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Supplementary Material

Synthesis, characterization and base hydrolysis of cobalt(III) complexes coordinated by substituted phenylthioether ligands

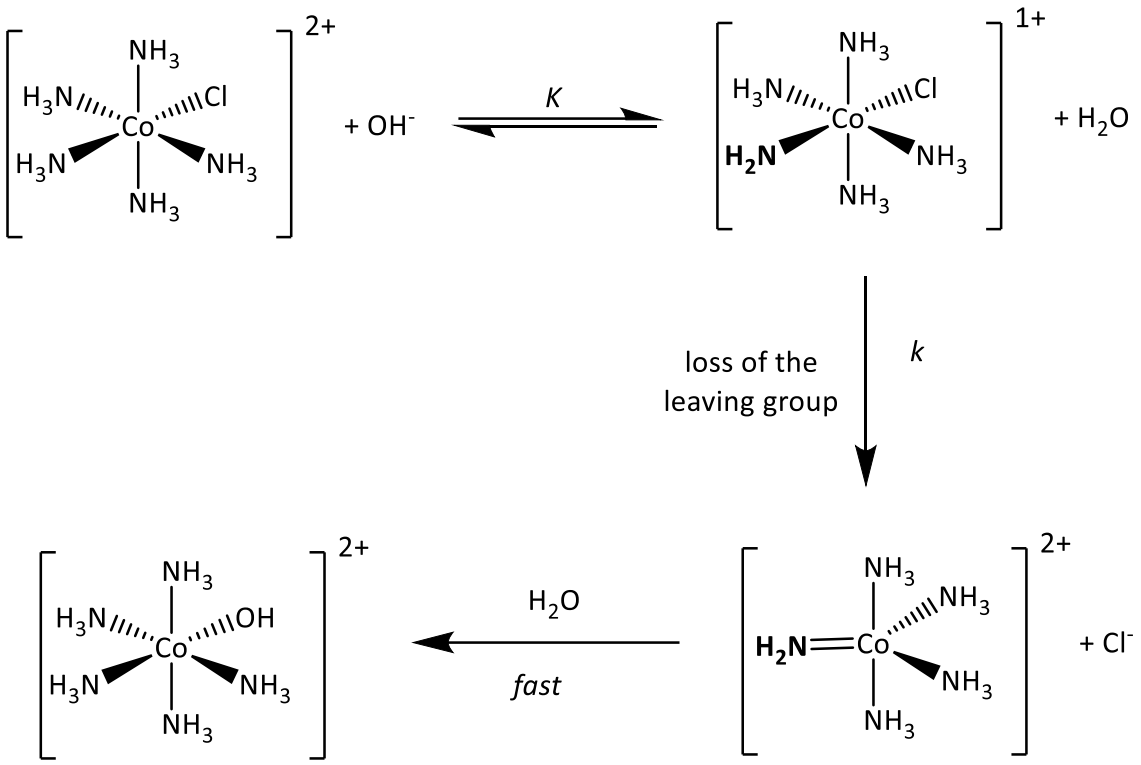
Lee Roecker[A,B,*], *Alicia Cohn*[B], *Thomas Cox*[B], *Rachel Ceaglske*[A], *Olivia Rick*[A], *Ella Miller Knagge*[A] and *Sean Parkin*[C,*]

[A]Department of Chemistry, Northern Michigan University, Marquette, MI 49855, USA

[B]Department of Chemistry, Gettysburg College, Gettysburg, PA 17325, USA

[C]Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA

*Correspondence to: Email: lroecker@nmu.edu, s.parkin@uky.edu



Scheme S1. The S_N1CB mechanism illustrated for the base hydrolysis of the $[(NH_3)_5CoCl]^{2+}$ ion.

Table S1. Bond lengths (Å) for the $[(en)_2Co(\underline{S}(phenyl)CH_2CH_2\underline{N}H_2)]^{3+}$ cation.

Co(1)-N(4)	1.955(2)	Co(1)-N(2)	1.977(2)
Co(1)-N(5)	1.978(2)	Co(1)-N(3)	1.981(2)
Co(1)-N(1)	1.986(2)	Co(1)-S(1)	2.2594(7)
S(1)-C(7)	1.774(3)	S(1)-C(6)	1.817(3)
N(1)-C(1)	1.491(3)	N(1)-H(1A)	0.91
N(1)-H(1B)	0.91	C(1)-C(2)	1.503(3)
C(1)-H(1C)	0.99	C(1)-H(1D)	0.99
C(2)-N(2)	1.495(3)	C(2)-H(2A)	0.99
C(2)-H(2B)	0.99	N(2)-H(2C)	0.91
N(2)-H(2D)	0.91	N(3)-C(3)	1.492(3)
N(3)-H(3A)	0.91	N(3)-H(3B)	0.91
C(3)-C(4)	1.506(3)	C(3)-H(3C)	0.99
C(3)-H(3D)	0.99	C(4)-N(4)	1.492(3)
C(4)-H(4A)	0.99	C(4)-H(4B)	0.99
N(4)-H(4C)	0.91	N(4)-H(4D)	0.91
N(5)-C(5)	1.489(3)	N(5)-H(5A)	0.91
N(5)-H(5B)	0.91	C(5)-C(6)	1.506(4)
C(5)-H(5C)	0.99	C(5)-H(5D)	0.99
C(6)-H(6A)	0.99	C(6)-H(6B)	0.99
C(7)-C(12)	1.392(4)	C(7)-C(8)	1.395(4)
C(8)-C(9)	1.386(4)	C(8)-H(8)	0.95
C(9)-C(10)	1.381(4)	C(9)-H(9)	0.95
C(10)-C(11)	1.389(4)	C(10)-H(10)	0.95
C(11)-C(12)	1.389(4)	C(11)-H(11)	0.95
C(12)-H(12)	0.95	Cl(1)-O(3)	1.4337(19)
Cl(1)-O(4)	1.4391(19)	Cl(1)-O(1)	1.4483(19)
Cl(1)-O(2)	1.4491(18)	Cl(2)-O(7)	1.4334(18)
Cl(2)-O(8)	1.4365(19)	Cl(2)-O(5)	1.4502(19)
Cl(2)-O(6)	1.4537(18)	Cl(3)-O(10)	1.4331(18)
Cl(3)-O(11)	1.439(2)	Cl(3)-O(9)	1.446(2)
Cl(3)-O(12)	1.4497(18)	O(1W)-H(1W)	0.78(3)
O(1W)-H(2W)	0.78(3)		

Table S2. Bond angles (°) for the $[(en)_2Co(\underline{S}(phenyl)CH_2CH_2\underline{N}H_2)]^{3+}$ cation.

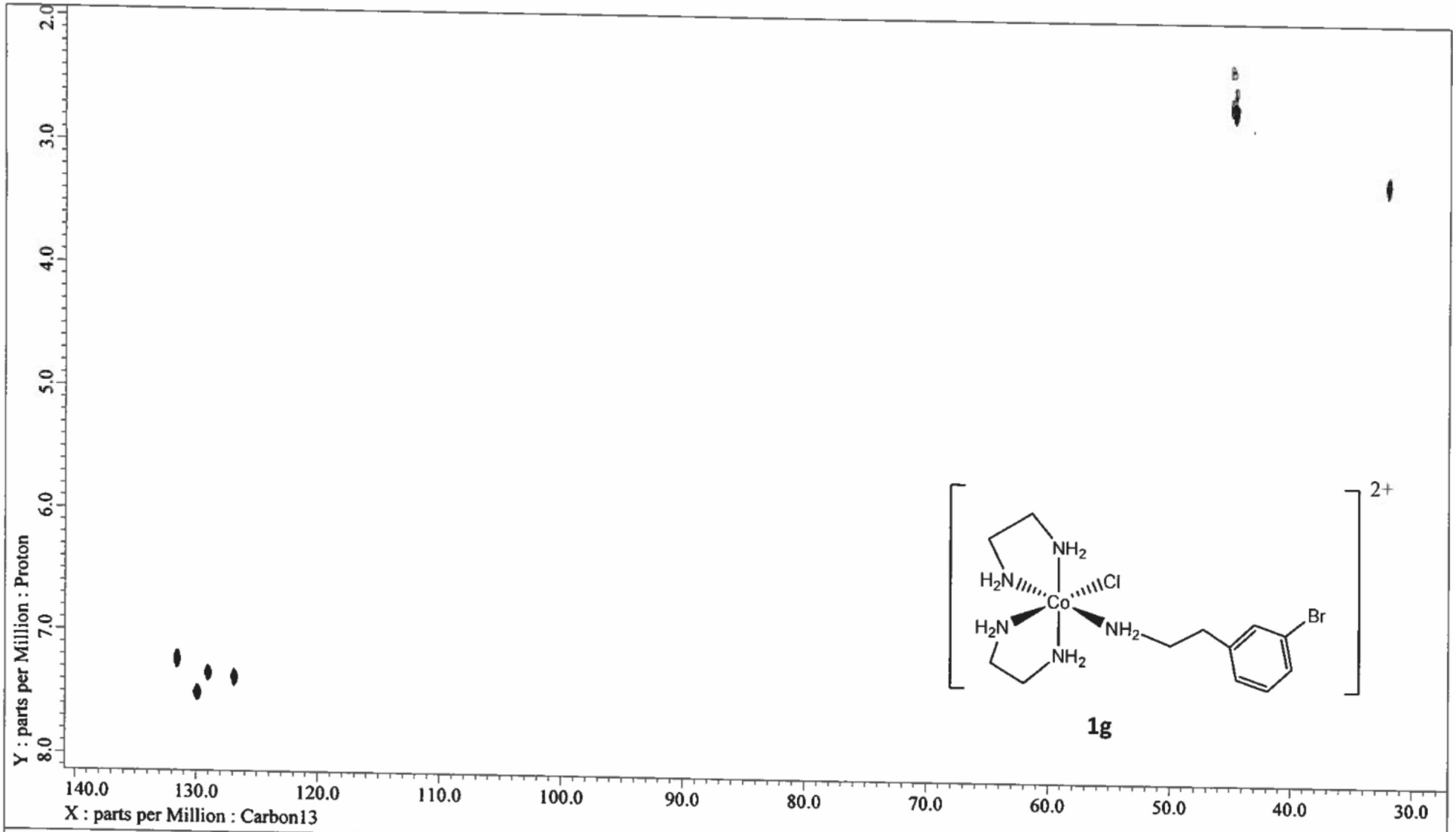
N(4)-Co(1)-N(2)	89.16(9)	N(4)-Co(1)-N(5)	92.90(9)
N(2)-Co(1)-N(5)	177.93(9)	N(4)-Co(1)-N(3)	85.57(8)
N(2)-Co(1)-N(3)	92.46(9)	N(5)-Co(1)-N(3)	87.52(9)
N(4)-Co(1)-N(1)	173.66(9)	N(2)-Co(1)-N(1)	84.86(8)
N(5)-Co(1)-N(1)	93.07(9)	N(3)-Co(1)-N(1)	92.54(8)
N(4)-Co(1)-S(1)	95.10(6)	N(2)-Co(1)-S(1)	94.39(6)
N(5)-Co(1)-S(1)	85.61(6)	N(3)-Co(1)-S(1)	173.13(7)
N(1)-Co(1)-S(1)	87.51(6)	C(7)-S(1)-C(6)	105.95(12)
C(7)-S(1)-Co(1)	115.45(8)	C(6)-S(1)-Co(1)	98.25(9)
C(1)-N(1)-Co(1)	108.49(15)	C(1)-N(1)-H(1A)	110
Co(1)-N(1)-H(1A)	110	C(1)-N(1)-H(1B)	110
Co(1)-N(1)-H(1B)	110	H(1A)-N(1)-H(1B)	108.4
N(1)-C(1)-C(2)	106.8(2)	N(1)-C(1)-H(1C)	110.4
C(2)-C(1)-H(1C)	110.4	N(1)-C(1)-H(1D)	110.4
C(2)-C(1)-H(1D)	110.4	H(1C)-C(1)-H(1D)	108.6
N(2)-C(2)-C(1)	107.1(2)	N(2)-C(2)-H(2A)	110.3
C(1)-C(2)-H(2A)	110.3	N(2)-C(2)-H(2B)	110.3
C(1)-C(2)-H(2B)	110.3	H(2A)-C(2)-H(2B)	108.6
C(2)-N(2)-Co(1)	110.31(15)	C(2)-N(2)-H(2C)	109.6
Co(1)-N(2)-H(2C)	109.6	C(2)-N(2)-H(2D)	109.6
Co(1)-N(2)-H(2D)	109.6	H(2C)-N(2)-H(2D)	108.1
C(3)-N(3)-Co(1)	108.16(15)	C(3)-N(3)-H(3A)	110.1
Co(1)-N(3)-H(3A)	110.1	C(3)-N(3)-H(3B)	110.1
Co(1)-N(3)-H(3B)	110.1	H(3A)-N(3)-H(3B)	108.4
N(3)-C(3)-C(4)	106.5(2)	N(3)-C(3)-H(3C)	110.4
C(4)-C(3)-H(3C)	110.4	N(3)-C(3)-H(3D)	110.4
C(4)-C(3)-H(3D)	110.4	H(3C)-C(3)-H(3D)	108.6
N(4)-C(4)-C(3)	107.3(2)	N(4)-C(4)-H(4A)	110.3
C(3)-C(4)-H(4A)	110.3	N(4)-C(4)-H(4B)	110.3
C(3)-C(4)-H(4B)	110.3	H(4A)-C(4)-H(4B)	108.5
C(4)-N(4)-Co(1)	110.09(15)	C(4)-N(4)-H(4C)	109.6
Co(1)-N(4)-H(4C)	109.6	C(4)-N(4)-H(4D)	109.6
Co(1)-N(4)-H(4D)	109.6	H(4C)-N(4)-H(4D)	108.2
C(5)-N(5)-Co(1)	115.18(16)	C(5)-N(5)-H(5A)	108.5
Co(1)-N(5)-H(5A)	108.5	C(5)-N(5)-H(5B)	108.5
Co(1)-N(5)-H(5B)	108.5	H(5A)-N(5)-H(5B)	107.5
N(5)-C(5)-C(6)	107.9(2)	N(5)-C(5)-H(5C)	110.1
C(6)-C(5)-H(5C)	110.1	N(5)-C(5)-H(5D)	110.1
C(6)-C(5)-H(5D)	110.1	H(5C)-C(5)-H(5D)	108.4
C(5)-C(6)-S(1)	104.89(17)	C(5)-C(6)-H(6A)	110.8
S(1)-C(6)-H(6A)	110.8	C(5)-C(6)-H(6B)	110.8

S(1)-C(6)-H(6B)	110.8 (	6A)-C(6)-H(6B)	108.8
C(12)-C(7)-C(8)	121.1(2)	C(12)-C(7)-S(1)	114.94(19)
C(8)-C(7)-S(1)	124.0(2)	C(9)-C(8)-C(7)	118.7(2)
C(9)-C(8)-H(8)	120.6	C(7)-C(8)-H(8)	120.6
C(10)-C(9)-C(8)	120.5(3)	C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7	C(9)-C(10)-C(11)	120.7(2)
C(9)-C(10)-H(10)	119.6	C(11)-C(10)-H(10)	119.6
C(12)-C(11)-C(10)	119.5(3)	C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2	C(11)-C(12)-C(7)	119.4(2)
C(11)-C(12)-H(12)	120.3	C(7)-C(12)-H(12)	120.3
O(3)-Cl(1)-O(4)	109.90(13)	O(3)-Cl(1)-O(1)	109.11(11)
O(4)-Cl(1)-O(1)	109.00(12)	O(3)-Cl(1)-O(2)	110.49(12)
O(4)-Cl(1)-O(2)	108.85(11)	O(1)-Cl(1)-O(2)	109.48(11)
O(7)-Cl(2)-O(8)	110.86(11)	O(7)-Cl(2)-O(5)	109.58(11)
O(8)-Cl(2)-O(5)	109.68(12)	O(7)-Cl(2)-O(6)	109.53(11)
O(8)-Cl(2)-O(6)	109.14(12)	O(5)-Cl(2)-O(6)	107.98(11)
O(10)-Cl(3)-O(11)	109.45(12)	O(10)-Cl(3)-O(9)	110.46(12)
O(11)-Cl(3)-O(9)	109.04(13)	O(10)-Cl(3)-O(12)	110.07(12)
O(11)-Cl(3)-O(12)	109.36(12)	O(9)-Cl(3)-O(12)	108.43(12)
H(1W)-O(1W)-H(2W)	106(3)		

Table S3. Values of k_{obsd}, s^{-1}, for the base hydrolysis reactions of $[(en)_2Co(S(C_6H_5R)CH_2CH_2NH_2)]^{3+}$ at 15 °C, μ = 0.10 M (NaCl).

