Supporting Information

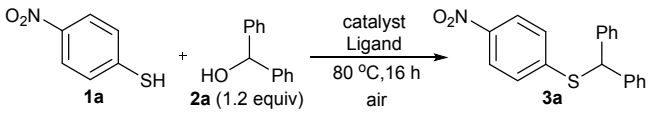
Direct substitution of benzylic alcohols with electron-deficient benezenethiols via π-benzylpalladium(II) in water

Hidemasa Hikawa,* Mariko Toyomoto, Shoko Kikkawa, and Isao Azumaya*

Faculty of Pharmaceutical Sciences, Toho University, Funabashi, Chiba 274-8510, Japan

hidemasa.hikawa@phar.toho-u.ac.jp and isao.azumaya @phar.toho-u.ac.jp

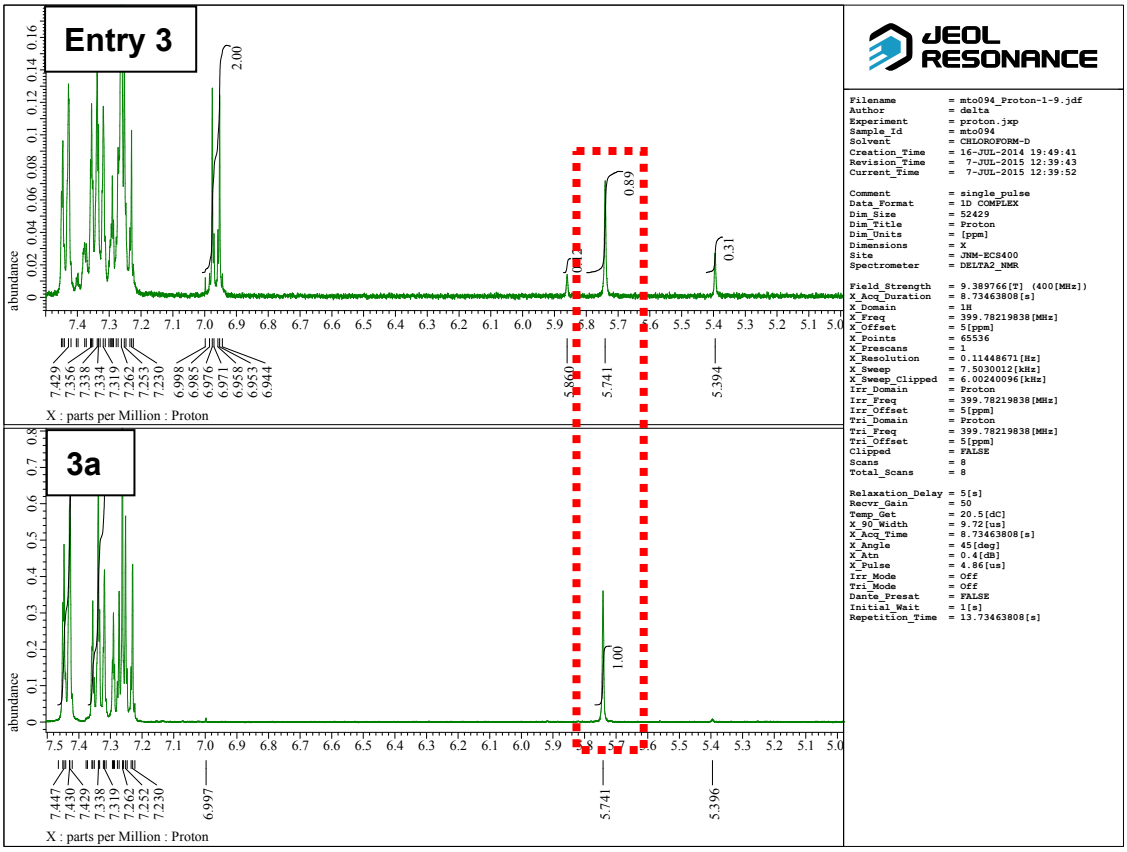
Table 1, Entry 9 (The yield was determined by ^{1}H NMR analysis of the crude product using *p*-nitroanisole as an internal standard.)



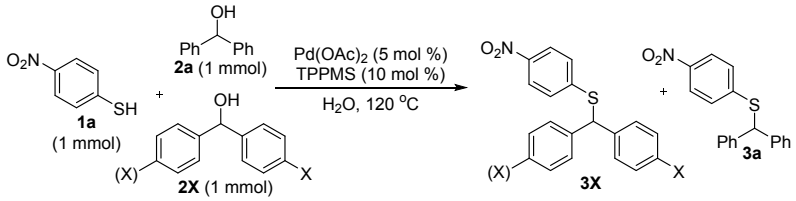
A mixture of 4-nitrobenzenethiol **1a** (155.4 mg, 1 mmol), $PdCl_2(MeCN)_2$ (13.0 mg, 0.05 mmol), TPPMS (36.7 mg, 0.1 mmol), and benzhydrol **2a** (221.6 mg, 1.2 mmol) in H_2O (4 mL) was heated at 80 °C in a sealed tube under air. After the reaction mixture was cooled, *p*-nitroanisole (153.3 mg, 1 mmol, internal standard) was added to the reaction mixture, which was extracted with $CDCl_3$ (8 mL), then the organic layer was analyzed by ^{1}H-NMR spectroscopy.

Conversion yield was calculated by integration.

	desired **3a**	*p*-nitroanisole **internal standard**
Signal δ	5.74 (methine -**H**)	6.97 (Ar-**H**)
Integral value	0.89 (1H)	2.00 (2H)
Calculated ratio	89% from **1a**	153 mg (1 mmol)

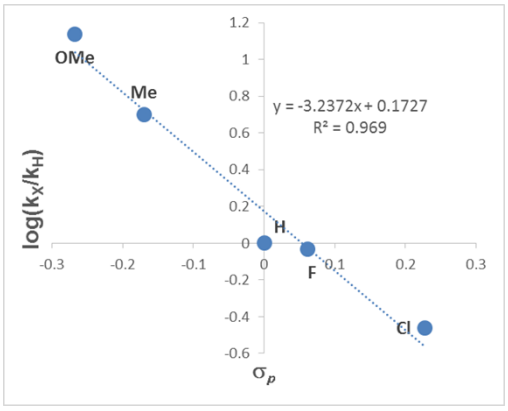


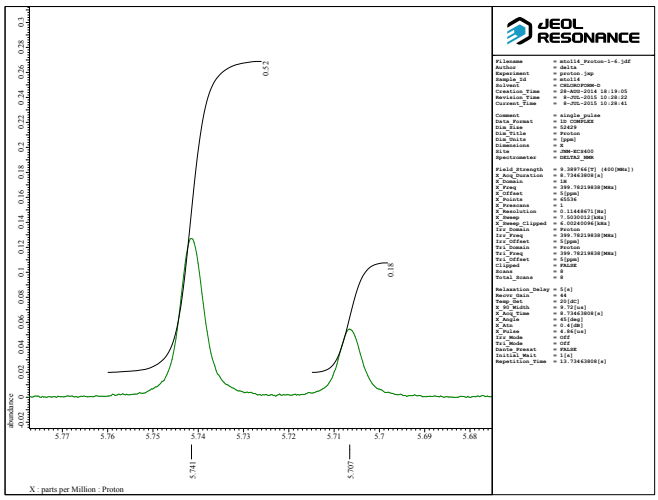
Hammett study



A mixture of 4-nitrobenzenethiol **1a** (155.4 mg, 1 mmol), $Pd(OAc)_2$ (11.7 mg, 0.05 mmol), TPPMS (36.7 mg, 0.1 mmol), benzhydryl alcohols **2X** (1 mmol), and benzhydrol **2a** (184.8 mg, 1 mmol) in H_2O (4 mL) was heated at 120 °C in a sealed tube under air. After the reaction mixture was cooled, *p*-nitroanisole (153 mg, 1 mmol, internal standard) was added to the reaction mixture, which was extracted with $CDCl_3$ (8 mL), then the organic layer was analyzed by ^{1}H-NMR spectroscopy.

	σ	log (k_X/k_H)
3b (diOMe)	-0.268	1.14
3d (Me)	-0.17	0.70
3c (diF)	0.062	-0.034
3a (H)	0	0
3e (Cl)	0.227	-0.46



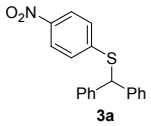


X=H, **3a**

[methine-H] (1H)]

δ: 5.74 ppm

Integrate: 0.52

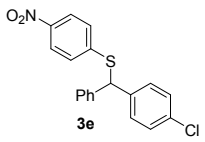


X=Cl, **3e**

[methine-H (1H)]

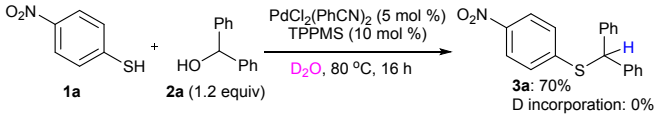
δ: 5.71 ppm

Integrate: 0.18



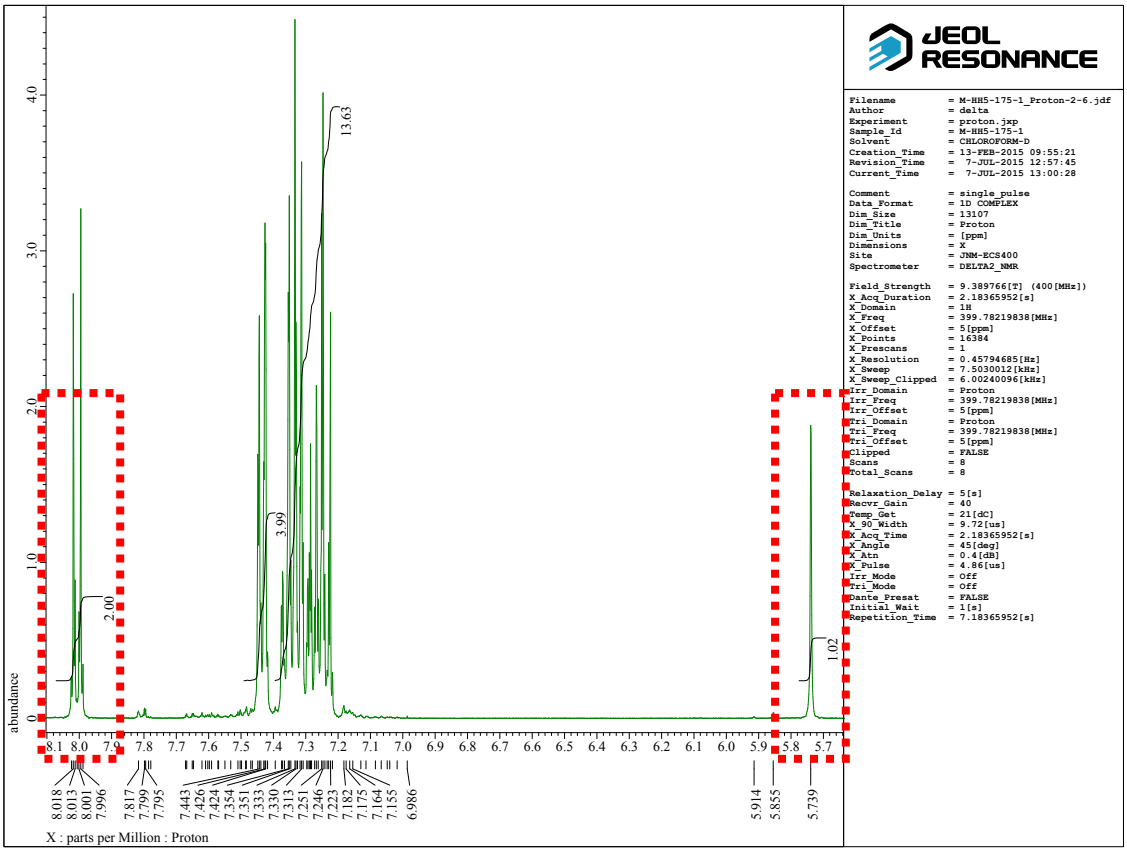
log (k_X/k_H) = log (0.18/0.52) = -0.46

Control experiment (Scheme 6A)

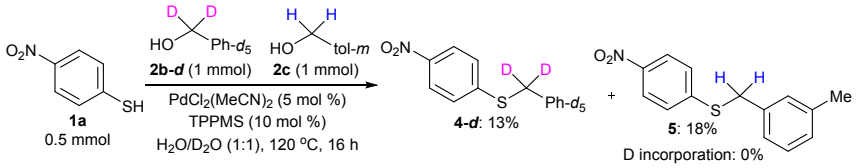


A mixture of 4-nitrobenzenethiol **1a** (77 mg, 0.5 mmol), $PdCl_2(MeCN)_2$ (6.5 mg, 0.025 mmol), sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 18 mg, 0.05 mmol), and benzhydrol **2a** (110 mg, 0.6 mmol), in D_2O (1.5 mL) was heated at 80 °C for 16 h in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give desired product **3a** (112 mg, 0.35 mmol, 70%).

