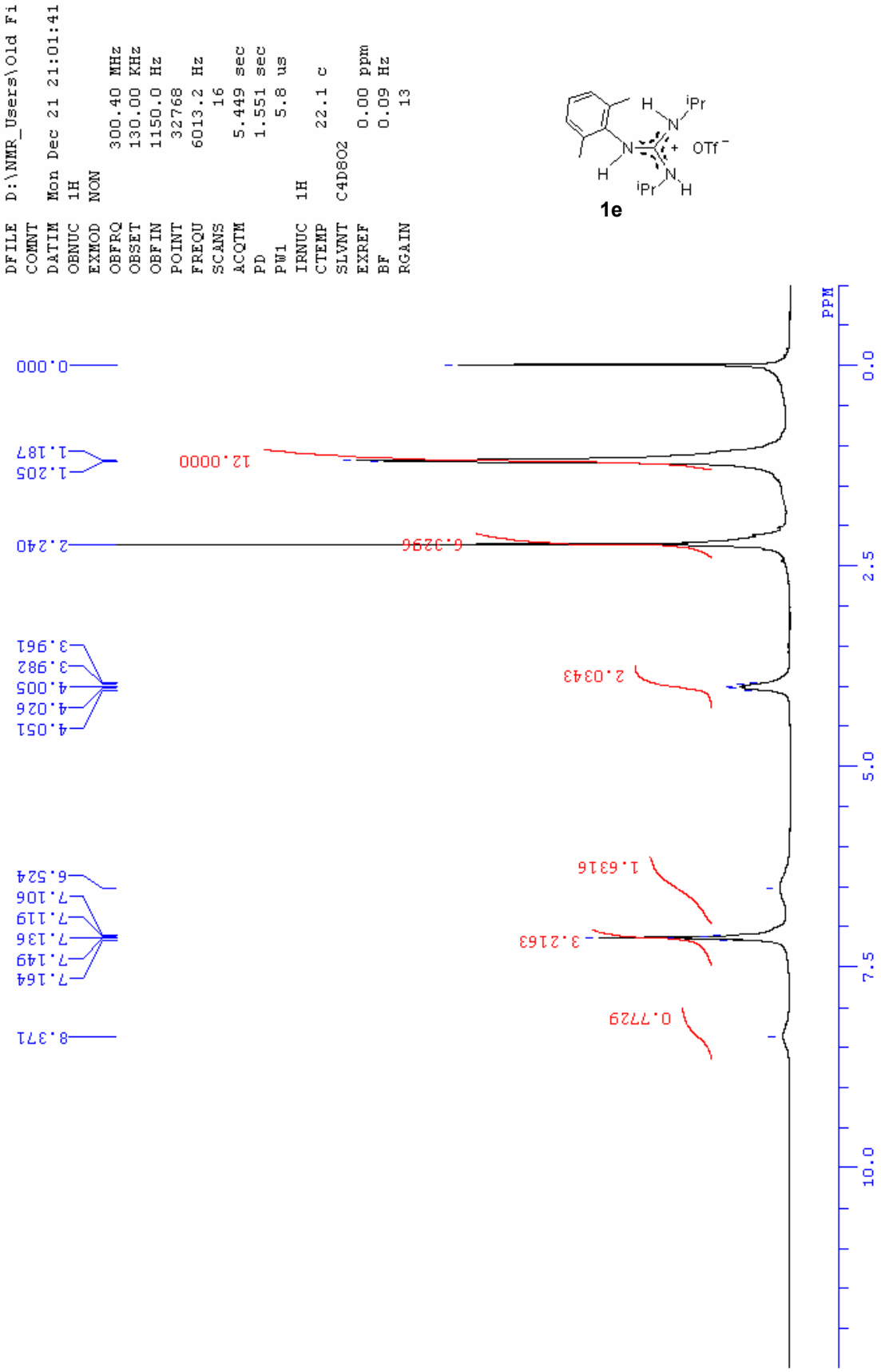
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CTEMP 22.1 c
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BF 0.09 Hz
RGAIN 13
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iPr
N
N
+
OTf⁻
H
N
iPr
H
1e
PPM
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2.5
5.0
7.5
10.0
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2.240
6.3296
3.961
3.982
4.005
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4.051
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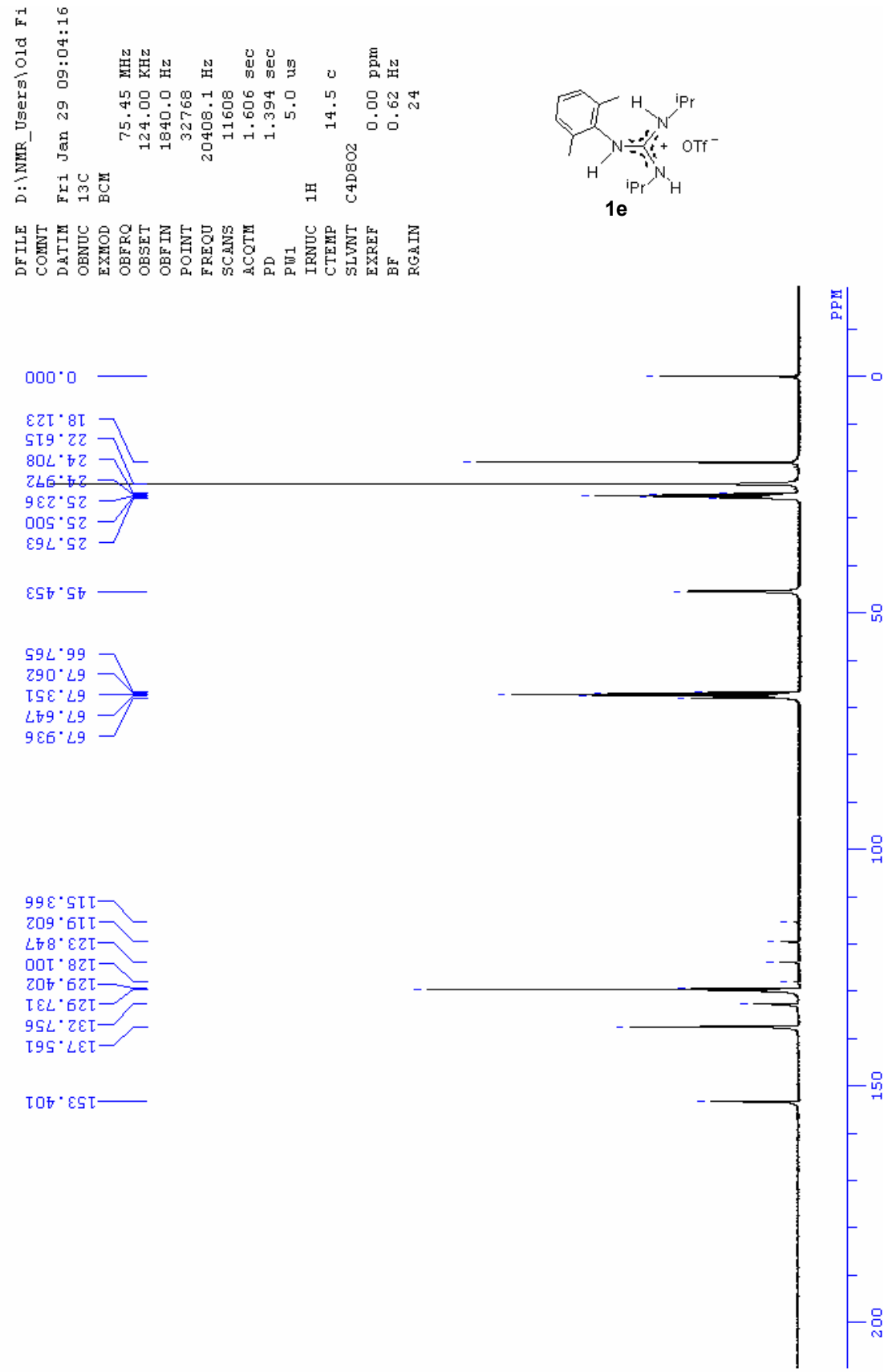
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BF 0.62 Hz
RGAIN 24
H
iPr
N
N
+
OTf⁻
H
iPr
N
H
1e
0.000
18.123
22.615
24.708
24.972
25.236