R	σ	$[OH^-]$, M	k_{obsd}, s^{-1}	k_{OH}, M^{-1} s^{-1}	$\log(K_R/K_H)$
4-methoxy	-0.27	0.0100	0.0101	1.01	-0.69
		0.0100	0.0103	1.03	
		0.0100	0.0100	1.00	
4-methyl	-0.17	0.0100	0.0163	1.63	-0.47
		0.0100	0.0168	1.68	
		0.0100	0.0170	1.70	
3-methyl	-0.07	0.0100	0.0270	2.70	-0.27
		0.0100	0.0263	2.63	
		0.0100	0.0260	2.60	
H	0.00	0.0100	0.0498	4.98	0.00
		0.0100	0.0496	4.96	
		0.0100	0.0478	4.78	
3-methoxy	0.12	0.0100	0.0562	5.62	0.05
		0.0100	0.0539	5.39	
		0.0100	0.0569	5.69	
		0.0050	0.0270	5.40	
4-bromo	0.23	0.0050	0.0776	15.5	0.50
		0.0050	0.0779	15.6	
		0.0050	0.0763	15.3	
3-bromo	0.37	0.0050	0.149	29.7	0.78
		0.0050	0.148	29.6	
		0.0050	0.143	28.5	

Figure S1. HETCOR NMR of **1g**, **2e** and **2f** in d_6-DMSO.



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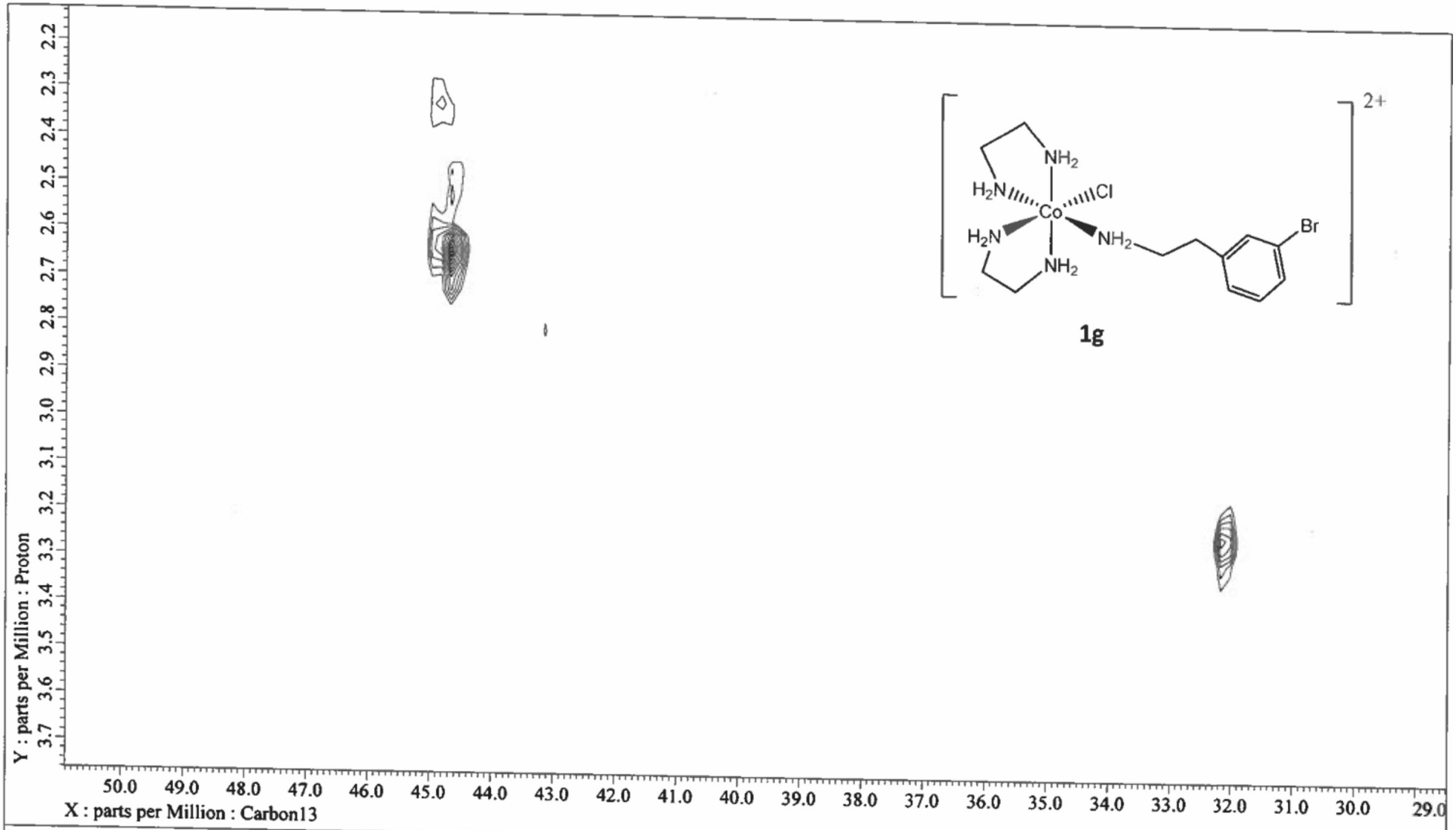

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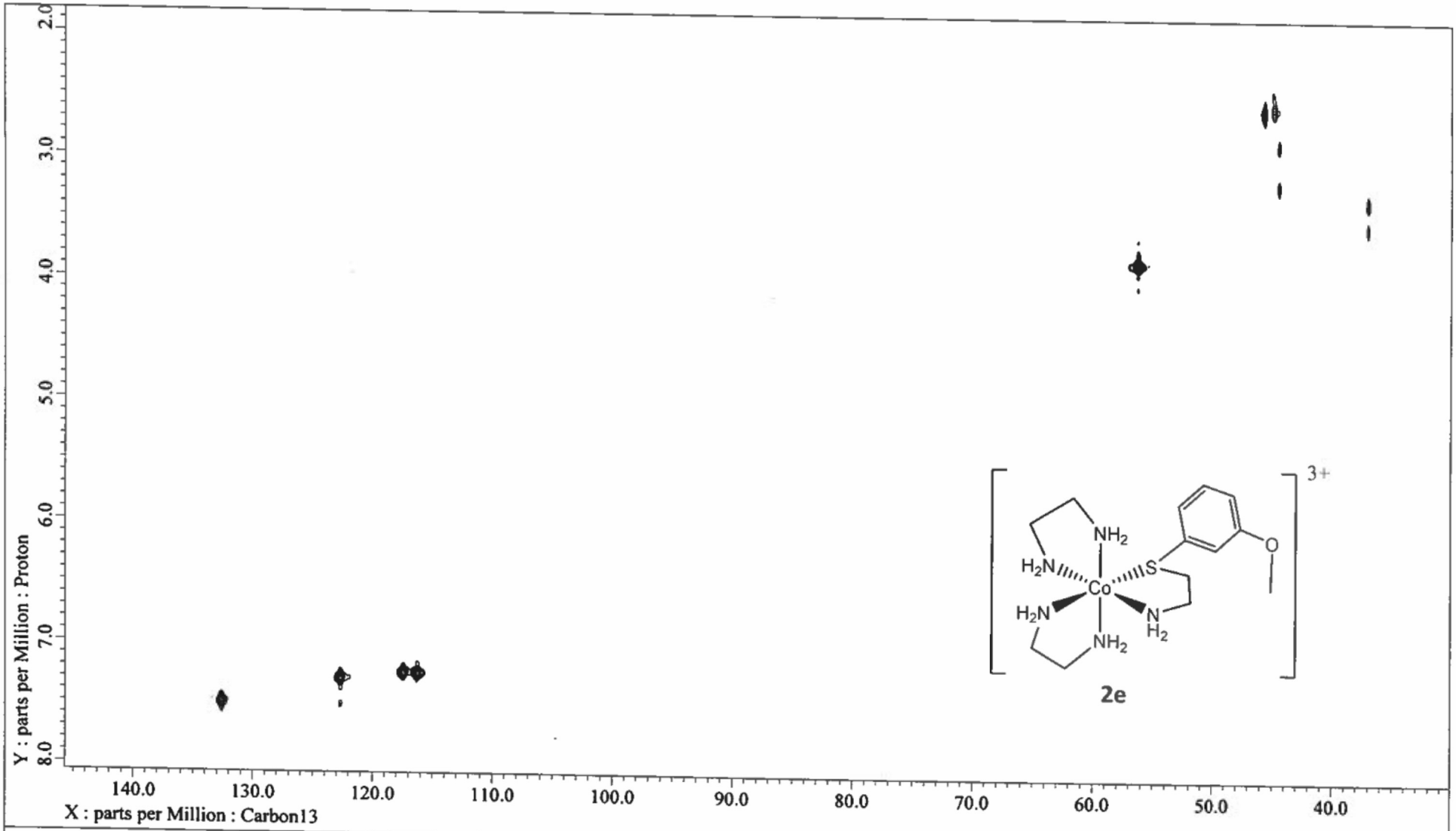

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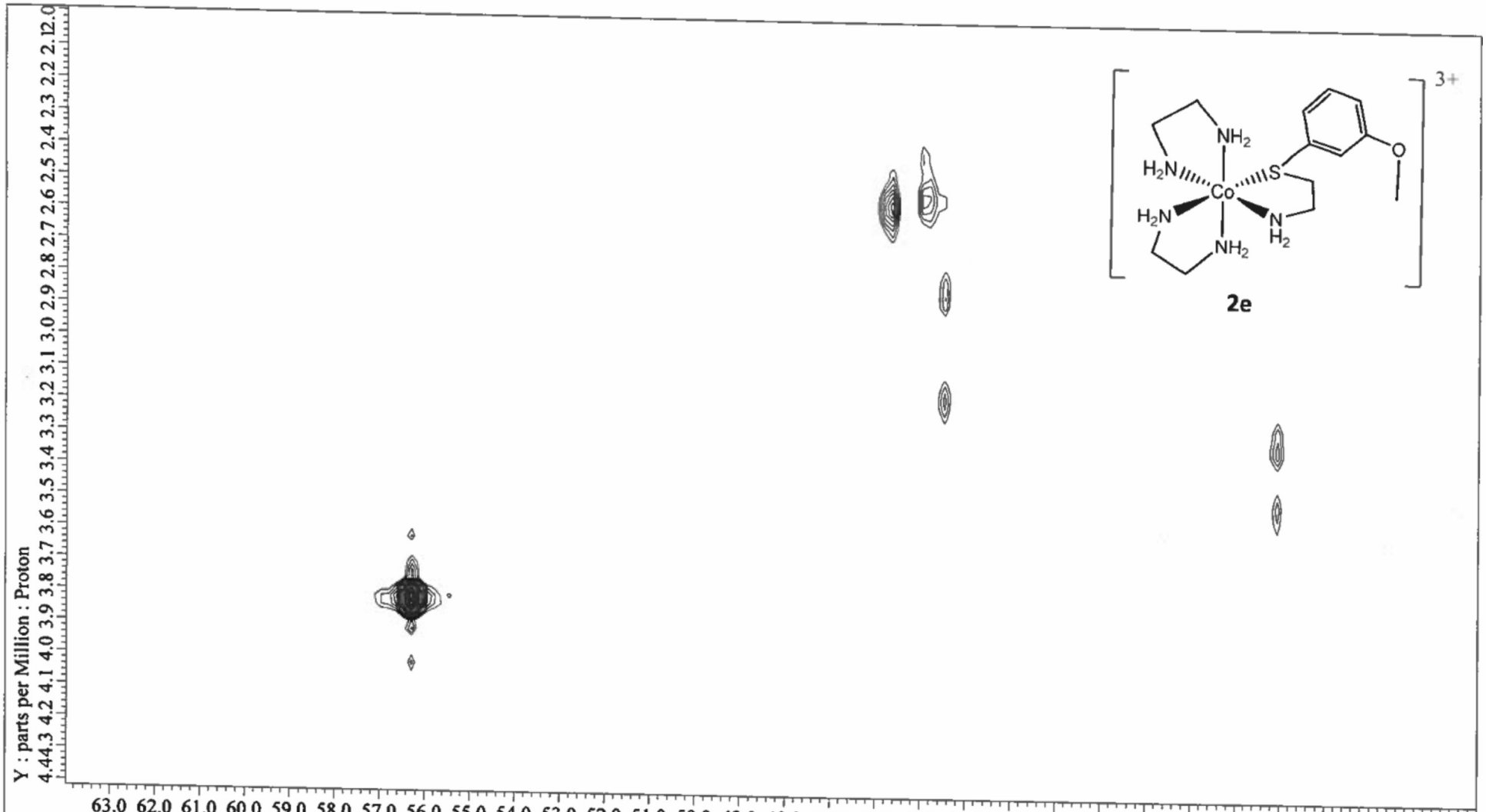

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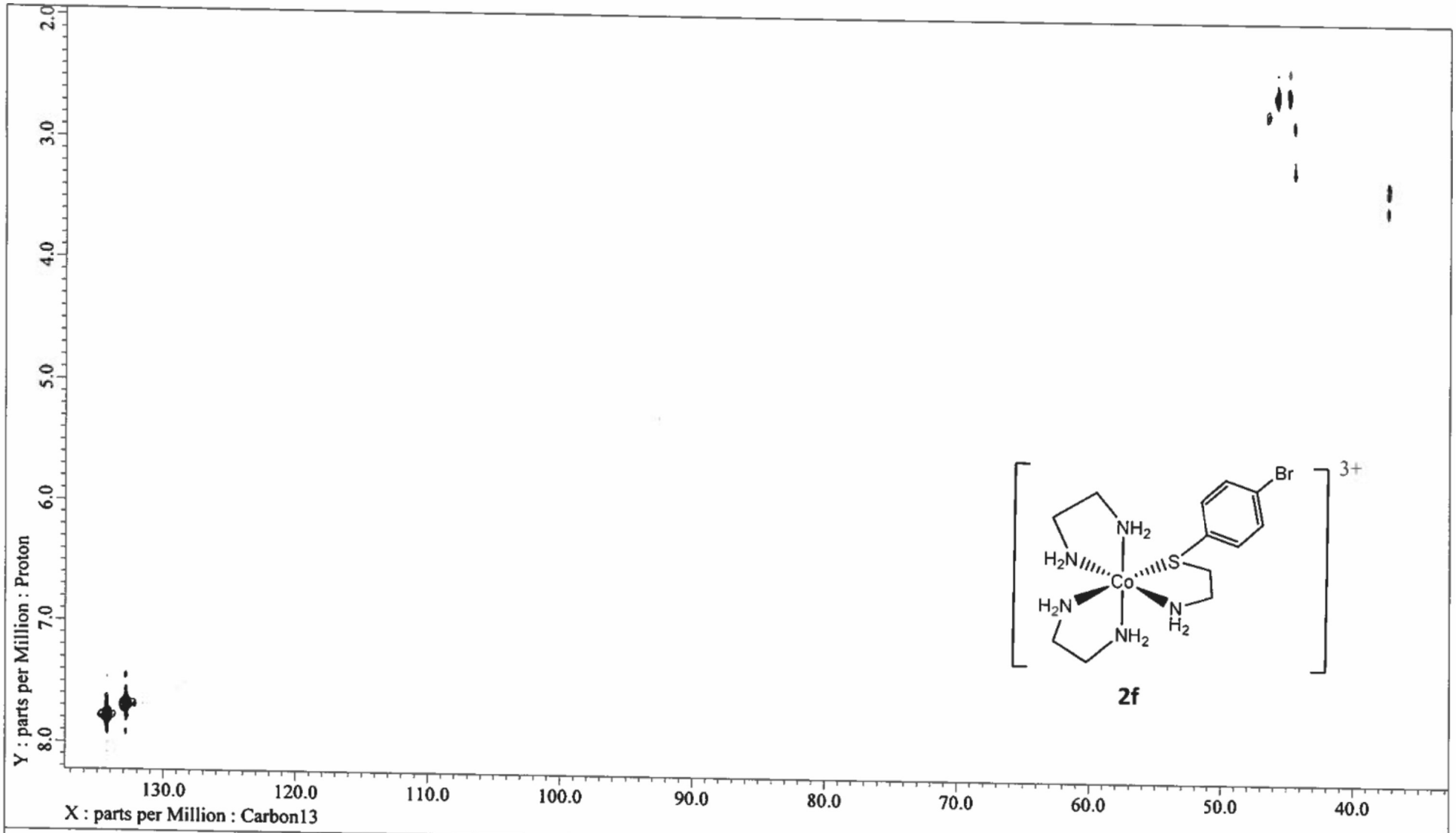
JEOL