Signal δ	8.01 (Ar-**H**)	5.74 (methin-**H**)
Integral value	2.0 (2H)	1.0 (1H)

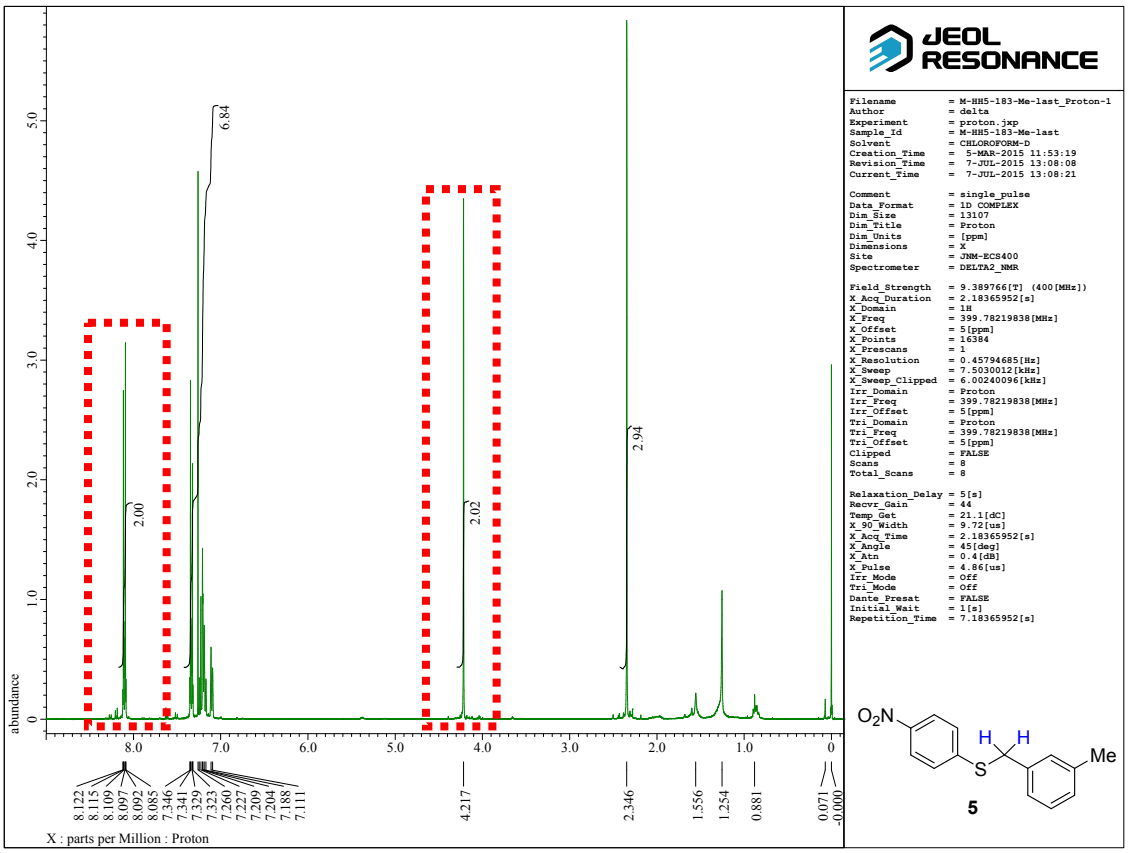


Control experiment (Scheme 6B)

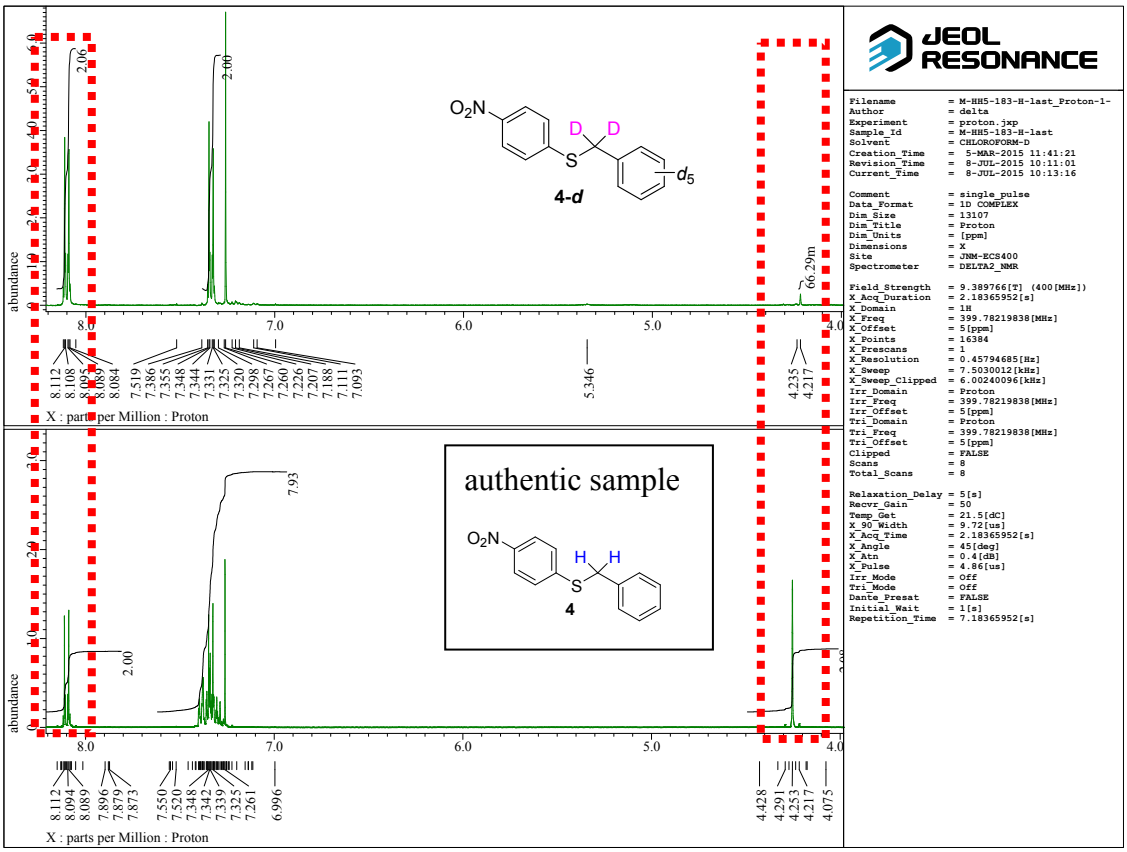


A mixture of 4-nitrobenzenethiol **1a** (77 mg, 0.5 mmol), $PdCl_2(MeCN)_2$ (6.5 mg, 0.025 mmol), sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 18 mg, 0.05 mmol), and benzyl alcohol-d_7 **2b-*d*** (114 mg, 1 mmol), and 3-methylbenzyl alcohol **2c** (122 mg, 1 mmol), in H_2O (2 mL) was heated at 120 °C for 16 h in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography and PTLC (silica gel, hexanes/EtOAc) to give desired product **4-*d*** (16 mg, 0.063 mmol, 13%) and **5** (23 mg, 0.09 mmol, 18%), respectively.

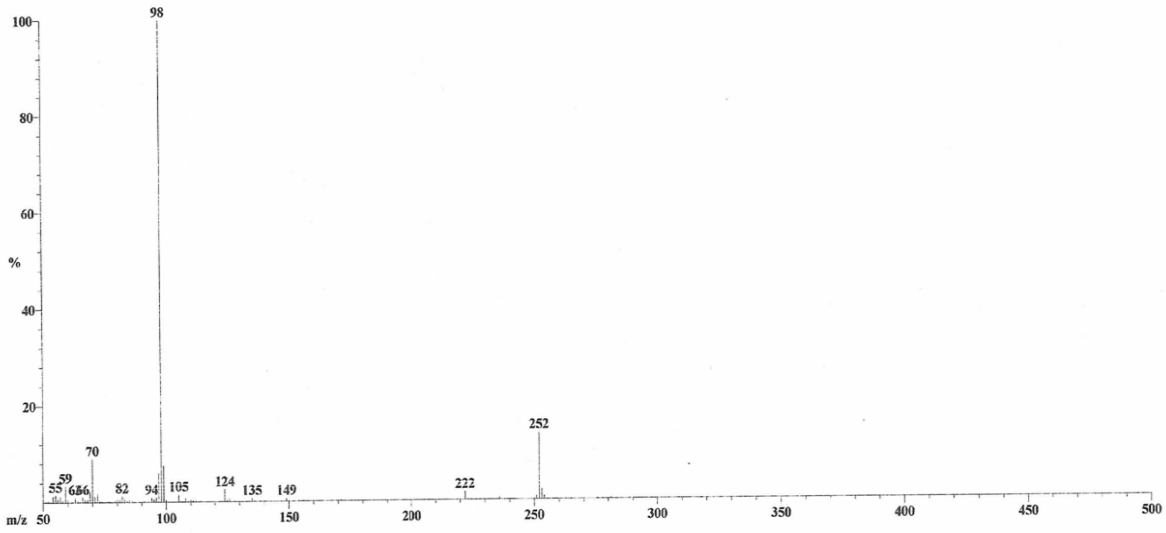
Signal δ	8.01 (Ar-**H**)	4.22 (methylene -**H**)
Integral value	2.0 (2H)	2.0 (2H)

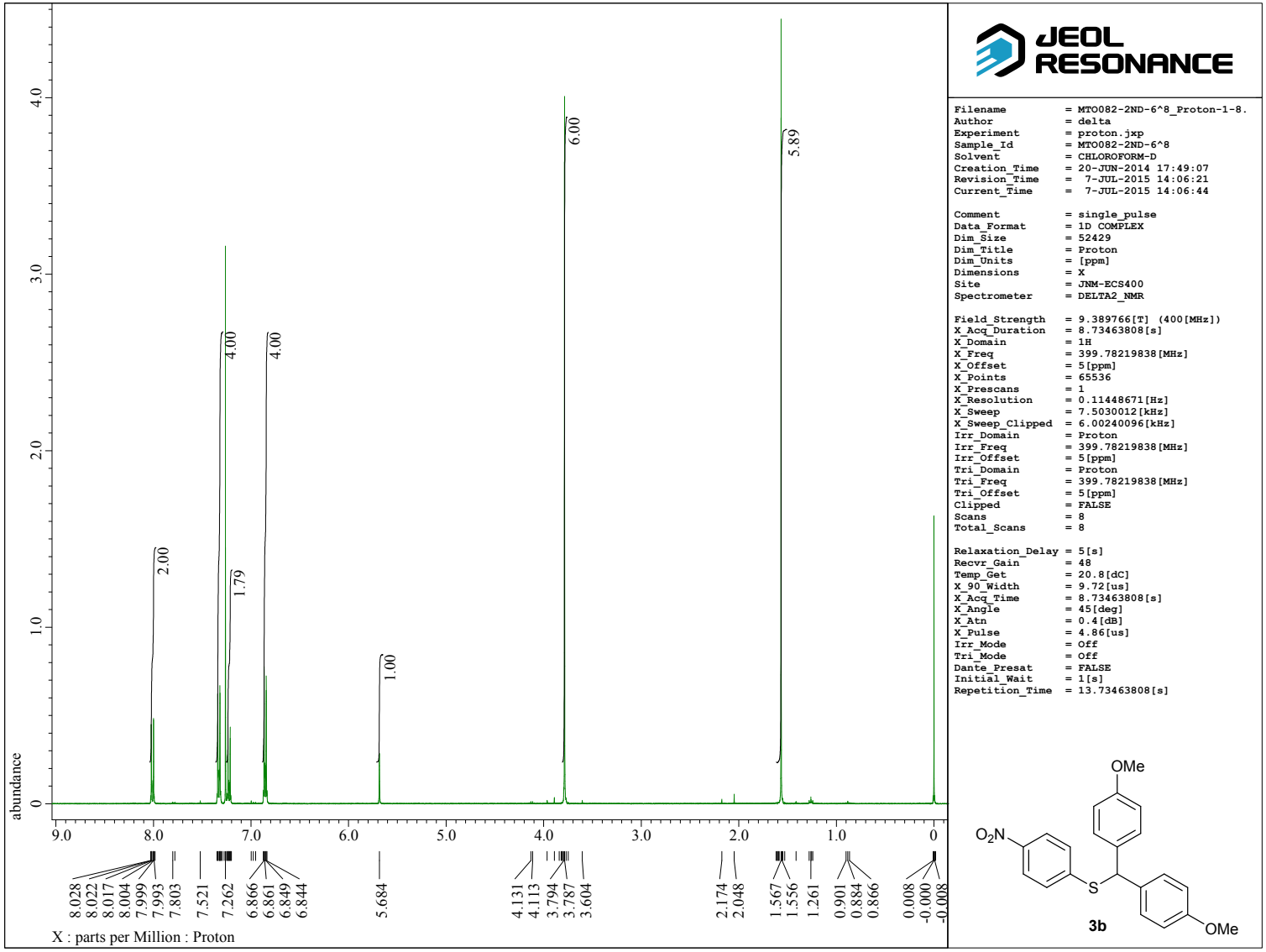


Signal δ	8.01 (Ar-**H**)	4.2 (methylene-**H**)
Integral value	2.0 (2H)	Not detected (2H)



MS (EI): *m/z* (%) 252 (M^+, 14.0), 98 (100).