25.500
25.763
45.453
66.765
67.062
67.351
67.647
67.936
115.366
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PPM
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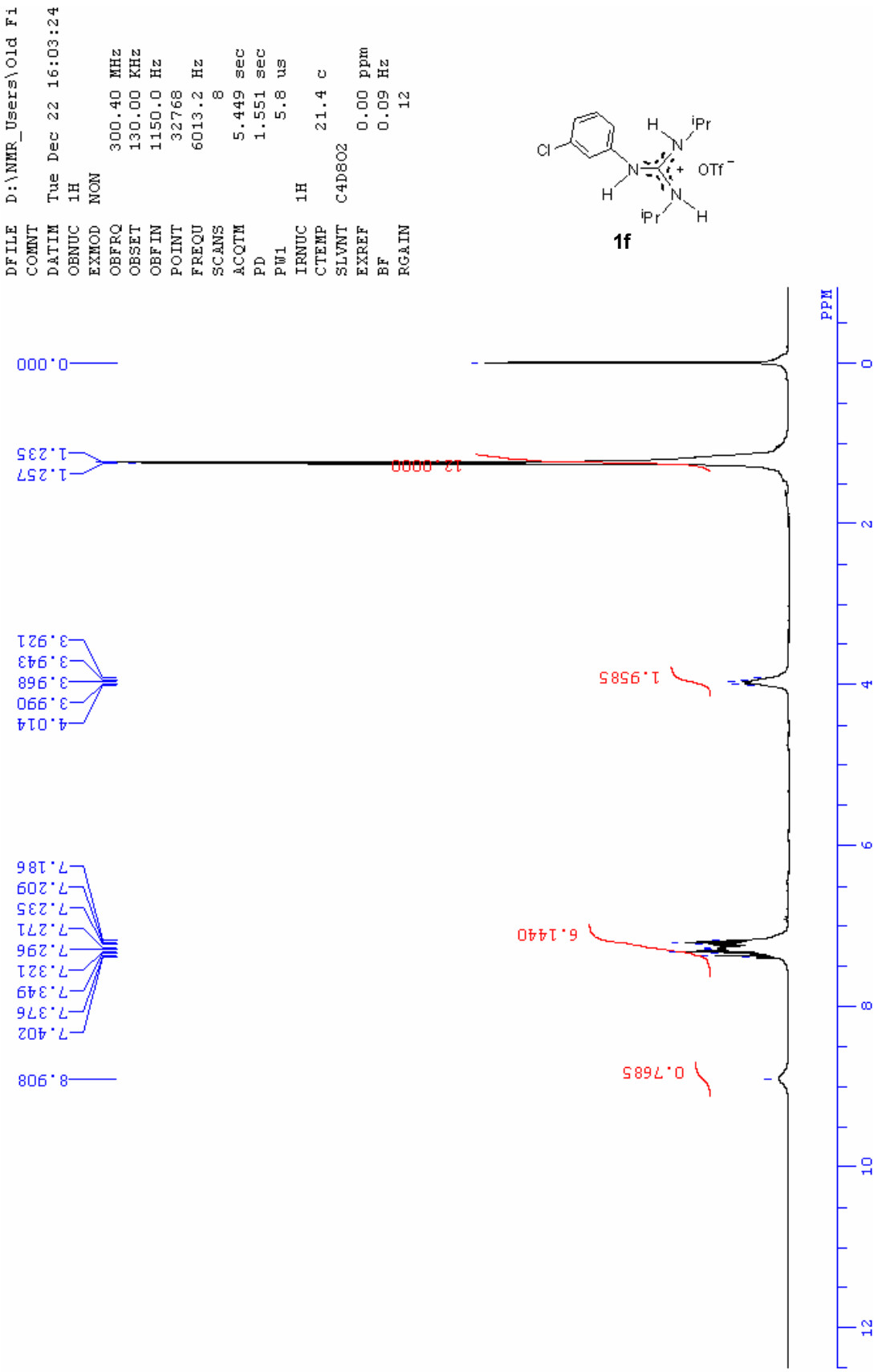
150
200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PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 21.4 c
SLVNT C4D8O2
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BF 0.09 Hz
RGAIN 12
Cl
H
N
iPr
OTf
1f
PPM
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12.0000
4.014
3.990
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3.943
3.921
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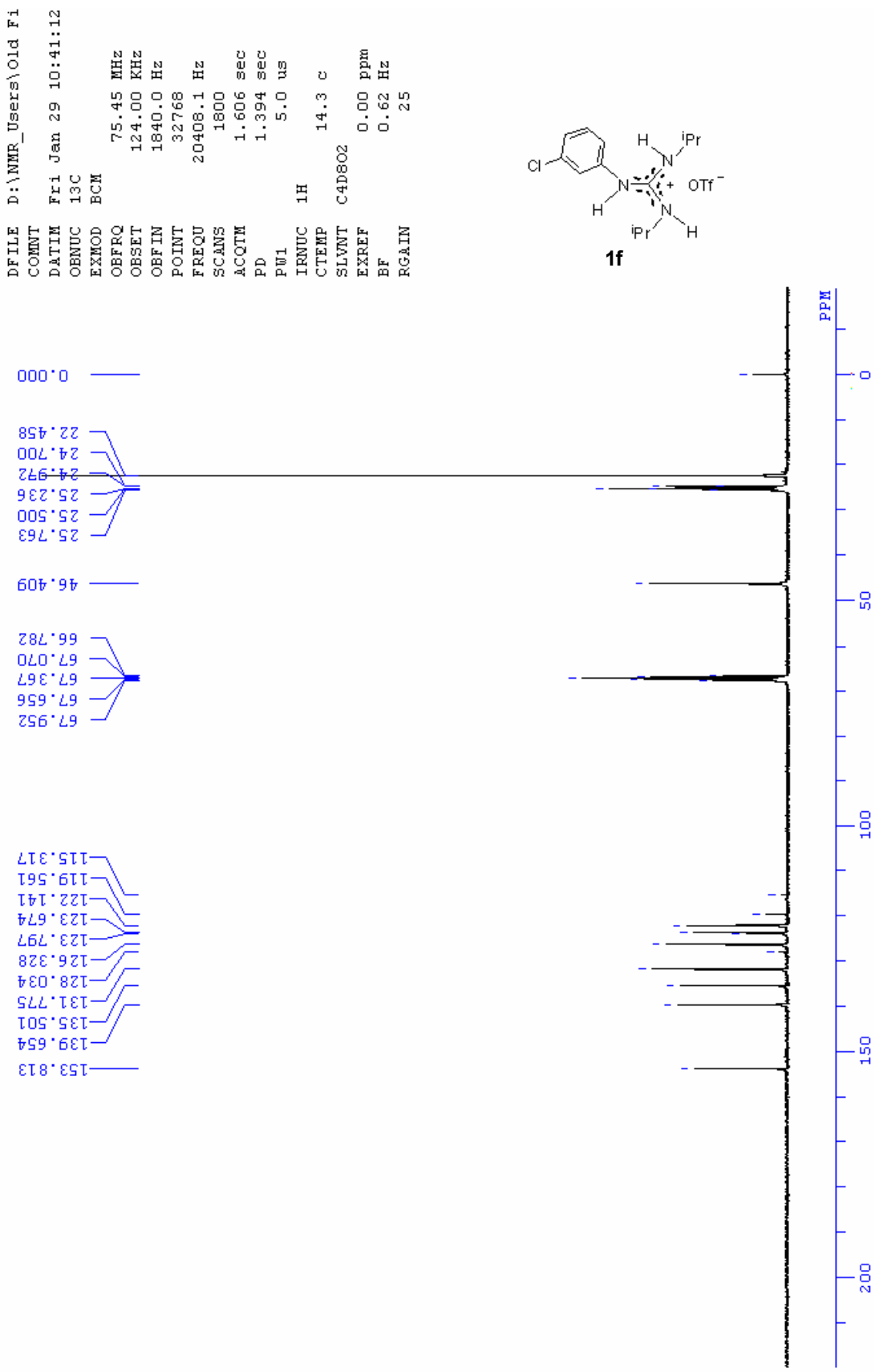
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PW1 5.0 us
