

## ***Supporting Information***

### **4-Disubstituted pyrazolin-3-ones — novel class of fungicides against phytopathogenic fungi**

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<sup>2</sup> Faculty of Chemical and Pharmaceutical Technology and Biomedical Products, D. I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Square, 125047 Moscow, Russia

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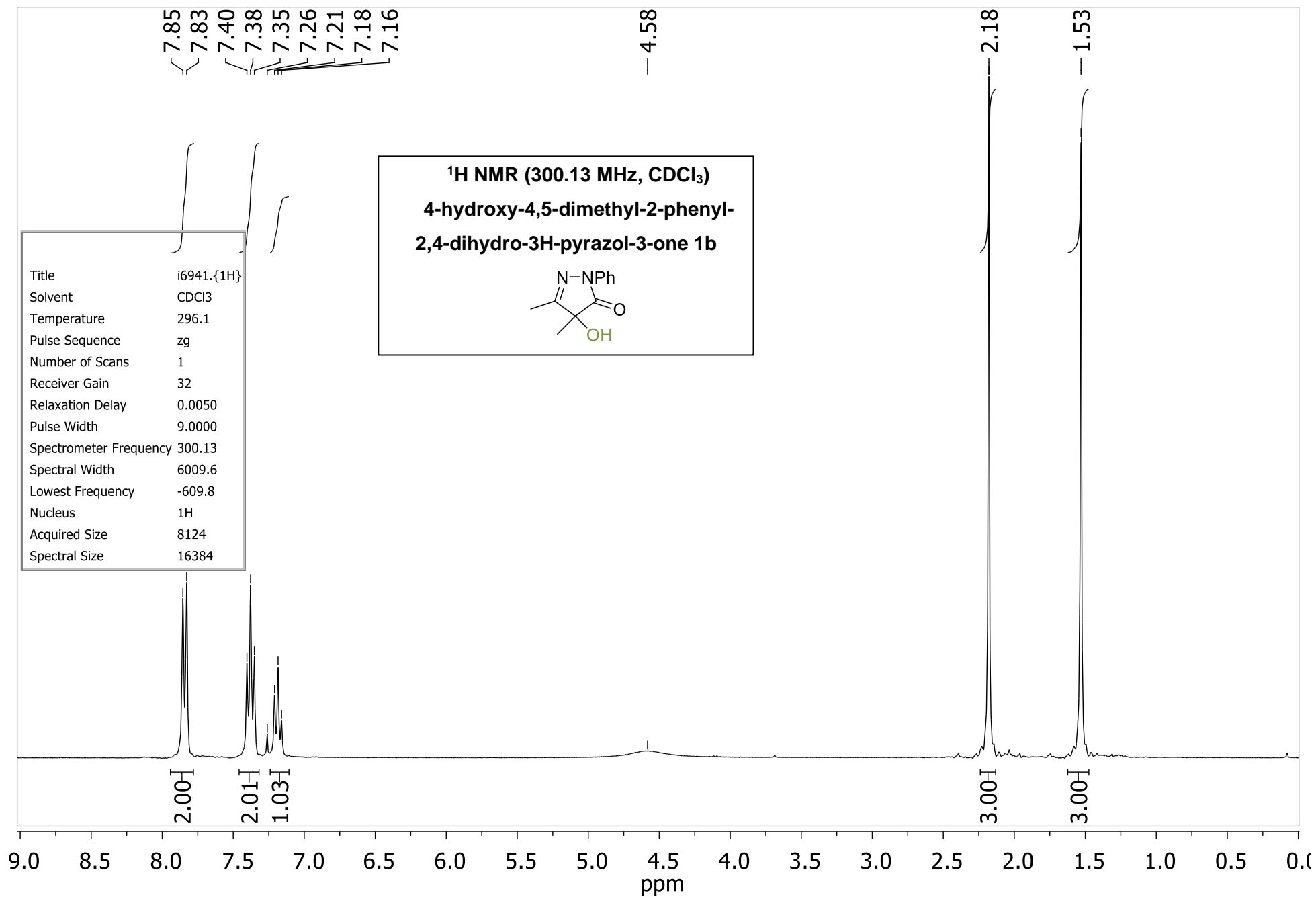
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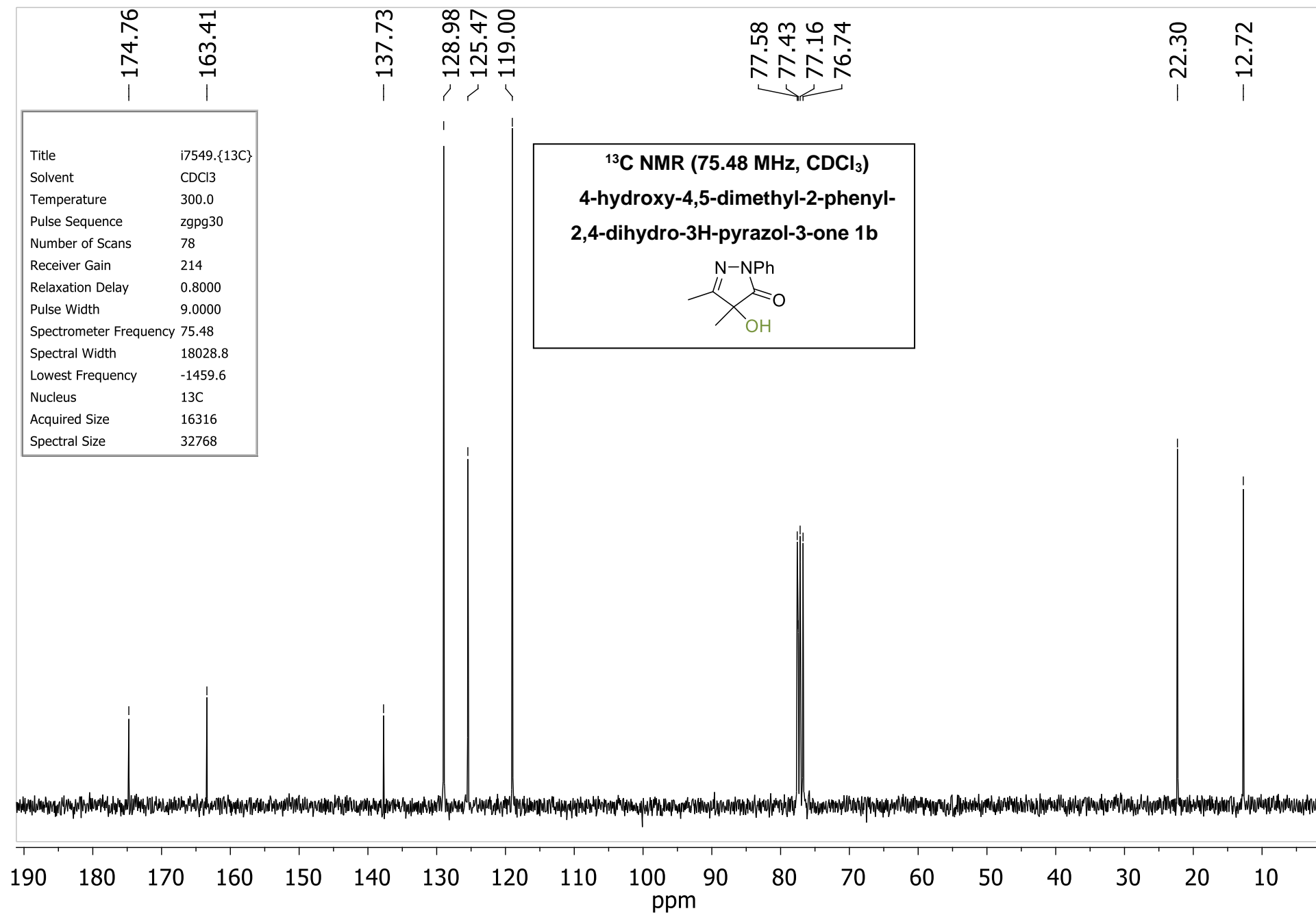
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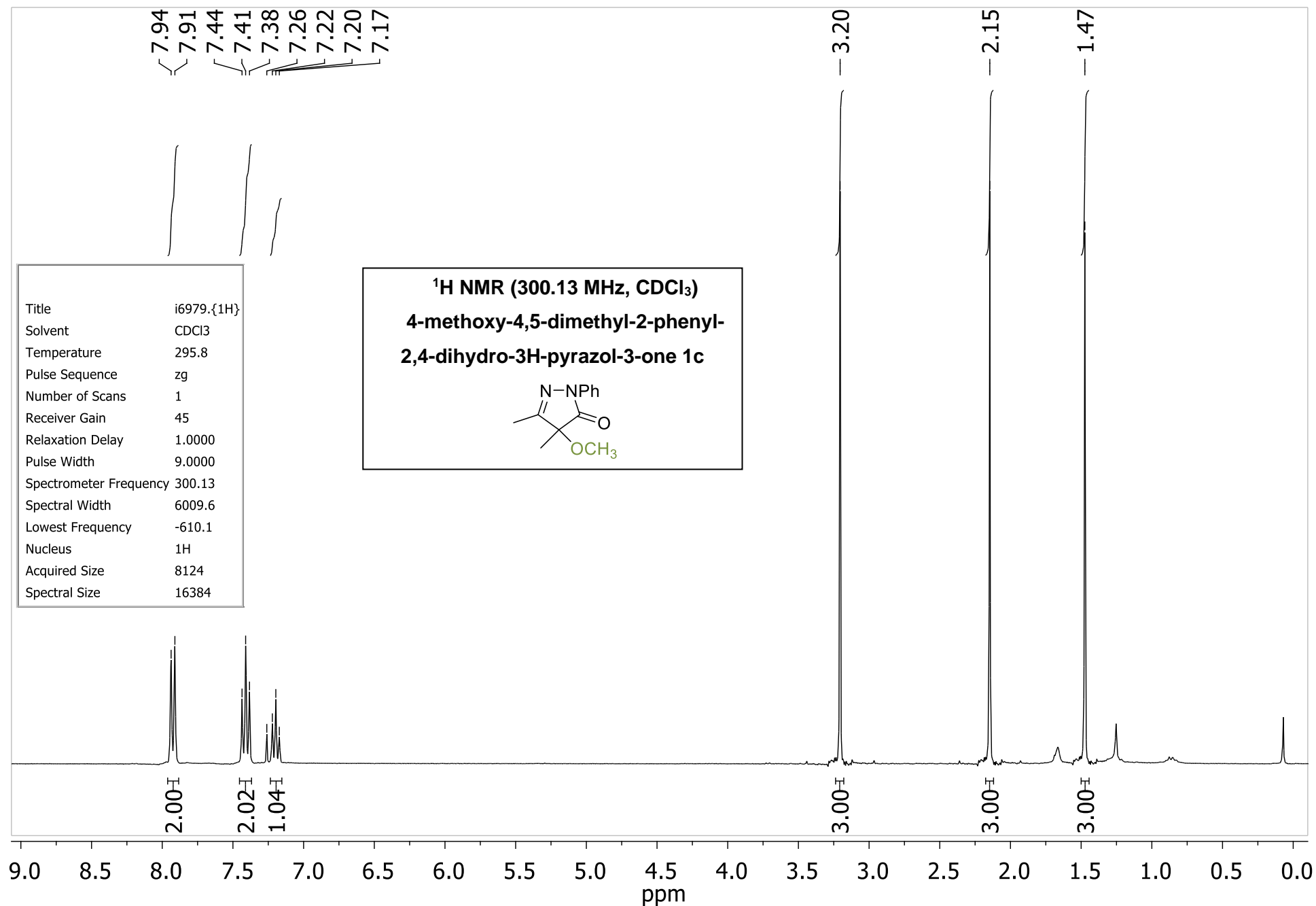
## General