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Dim_Units	= [ppm] [ppm]	Y_Offset	= 5.07801[ppm]	Y_Pulse	= 7.4[us]
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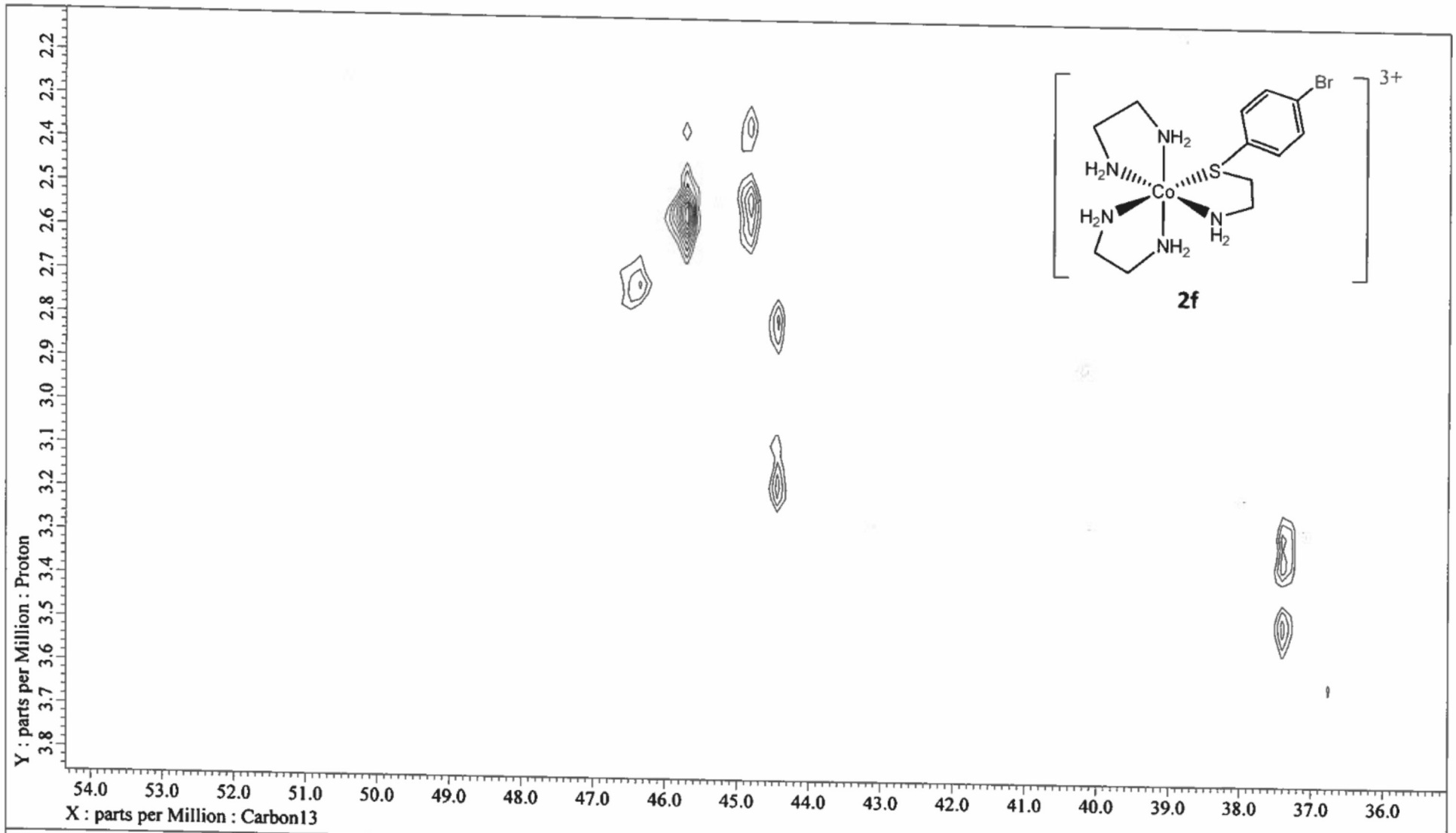
Site	= NMU ECZ400 NMR	Y_Prescans	= 0	Irr_Atn_Dec_Calc	= 25.5[dB]
Spectrometer	= DELTA2_NMR	Y_Resolution	= 19.67884131[Hz]	Irr_Atn_Dec_Default_Calc	= 25.5[dB]
		Y_Sweep	= 2.51889169[kHz]	Irr_Dec_Bandwidth_Hz	= 5.28846154[kHz]

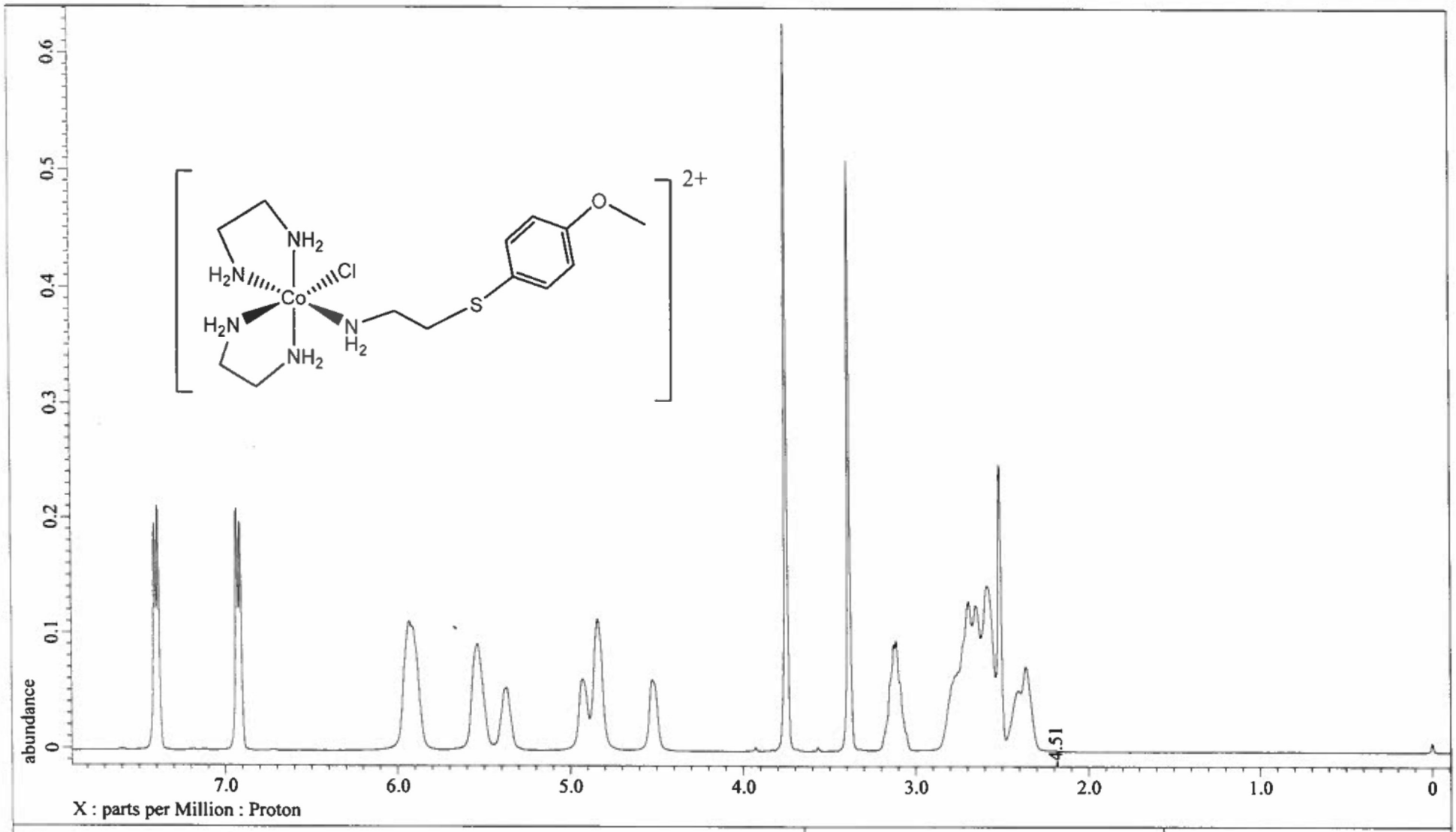
JEOL



2f

Filename	= LR 4 bromo biden_h	Field_Strength	= 9.389766[T] (400[M	Clipped	= FALSE
Author	= Lee_Roecker	X_Acq_Duration	= 77.66016[ms]	Scans	= 8
Experiment	= hetcor.jxp	X_Domain	= 13C	Total_Scans	= 1024
Sample_Id	= LR 4 bromo biden	X_Freq	= 100.52530333[MHz]		
Solvent	= DMSO-D6	X_Offset	= 85.05575[ppm]	Relaxation_Delay	= 1.5[s]
Actual_Start_Time	= 8-NOV-2023 15:26:	X_Points	= 1024	Recvr_Gain	= 56
Revision_Time	= 11-JAN-2024 16:09:	X_Prescans	= 4	Temp_Get	= 22.9[dC]
		X_Resolution	= 12.87661524[Hz]	X_Acq_Time	= 77.66016[ms]
Comment	= Heteronuclear Shif	X_Sweep	= 13.18565401[kHz]	X_Atn	= 5[dB]
Data_Format	= 2D RRAL RRAL	X_Sweep_Clipped	= 10.54852321[kHz]	X_Pulse	= 11.4[us]
Dim_Size	= 819, 256	Y_Domain	= 1H	Y_Acq_Time	= 50.816[ms]
Dim_Title	= Carbon13 Proton	Y_Freq	= 399.78219838[MHz]	Y_Atn	= 3[dB]
Dim_Units	= [ppm] [ppm]	Y_Offset	= 5.07801[ppm]	Y_Pulse	= 7.4[us]
Dimensions	= X Y	Y_Points	= 128	Irr_Atn_Dec	= 25.5[dB]
Site	= NMU ECZ400 NMR	Y_Prescans	= 0	Irr_Atn_Dec_Calc	= 25.5[dB]
Spectrometer	= DELTA2_NMR	Y_Resolution	= 19.67884131[Hz]	Irr_Atn_Dec_Default_Calc	= 25.5[dB]
		Y_Sweep	= 2.51889169[kHz]	Irr_Dec_Bandwidth_Hz	= 5.28846154[kHz]

Figure S2. ^{1}H and ^{13}C NMR of the intermediate complexes (**1a – 1g**) in d_6-DMSO.

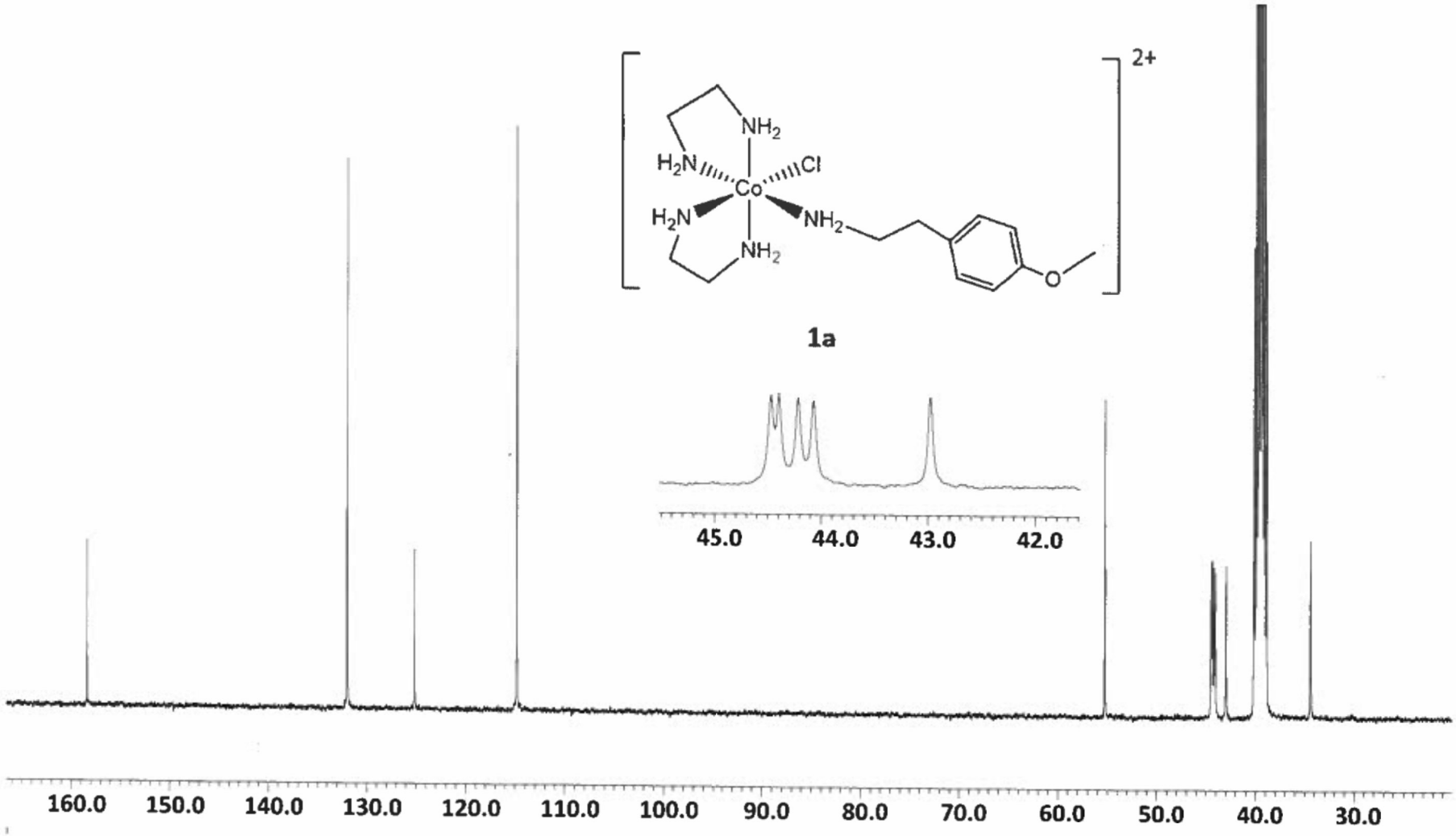


Filename	= LR Elle p 19 Cl 4 MeO	X_Acq_Duration	= 2.18628096[s]
Author	= Lee_Roecker	X_Domain	= 1H
Experiment	= proton.jxp	X_Freq	= 399.78219838[MHz]
Sample_Id	= LR Elle p 19 Cl 4 MeO	X_Offset	= 5[ppm]
Solvent	= DMSO-D6	X_Points	= 16384
Actual_Start_Time	= 5-DEC-2022 07:14:32	X_Prescans	= 1
Revision_Time	= 19-DEC-2023 17:25:26	X_Resolution	= 0.45739775[Hz]
		X_Sweep	= 7.4940048[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]
Dim_Size	= 13107	Irr_Domain	= Proton
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Tri_Domain	= Proton
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]
		Clipped	= FALSE
Field_Strength	= 9.389766[T] (400[MHz]	Scans	= 16

```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid3( 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
thresh( 2[%], 1 )
peak_pick( 0[Hz], 0.1[ppm], Both, 0[Hz] )
norm_smallest_int( 1.0, 0[Hz], 25[Hz] )

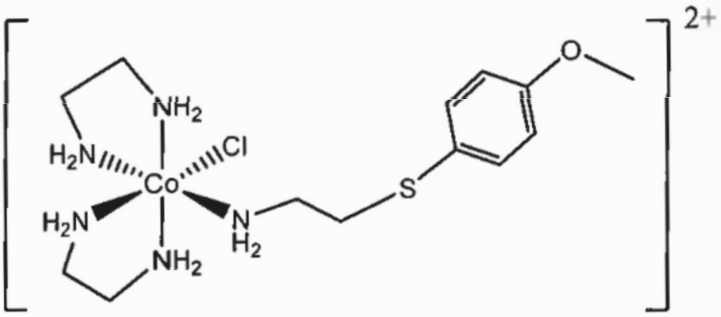
Derived from: LR Elle p 19 Cl 4 MeO_PROTON-
```

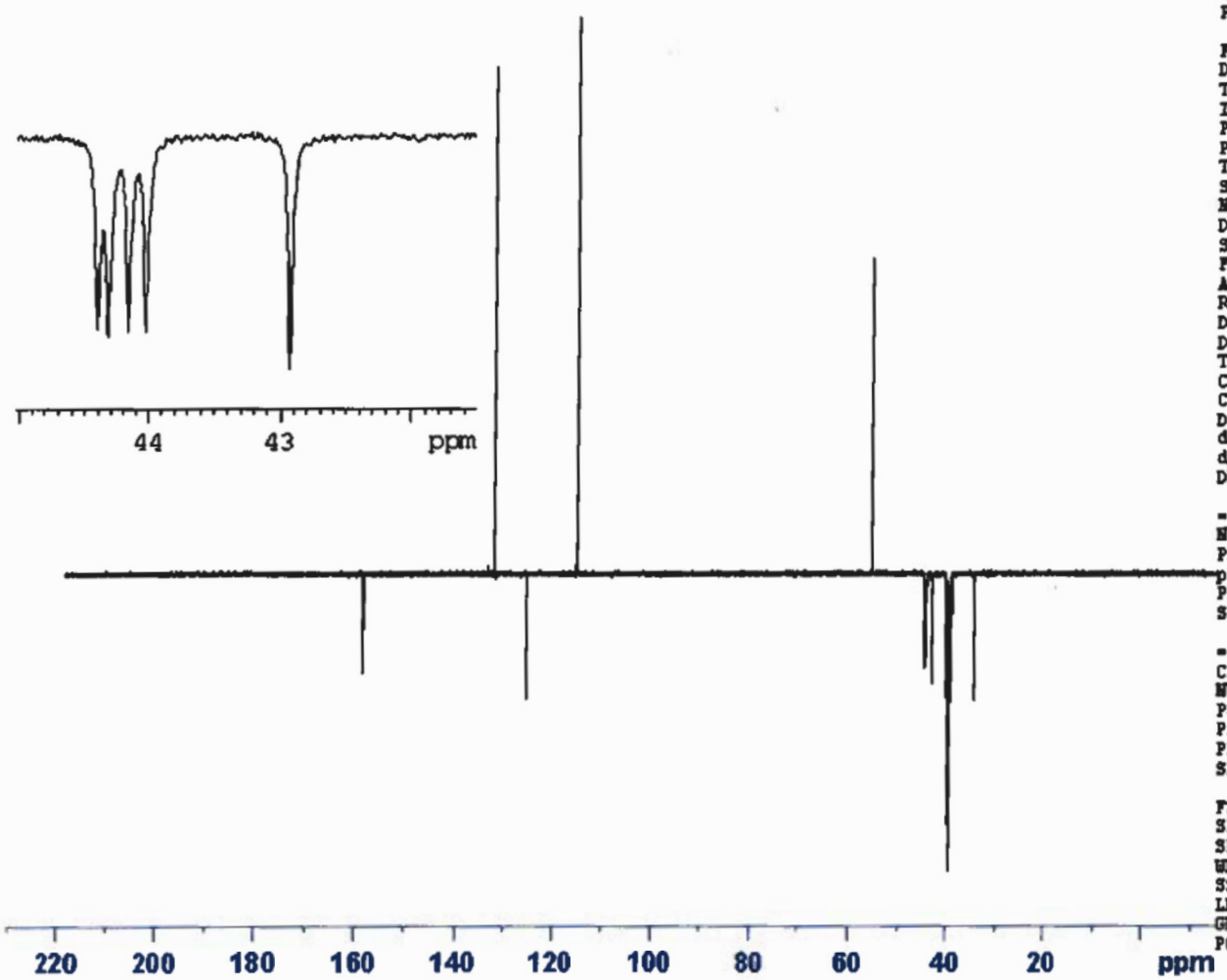
JEOL


2+
NH2
H2N
Cl
Co
H2N
NH2
NH2
O
1a
45.0
44.0
43.0
42.0
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
δ, ppm

APT (Attached Proton Test) NMR Experiment.