IRNUC 1H
CTEMP 14.3 c
SLVNT C4D8O2
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RGAIN 25
Cl
H
iPr
N
N
+
OTf⁻
H
N
iPr
H
1f
PPM
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24.972
25.236
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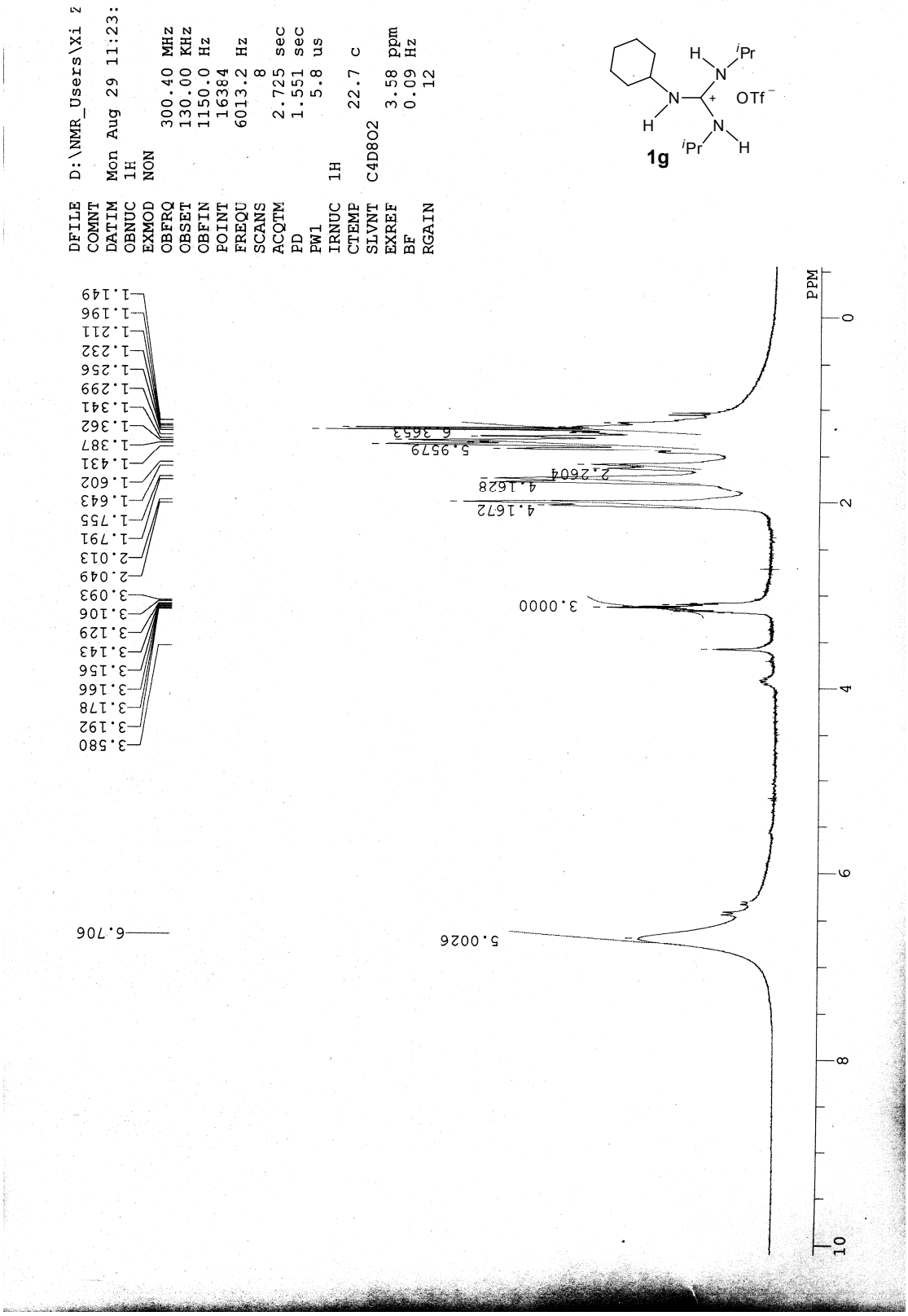
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PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.7 c
SLVNT C4D8O2
EXREF 3.58 ppm
BF 0.09 Hz
RGAIN 12
1g
OTf
PPM
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2.2604
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6.3653
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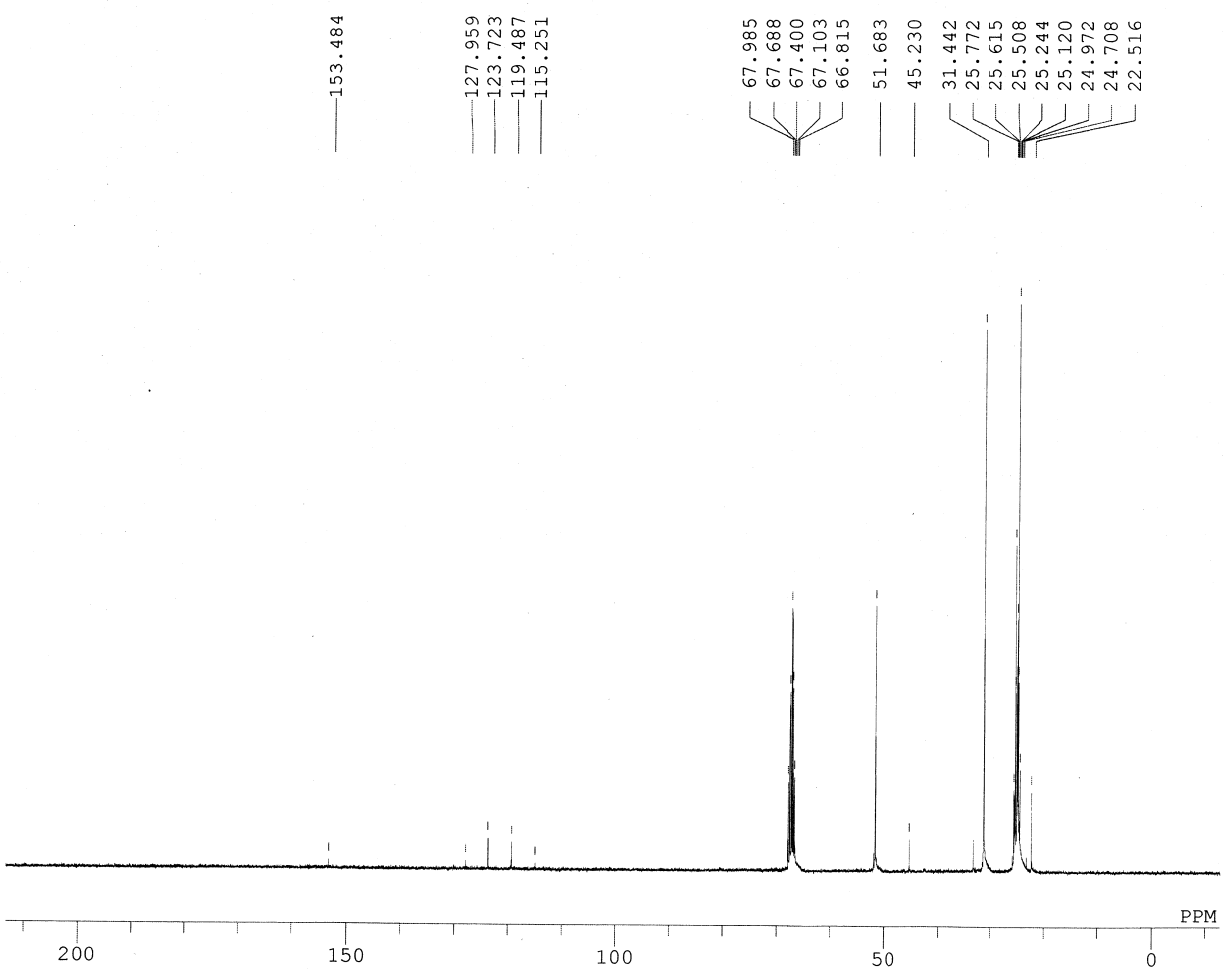