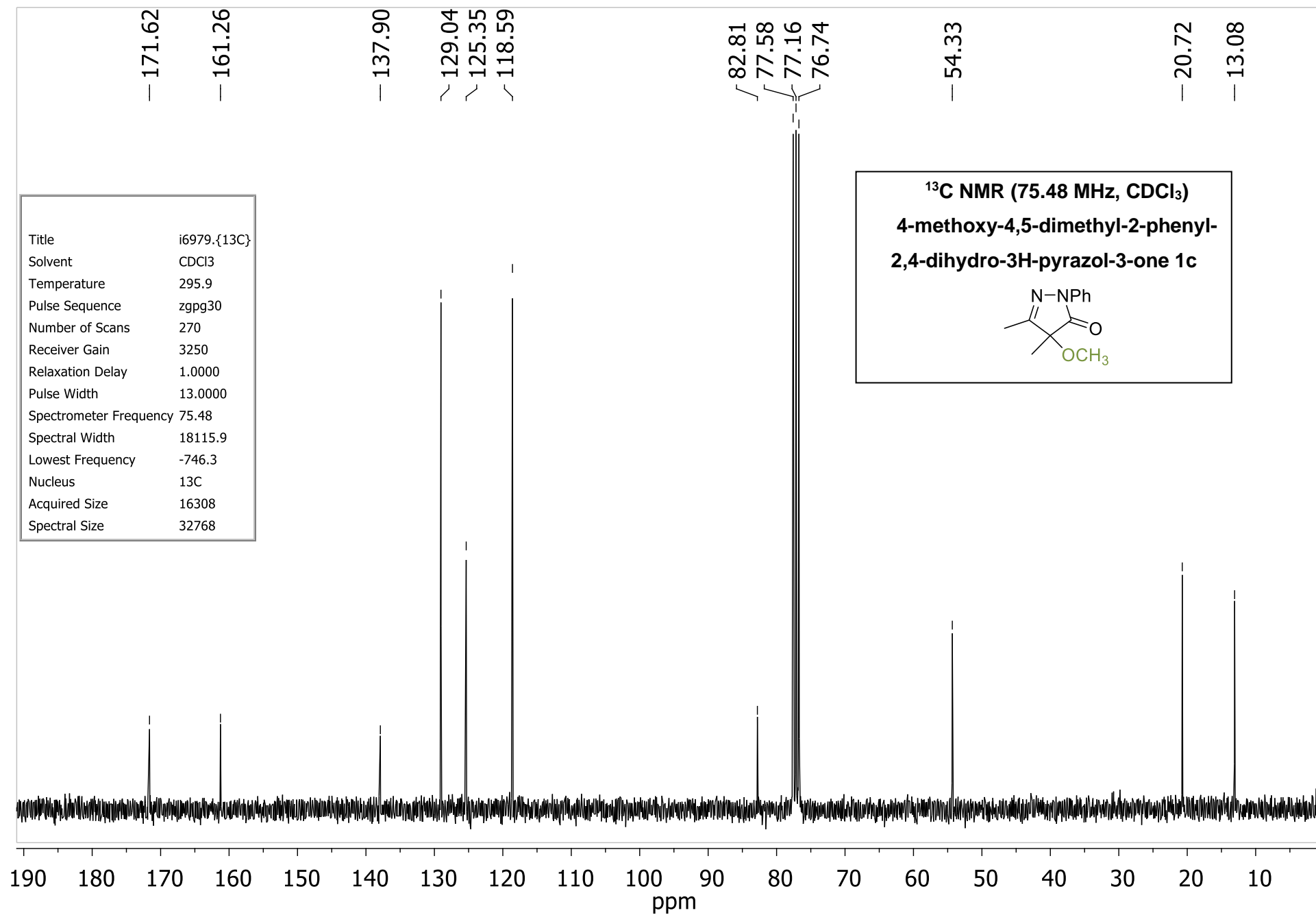
In all experiments RT stands for 22–25 °C.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE II 300 and Bruker Fourier 300HD (300.13 and 75.47 MHz, respectively) spectrometers in  $\text{CDCl}_3$  and  $\text{DMSO}-\text{D}_6$ . Residual signals of  $\text{CDCl}_3$  (7.26 in  $^1\text{H}$  NMR, 77.16 in  $^{13}\text{C}$  NMR) or  $\text{DMSO}-\text{d}_6$  (2.50 in  $^1\text{H}$  NMR, 39.52 in  $^{13}\text{C}$  NMR) were used as reference signals for precise chemical shift determination. FT-IR spectra were recorded on Bruker Alpha instrument. IR spectra were registered in KBr pellets for solid compounds, and liquid compounds were placed between two KBr windows to make a thin layer. High resolution mass spectra (HR-MS) were measured on a Bruker maXis instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from  $m/z$  50 to  $m/z$  3000 Da; external calibration with Electrospray Calibrant Solution (Fluka). A syringe injection was used for acetonitrile solutions of synthesized compounds (flow rate 3  $\mu\text{L}/\text{min}$ ). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

## **Spectral data of the 4-substituted pyrazolin-3-ones**

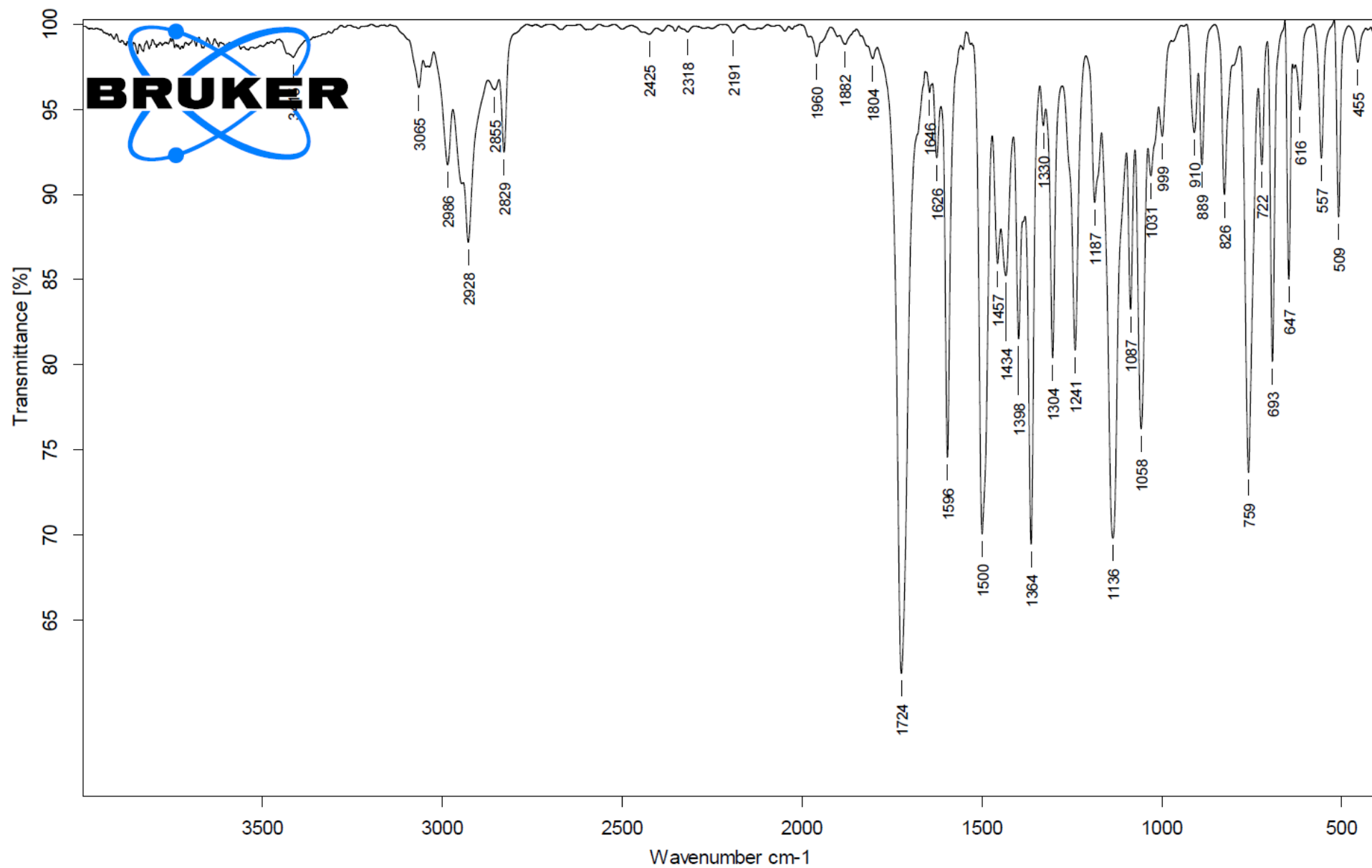












## Display Report

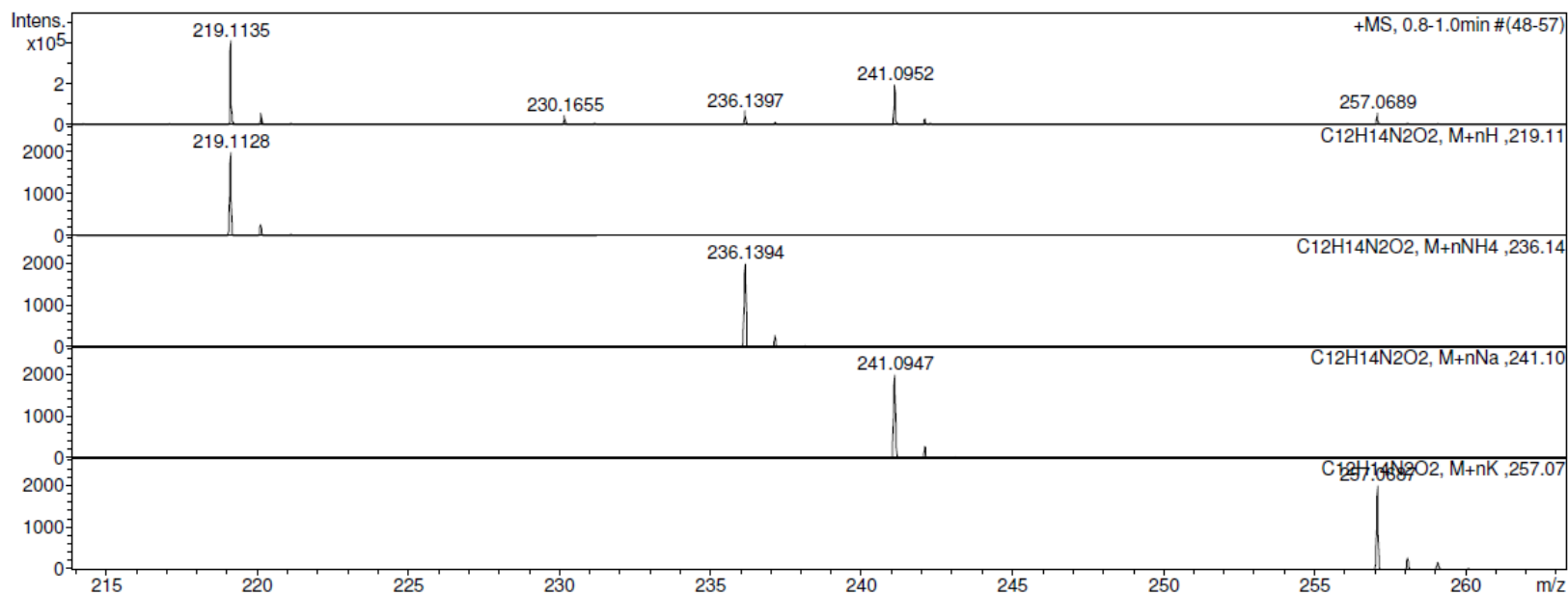
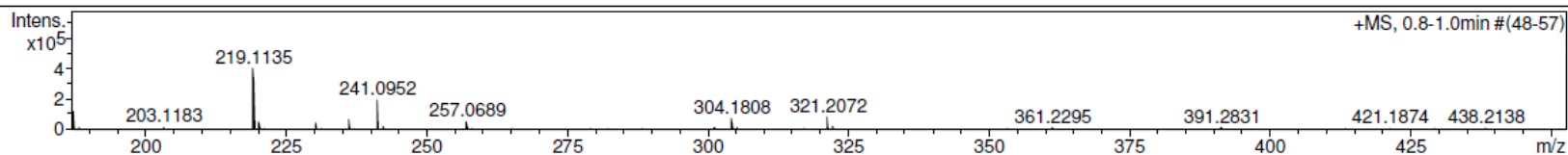
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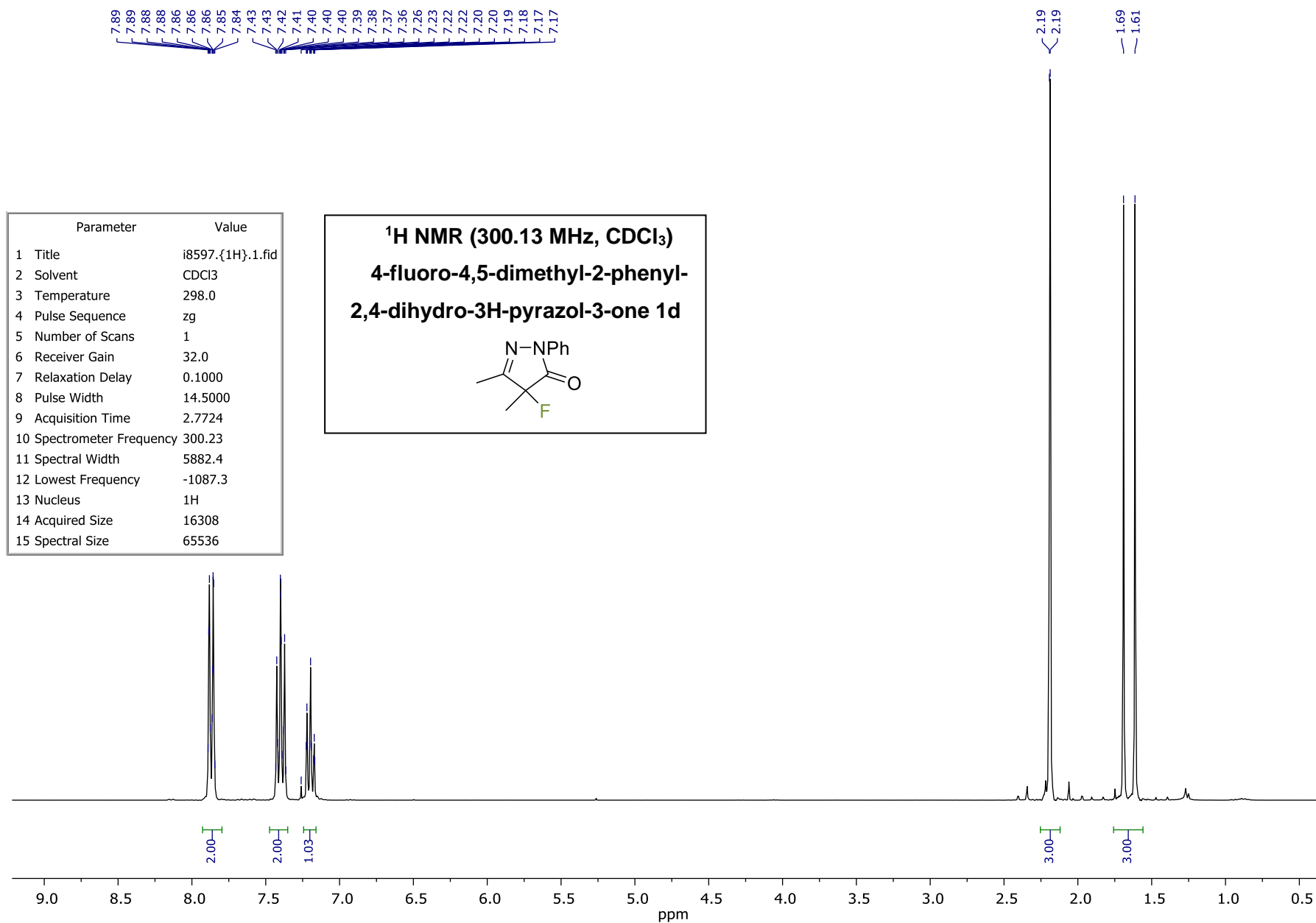
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Method tune\_low.m  
Sample Name /TERN LL-1622  
Comment C12H14N2O2 mH 219.1128 calibrant added, CH3CN