In an APT experiment, carbon atoms attached to 0 or 2 hydrogen atoms appear in one direction while those attached to 1 or 3 hydrogen atoms appear in the other direction.





BRUKER

```
Current Data Parameters
NAME                 Apr17-2008
EXPNO                        21
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20080417
Time                      20.31
INSTRUM                   spect
PROBHD     5 mm BBO BB-1H
PULPROG                   jmod
TD                       65536
SOLVENT                    DMSO
NS                         2000
DS                            4
SWH                23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                        16384
DW                     20.850 usec
DE                      6.50 usec
TE                     300.0 K
CNST2              145.0000000
CNST11               1.0000000
D1                   2.00000000 sec
d13                  0.00000300 sec
d20                  0.00689655 sec
DELTA                0.00000987 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                       7.75 usec
p2                      15.50 usec
PL1                     -4.00 dB
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    14.20 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6128193 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          1.40
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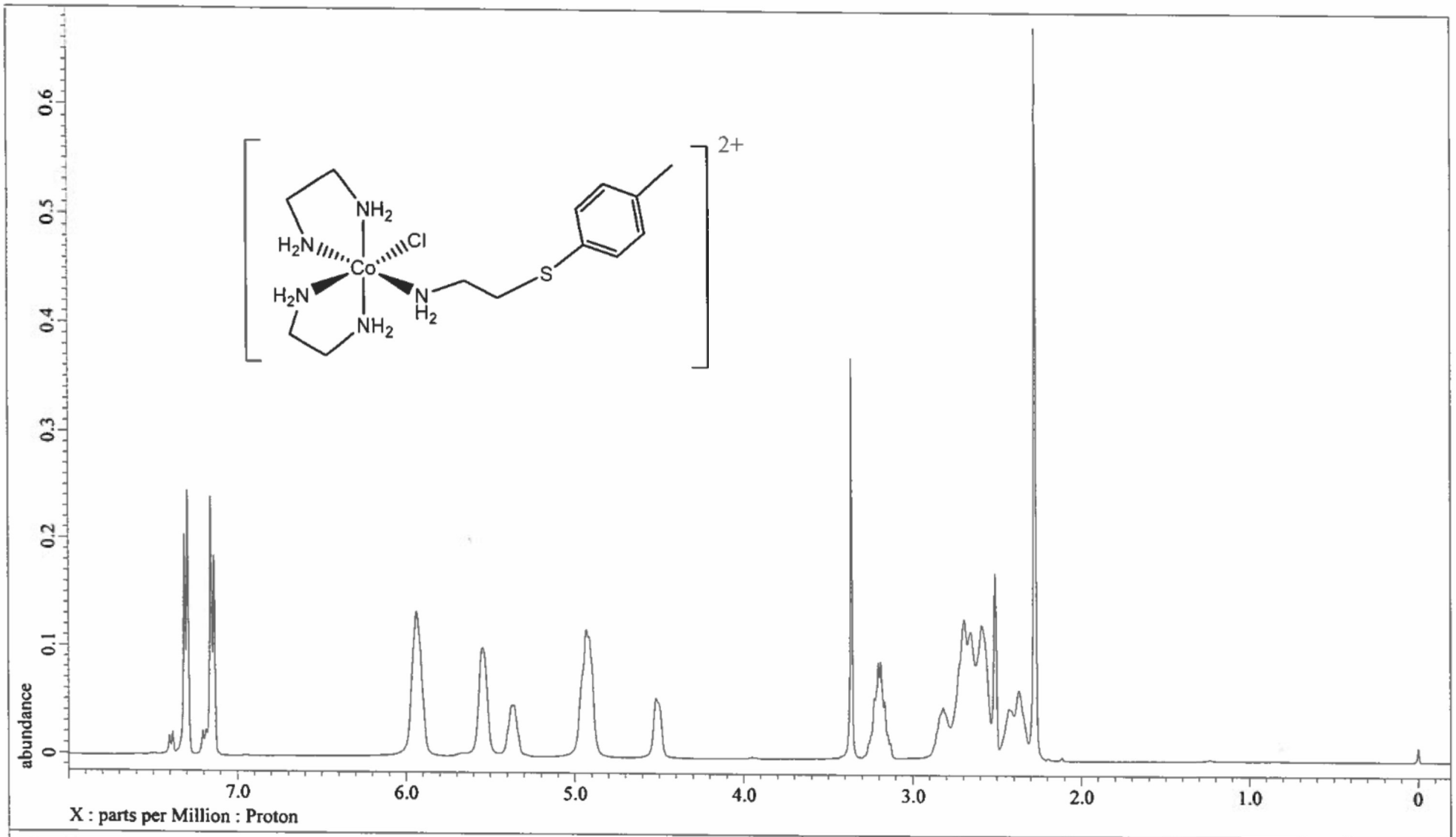
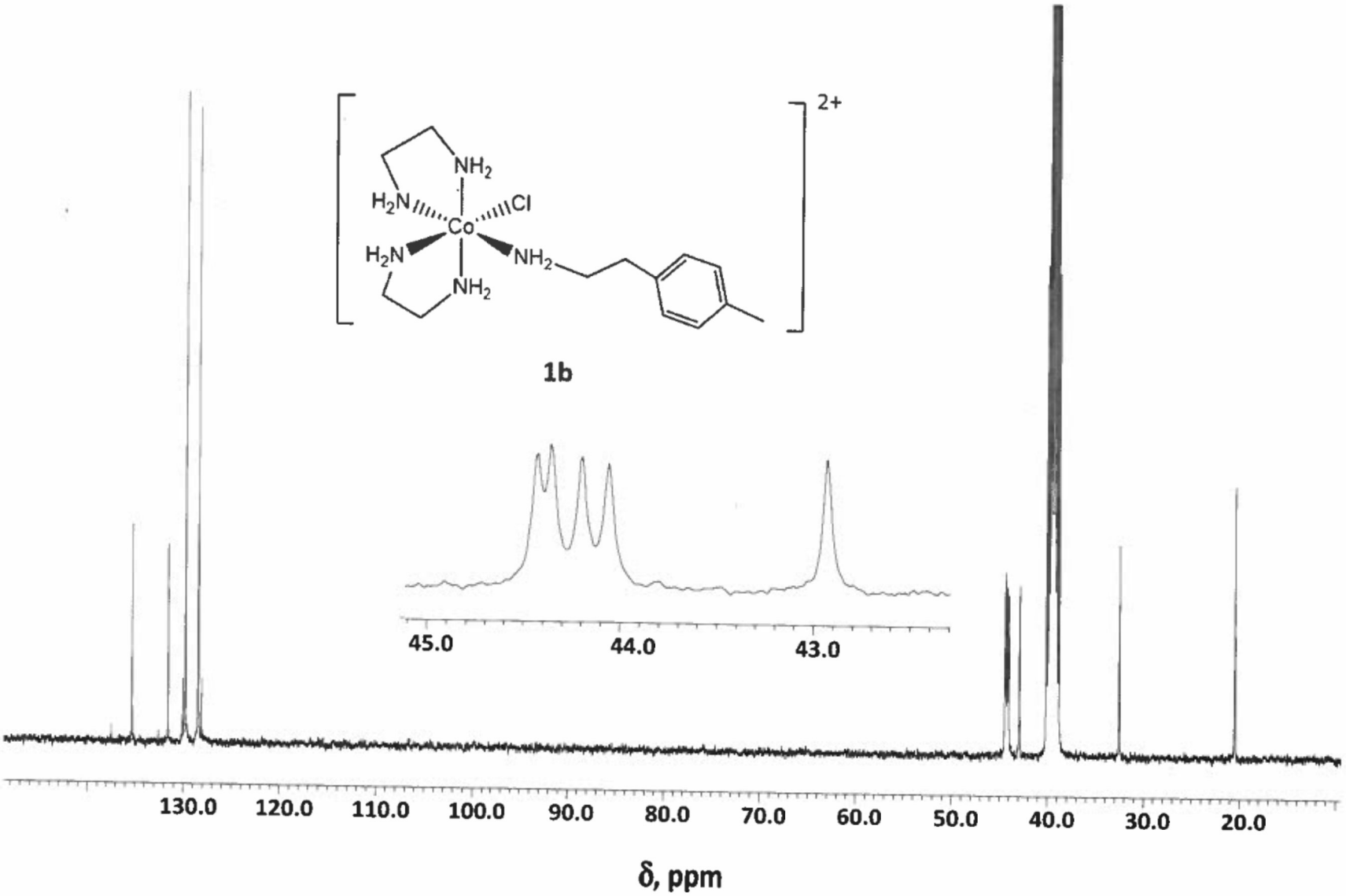
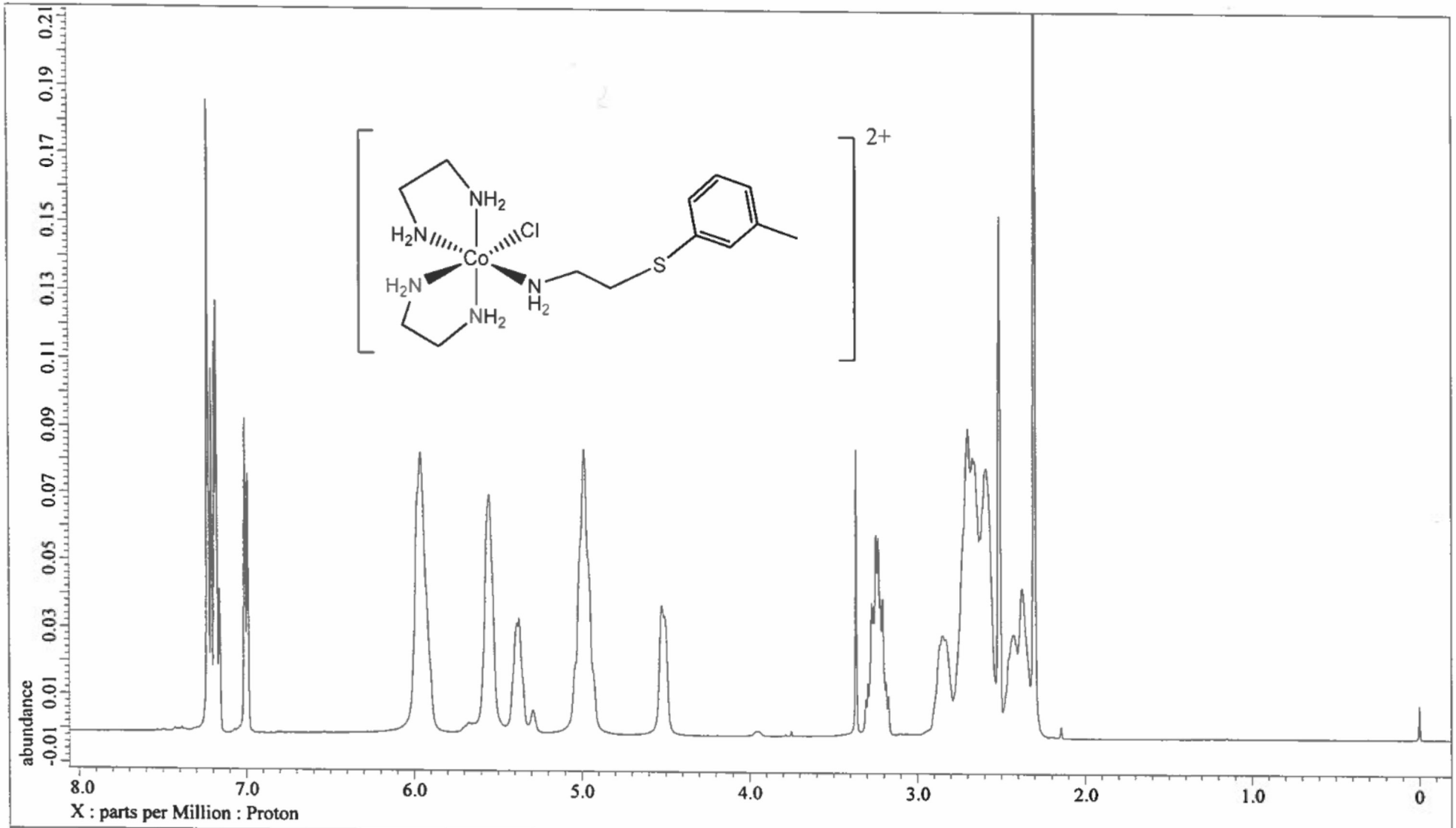
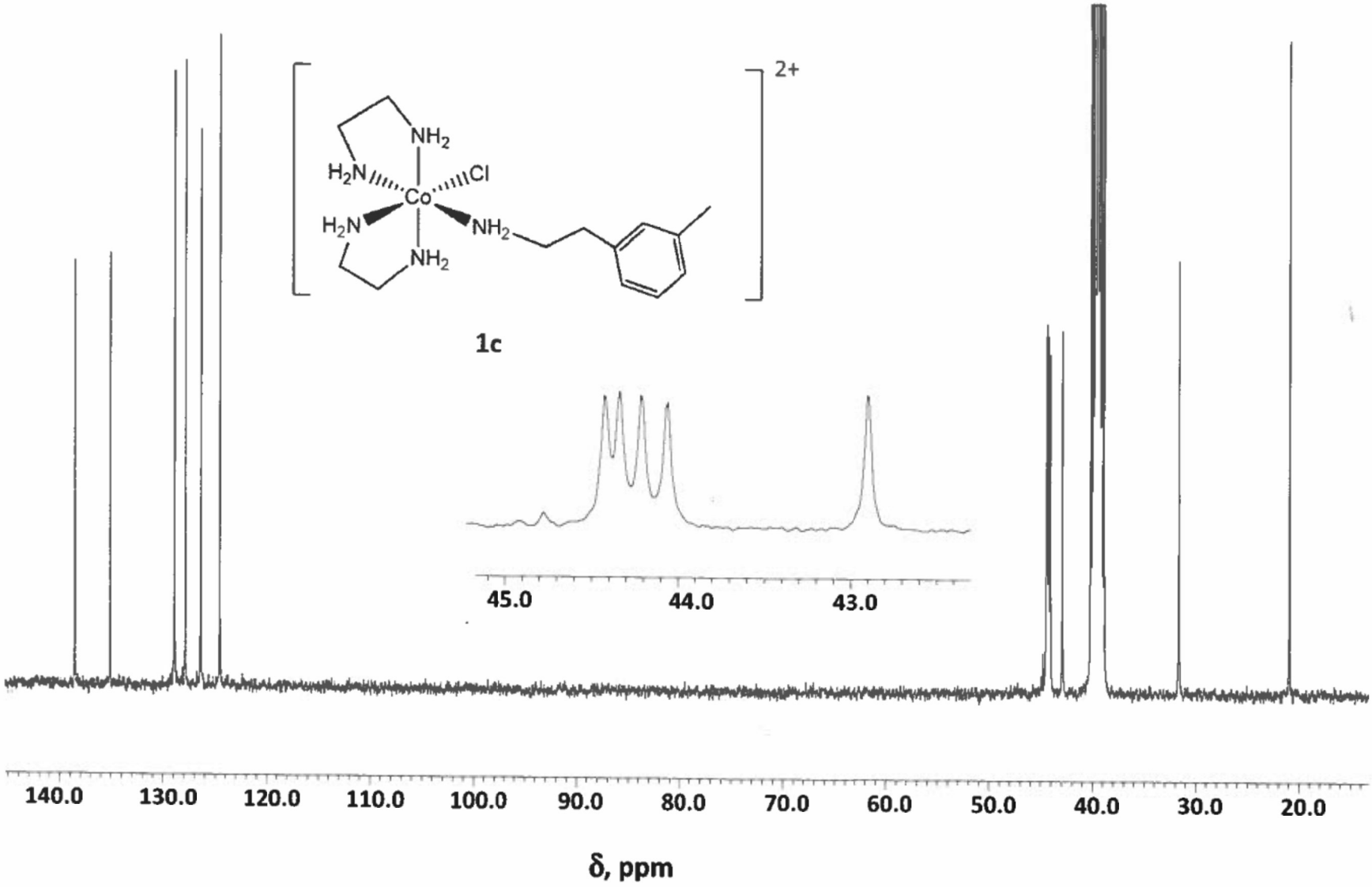


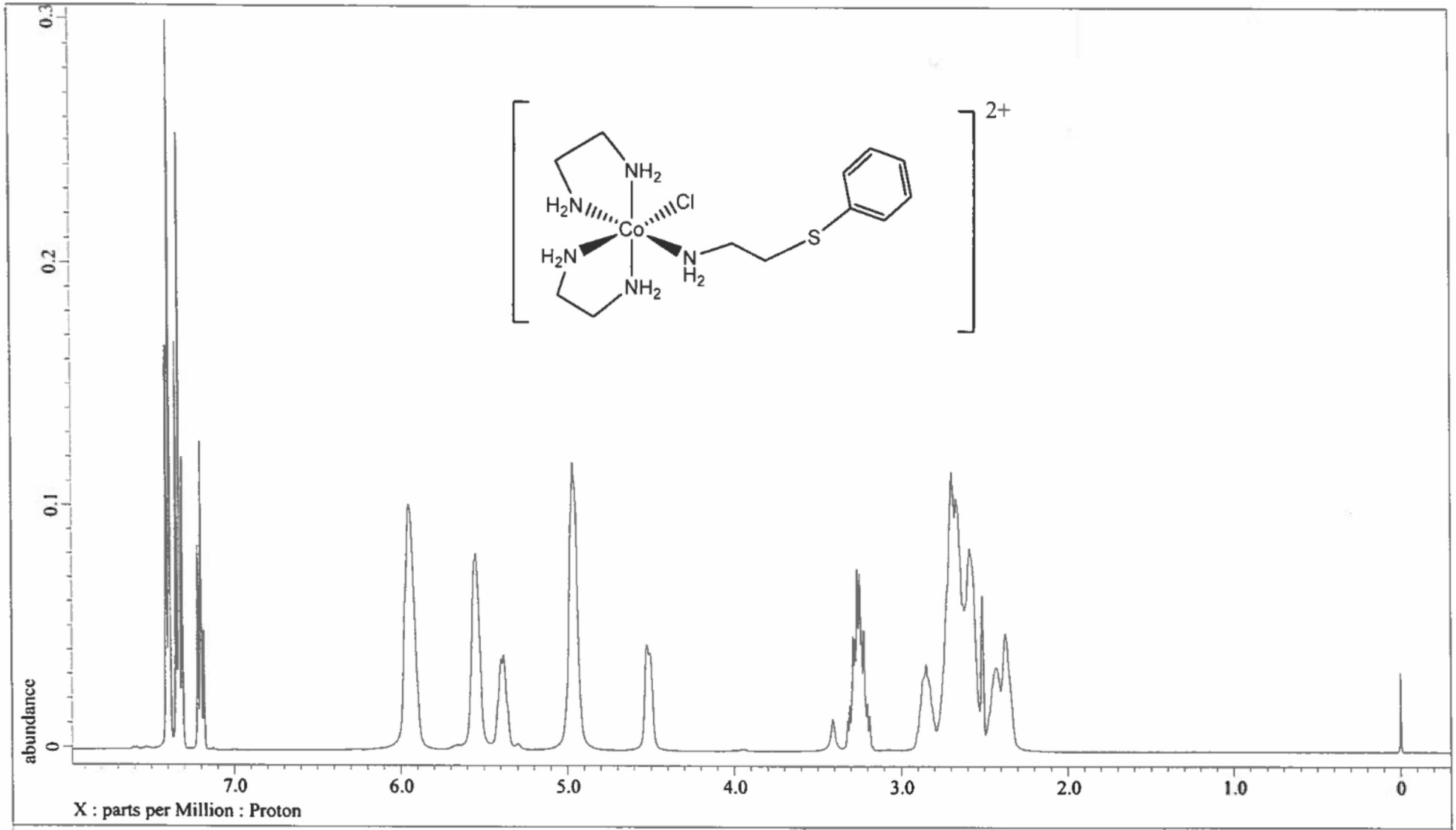
Filename	= Lee 4Me Cl_proton-2-3	Field_Strength	= 9.389766[T] (400[MHz])	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= Lee 4Me Cl	X_Freq	= 399.78219838[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 17-AUG-2023 13:01:59	X_Points	= 16384	machinephase
Revision_Time	= 19-DEC-2023 16:58:22	X_Prescans	= 1	ppm
		X_Resolution	= 0.45739775[Hz]	
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: Lee 4Me Cl_proton-2-1.jdf
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]	
Dim_Size	= 13107	Irr_Domain	= Proton	
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]	
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]	
Dimensions	= X	Tri_Domain	= Proton	
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]	
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]	
		Clipped	= FALSE	


2+
NH2
H2N
Cl
Co
H2N
NH2
NH2
1b
45.0
44.0
43.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
δ, ppm

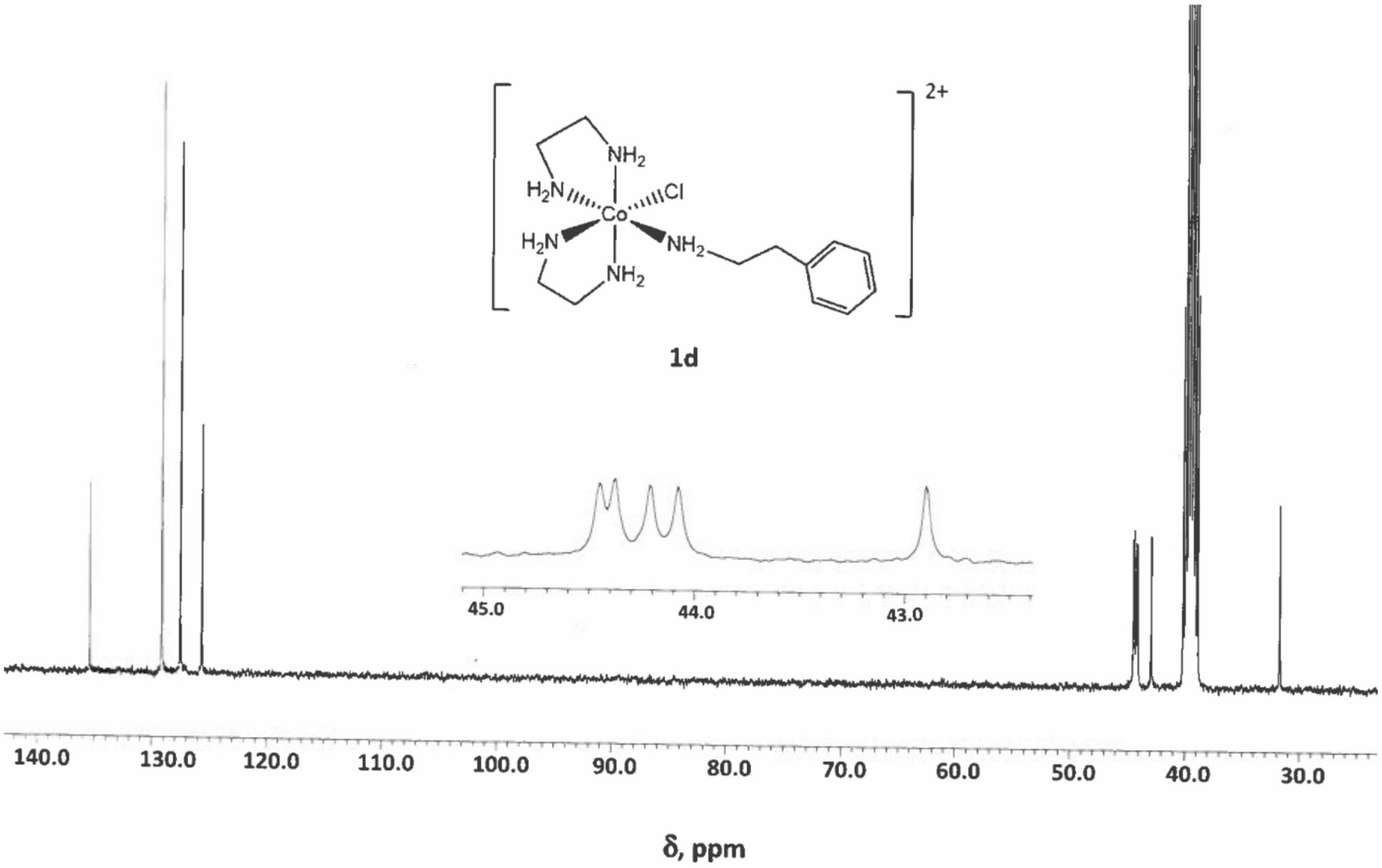


Filename	= LR 3ME chloro p34_pro	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR 3ME chloro p34	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 9-OCT-2023 16:30:57	X_Points	= 16384	machinephase	
Revision_Time	= 19-DEC-2023 16:54:26	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: LR 3ME chloro p34_proton-2-1.	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		

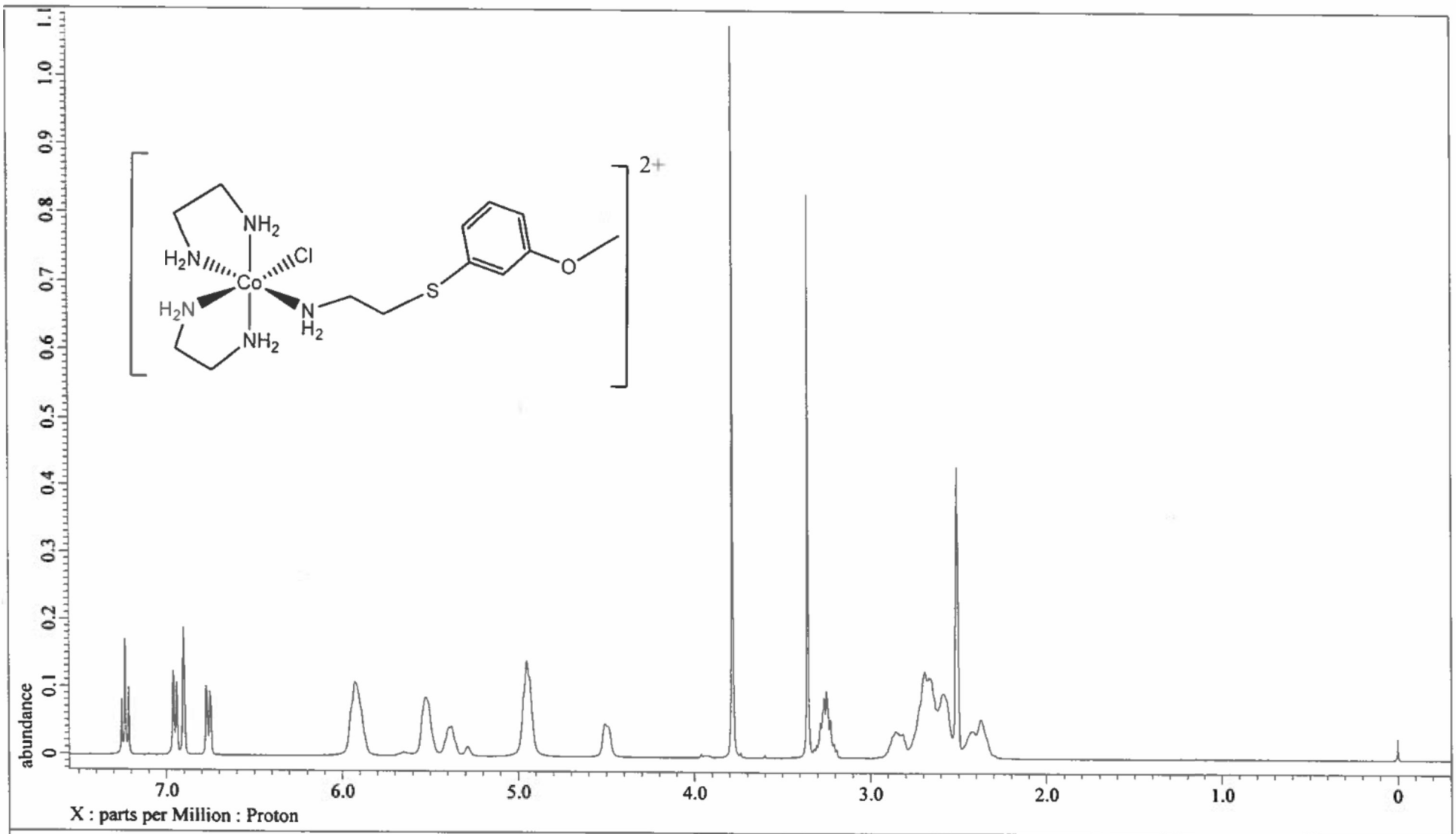

2+
NH2
H2N
Co
Cl
H2N
NH2
NH2
1c
45.0
44.0
43.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
δ, ppm



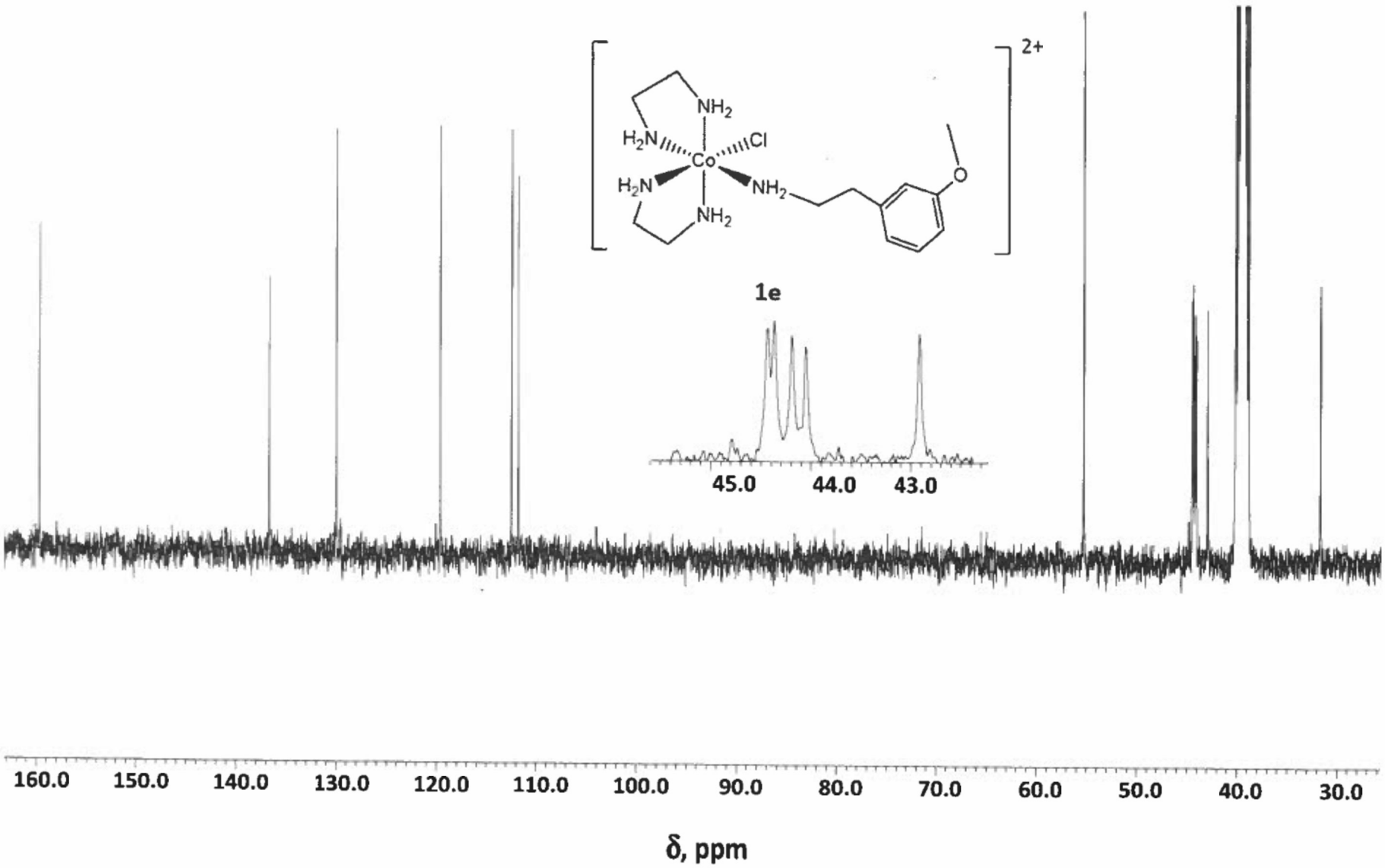
Filename	= OR cobalt thiolphenyl	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= OR cobalt thiolphenyl	X_Freq	= 399.78219838[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 26-OCT-2021 11:22:44	X_Points	= 16384	machinephase