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SCANS         1296
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.2 us
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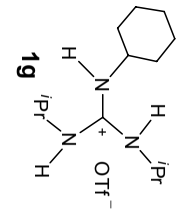

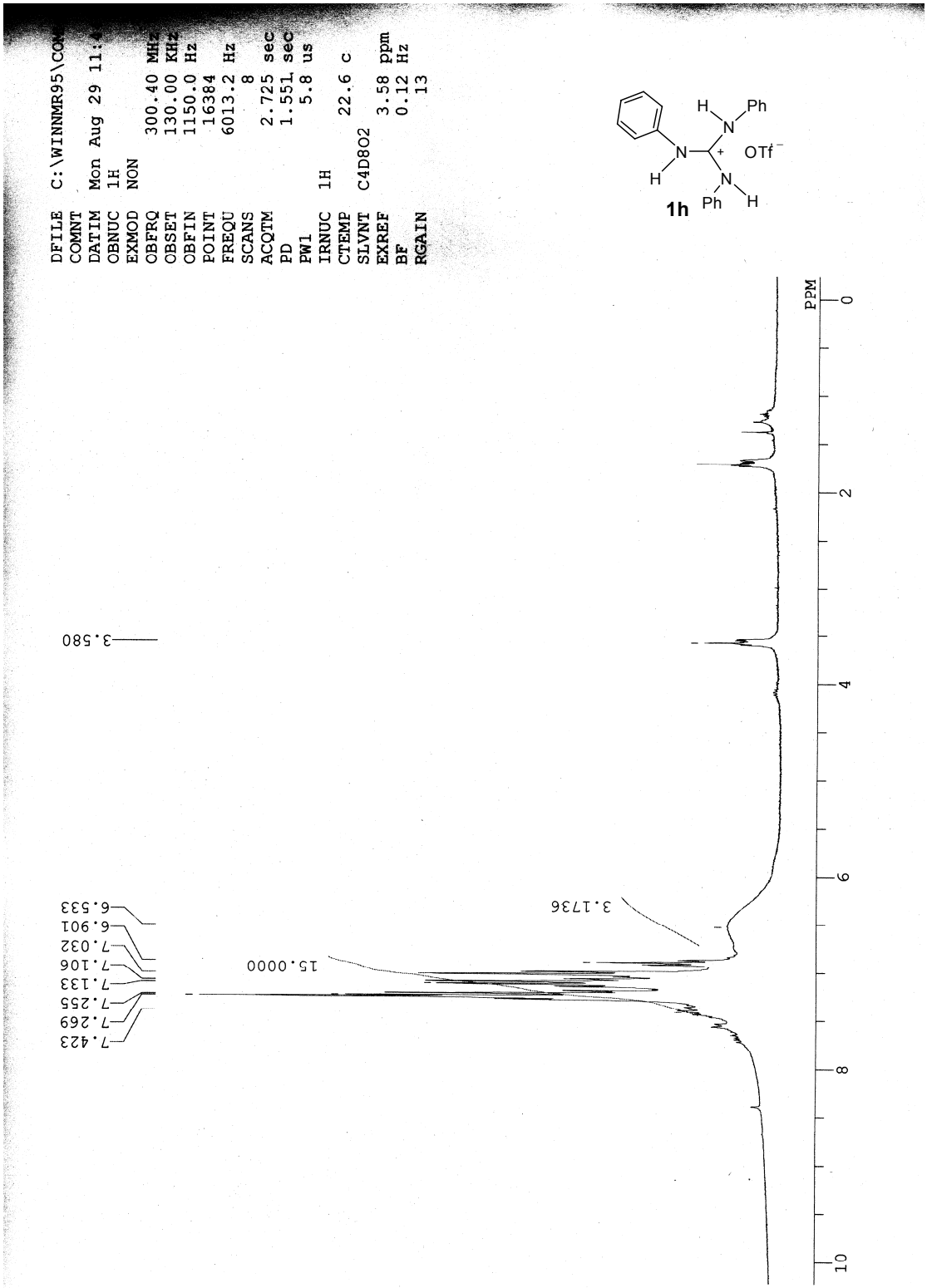
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FREQU 6013.2 Hz
SCANS 8
ACQTM 2.725 sec
PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.6 c
SLVNT C4D8O2
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BF 0.12 Hz
RGAIN 13
H
Ph
N
N
OTf
H
N
Ph
H
1h
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6.533
6.901
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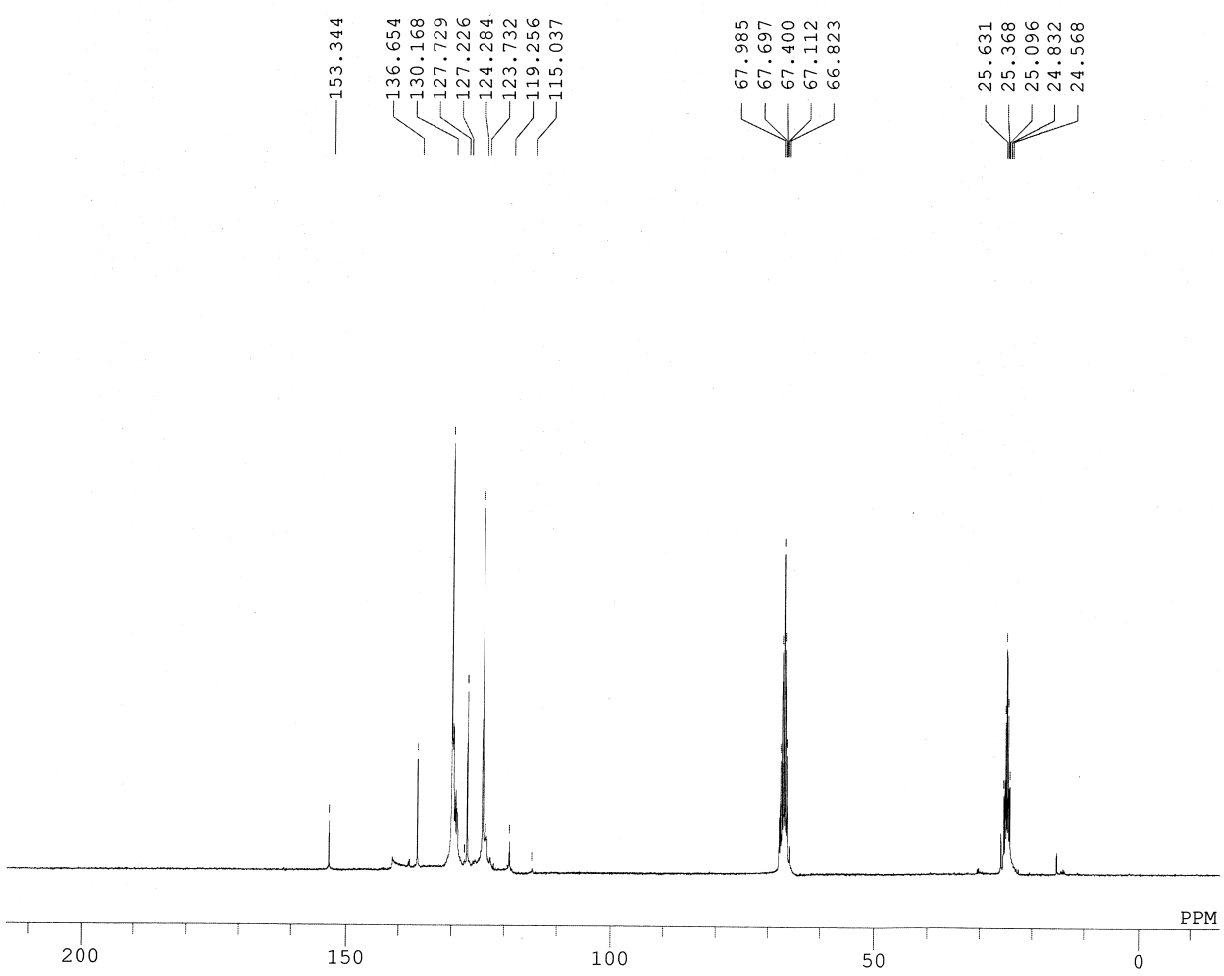
8
10