Acquisition Date 13.10.2022 10:46:40  
Operator BDAL@DE  
Instrument / Ser# microTOF 10248

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





168.33  
168.04

158.23  
158.01

137.43

128.96  
125.48

118.53

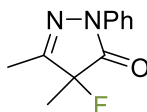
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77.58  
77.16  
76.74

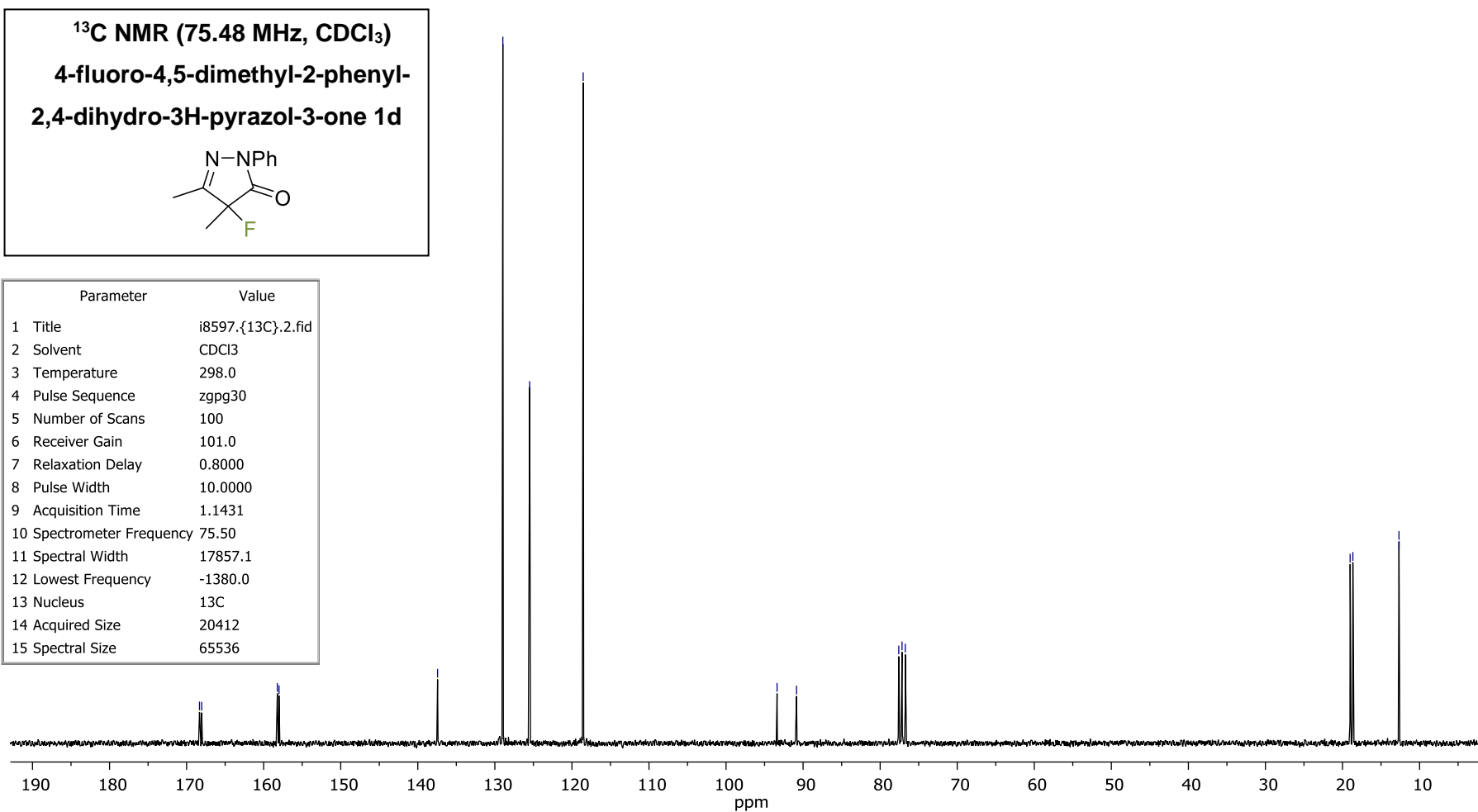
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18.65  
12.67  
12.65

**<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>)**

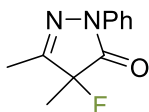
**4-fluoro-4,5-dimethyl-2-phenyl-  
2,4-dihydro-3H-pyrazol-3-one 1d**



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2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.0
4 Pulse Sequence	zgpg30
5 Number of Scans	100
6 Receiver Gain	101.0
7 Relaxation Delay	0.8000
8 Pulse Width	10.0000
9 Acquisition Time	1.1431
10 Spectrometer Frequency	75.50
11 Spectral Width	17857.1
12 Lowest Frequency	-1380.0
13 Nucleus	<sup>13</sup> C
14 Acquired Size	20412
15 Spectral Size	65536



**<sup>19</sup>F NMR (282.47 MHz, CDCl<sub>3</sub>)**  
**4-fluoro-4,5-dimethyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 1d**



1	Title	BUD495- <sup>19</sup> F-2.fid
2	Solvent	CDCl <sub>3</sub>
3	Temperature	298.0
4	Pulse Sequence	zg30
5	Number of Scans	16
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7	Relaxation Delay	2.0000
8	Pulse Width	15.0000
9	Acquisition Time	1.8677
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11	Spectral Width	68493.2
12	Lowest Frequency	-62496.4
13	Nucleus	<sup>19</sup> F
14	Acquired Size	127924
15	Spectral Size	262144