Revision_Time	= 19-DEC-2023 17:30:09	X_Prescans	= 1	ppm
		X_Resolution	= 0.45739775[Hz]	
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: OR cobalt thiolphenyl_proton-
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]	
Dim_Size	= 13107	Irr_Domain	= Proton	
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]	
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]	
Dimensions	= X	Tri_Domain	= Proton	
Site	= KMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]	
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]	
		Clipped	= FALSE	

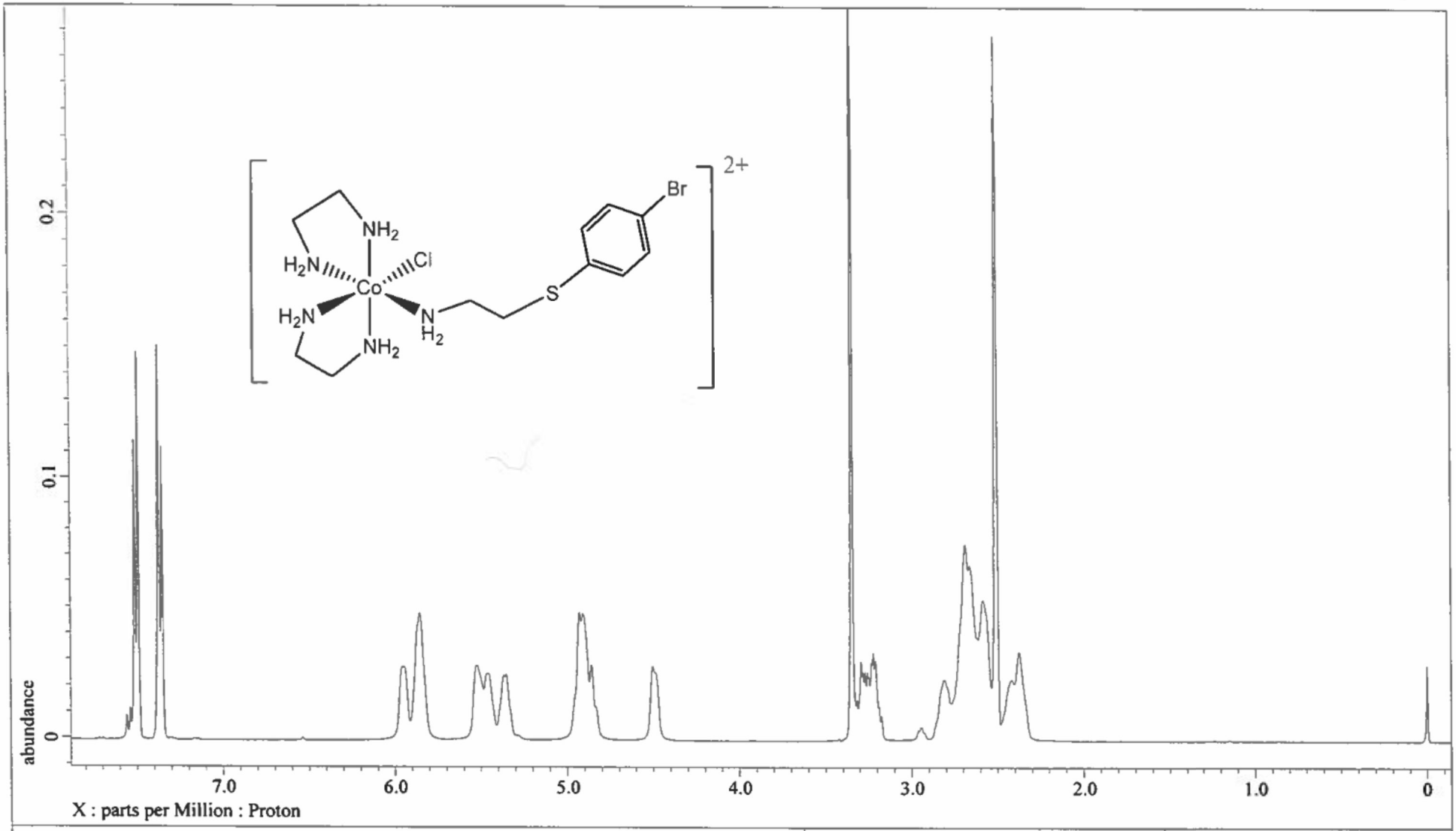

2+
NH2
H2N
Co
Cl
H2N
NH2
NH2
45.0
44.0
43.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
δ, ppm

1d



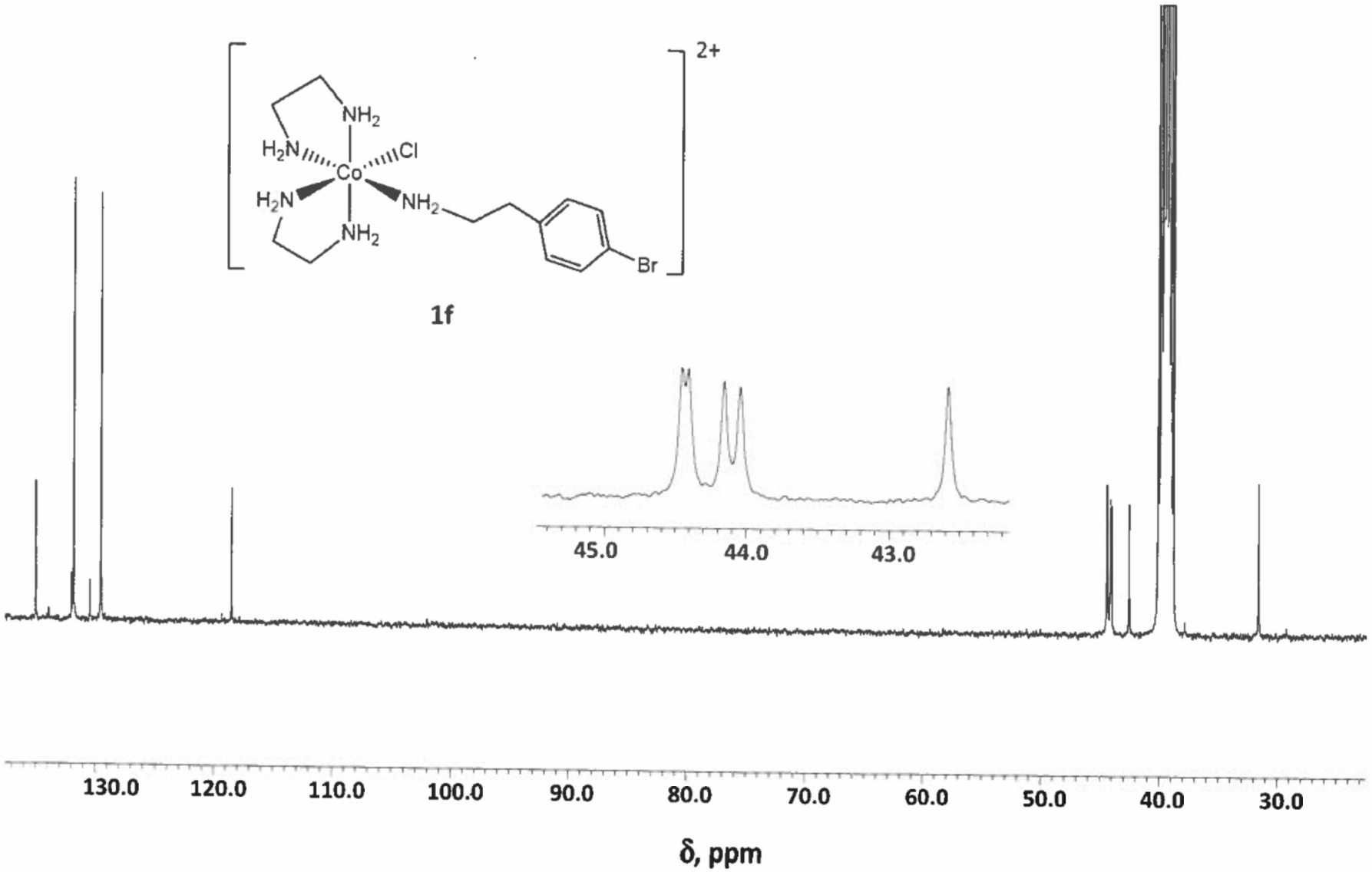
Filename	= 4methoxy ella chloror	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= 4methoxy ella chloror	X_Freq	= 399.78219838[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 30-MAR-2023 12:53:09	X_Points	= 16384	machinephase
Revision_Time	= 19-DEC-2023 17:19:31	X_Prescans	= 1	ppm
		X_Resolution	= 0.45739775[Hz]	
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: 4methoxy ella chloror_proton-
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]	
Dim_Size	= 13107	Irr_Domain	= Proton	
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]	
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]	
Dimensions	= X	Tri_Domain	= Proton	
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]	
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]	
		Clipped	= FALSE	


NH2
H2N
Co
Cl
H2N
NH2
NH2
O
2+
1e
45.0
44.0
43.0
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
δ, ppm

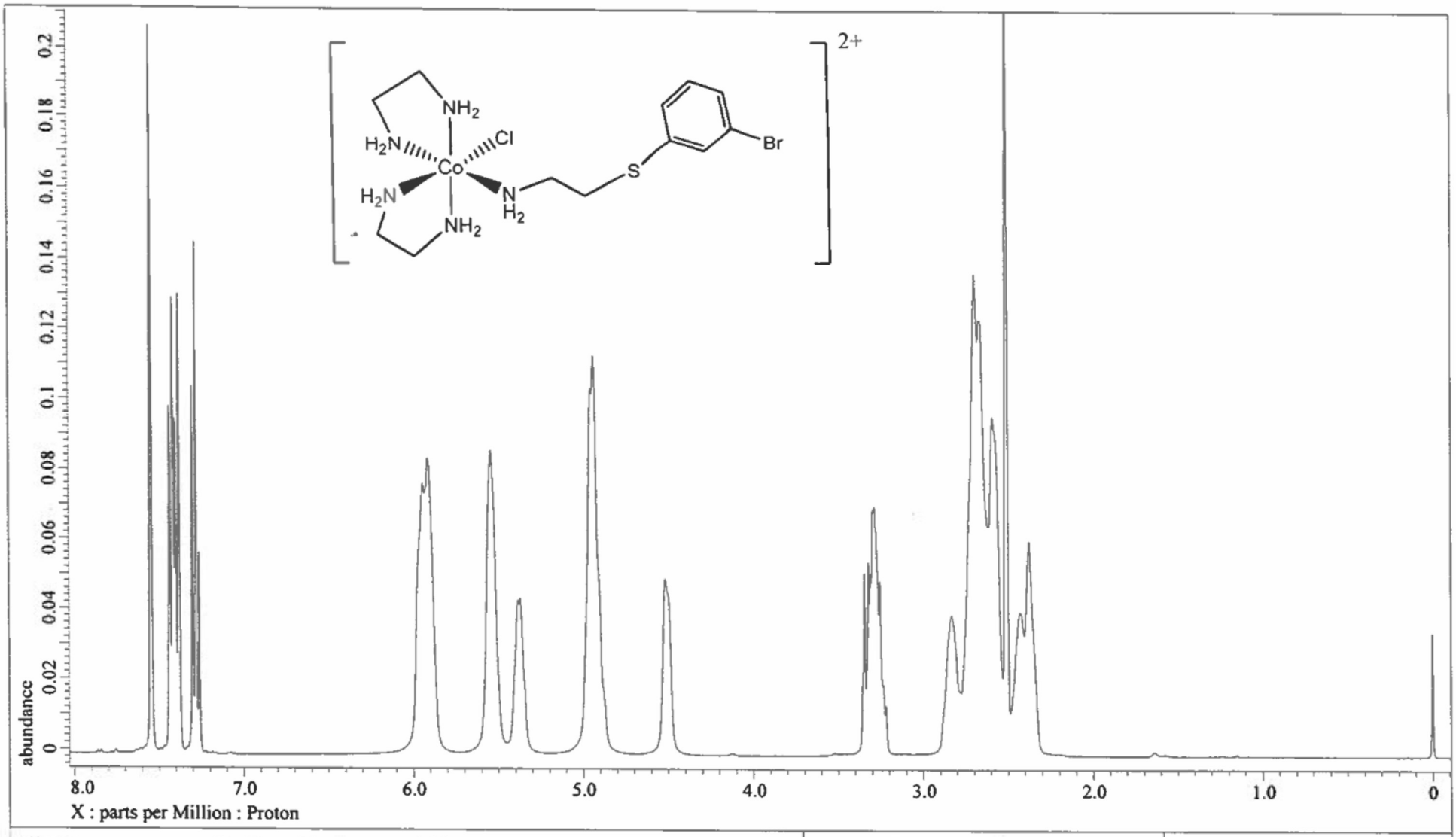


Filename	= Lee 4Br Cl RC p67_pro	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= Lee 4Br Cl RC p67	X_Freq	= 399.78219838[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 15-AUG-2023 16:08:39	X_Points	= 16384	machinephase
Revision_Time	= 19-DEC-2023 17:05:18	X_Prescans	= 1	ppm
		X_Resolution	= 0.45739775[Hz]	
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: Lee 4Br Cl RC p67_proton-2-1.
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]	
Dim_Size	= 13107	Irr_Domain	= Proton	
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]	
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]	
Dimensions	= X	Tri_Domain	= Proton	
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]	
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]	
		Clipped	= FALSE	

JEOL


2+
NH2
H2N
Cl
Co
H2N
NH2
NH2
Br
45.0
44.0
43.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
δ, ppm

1f

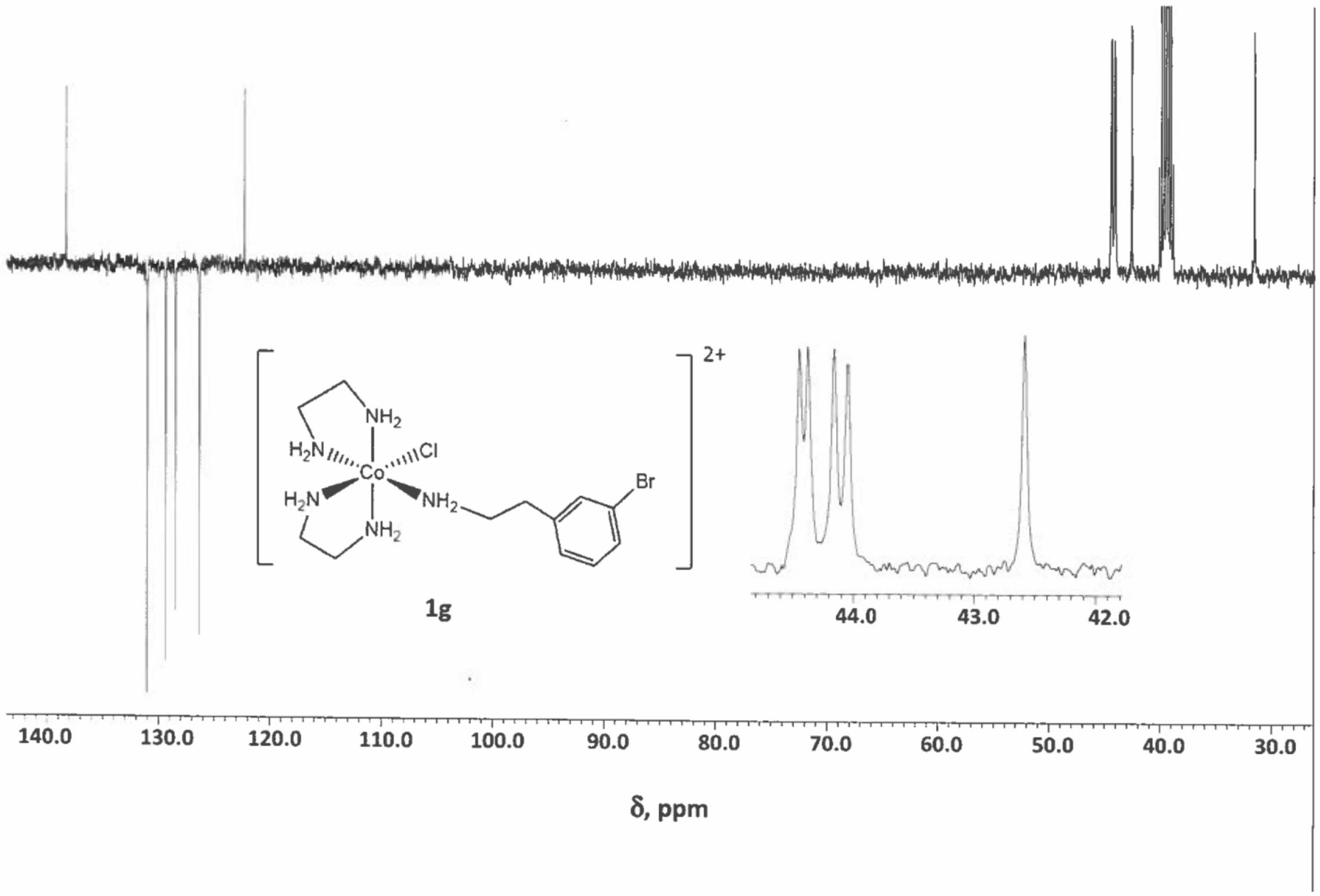


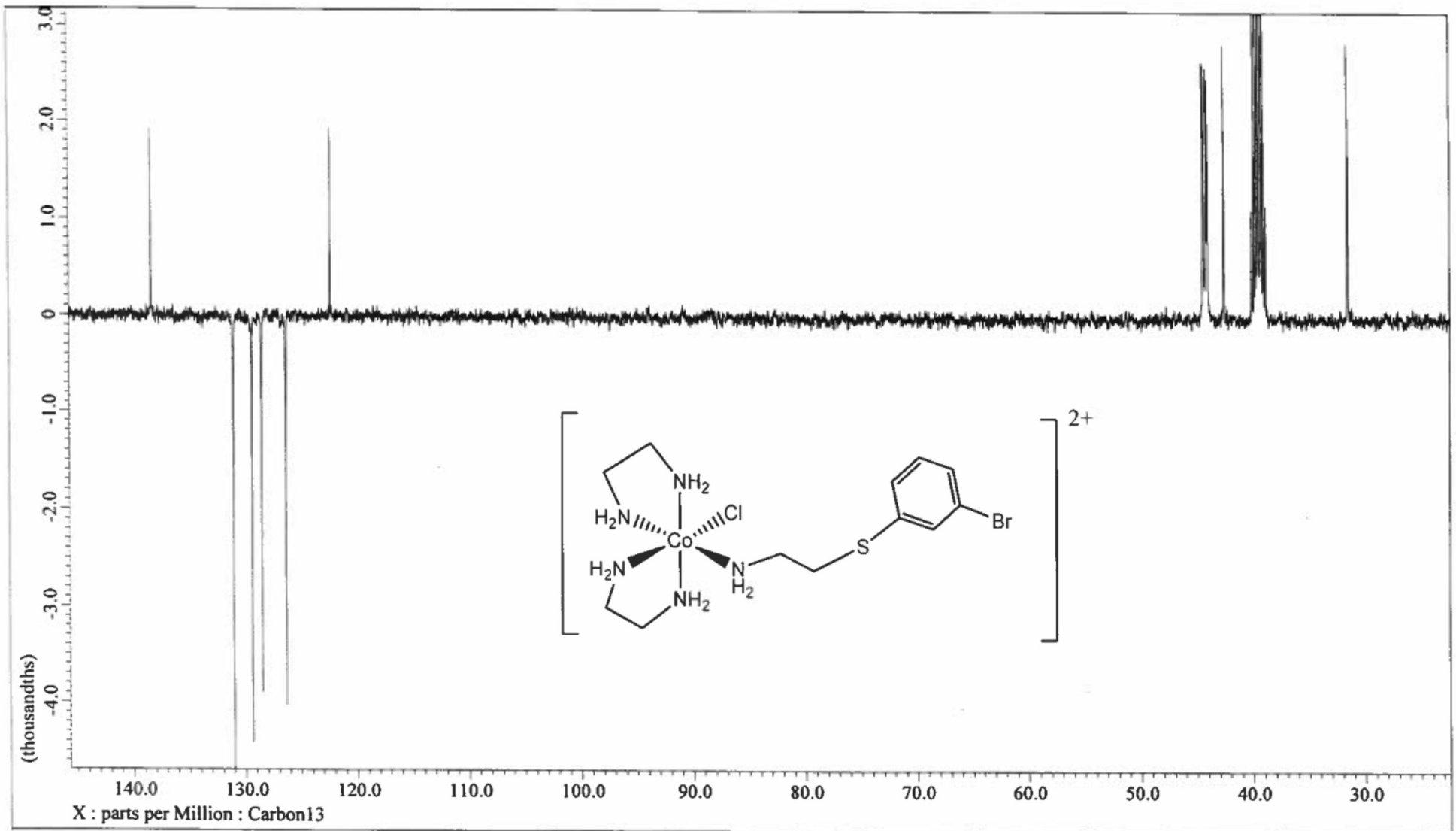
Filename	= LR chloro 3 bromo_pro	Field_Strength	= 9.389766[T] (400[MHz]
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]
Experiment	= proton.jxp	X_Domain	= 1H
Sample_Id	= LR chloro 3 bromo	X_Freq	= 399.78219838[MHz]
Solvent	= DMSO-D6	X_Offset	= 5[ppm]
Actual_Start_Time	= 8-NOV-2023 07:51:36	X_Points	= 16384
Revision_Time	= 19-DEC-2023 16:52:49	X_Prescans	= 1
		X_Resolution	= 0.45739775[Hz]
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]
Dim_Size	= 13107	Irr_Domain	= Proton
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Tri_Domain	= Proton
Site	= KMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]
		Clipped	= FALSE