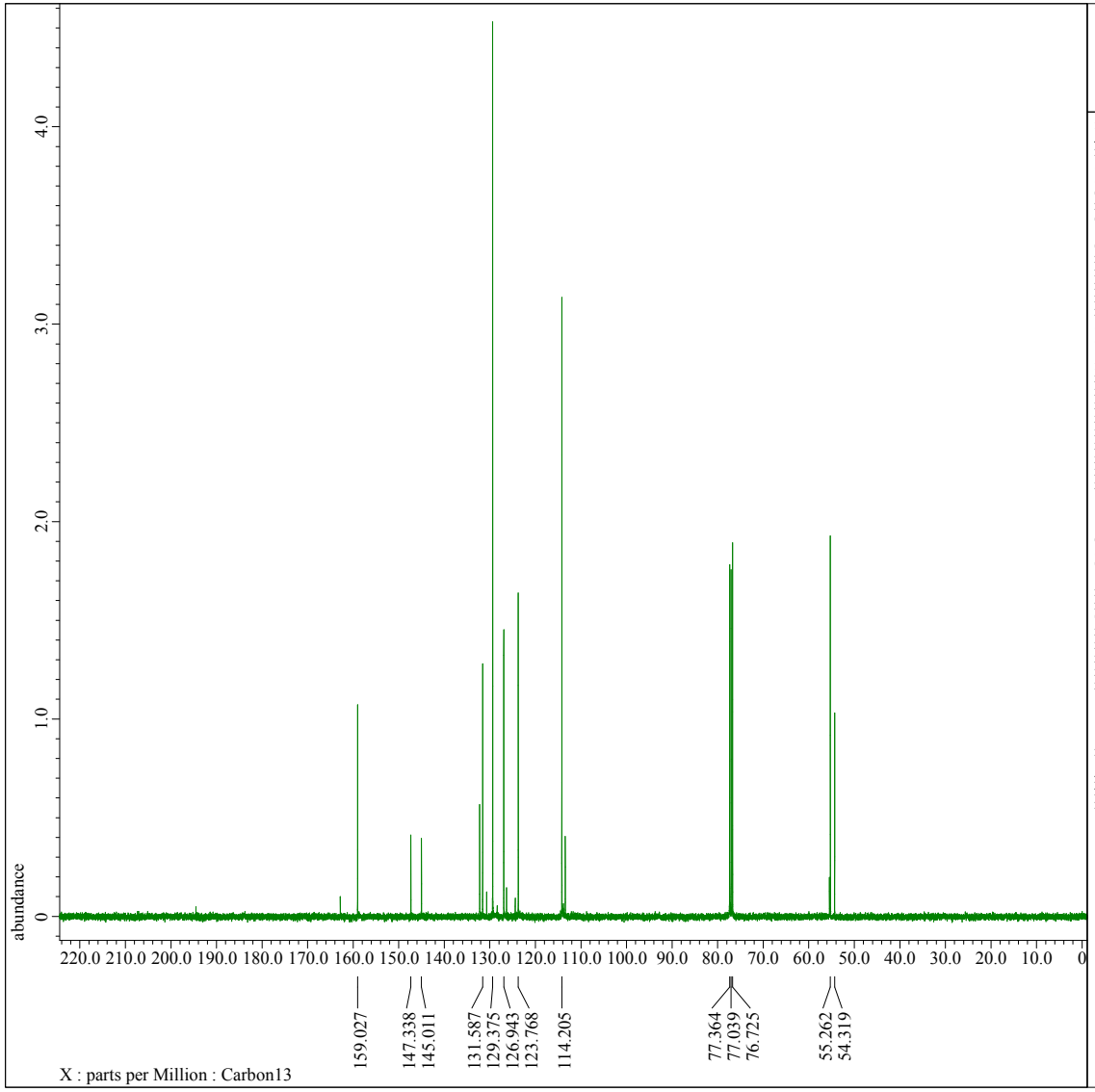




JEOL RESONANCE

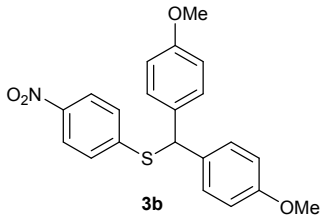
```
Filename          = MTO082-2ND-6^8_Proton-1-8.
Author            = delta
Experiment        = proton.jxp
Sample_Id         = MTO082-2ND-6^8
Solvent           = CHLOROFORM-D
Creation_Time     = 20-JUN-2014 17:49:07
Revision_Time     =  7-JUL-2015 14:06:21
Current_Time      =  7-JUL-2015 14:06:44

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 48
Temp_Get          = 20.8[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```


3b

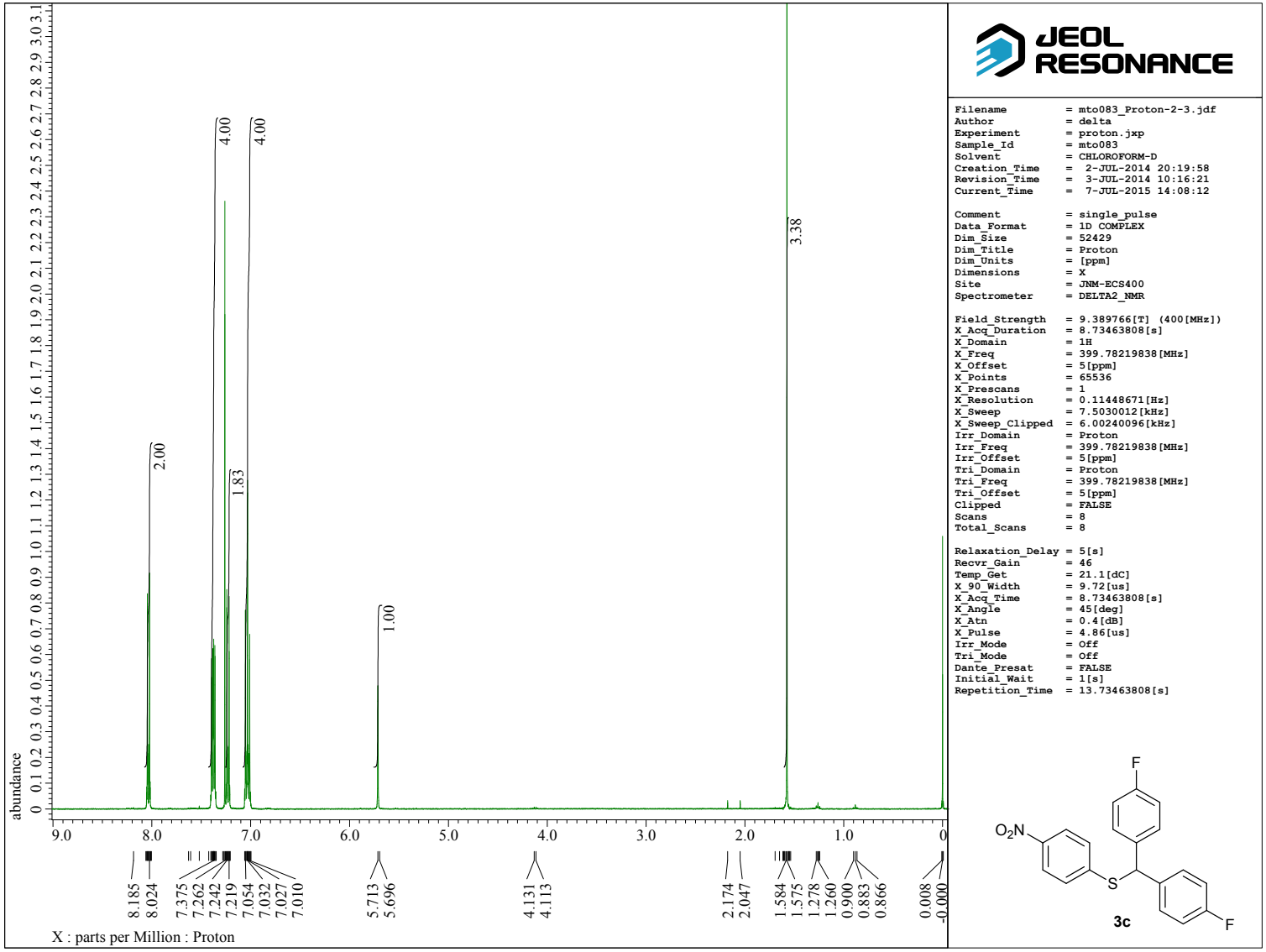


JEOL RESONANCE

```
Filename          = M-3b-toyo_Carbon-1-4.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = M-3b-toyo
Solvent           = CHLOROFORM-D
Creation_Time     = 15-SEP-2015 13:05:24
Revision_Time     = 15-SEP-2015 13:31:19
Current_Time      = 15-SEP-2015 13:32:55

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 331
Total_Scans       = 331

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.8[dC]
X_90_Width        = 7.63[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 3.3[dB]
X_Pulse           = 2.54333333[us]
Irr_Atn_Dec       = 21.538[dB]
Irr_Atn_Noe       = 21.538[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```



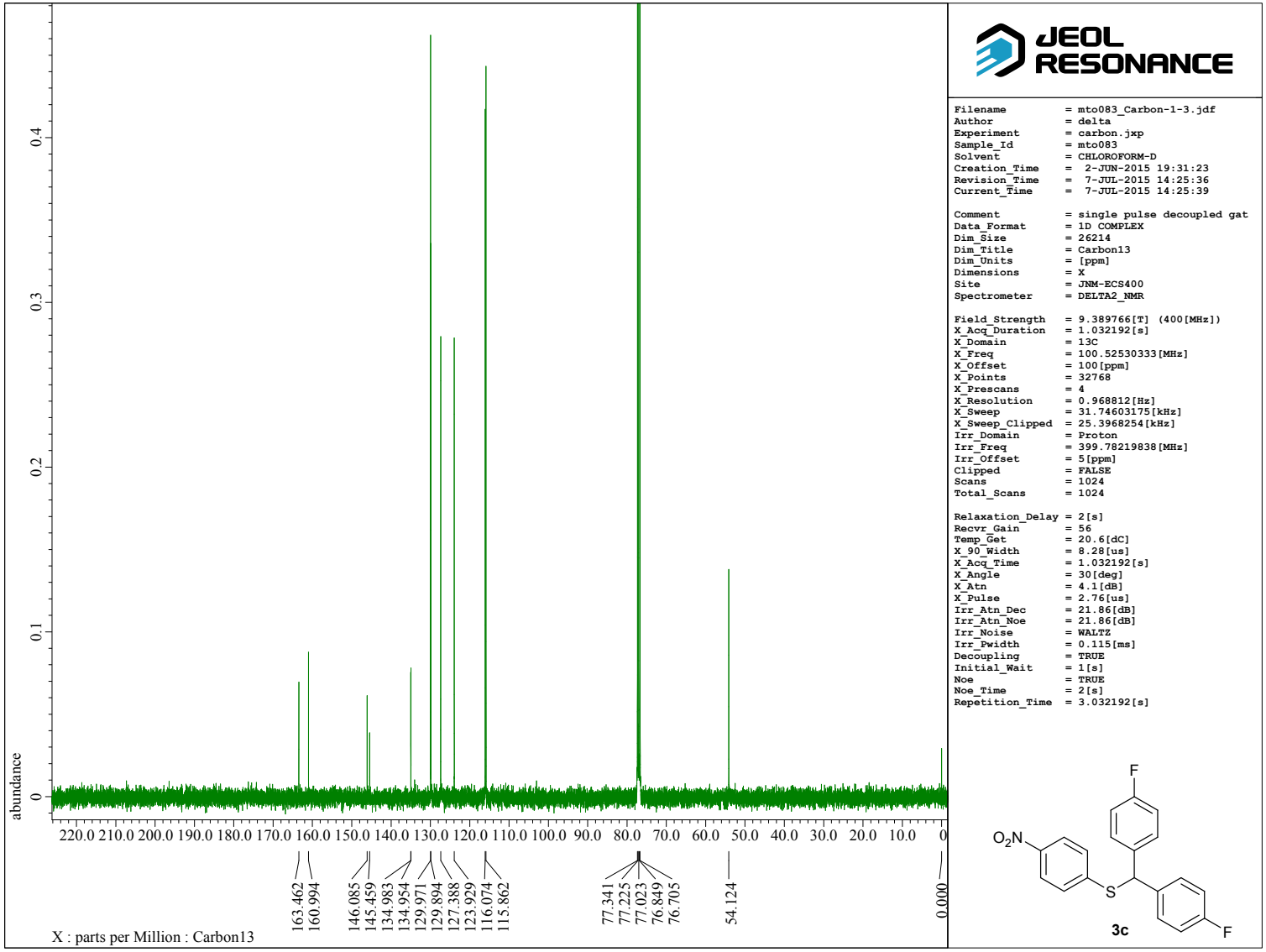
3b



JEOL RESONANCE

Filename	= mto083_Proton-2-3.jdf
Author	= delta
Experiment	= proton.jxp
Sample_Id	= mto083
Solvent	= CHLOROFORM-D
Creation_Time	= 2-JUL-2014 20:19:58
Revision_Time	= 3-JUL-2014 10:16:21
Current_Time	= 7-JUL-2015 14:08:12
Comment	= single_pulse
Data_Format	= 1D COMPLEX
Dim_Size	= 52429
Dim_Title	= Proton
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 8.73463808[s]
X_Domain	= 1H
X_Freq	= 399.78219838[MHz]
X_Offset	= 5[ppm]
X_Points	= 65536
X_Prescans	= 1
X_Resolution	= 0.11448671[Hz]
X_Sweep	= 7.5030012[kHz]
X_Sweep_Clipped	= 6.00240096[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Tri_Domain	= Proton
Tri_Freq	= 399.78219838[MHz]
Tri_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 8
Total_Scans	= 8
Relaxation_Delay	= 5[s]
Recvr_Gain	= 46
Temp_Get	= 21.1[dC]
X_90_Width	= 9.72[us]
X_Acq_Time	= 8.73463808[s]
X_Angle	= 45[deg]
X_Atn	= 0.4[dB]
X_Pulse	= 4.86[us]
Irr_Mode	= Off
Tri_Mode	= Off
Dante_Presat	= FALSE
Initial_Wait	= 1[s]
Repetition_Time	= 13.73463808[s]