-166.60  
-166.68  
-166.76  
-166.85

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210  
ppm

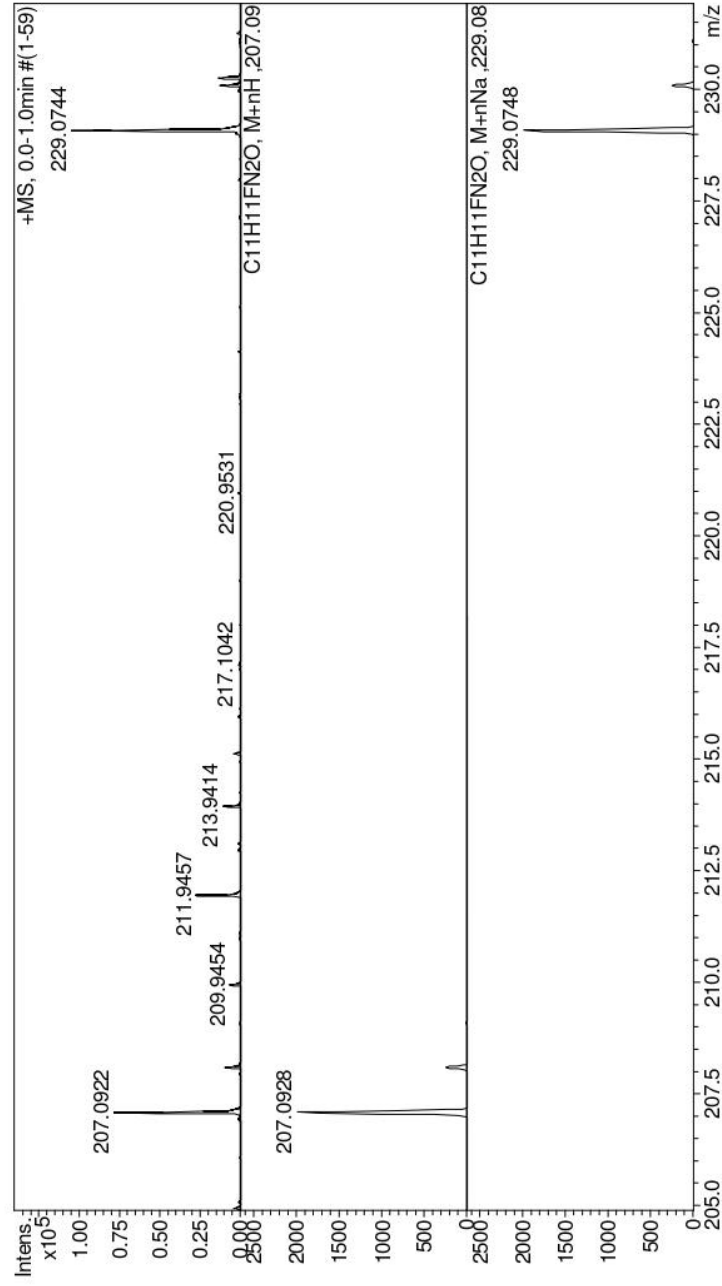
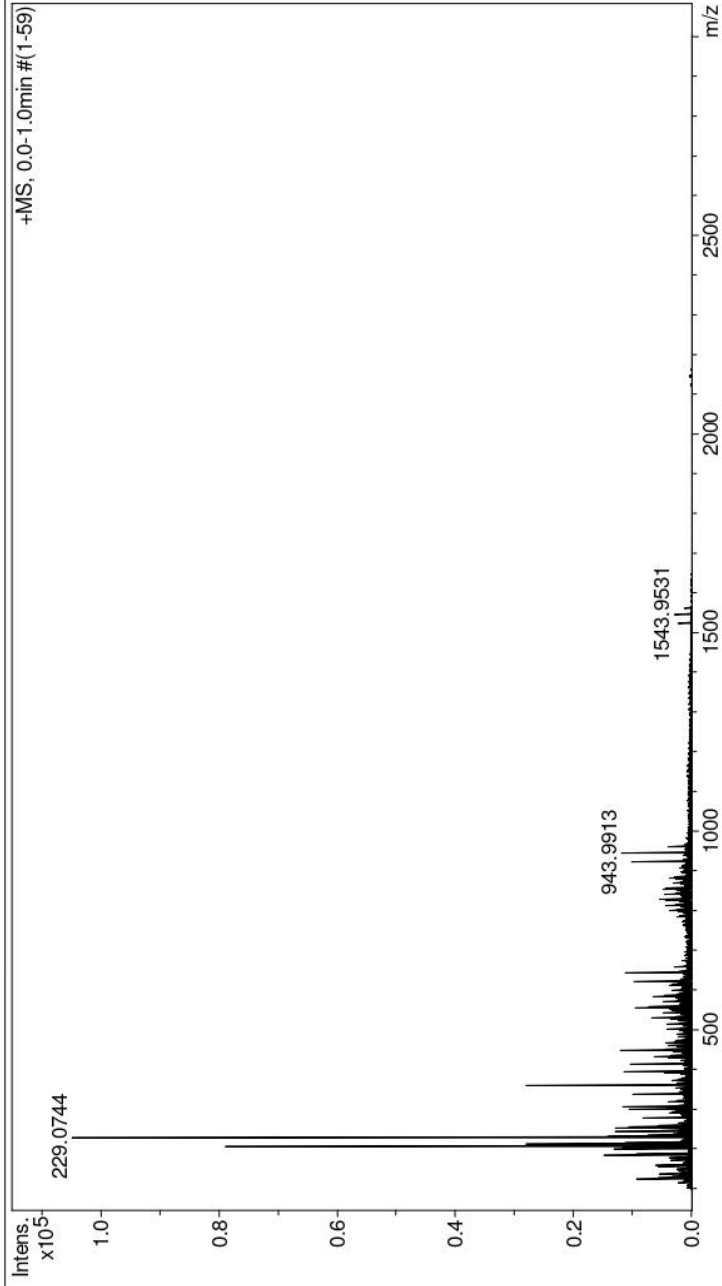
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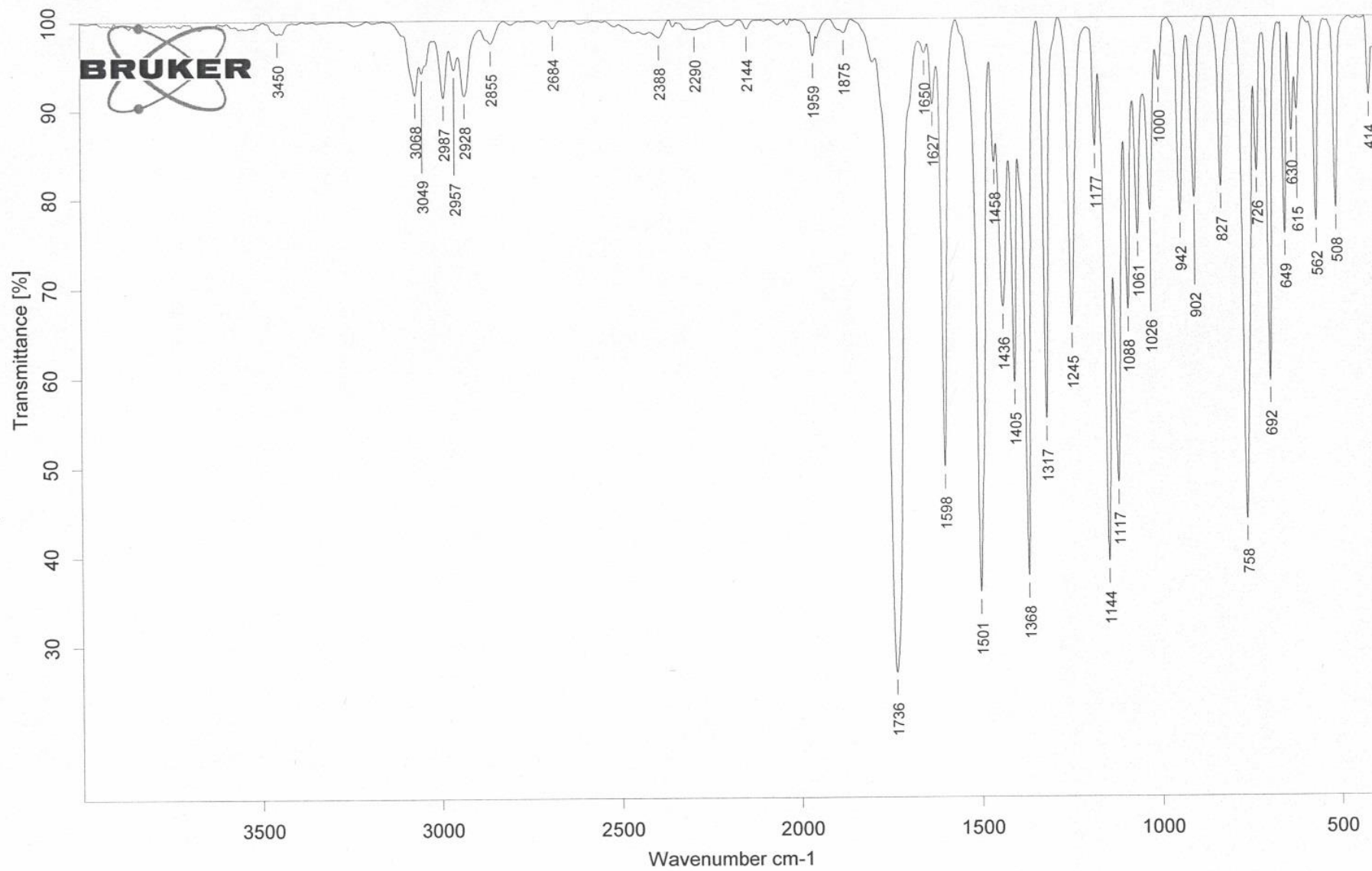
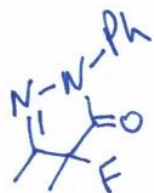
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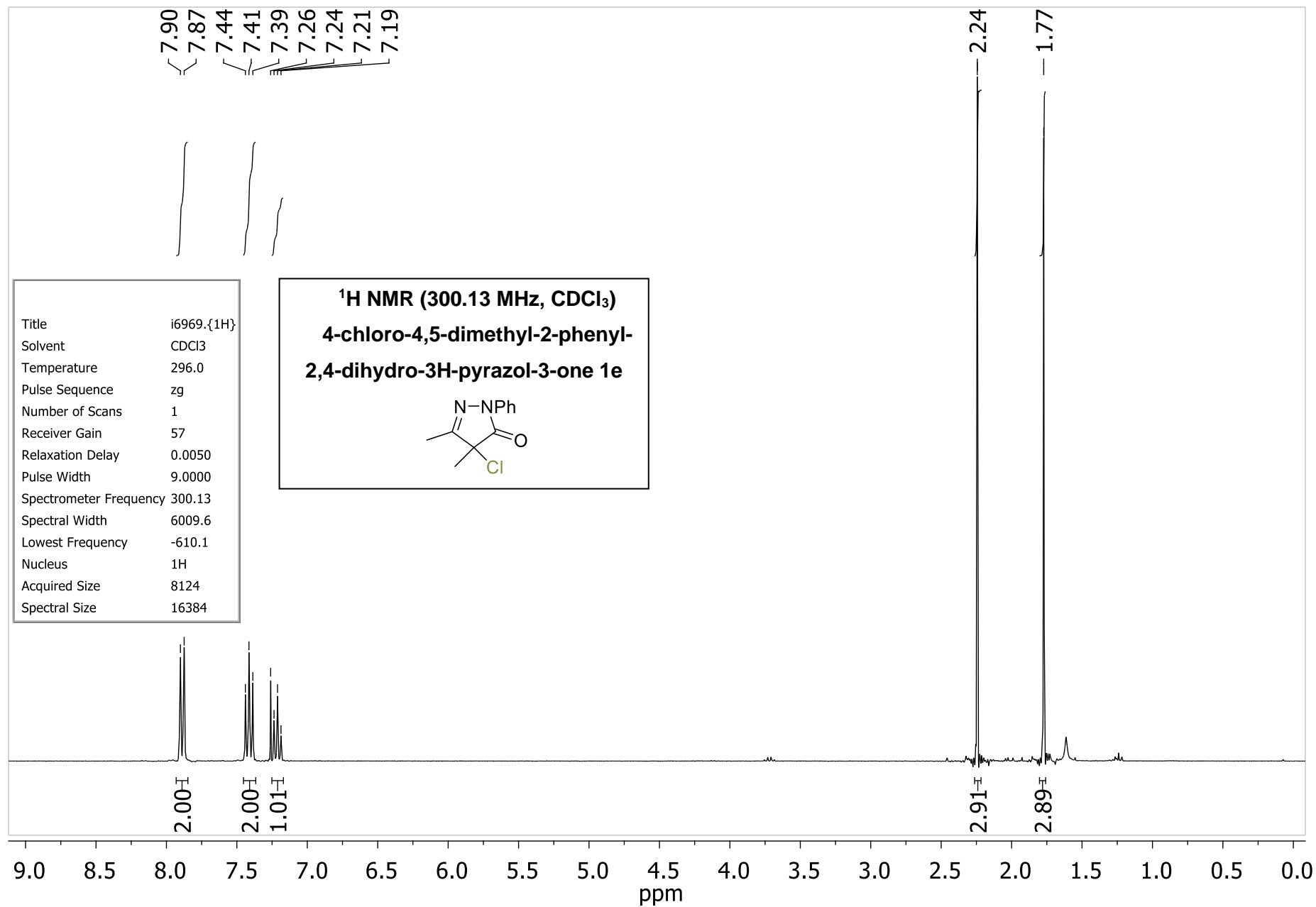
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Sample Name /TERN BUD-925 Instrument / Ser# microTOF 10248  
Comment CH3OH 1000 %, dil. 2000, calibrant added

## Acquisition Parameter

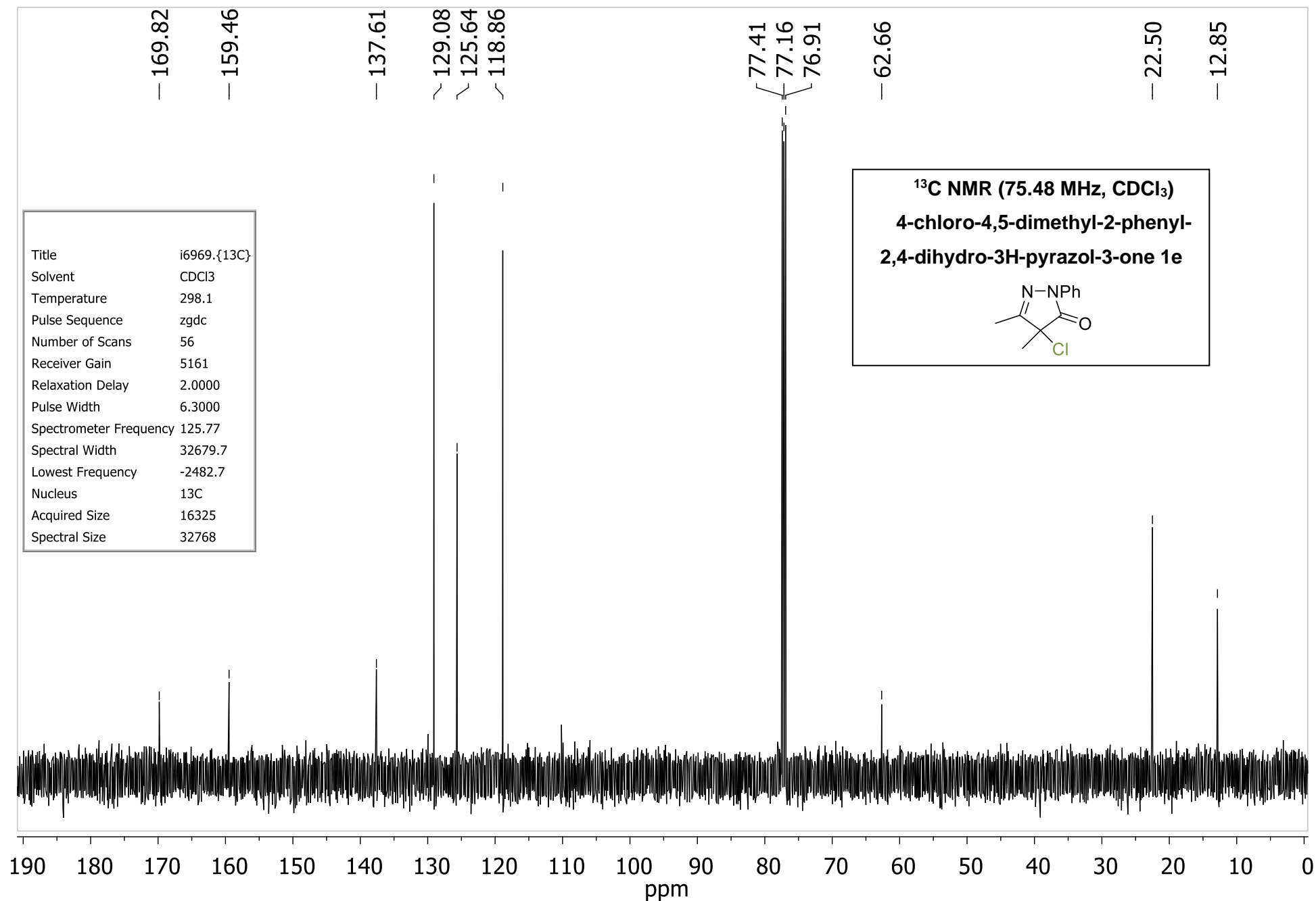
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Waste