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PW1             4.2 us
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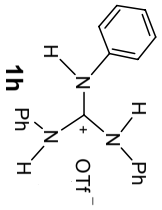

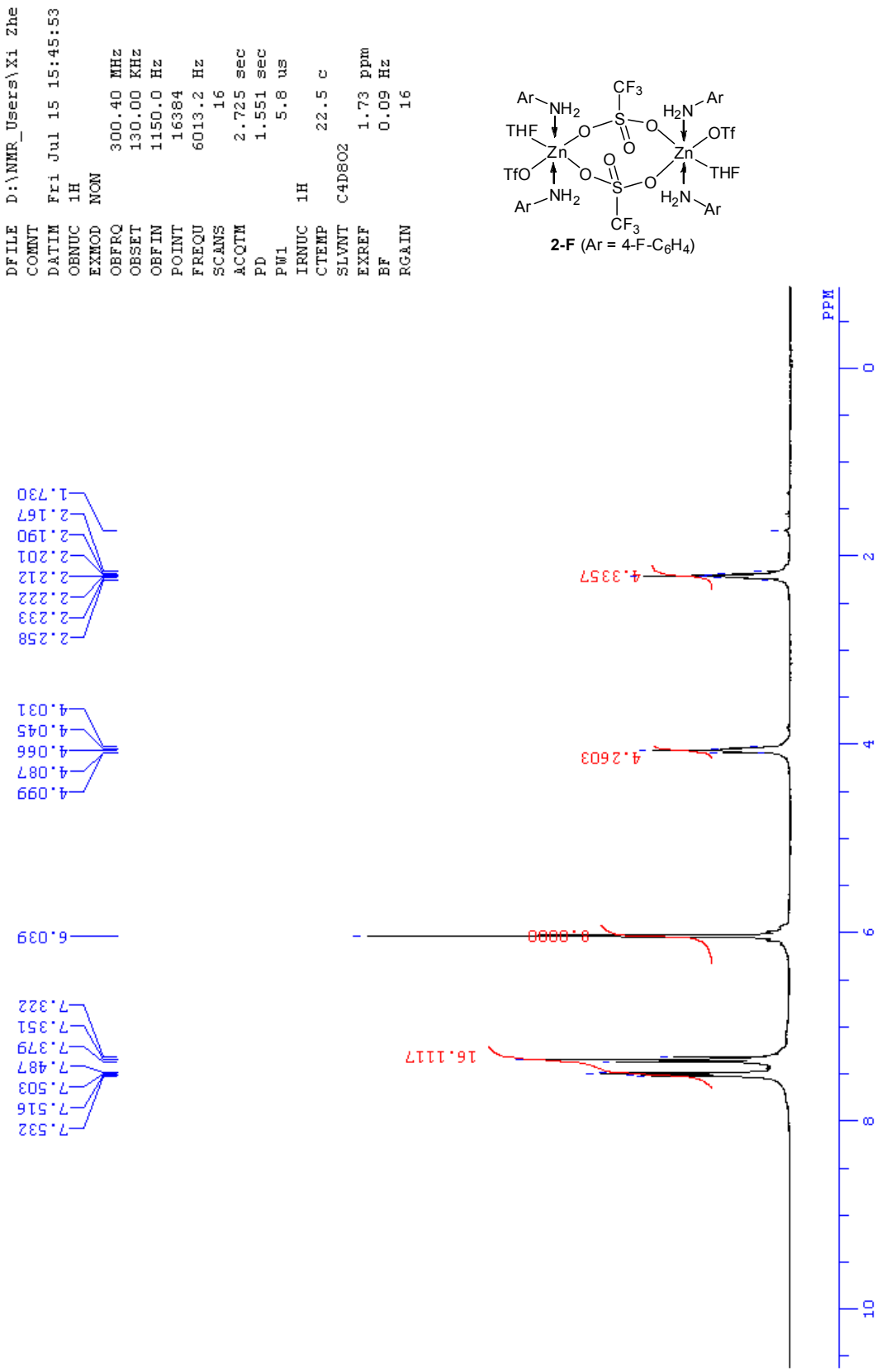
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PD 1.551 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.5 c
SLVNT C4D8O2
EXREF 1.73 ppm
BF 0.09 Hz
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Ar
NH2
THF
Zn
TfO
CF3
S
O
H2N
OTf
2-F (Ar = 4-F-C6H4)
PPM
0
2
4
6
8
10
16.1117
0.8880
4.2603
4.3357
7.532
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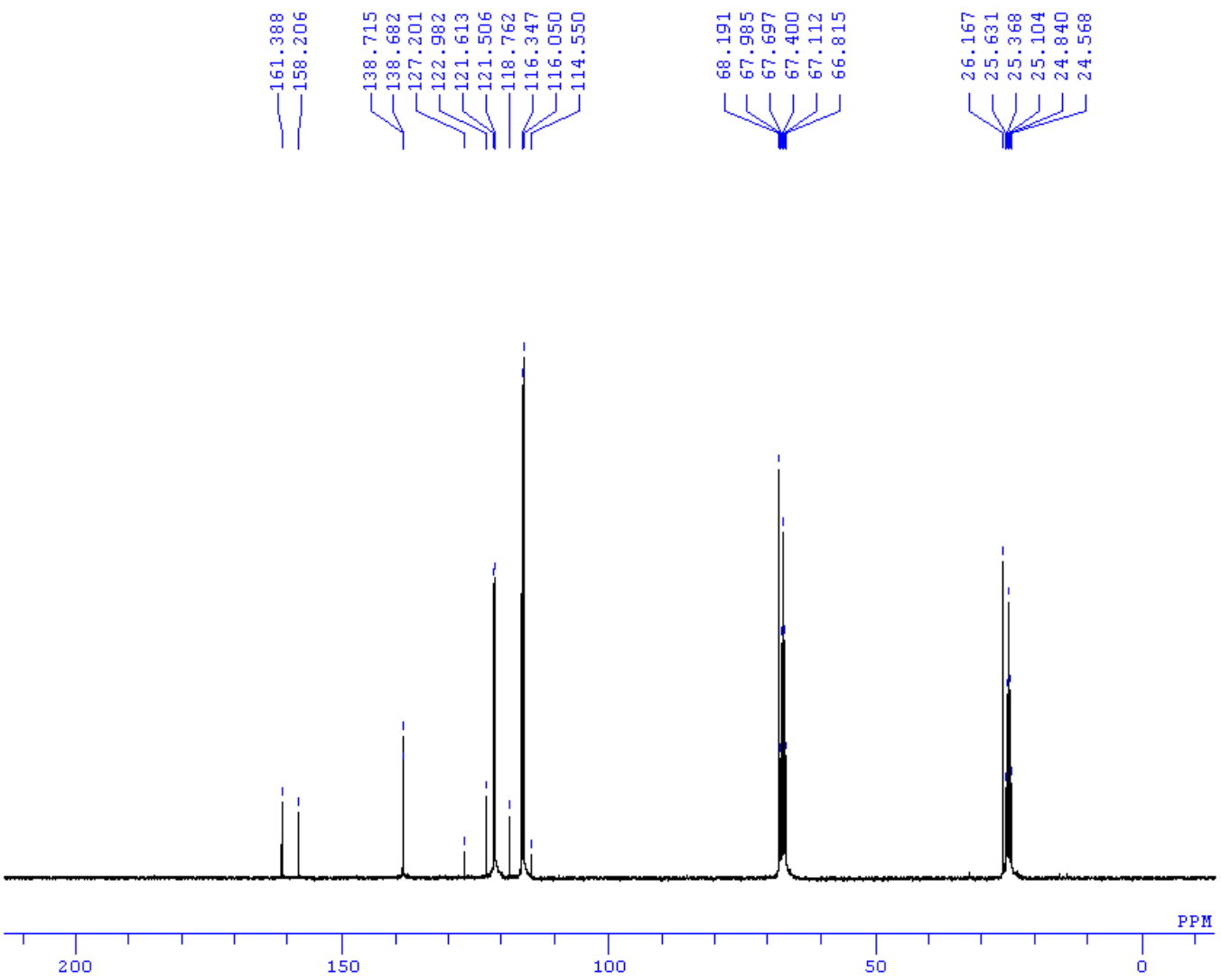