```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: LR chloro 3 bromo_proton-3-1.
```

JEOL


NH2
H2N
Co
Cl
H2N
NH2
NH2
Br
2+
1g
44.0
43.0
42.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
δ, ppm



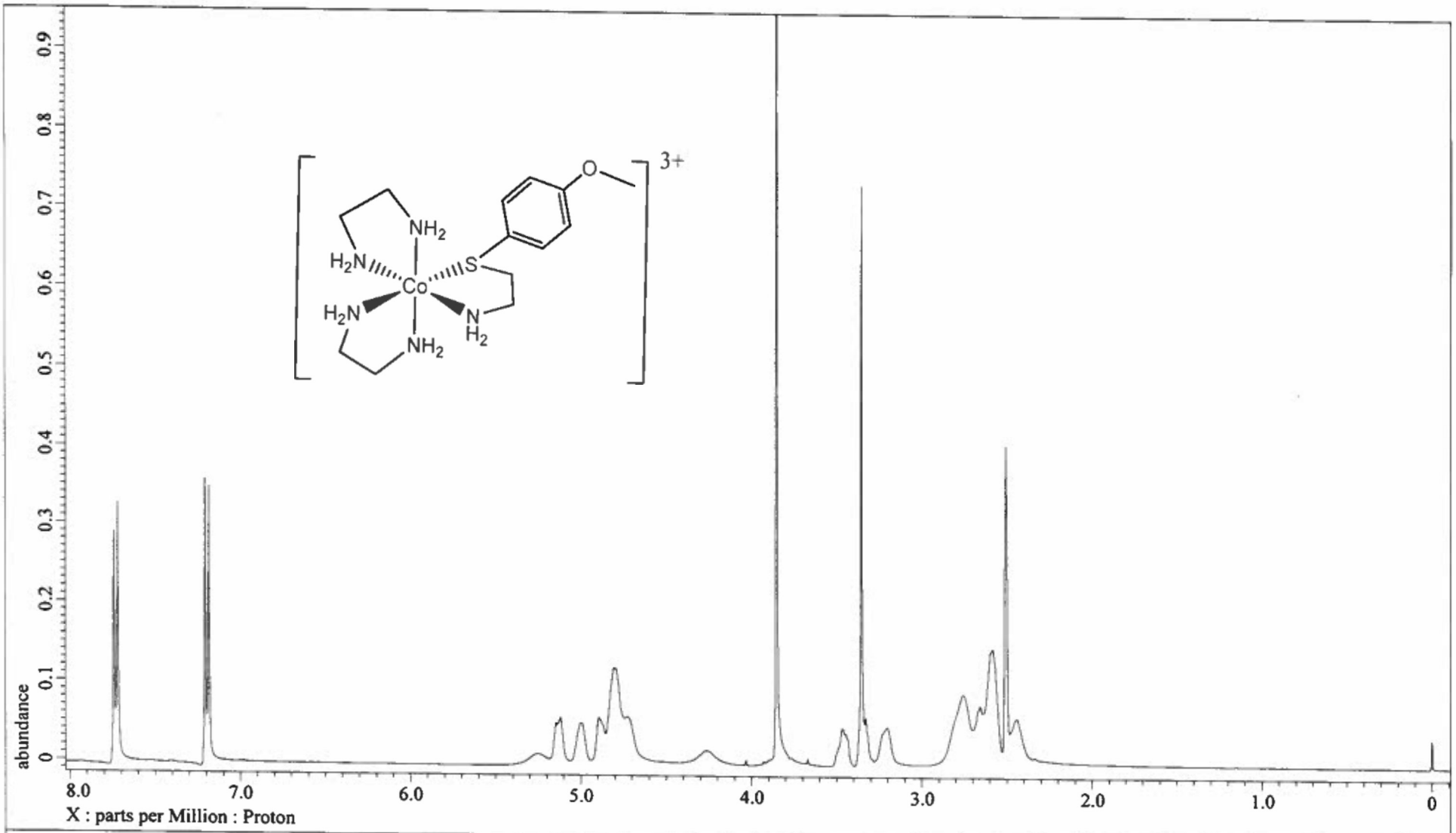
Filename	= LR chloro 3 bromo_	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= apt.jxp	X_Domain	= 13C
Sample_Id	= LR chloro 3 bromo	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 8-NOV-2023 11:10:	X_Points	= 32768
Revision_Time	= 19-DEC-2023 16:51:	X_Prescans	= 4
		X_Resolution	= 0.96330739[Hz]
Comment	= APT Experiment	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= TRUE
Site	= NMU ECZ400 NMR	Scans	= 1776
Spectrometer	= DELTA2_NMR	Total_Scans	= 1776