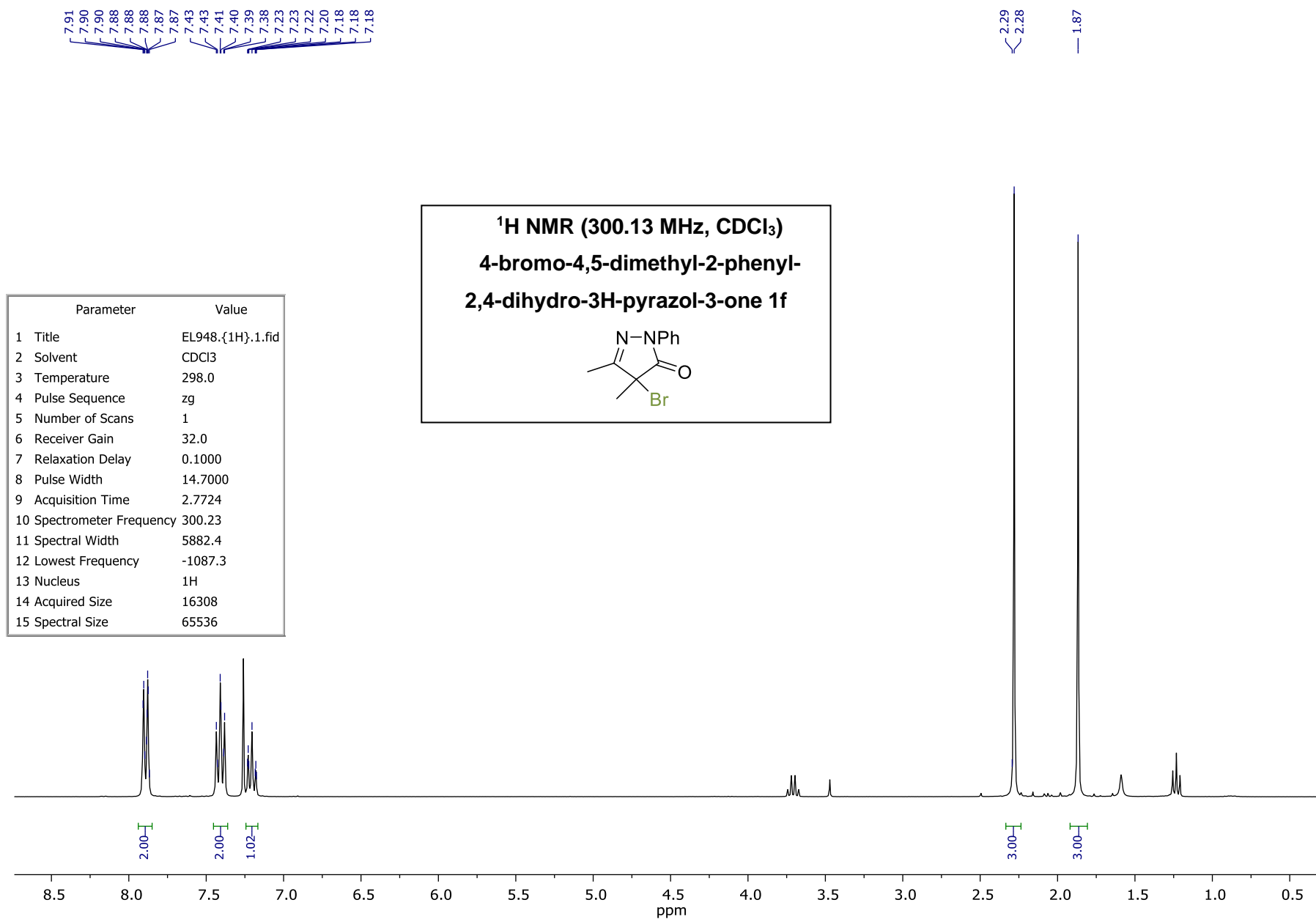




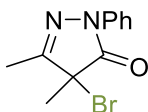




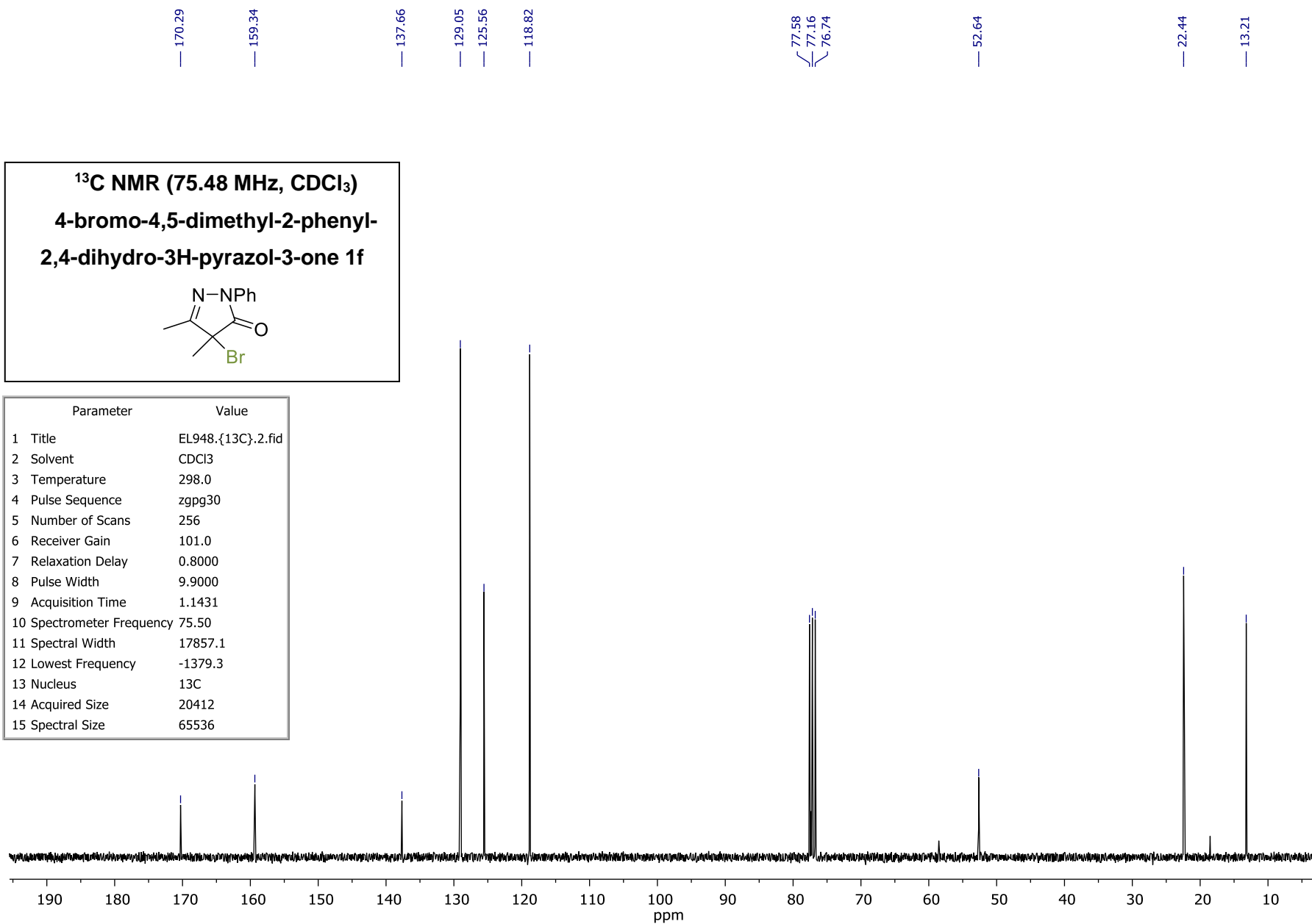




**$^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ )**  
**4-bromo-4,5-dimethyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 1f**



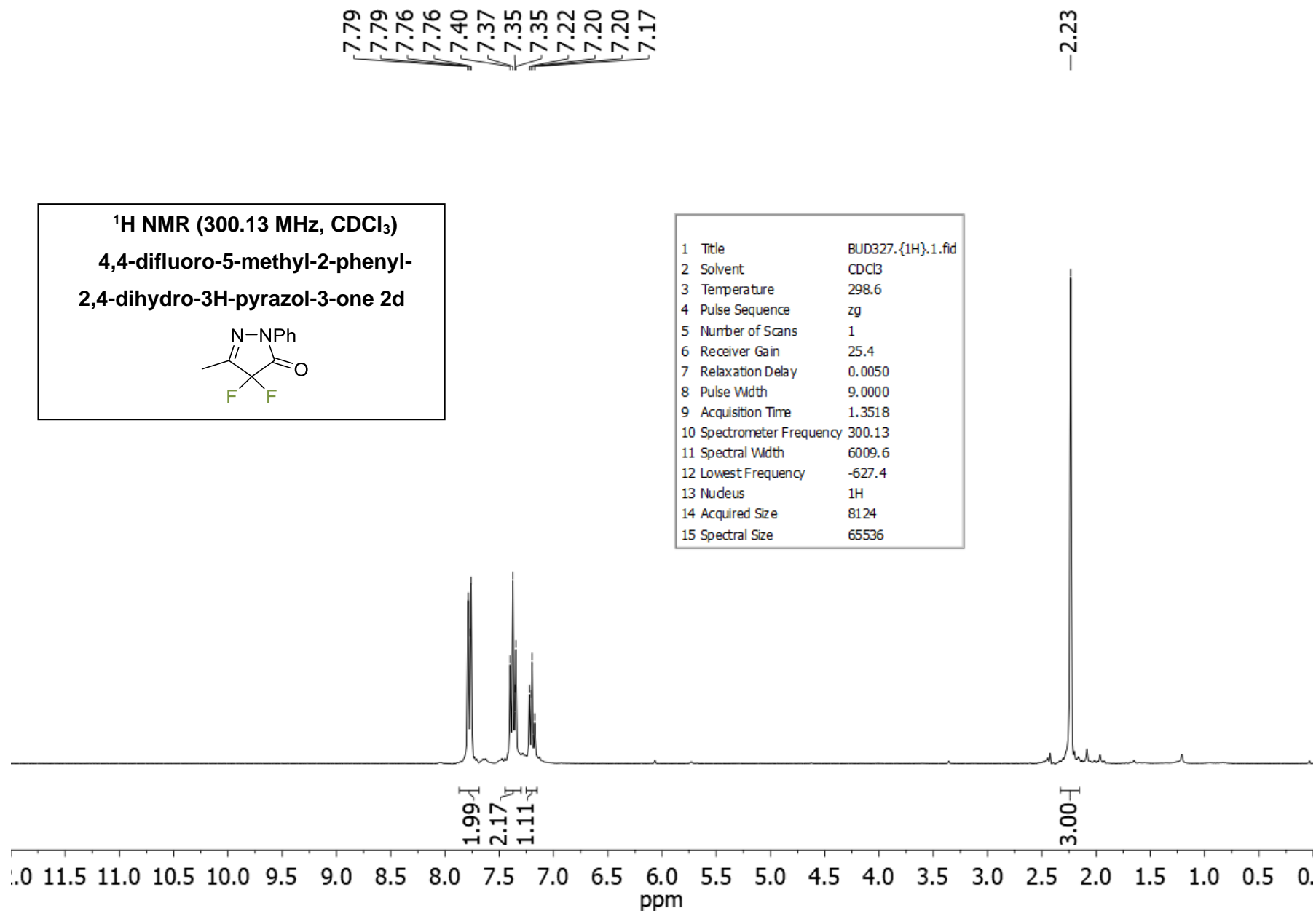
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4 Pulse Sequence	zgpg30
5 Number of Scans	256
6 Receiver Gain	101.0
7 Relaxation Delay	0.8000
8 Pulse Width	9.9000
9 Acquisition Time	1.1431
10 Spectrometer Frequency	75.50
11 Spectral Width	17857.1
12 Lowest Frequency	-1379.3
13 Nucleus	$^{13}\text{C}$
14 Acquired Size	20412
15 Spectral Size	65536



**<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)**  
**4,4-difluoro-5-methyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 2d**



1	Title	BUD327.{1H}.1.fid
2	Solvent	CDCl3
3	Temperature	298.6
4	Pulse Sequence	zg
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11	Spectral Width	6009.6
12	Lowest Frequency	-627.4
13	Nucleus	1H
14	Acquired Size	8124
15	Spectral Size	65536



<sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>)