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SCANS          5068
ACQTM         1.606 sec
PD            1.394 sec
PW1             4.2 us
IRNUC   1H
CTEMP          23.3 c
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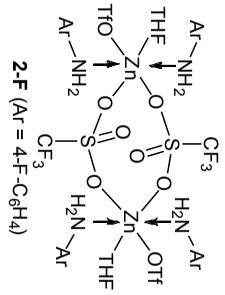
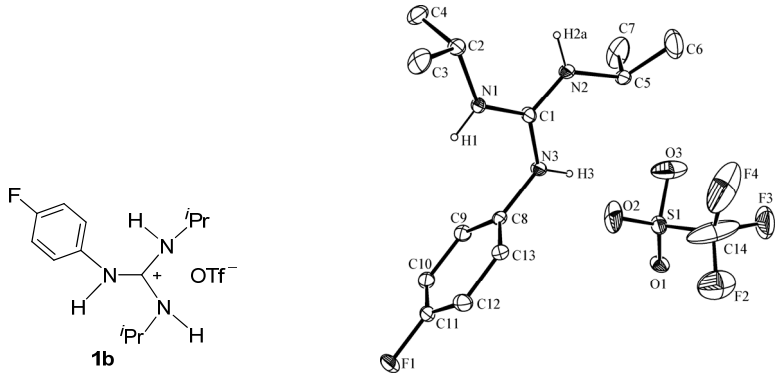