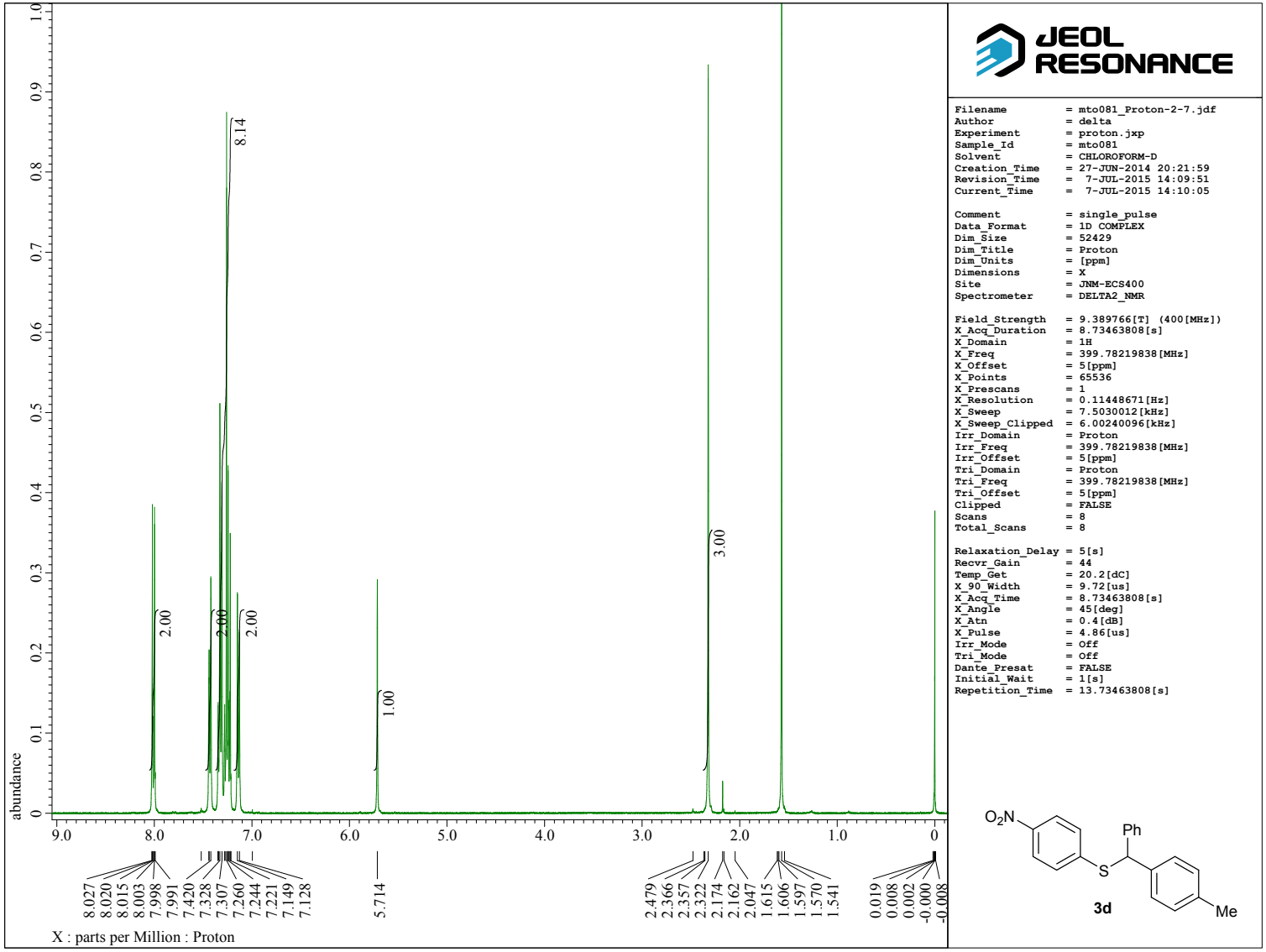
3c



JEOL RESONANCE

```
Filename          = mto083_Carbon-1-3.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = mto083
Solvent           = CHLOROFORM-D
Creation_Time     =  2-JUN-2015 19:31:23
Revision_Time     =  7-JUL-2015 14:25:36
Current_Time      =  7-JUL-2015 14:25:39

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.032192[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.968812[Hz]
X_Sweep           = 31.74603175[kHz]
X_Sweep_Clipped   = 25.3968254[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 56
Temp_Get          = 20.6[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.032192[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.032192[s]
```

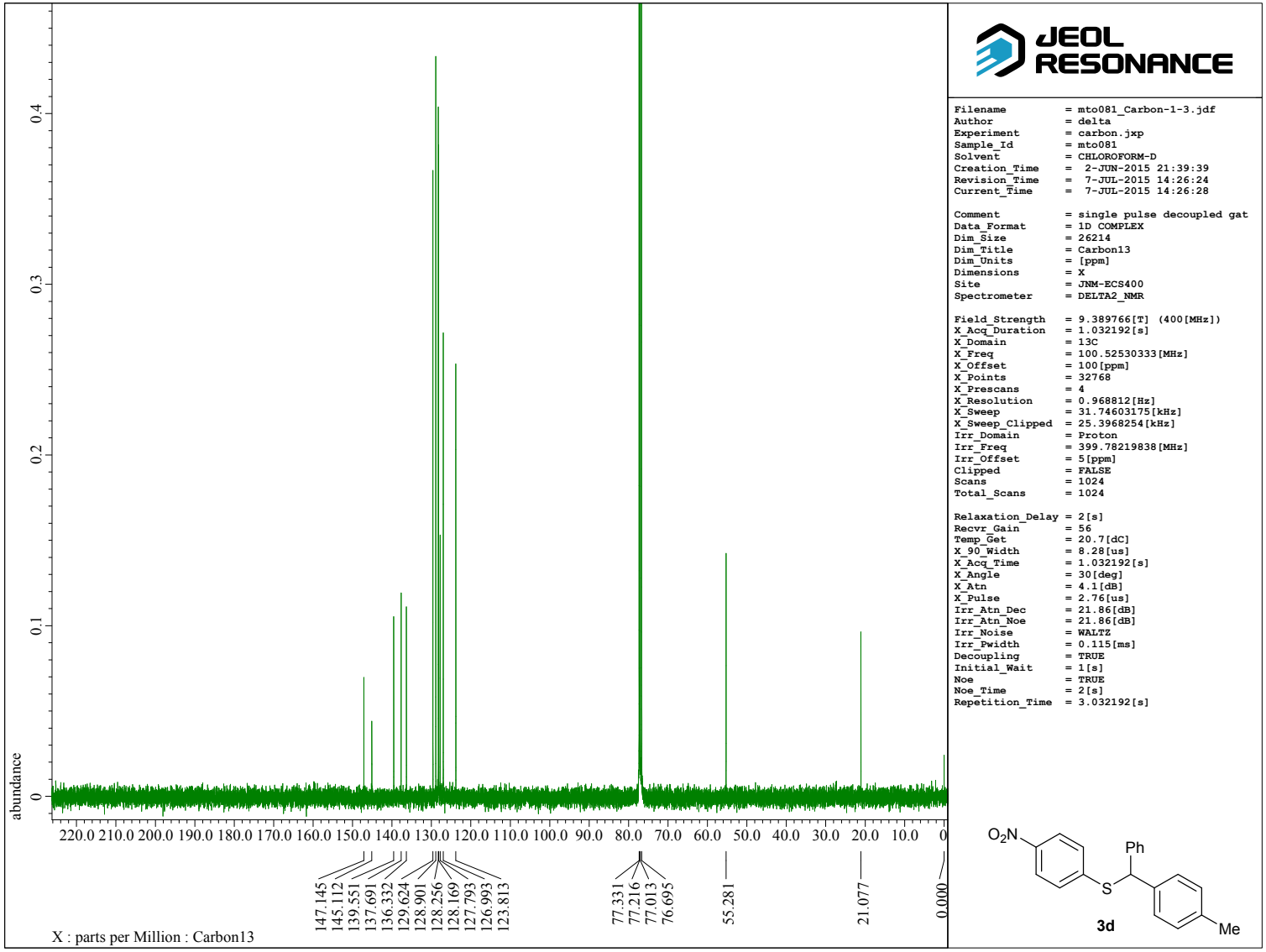

3c



JEOL RESONANCE

```
Filename          = mto081_Proton-2-7.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto081
Solvent           = CHLOROFORM-D
Creation_Time     = 27-JUN-2014 20:21:59
Revision_Time     =  7-JUL-2015 14:09:51
Current_Time      =  7-JUL-2015 14:10:05

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 44
Temp_Get          = 20.2[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```

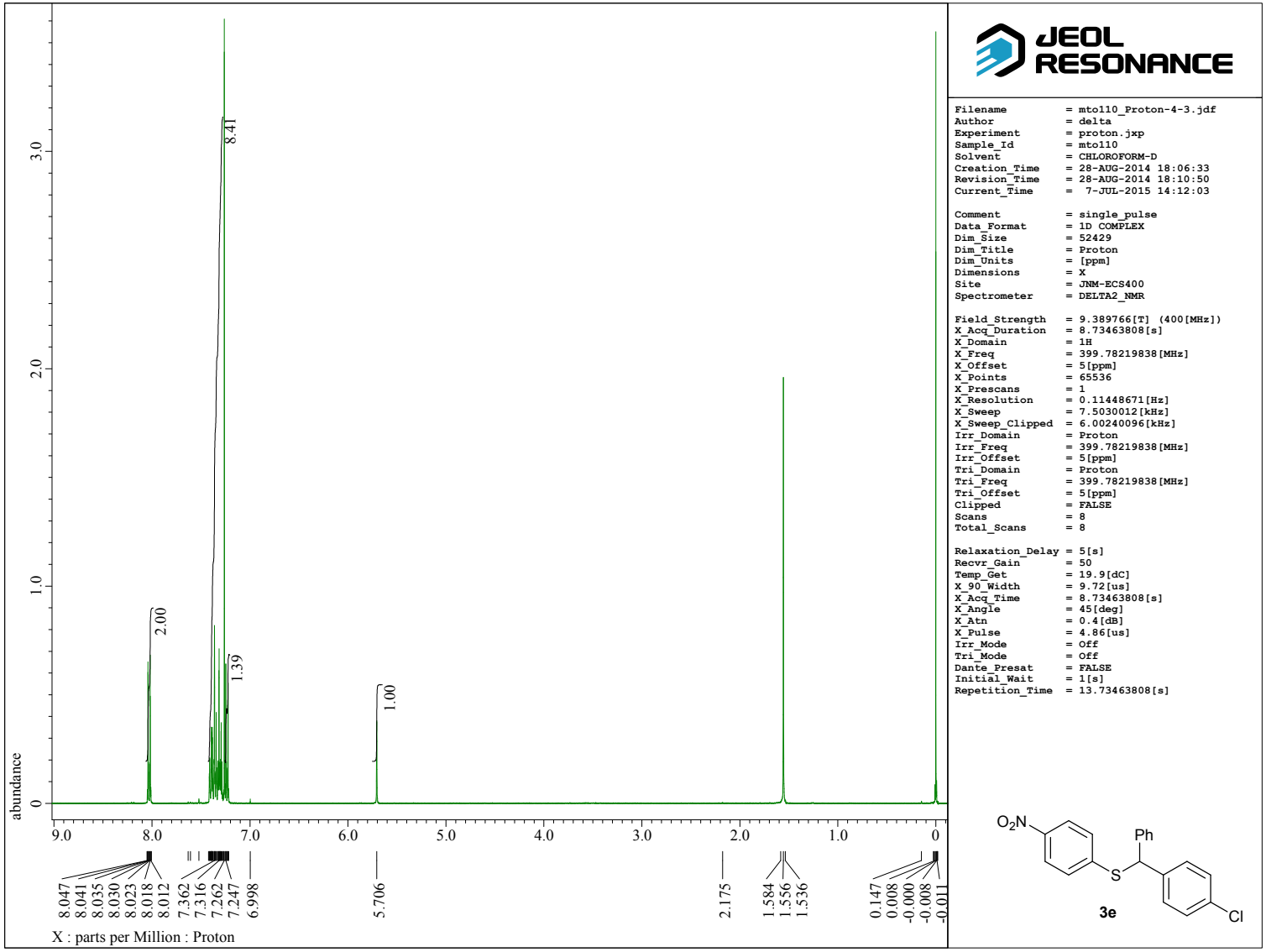

3d



JEOL RESONANCE

```
Filename          = mto081_Carbon-1-3.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = mto081
Solvent           = CHLOROFORM-D
Creation_Time     =  2-JUN-2015 21:39:39
Revision_Time     =  7-JUL-2015 14:26:24
Current_Time      =  7-JUL-2015 14:26:28