4,4-difluoro-5-methyl-2-phenyl-  
2,4-dihydro-3H-pyrazol-3-one 2d



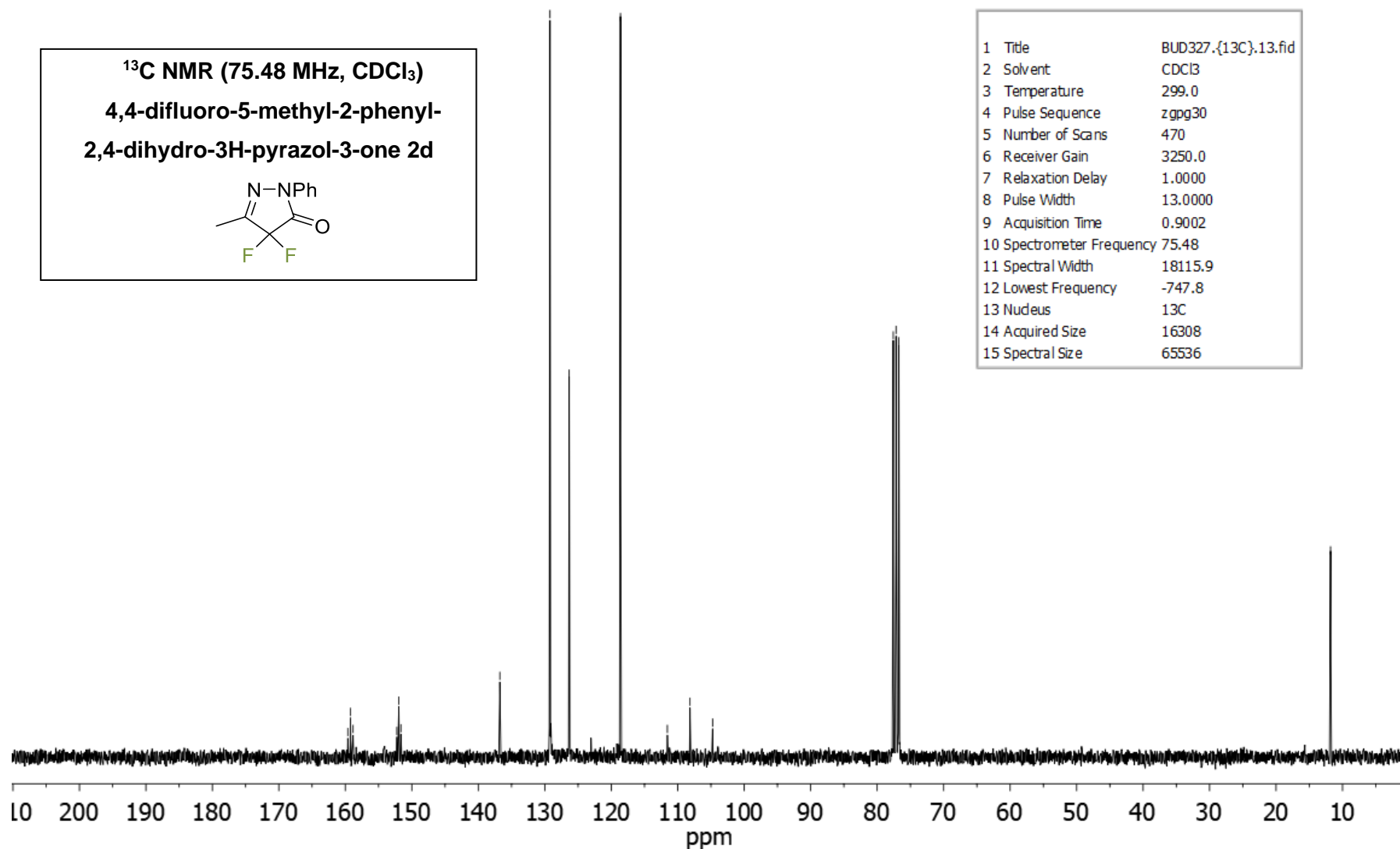
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108.15  
104.75

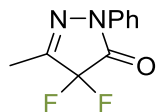
77.58  
77.16  
76.74

11.80

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7	Relaxation Delay	1.0000
8	Pulse Width	13.0000
9	Acquisition Time	0.9002
10	Spectrometer Frequency	75.48
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13	Nucleus	13C
14	Acquired Size	16308
15	Spectral Size	65536



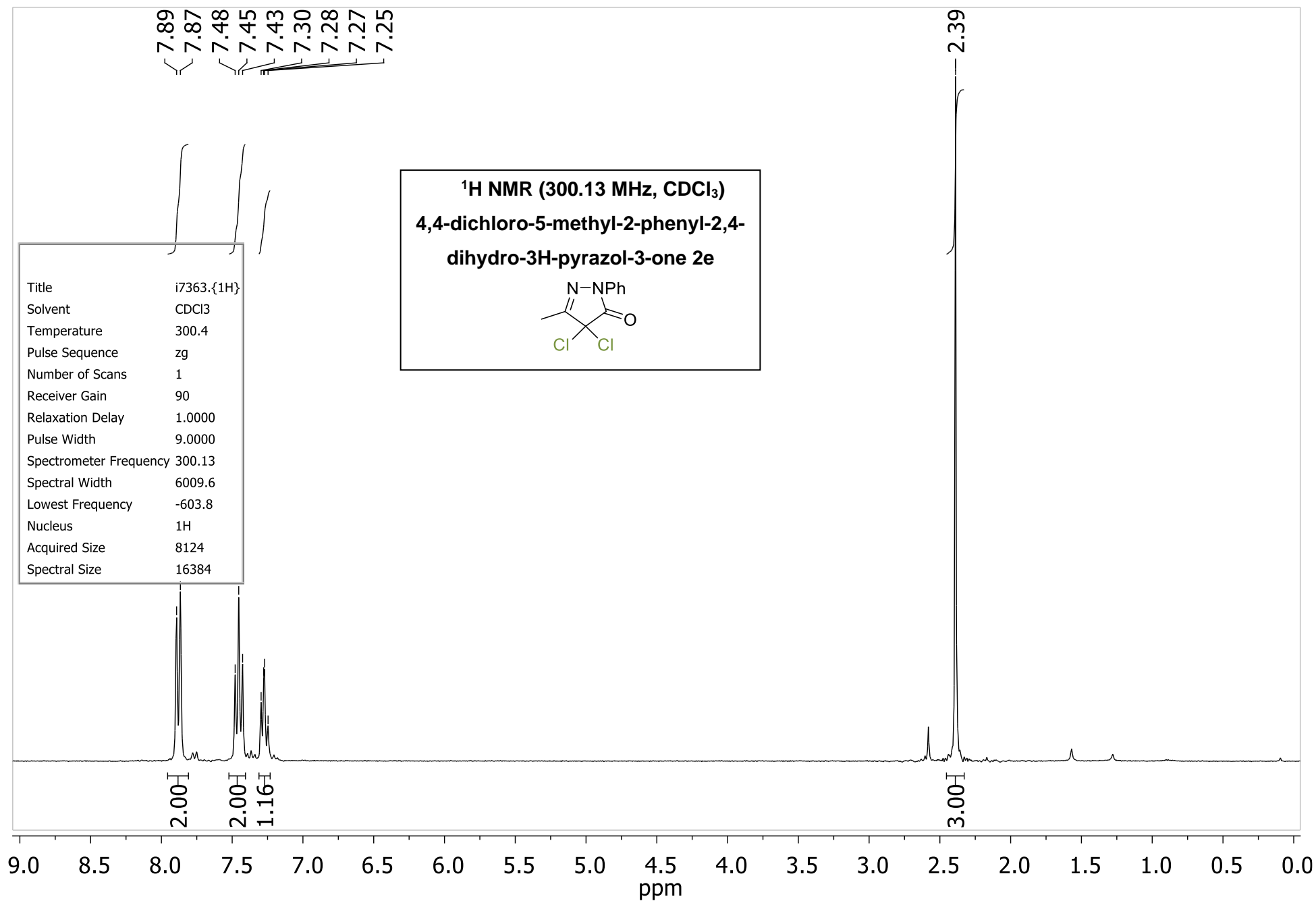
**<sup>19</sup>F NMR (282.39 MHz, CDCl<sub>3</sub>)**  
**4,4-difluoro-5-methyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 2d**

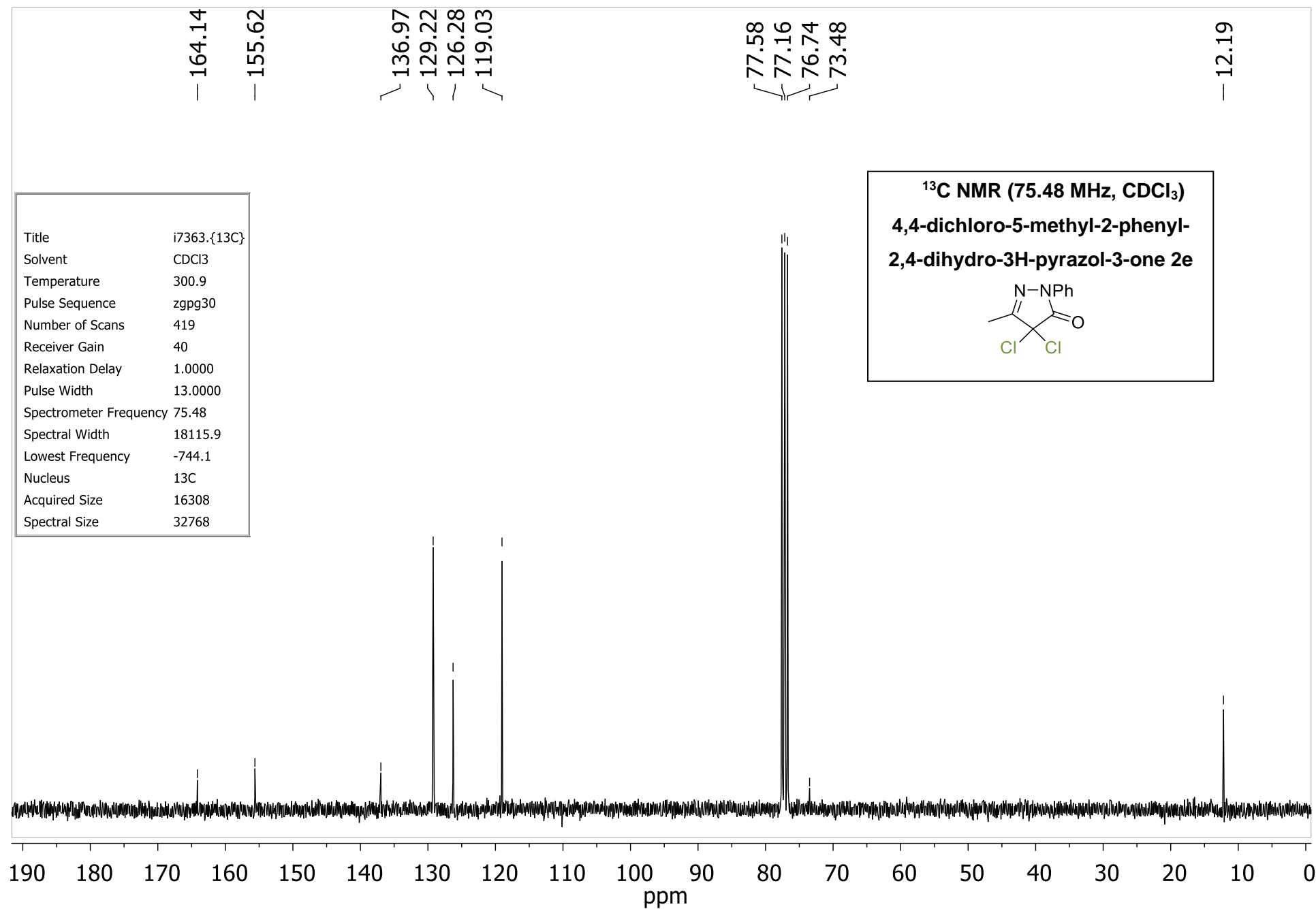


— -123.13

1	Title	BUD327.{19F}.19.fid
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3	Temperature	298.7
4	Pulse Sequence	zg
5	Number of Scans	1
6	Receiver Gain	2300.0
7	Relaxation Delay	0.3000
8	Pulse Width	6.0000
9	Acquisition Time	0.2449
10	Spectrometer Frequency	282.39
11	Spectral Width	138888.9
12	Lowest Frequency	-83785.3
13	Nucleus	19F
14	Acquired Size	34018
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ppm





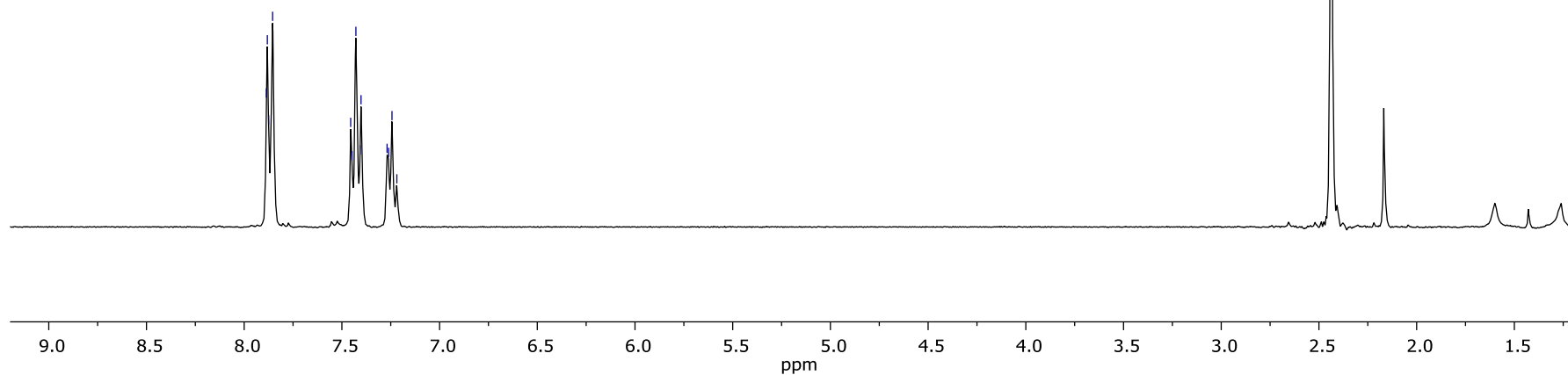
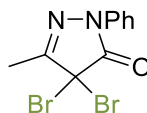