2-F (Ar = 4-F-C_6H_4)

2) X-ray Crystallographic Studies for 1b, 1d, and 2-F

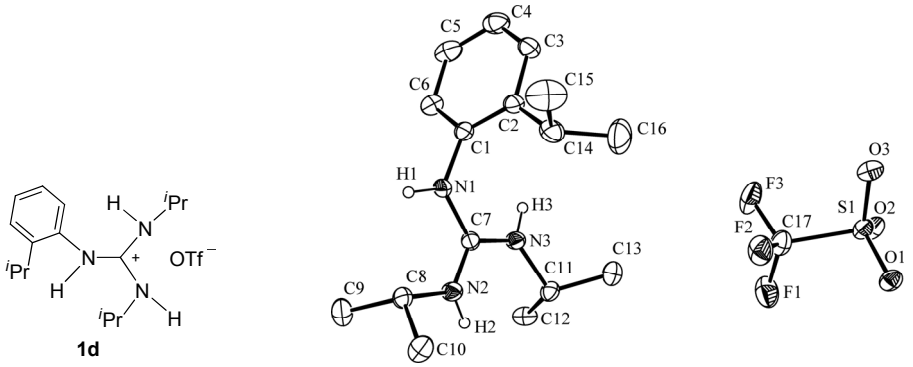
Data collections of **1b** and **2-F** were performed at −100 °C and −150 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated MoKα radiation (λ = 0.71073 Å), respectively. The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) to yield the reflection data file. Data collections of **1d** were performed at –100 °C on a Rigaku SATURN 724+ CCD diffractometer, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the CrystalClear (Rigaku Inc., 2008) program package. The raw frame data were processed using the CrystalClear (Rigaku Inc., 2008) to yield the reflection data file. The structures were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for **1b**, **1d**, and **2-F** were given only in Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-835290 (**1b**), CCDC-741355 (**1d**), and CCDC-835291 (**2-F**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