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.032192[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.968812[Hz]
X_Sweep           = 31.74603175[kHz]
X_Sweep_Clipped   = 25.3968254[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 56
Temp_Get          = 20.7[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.032192[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.032192[s]
```

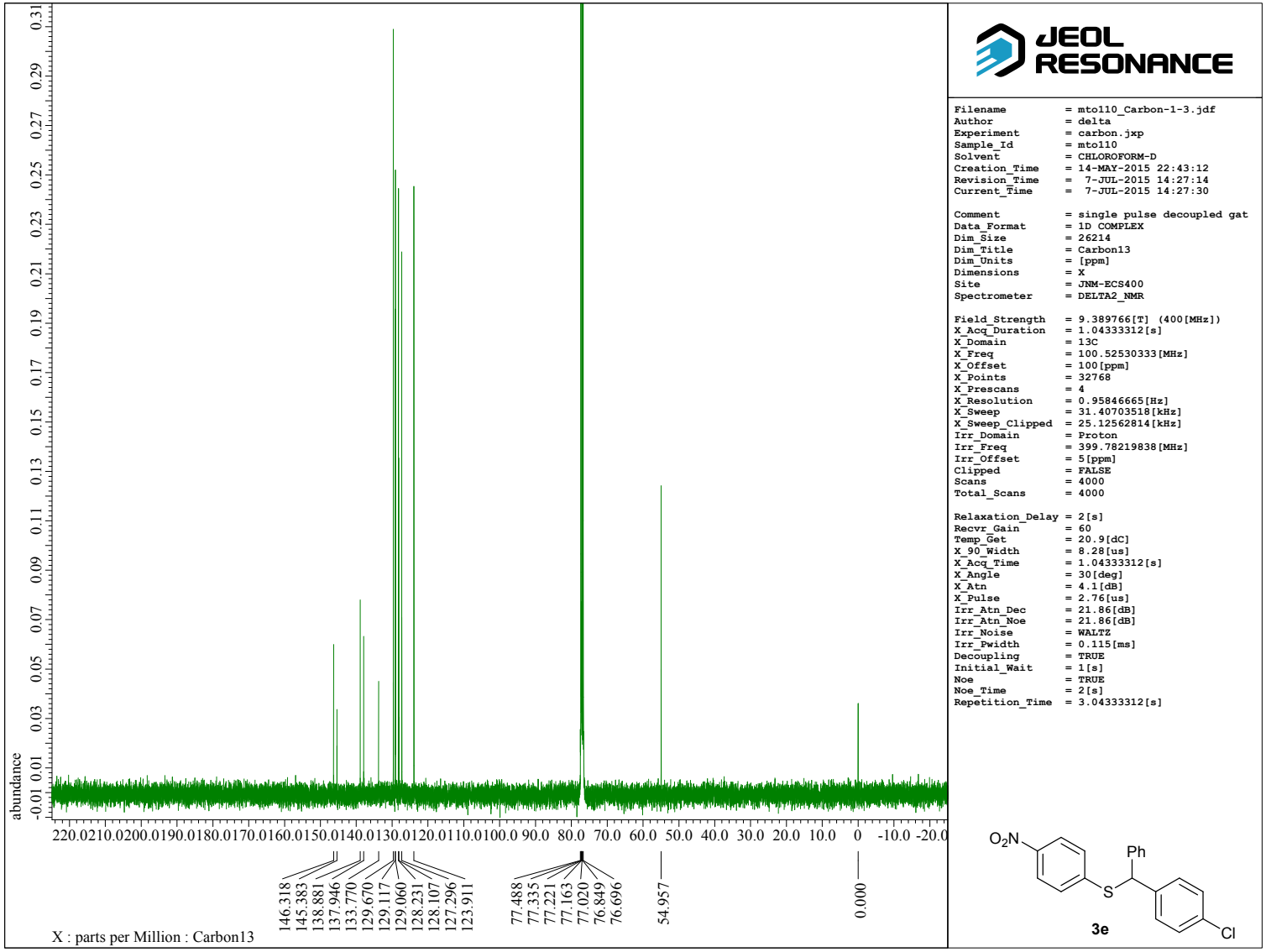

3d

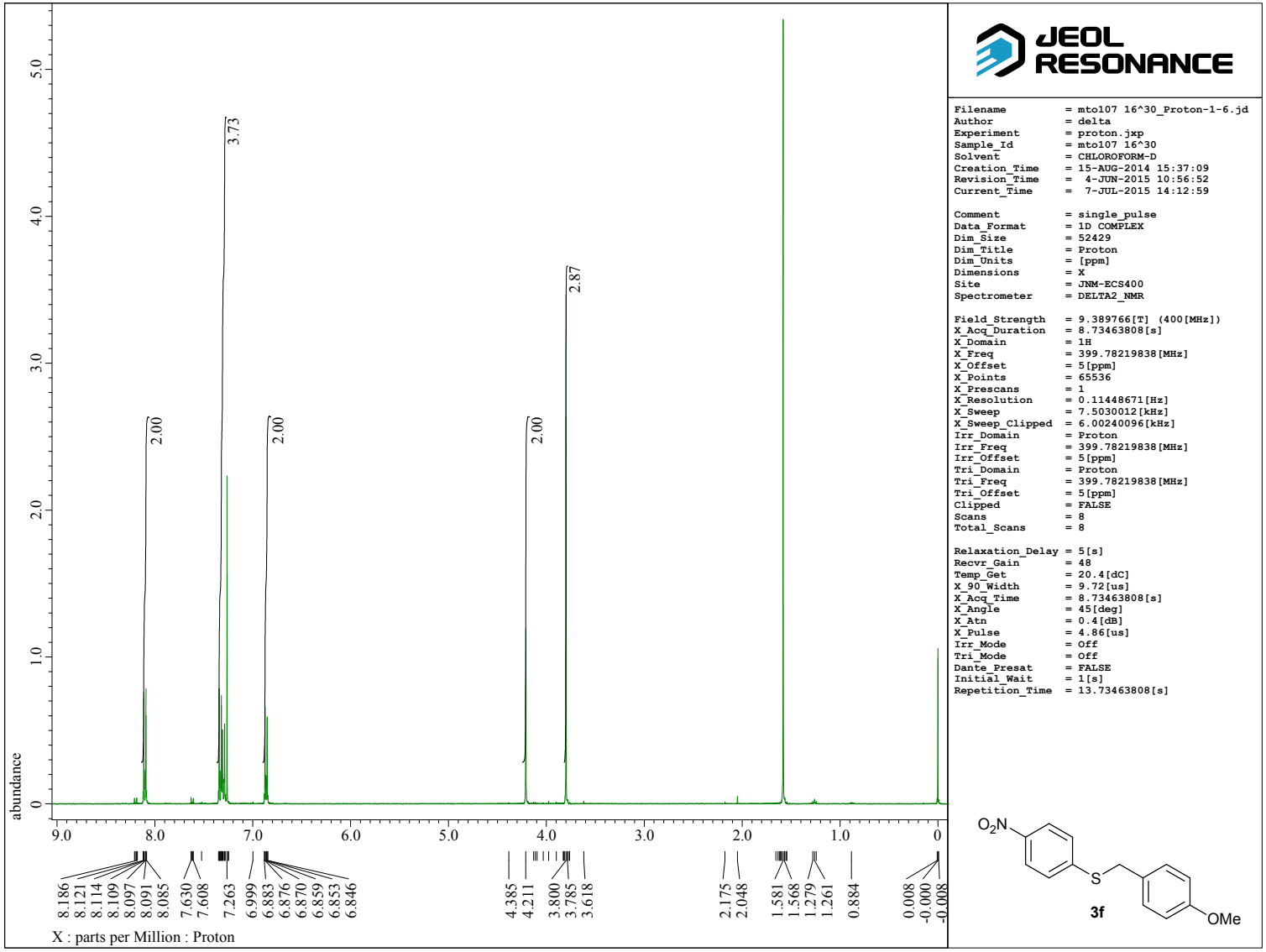


JEOL RESONANCE

```
Filename          = mto110_Proton-4-3.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto110
Solvent           = CHLOROFORM-D
Creation_Time     = 28-AUG-2014 18:06:33
Revision_Time     = 28-AUG-2014 18:10:50
Current_Time      =  7-JUL-2015 14:12:03

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 50
Temp_Get          = 19.9[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```


3e

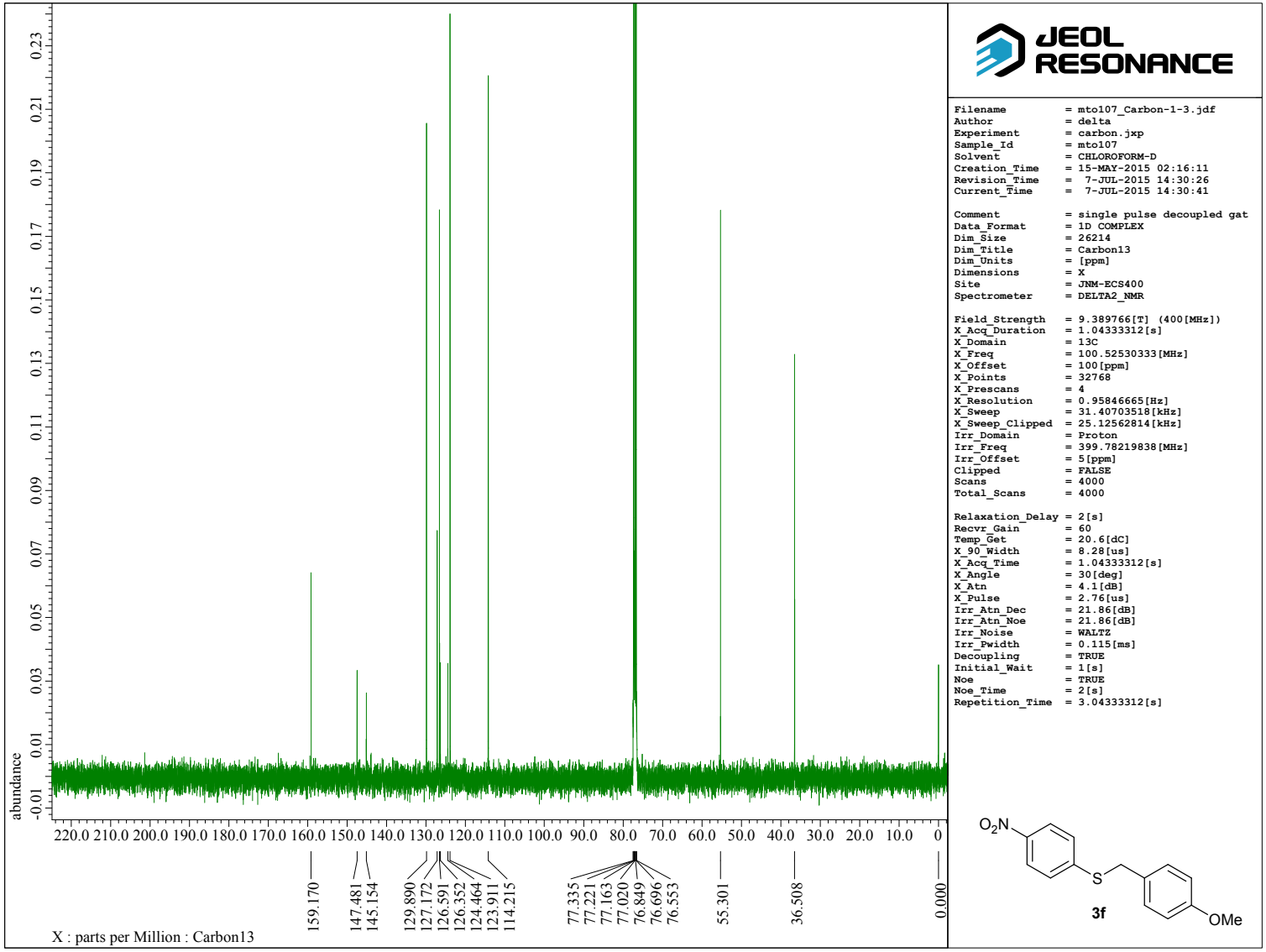

abundance
X : parts per Million : Carbon13
146.318
145.383
138.881
137.946
133.770
129.670
129.117
129.060
128.231
128.107
127.296
123.911
77.488
77.335
77.221
77.163
77.020
76.849
76.696
54.957
0.000
JEOL RESONANCE
Filename = mto110_Carbon-1-3.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = mto110
Solvent = CHLOROFORM-D
Creation_Time = 14-MAY-2015 22:43:12
Revision_Time = 7-JUL-2015 14:27:14
Current_Time = 7-JUL-2015 14:27:30
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 4000
Total_Scans = 4000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.9[dC]
X_90_Width = 8.28[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.1[dB]
X_Pulse = 2.76[us]
Irr_Atn_Dec = 21.86[dB]
Irr_Atn_Noe = 21.86[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.04333312[s]
O2N
Ph
S
Cl
3e