```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

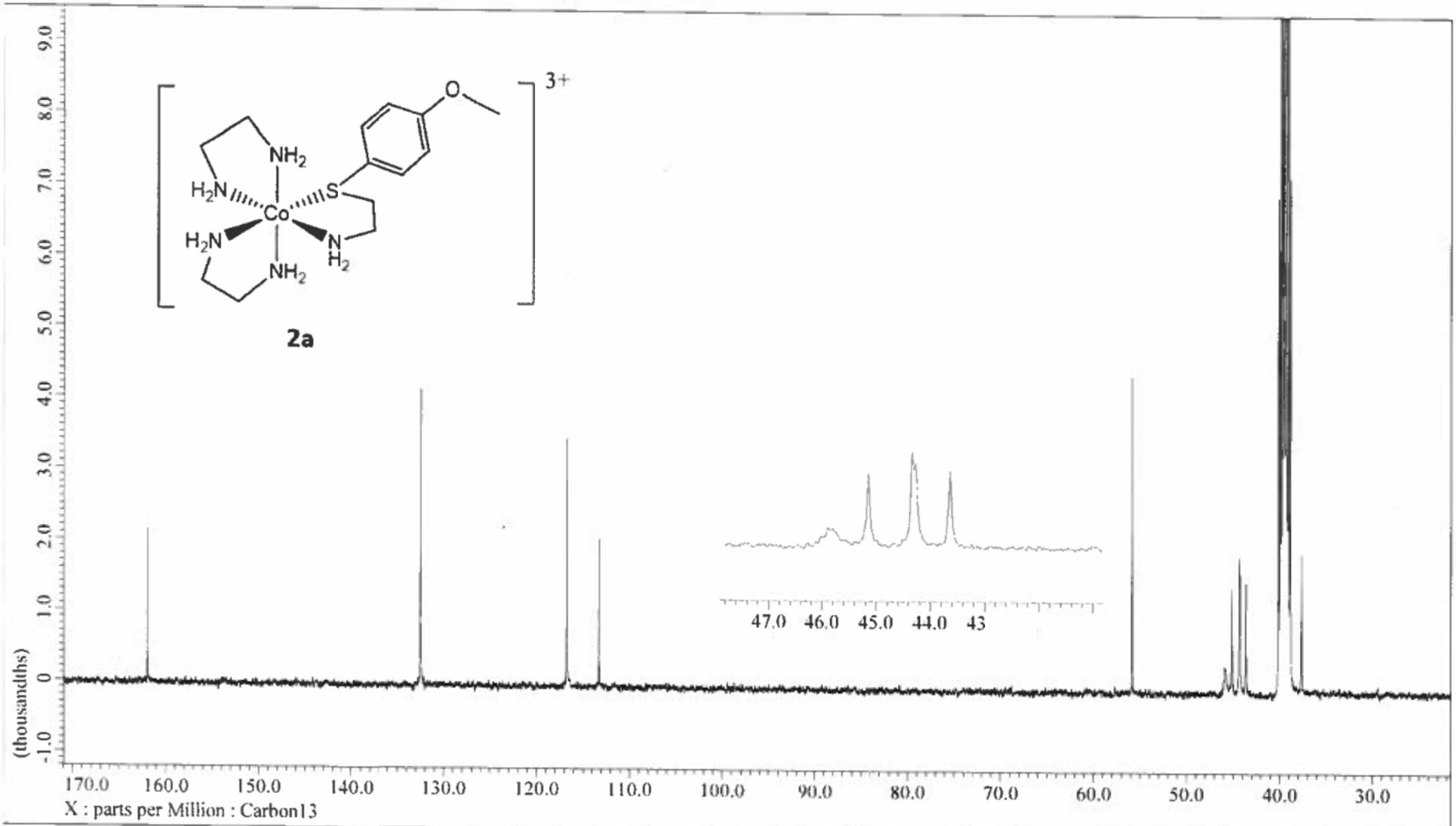
Derived from: LR chloro 3 bromo_apt-3-1.jdf
```

JEOL

Figure S3. ^{1}H and ^{13}C NMR of the bidentate thioether complexes (**2a – 2g**) in d_6-DMSO.



Filename	= Recryst. 4MeOHFinal f	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= Recryst. 4MeOHFinal f	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 30-MAR-2023 14:11:08	X_Points	= 16384	machinephase	
Revision_Time	= 19-DEC-2023 15:53:21	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: Recryst. 4MeOHFinal from OR_p	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		



Filename	= LR 4MEO NS_carbon-	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= carbon.jxp	X_Domain	= 13C
Sample_Id	= LR 4MEO NS	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 14-MAY-2024 12:34:	X_Points	= 32768
Revision_Time	= 14-MAY-2024 16:02:	X_Prescans	= 4
		X_Resolution	= 0.96330739[Hz]
Comment	= single pulse decou	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= TRUE
Site	= NMU ECZ400 NMR	Scans	= 4218
Spectrometer	= DELTA2_NMR	Total_Scans	= 4218

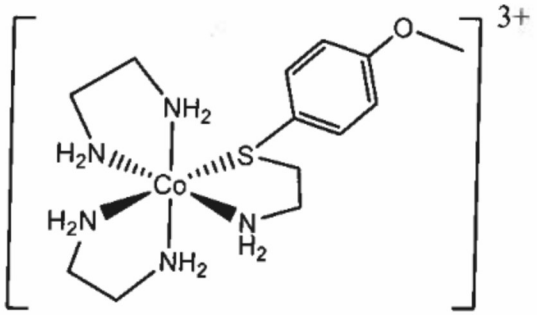
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

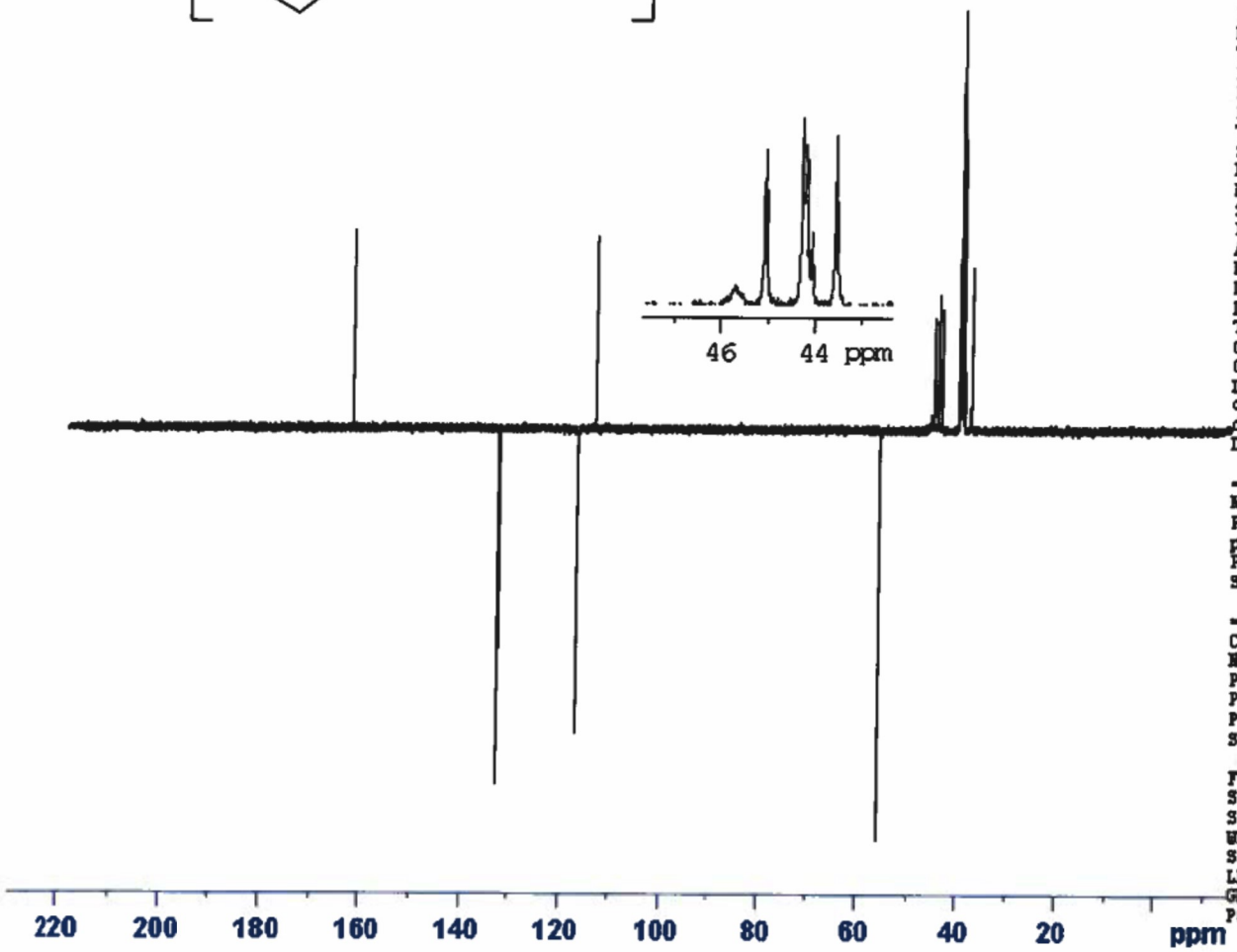
Derived from: LR 4MEO NS_carbon-2-1.jdf
```

JEOL

APT (Attached Proton Test) NMR Experiment.