SFigure 1. ORTEP drawing of **1b** with 20% thermal ellipsoids. Hydrogen atoms, except those on the nitrogen atoms, are omitted for clarity.

STable 1. Crystal data and structure refinement for **1b**.

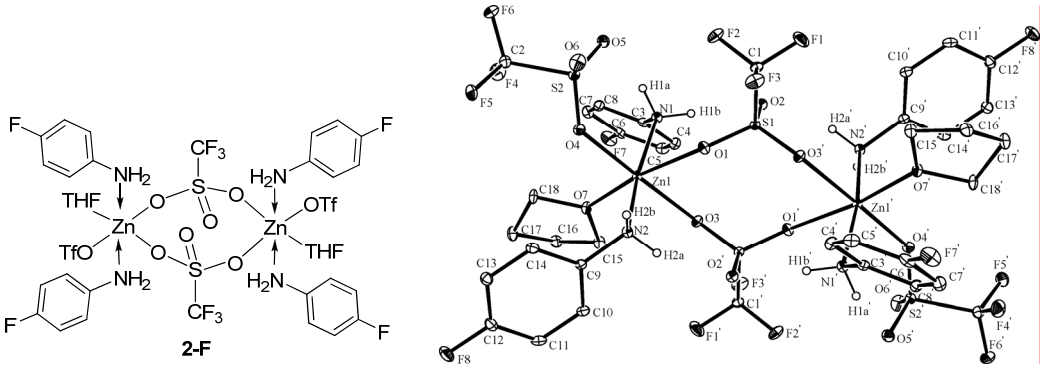
Identification code	**1b**	
Empirical formula	$C_{14}H_{21}F_4N_3O_3S$	
Formula weight	387.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1088(18) Å	α= 76.98(3) °
	b = 10.016(2) Å	β= 76.48(3) °
	c = 11.801(2) Å	γ = 69.03(3) °
Volume	965.5(3) $Å^3$	
Z	2	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	404	
Crystal size	0.30 x 0.30 x 0.10 mm^3	
Theta range for data collection	2.20 to 27.48°.	
Index ranges	-11<=h<=11, -12<=k<=12, -15<=l<=15	
Reflections collected	6320	
Independent reflections	4151 [R(int) = 0.0567]	
Completeness to theta = 27.48°	94.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9782 and 0.9366	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4151 / 3 / 231	
Goodness-of-fit on F^2	1.198	
Final R indices [I>2sigma(I)]	R1 = 0.1099, wR2 = 0.2833	
R indices (all data)	R1 = 0.2124, wR2 = 0.3183	
Extinction coefficient	0.022(8)	
Largest diff. peak and hole	1.048 and -0.470 e. $Å^{-3}$	



SFigure 2. ORTEP drawing of **1d** with 30% thermal ellipsoids. Hydrogen atoms, except those on the nitrogen atoms, are omitted for clarity.

STable 2. Crystal data and structure refinement for **1d.**

Identification code	**1d**
Empirical formula	$C_{17}H_{28}F_3N_3O_3S$
Formula weight	411.48
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 16.419(3) Å α = 90 °.
	b = 12.458(3) Å β = 90 °.
	c = 10.520(2) Å γ = 90 °.
Volume	2151.8(7) Å ^{3}
Z, Calculated density	4, 1.270 Mg/m^3
Absorption coefficient	0.196 mm^{-1}
F(000)	872
Crystal size	0.30 x 0.29 x 0.13 mm
Theta range for data collection	2.82 to 27.49 °.
Limiting indices	-14 <= h <= 21, -16 <= k <= 16, -13 <= l <= 12
Reflections collected / unique	16883 / 4604 [$R_{(int)}$ = 0.0369]
Completeness to theta = 27.49 °	99.7 %
Absorption correction	Numerical
Max. and min. transmission	0.9749 and 0.9435
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4604 / 1 / 244
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R_1 = 0.0441, wR_2 = 0.0945
R indices (all data)	R_1 = 0.0482, wR_2 = 0.0977
Absolute structure parameter	0.00(8)
Largest diff. peak and hole	0.185 and -0.200 e. Å $^{-3}$



SFigure 3. ORTEP drawing of **2-F** with 20% thermal ellipsoids. Hydrogen atoms, except those on the nitrogen atoms, are omitted for clarity.

STable 3. Crystal data and structure refinement for **2-F**.

Identification code	**2-F**	
Empirical formula	$C_{36}H_{40}F_{16}N_4O_{14}S_4Zn_2$	
Formula weight	1315.70	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.610(2) Å	α= 67.54(3) °
	b = 11.128(2) Å	β= 80.01(3) °
	c = 11.191(2) Å	γ = 87.03(3) °
Volume	1202.4(4) $Å^3$	
Z	1	
Density (calculated)	1.817 Mg/m^3	
Absorption coefficient	1.301 mm^{-1}	
F(000)	664	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	1.95 to 27.48°.	
Index ranges	-13<=h<=13, -14<=k<=14, -14<=l<=13	
Reflections collected	10110	
Independent reflections	5359 [R(int) = 0.0556]	
Completeness to theta = 27.48°	97.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7809 and 0.5623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5359 / 0 / 344	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1388	
R indices (all data)	R1 = 0.0705, wR2 = 0.1466	
Extinction coefficient	0.017(2)	
Largest diff. peak and hole	0.873 and -1.655 e. $Å^{-3}$	