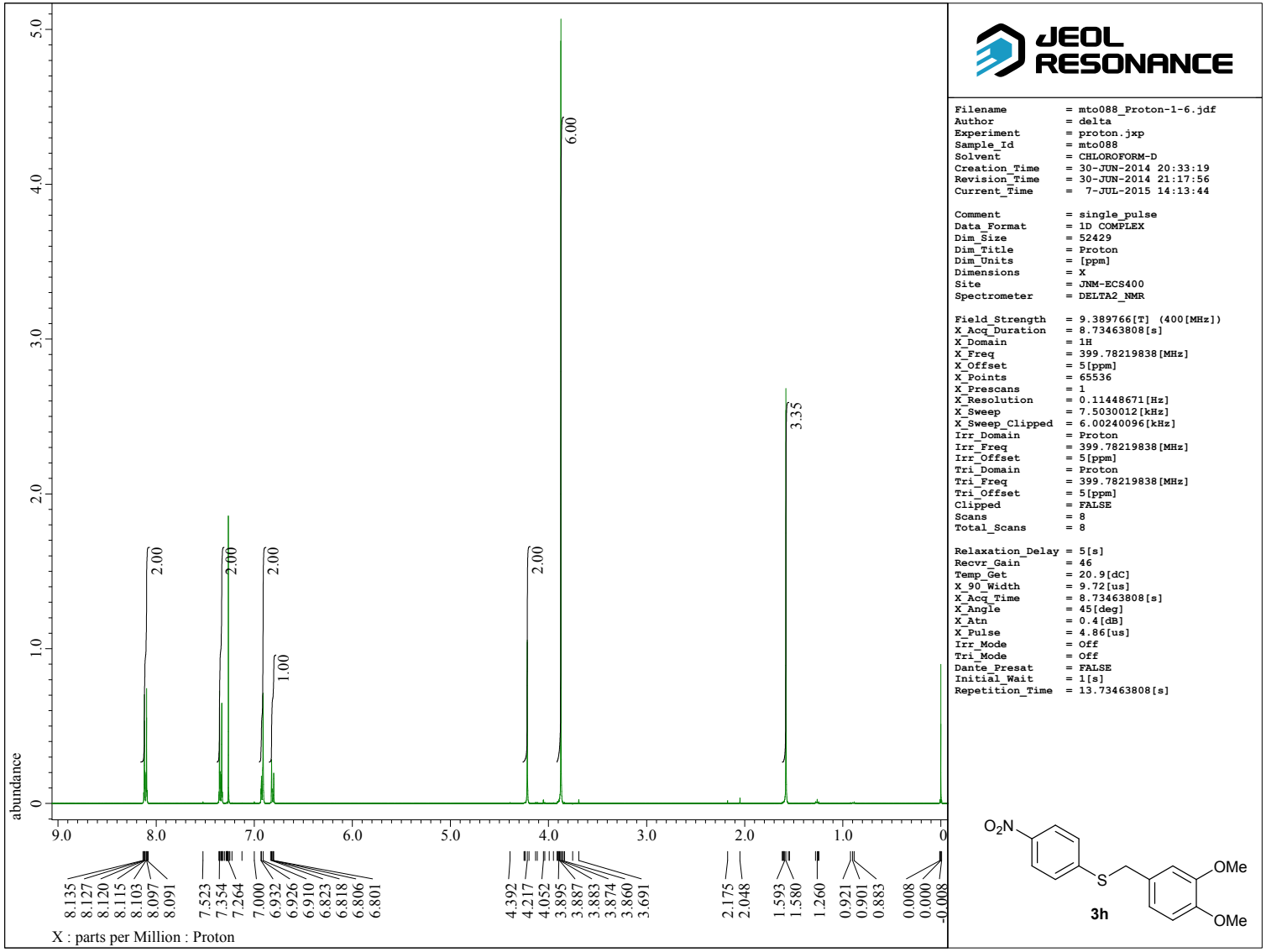


JEOL RESONANCE

```
Filename          = mto107 16^30_Proton-1-6.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto107 16^30
Solvent           = CHLOROFORM-D
Creation_Time     = 15-AUG-2014 15:37:09
Revision_Time     =  4-JUN-2015 10:56:52
Current_Time      =  7-JUL-2015 14:12:59

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Get          = 20.4[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```


3f

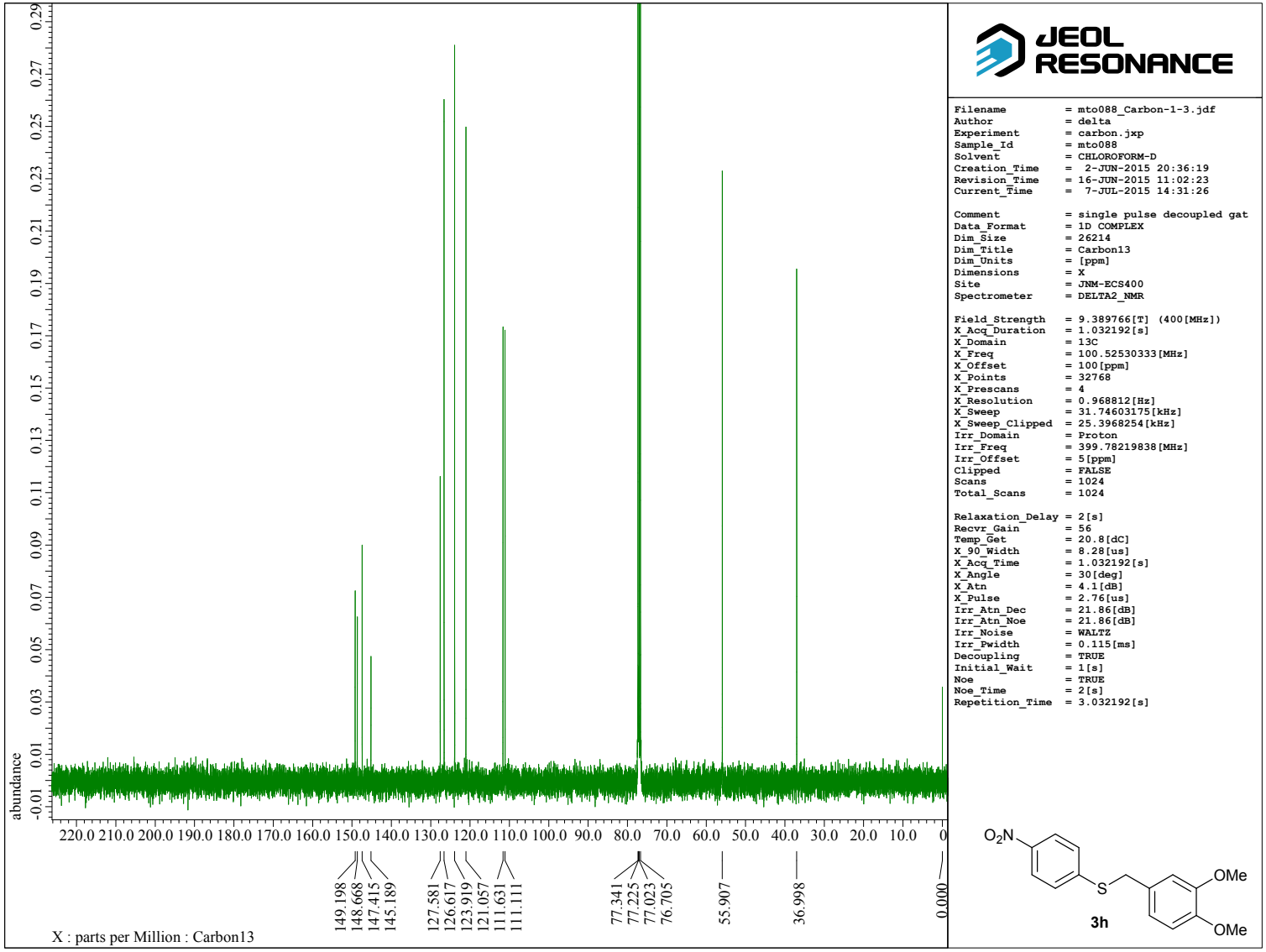

abundance
-0.01
0.01
0.03
0.05
0.07
0.09
0.11
0.13
0.15
0.17
0.19
0.21
0.23
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.170
147.481
145.154
129.890
127.172
126.591
126.352
124.464
123.911
114.215
77.335
77.221
77.163
77.020
76.849
76.696
76.553
55.301
36.508
0.000
X : parts per Million : Carbon13
JEOL RESONANCE
Filename = mto107_Carbon-1-3.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = mto107
Solvent = CHLOROFORM-D
Creation_Time = 15-MAY-2015 02:16:11
Revision_Time = 7-JUL-2015 14:30:26
Current_Time = 7-JUL-2015 14:30:41
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 4000
Total_Scans = 4000
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 20.6[dC]
X_90_Width = 8.28[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 4.1[dB]
X_Pulse = 2.76[us]
Irr_Atn_Dec = 21.86[dB]
Irr_Atn_Noe = 21.86[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 3.04333312[s]
O2N
S
OMe
3f



JEOL RESONANCE

```
Filename          = mto088_Proton-1-6.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto088
Solvent           = CHLOROFORM-D
Creation_Time     = 30-JUN-2014 20:33:19
Revision_Time     = 30-JUN-2014 21:17:56
Current_Time      =  7-JUL-2015 14:13:44

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 20.9[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```

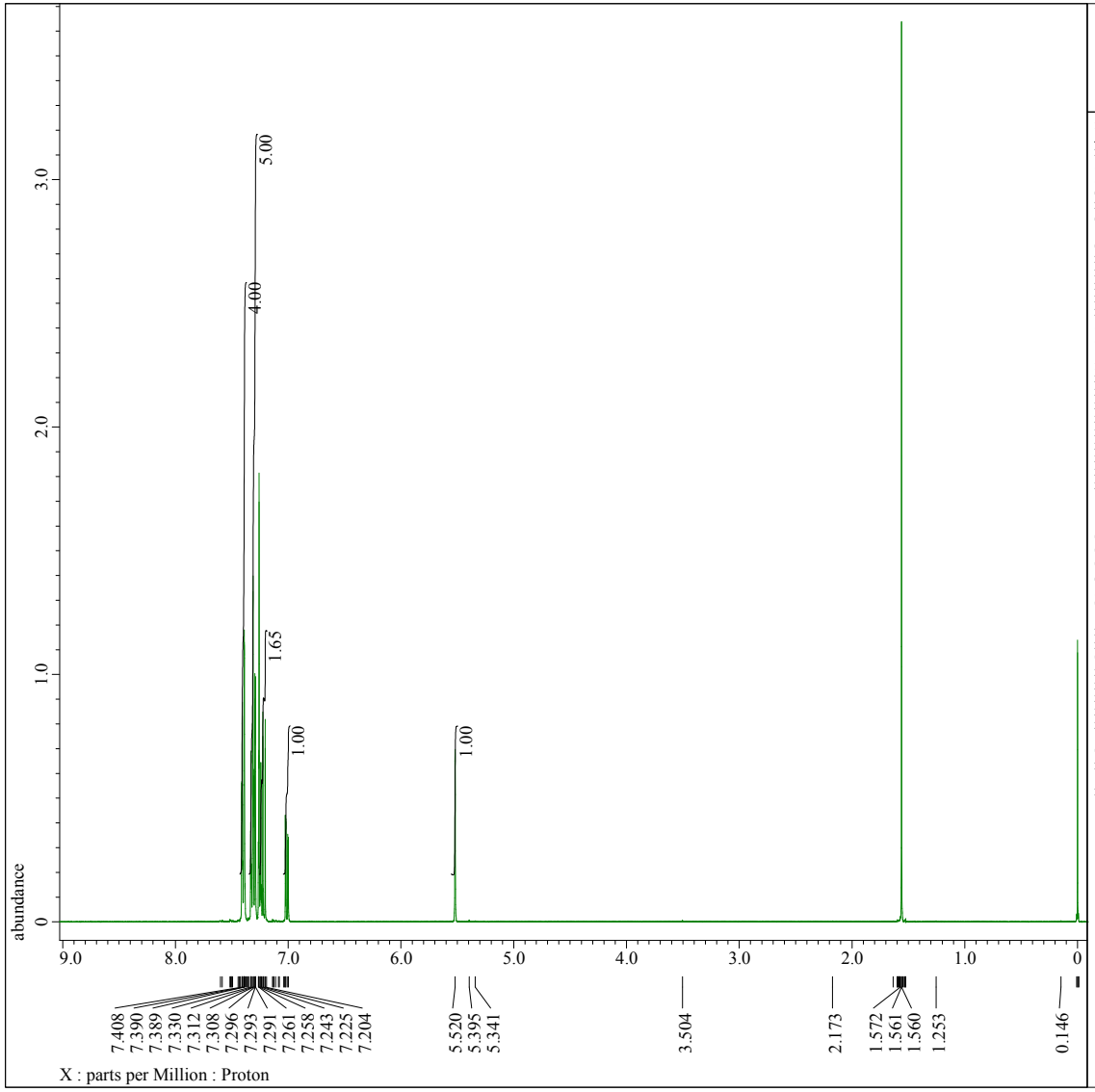

3h



JEOL RESONANCE

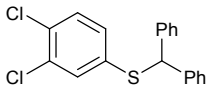
```
Filename          = mto088_Carbon-1-3.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = mto088
Solvent           = CHLOROFORM-D
Creation_Time     =  2-JUN-2015 20:36:19
Revision_Time     = 16-JUN-2015 11:02:23
Current_Time      =  7-JUL-2015 14:31:26

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.032192[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.968812[Hz]
X_Sweep           = 31.74603175[kHz]
X_Sweep_Clipped   = 25.3968254[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 56
Temp_Get          = 20.8[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.032192[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.032192[s]
```