7.89  
7.88  
7.87  
7.85  
7.46  
7.45  
7.43  
7.41  
7.40  
7.27  
7.26  
7.24  
7.22

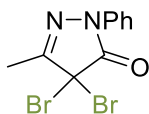
2.44

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8 Pulse Width	9.0000
9 Acquisition Time	1.3518
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13 Nucleus	1H
14 Acquired Size	8124
15 Spectral Size	65536

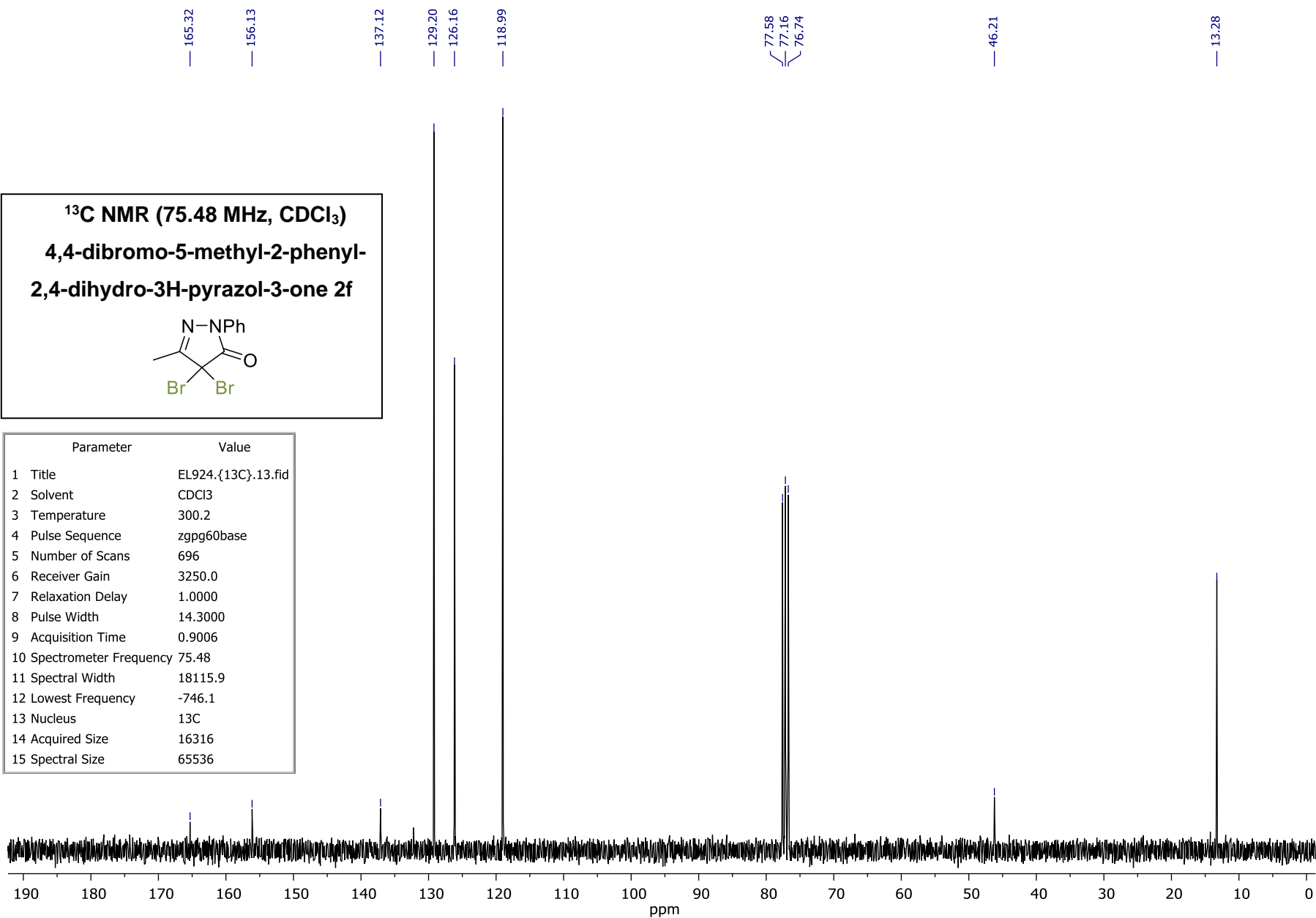
**<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)**  
**4,4-dibromo-5-methyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 2f**

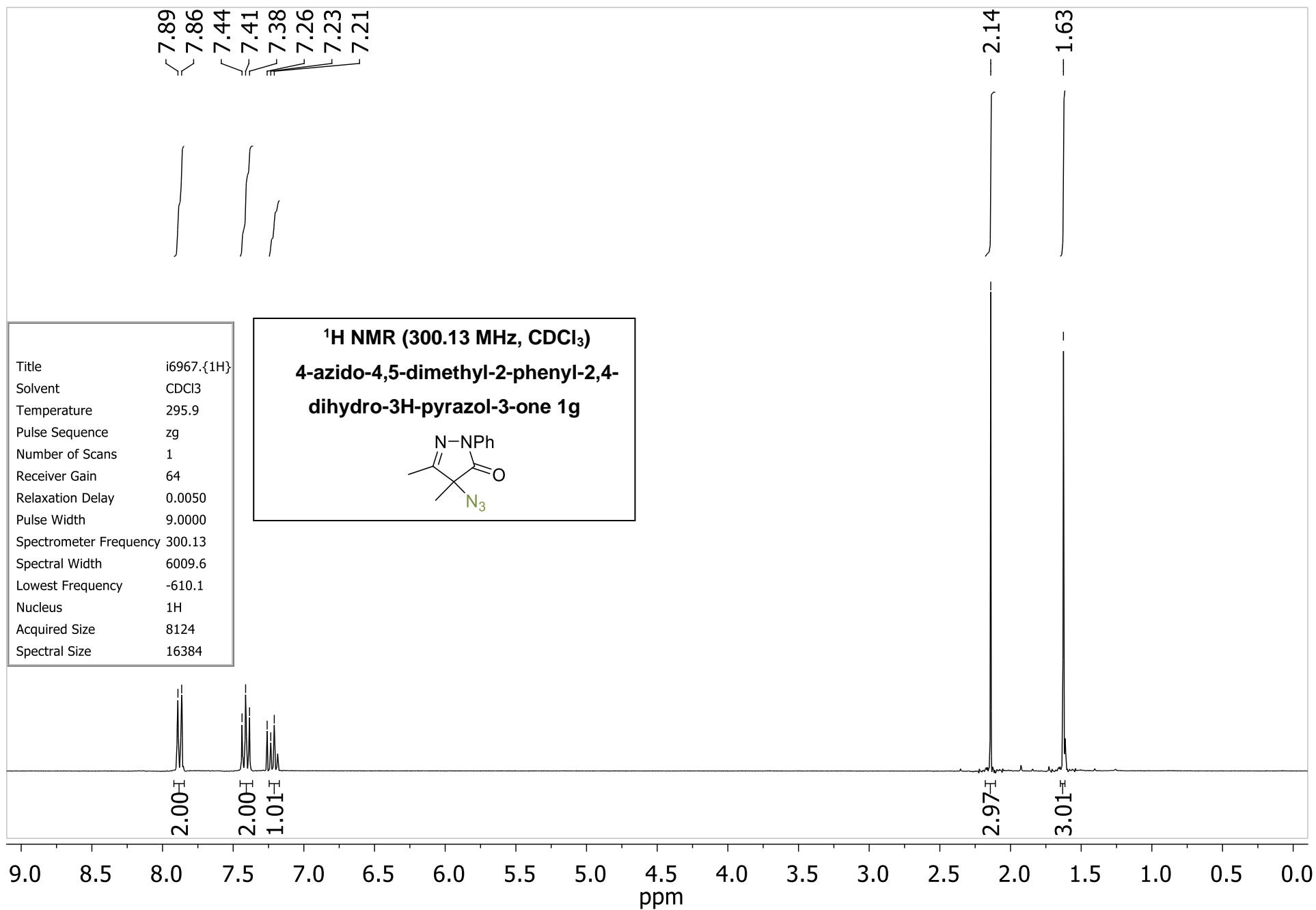


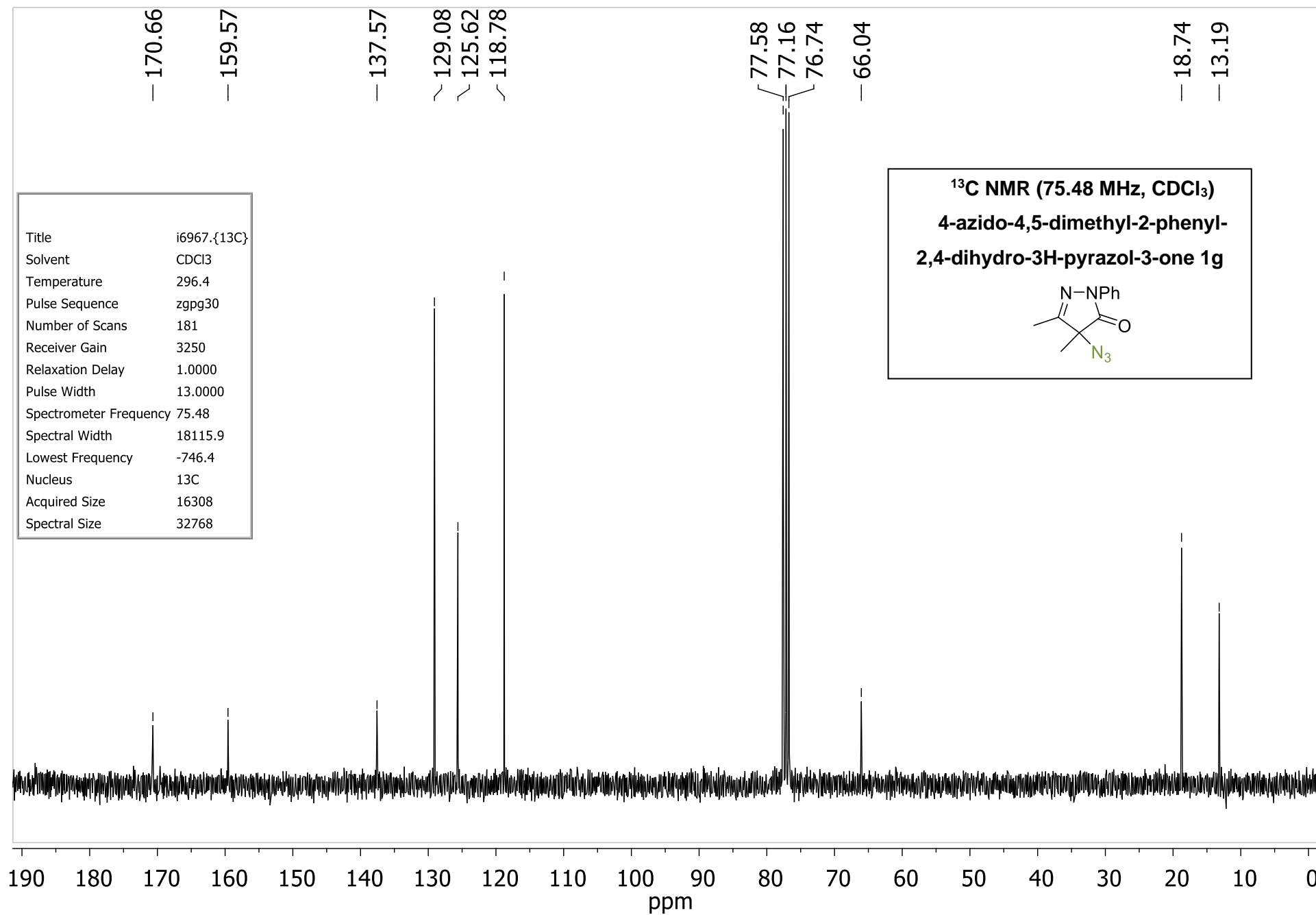
**$^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ )**  
**4,4-dibromo-5-methyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 2f**



Parameter	Value
1 Title	EL924.{ $^{13}\text{C}$ }.13.fid
2 Solvent	$\text{CDCl}_3$
3 Temperature	300.2
4 Pulse Sequence	zgpg60base
5 Number of Scans	696
6 Receiver Gain	3250.0
7 Relaxation Delay	1.0000
8 Pulse Width	14.3000
9 Acquisition Time	0.9006
10 Spectrometer Frequency	75.48
11 Spectral Width	18115.9
12 Lowest Frequency	-746.1
13 Nucleus	$^{13}\text{C}$
14 Acquired Size	16316
15 Spectral Size	65536