3h

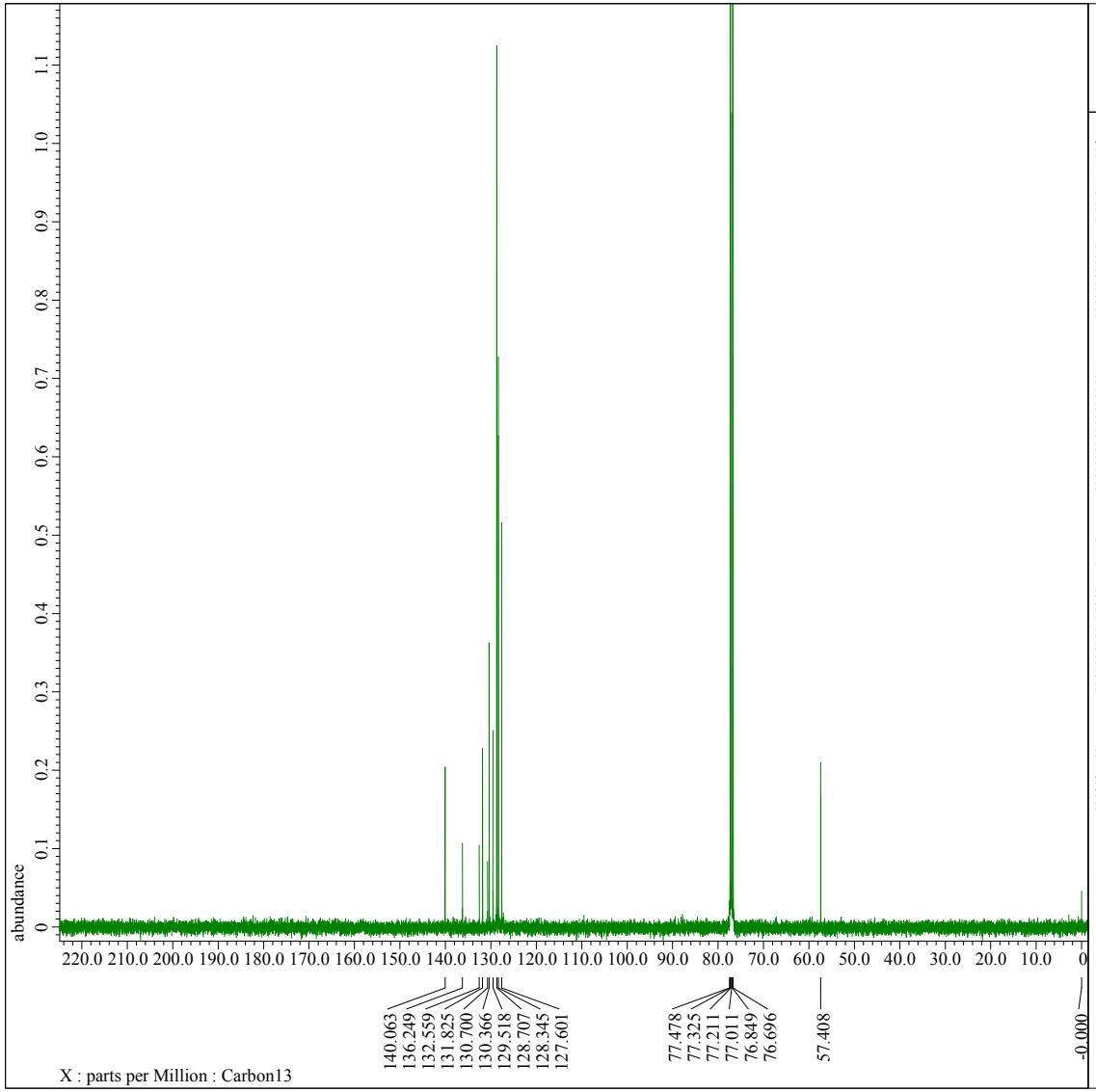


JEOL RESONANCE

```
Filename          = mto103 fr2^3_Proton-1-3.jd
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto103 fr2^3
Solvent           = CHLOROFORM-D
Creation_Time     = 28-JUL-2014 18:10:50
Revision_Time     = 28-JUL-2014 19:06:40
Current_Time      =  7-JUL-2015 14:15:03

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 20.5[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```

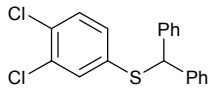


3i

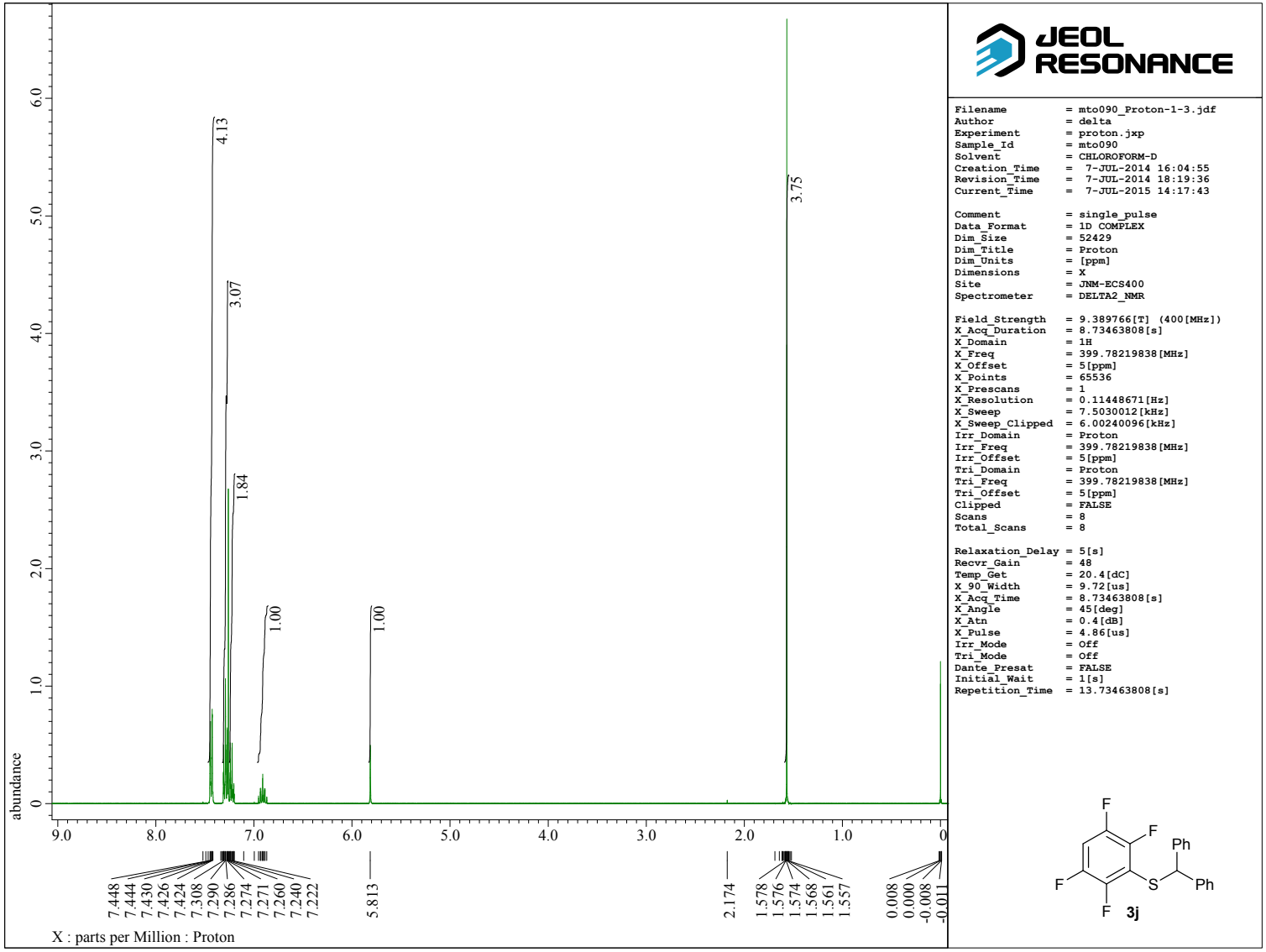


JEOL RESONANCE

```
Filename          = mto103_Carbon-1-3.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = mto103
Solvent           = CHLOROFORM-D
Creation_Time     =  9-JUN-2015 19:15:09
Revision_Time     = 16-JUN-2015 11:31:03
Current_Time      =  7-JUL-2015 14:32:06

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.2[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```



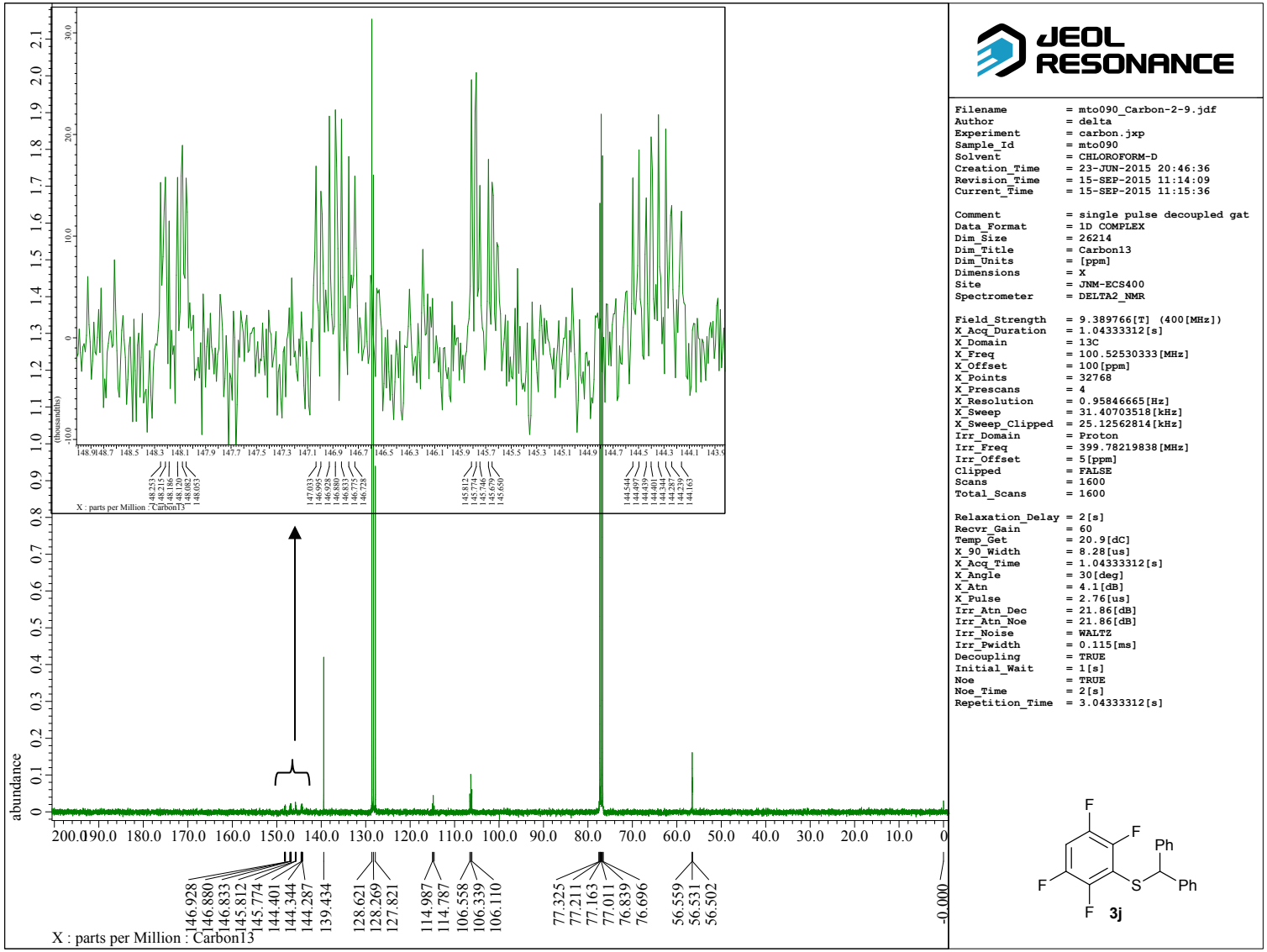
3i



JEOL RESONANCE

```
Filename          = mto090_Proton-1-3.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = mto090
Solvent           = CHLOROFORM-D
Creation_Time     =  7-JUL-2014 16:04:55
Revision_Time     =  7-JUL-2014 18:19:36
Current_Time      =  7-JUL-2015 14:17:43

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 8.73463808[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.11448671[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Get          = 20.4[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 8.73463808[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 13.73463808[s]
```

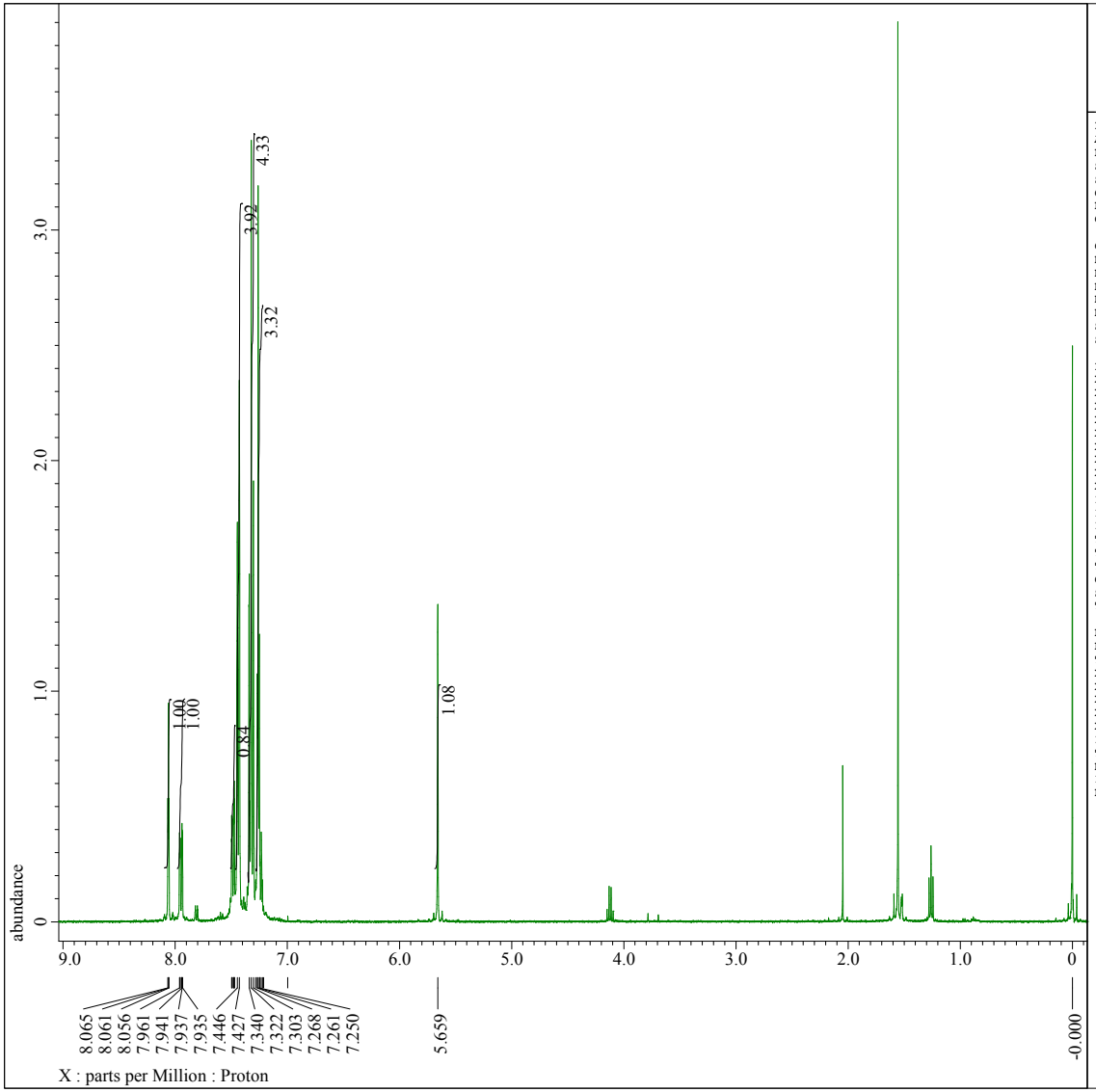

3j



JEOL RESONANCE

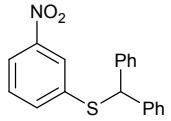
Filename	= mto090_Carbon-2-9.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= mto090
Solvent	= CHLOROFORM-D
Creation_Time	= 23-JUN-2015 20:46:36
Revision_Time	= 15-SEP-2015 11:14:09
Current_Time	= 15-SEP-2015 11:15:36
Comment	= single pulse decoupled gat
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECS400
Spectrometer	= DELTA2_NMR
Field_Strength	= 9.389766[T] (400[MHz])
X_Acq_Duration	= 1.04333312[s]
X_Domain	= 13C
X_Freq	= 100.52530333[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 0.95846665[Hz]
X_Sweep	= 31.40703518[kHz]
X_Sweep_Clipped	= 25.12562814[kHz]
Irr_Domain	= Proton
Irr_Freq	= 399.78219838[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 1600
Total_Scans	= 1600
Relaxation_Delay	= 2[s]
Recvr_Gain	= 60
Temp_Get	= 20.9[dC]
X_90_Width	= 8.28[us]
X_Acq_Time	= 1.04333312[s]
X_Angle	= 30[deg]
X_Atn	= 4.1[dB]
X_Pulse	= 2.76[us]
Irr_Atn_Dec	= 21.86[dB]
Irr_Atn_Noe	= 21.86[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 0.115[ms]
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Repetition_Time	= 3.04333312[s]

3j

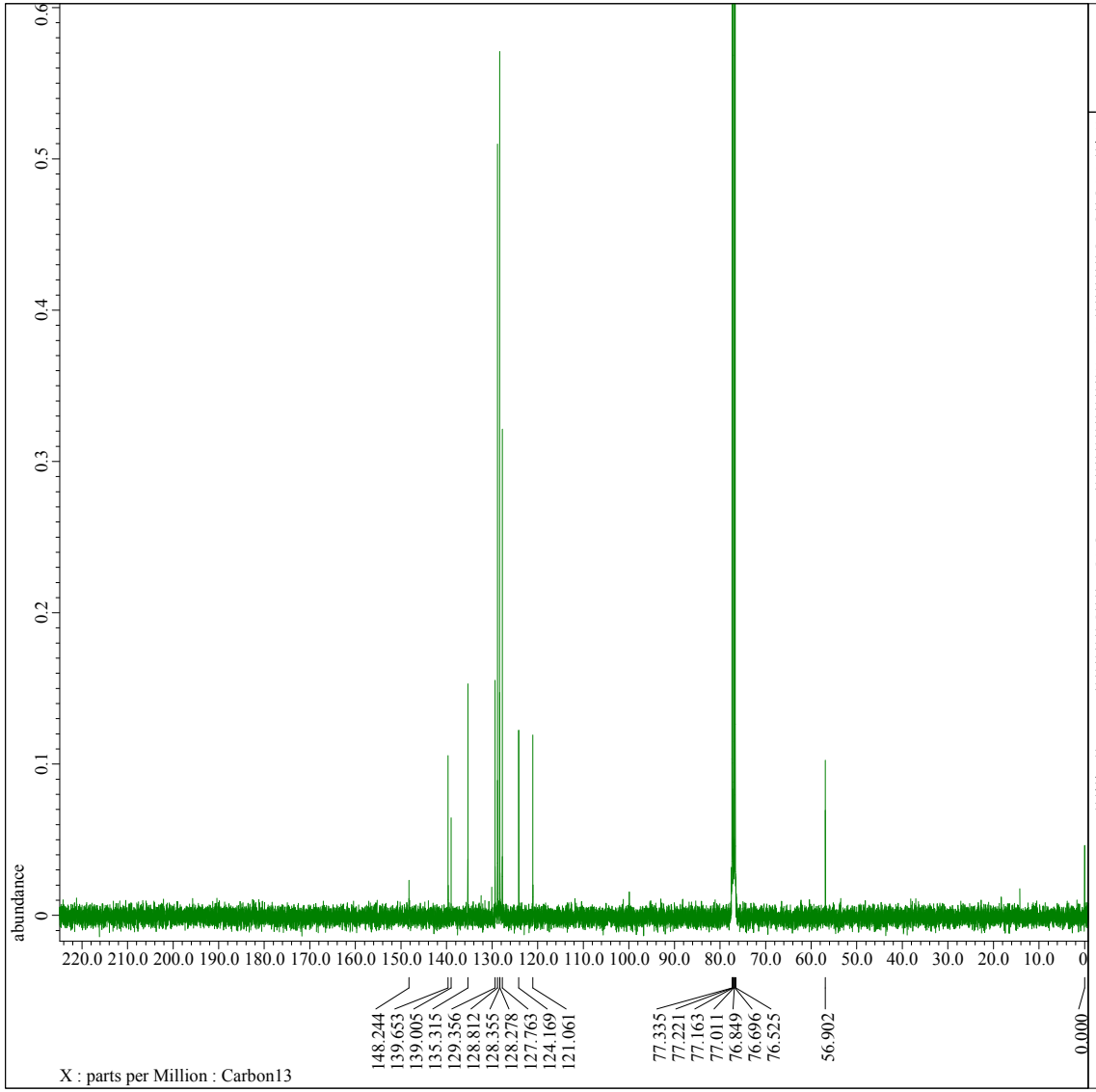


JEOL RESONANCE

```
Filename          = M-HH6-14-2_Proton-1-7.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = M-HH6-14-2
Solvent           = CHLOROFORM-D
Creation_Time     = 14-APR-2015 17:03:59
Revision_Time     = 15-SEP-2015 11:34:21
Current_Time      = 15-SEP-2015 11:42:21

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 2.18365952[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45794685[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Get          = 20.2[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 2.18365952[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.18365952[s]
```

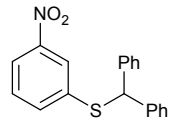


3l

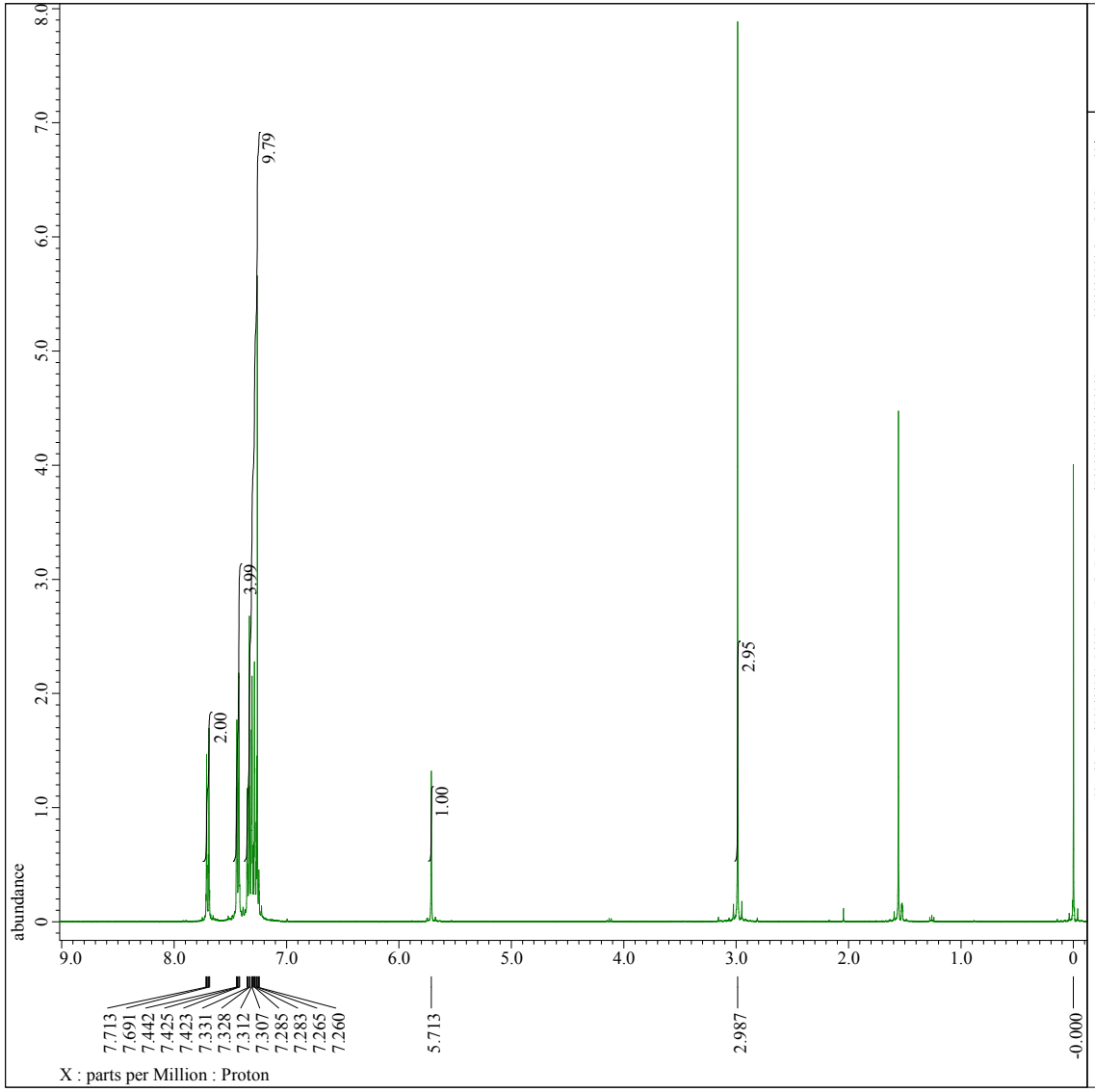


JEOL RESONANCE

```
Filename          = mto14-2_Carbon-1-4.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = mto14-2
Solvent           = CHLOROFORM-D
Creation_Time     =  1-MAY-2015 00:05:57
Revision_Time     =  7-JUL-2015 14:21:51
Current_Time      =  7-JUL-2015 14:22:08

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1600
Total_Scans       = 1600

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.8[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```

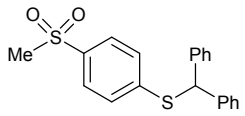


3l

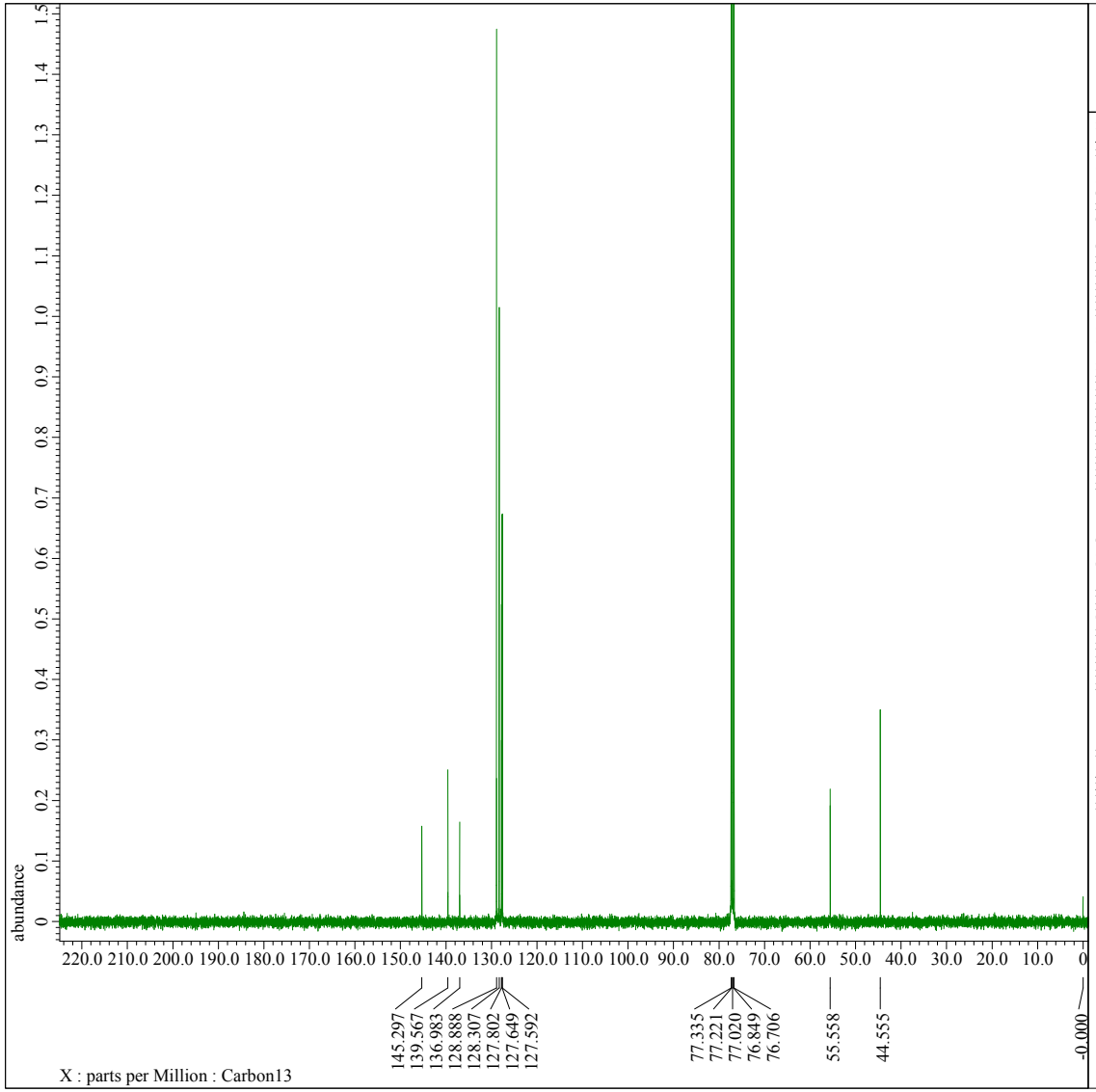


JEOL RESONANCE

```
Filename          = M-HH6-14-3_Proton-1-5.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = M-HH6-14-3
Solvent           = CHLOROFORM-D
Creation_Time     = 14-APR-2015 17:16:06
Revision_Time     = 15-SEP-2015 11:47:09
Current_Time      = 15-SEP-2015 11:47:20

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 2.18365952[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45794685[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 48
Temp_Get          = 21.2[dC]
X_90_Width        = 9.72[us]
X_Acq_Time        = 2.18365952[s]
X_Angle           = 45[deg]
X_Atn             = 0.4[dB]
X_Pulse           = 4.86[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.18365952[s]
```

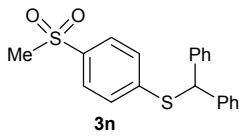


3n



JEOL RESONANCE

```
Filename          = 14-3_Carbon-1-2.jdf
Author            = delta
Experiment        = carbon.jxp
Sample_Id         = 14-3
Solvent           = CHLOROFORM-D
Creation_Time     = 23-JUN-2015 19:41:37
Revision_Time     = 24-JUN-2015 11:25:28
Current_Time      =  7-JUL-2015 14:23:47

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 1.04333312[s]
X_Domain          = 13C
X_Freq            = 100.52530333[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95846665[Hz]
X_Sweep           = 31.40703518[kHz]
X_Sweep_Clipped   = 25.12562814[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 20.2[dC]
X_90_Width        = 8.28[us]
X_Acq_Time        = 1.04333312[s]
X_Angle           = 30[deg]
X_Atn             = 4.1[dB]
X_Pulse           = 2.76[us]
Irr_Atn_Dec       = 21.86[dB]
Irr_Atn_Noe       = 21.86[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 0.115[ms]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.04333312[s]
```



3n