# Display Report

## Analysis Info

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Method tune\_low.m

Operator BDAL@DE

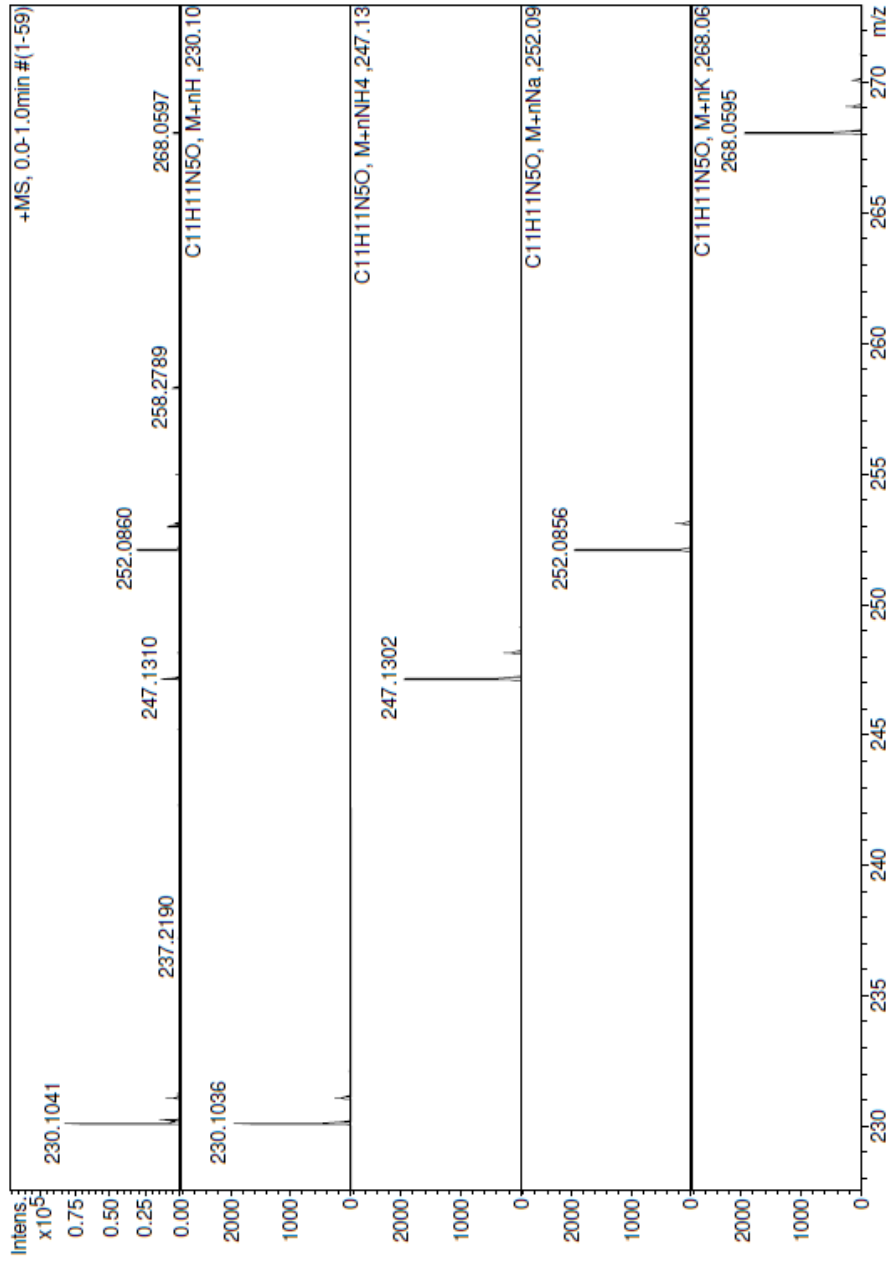
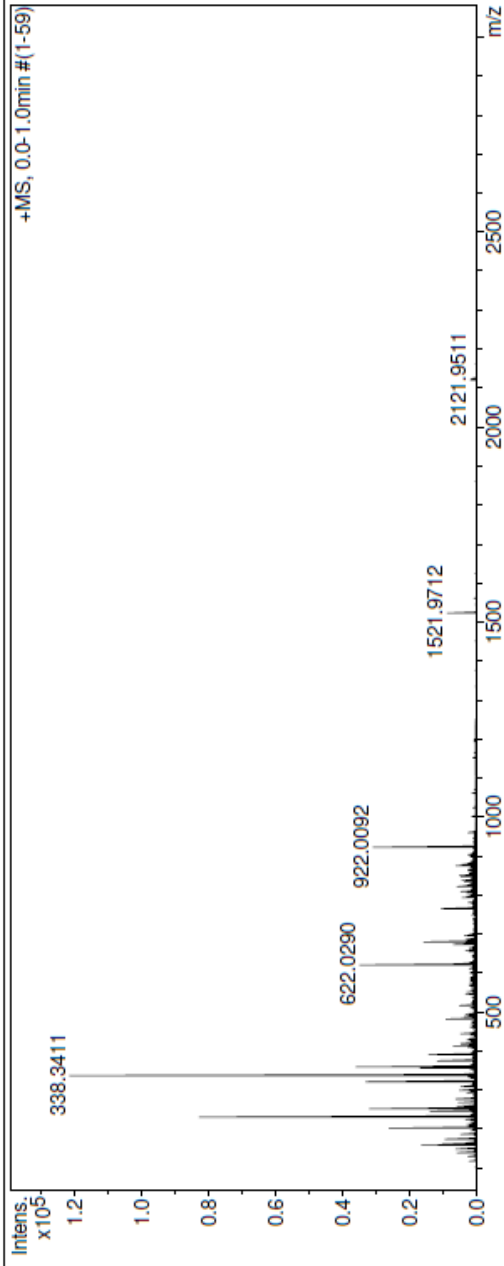
Sample Name /TERN LL-564

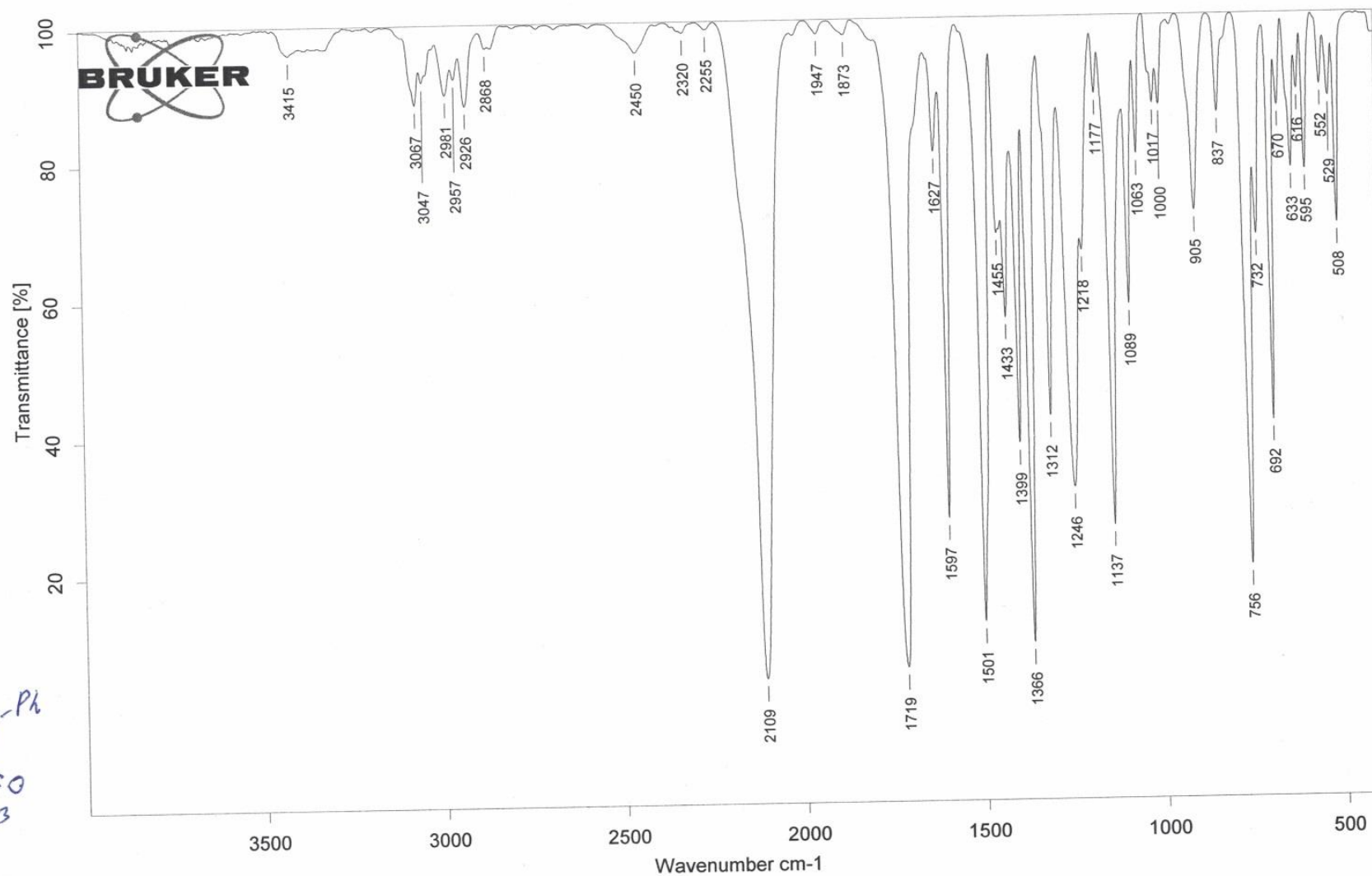
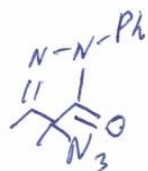
Instrument / Ser# microTOF 10248

Comment CH3CN 100 %, dil. 200, calibrant added

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z			Set Divert Valve	Waste





D:\ИЛ\Лопатьева LL-564.0

Лопатьева LL-564

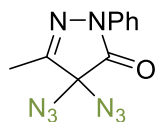
КВг тонкий слой

10.02.2021

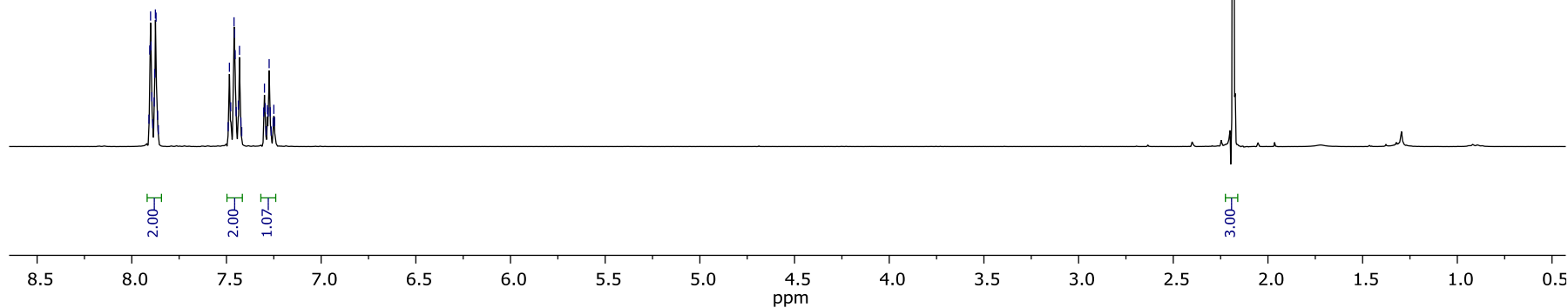


**<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>)**

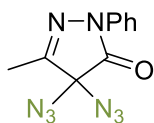
**4,4-diazido-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one 2g**



Parameter	Value
1 Title	EL980.{1H}.1.fid
2 Solvent	CDCl3
3 Temperature	298.0
4 Pulse Sequence	zg
5 Number of Scans	1
6 Receiver Gain	32.0
7 Relaxation Delay	0.1000
8 Pulse Width	14.7000
9 Acquisition Time	2.7724
10 Spectrometer Frequency	300.23
11 Spectral Width	5882.4
12 Lowest Frequency	-1087.3
13 Nucleus	1H
14 Acquired Size	16308
15 Spectral Size	65536



**$^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ )**  
**4,4-diazido-5-methyl-2-phenyl-**  
**2,4-dihydro-3H-pyrazol-3-one 2g**



Parameter	Value
1 Title	EL980.{ $^{13}\text{C}$ }.2.fid
2 Solvent	$\text{CDCl}_3$
3 Temperature	298.0
4 Pulse Sequence	zgpg30
5 Number of Scans	256
6 Receiver Gain	101.0
7 Relaxation Delay	0.8000
8 Pulse Width	9.9000
9 Acquisition Time	1.1431
10 Spectrometer Frequency	75.50
11 Spectral Width	17857.1
12 Lowest Frequency	-1373.8
13 Nucleus	$^{13}\text{C}$
14 Acquired Size	20412
15 Spectral Size	65536