In an APT experiment, carbon atoms attached to 0 or 2 hydrogen atoms appear in one direction while those attached to 1 or 3 hydrogen atoms appear in the other direction.





BRUKER

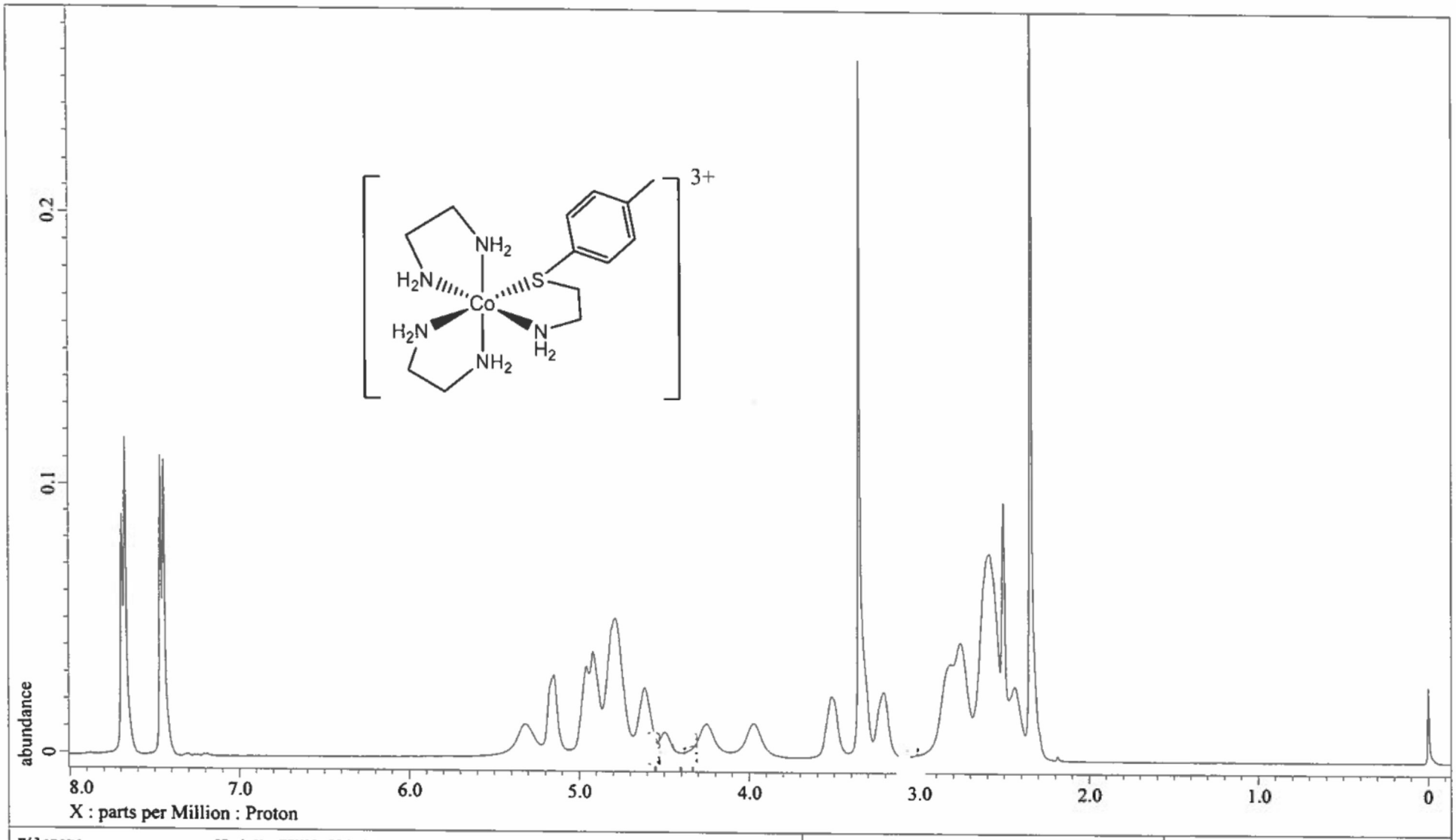
```
Current Data Parameters
NAME                 Apr25-2008
EXPNO                        11
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20080425
Time                      14.24
INSTRUM                   spect
PROBHD     5 mm BBO BB-1H
PULPROG                   jmod
TD                       65536
SOLVENT                   DMSO
NS                        2000
DS                           4
SWH                23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                       16384
DW                    20.850 usec
DE                     6.50 usec
TE                     300.0 K
CNST2                145.0000000
CNST11                 1.0000000
D1                 2.00000000 sec
d13                0.00000300 sec
d20                0.00689655 sec
DELTA              0.00000987 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                        7.75 usec
p2                       15.50 usec
PL1                      -4.00 dB
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    14.20 dB
SFO2               400.1316005 MHz

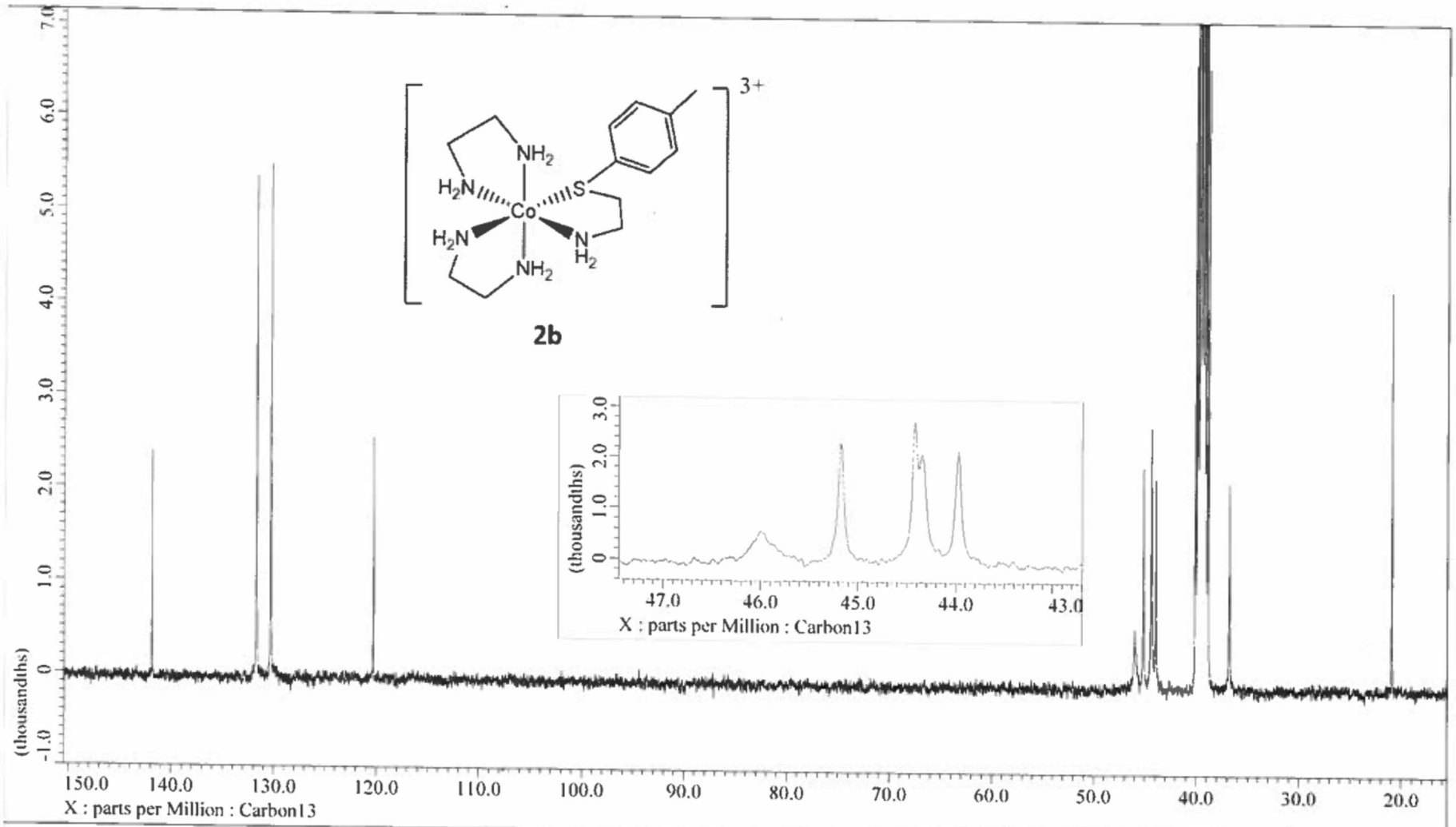
F2 - Processing parameters
SI                         32768
SF                 100.6128193 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```



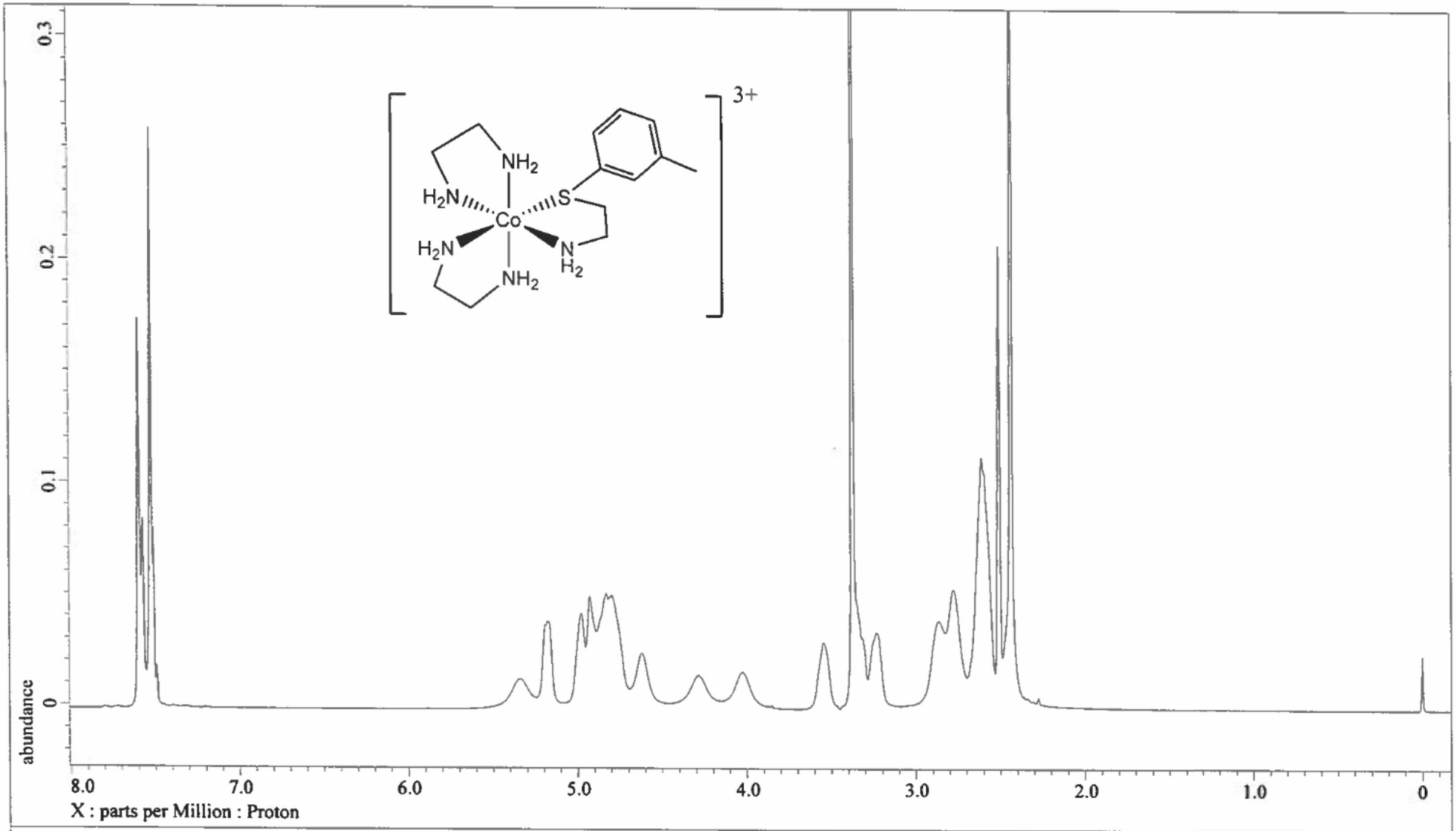
Filename	= OR 4-Me FINAL_PROTON_	X_Acq_Duration	= 2.18628096[s]
Author	= Lee_Roecker	X_Domain	= 1H
Experiment	= proton.jxp	X_Freq	= 399.78219838[MHz]
Sample_Id	= OR 4-Me FINAL	X_Offset	= 5[ppm]
Solvent	= DMSO-D6	X_Points	= 16384
Actual_Start_Time	= 14-JAN-2022 12:58:22	X_Prescans	= 1
Revision_Time	= 19-DEC-2023 15:59:18	X_Resolution	= 0.45739775[Hz]
		X_Sweep	= 7.4940048[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]
Dim_Size	= 13107	Irr_Domain	= Proton
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Tri_Domain	= Proton
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]
		Clipped	= FALSE
Field_Strength	= 9.389766[T] (400[MHz]	Scans	= 16

```
---- PROCESSING PARAMETERS ----
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
thresh : 2[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Both : 0[Hz]
norm_smallest_int : 1.0 : 0[Hz] : 25[Hz]
```

JEOL

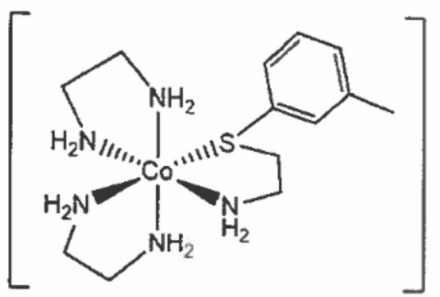


Filename	= LR 4ME old_carbon-	Field_Strength	= 9.389766[T] (400[M	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]	sexp(2.0[Hz], 0.0[s])	
Experiment	= carbon.jxp	X_Domain	= 13C	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR 4ME old	X_Freq	= 100.52530333[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 100[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 15-MAY-2024 08:26:	X_Points	= 32768	machinephase	
Revision_Time	= 15-MAY-2024 13:11:	X_Prescans	= 4	ppm	
		X_Resolution	= 0.96330739[Hz]		
Comment	= single pulse decou	X_Sweep	= 31.56565657[kHz]	Derived from: LR 4ME old_carbon-1-1.jdf	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]		
Dim_Size	= 26214	Irr_Domain	= Proton		
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Clipped	= TRUE		
Site	= NMU ECZ400 NMR	Scans	= 2401		
Spectrometer	= DELTA2_NMR	Total_Scans	= 2401		



Filename	= LR 3 ME BIDEN p42_pro	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR 3 ME BIDEN p42	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 25-JAN-2024 14:36:42	X_Points	= 16384	machinephase	
Revision_Time	= 25-JAN-2024 14:35:16	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: LR 3 ME BIDEN p42_proton-1-1.	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		

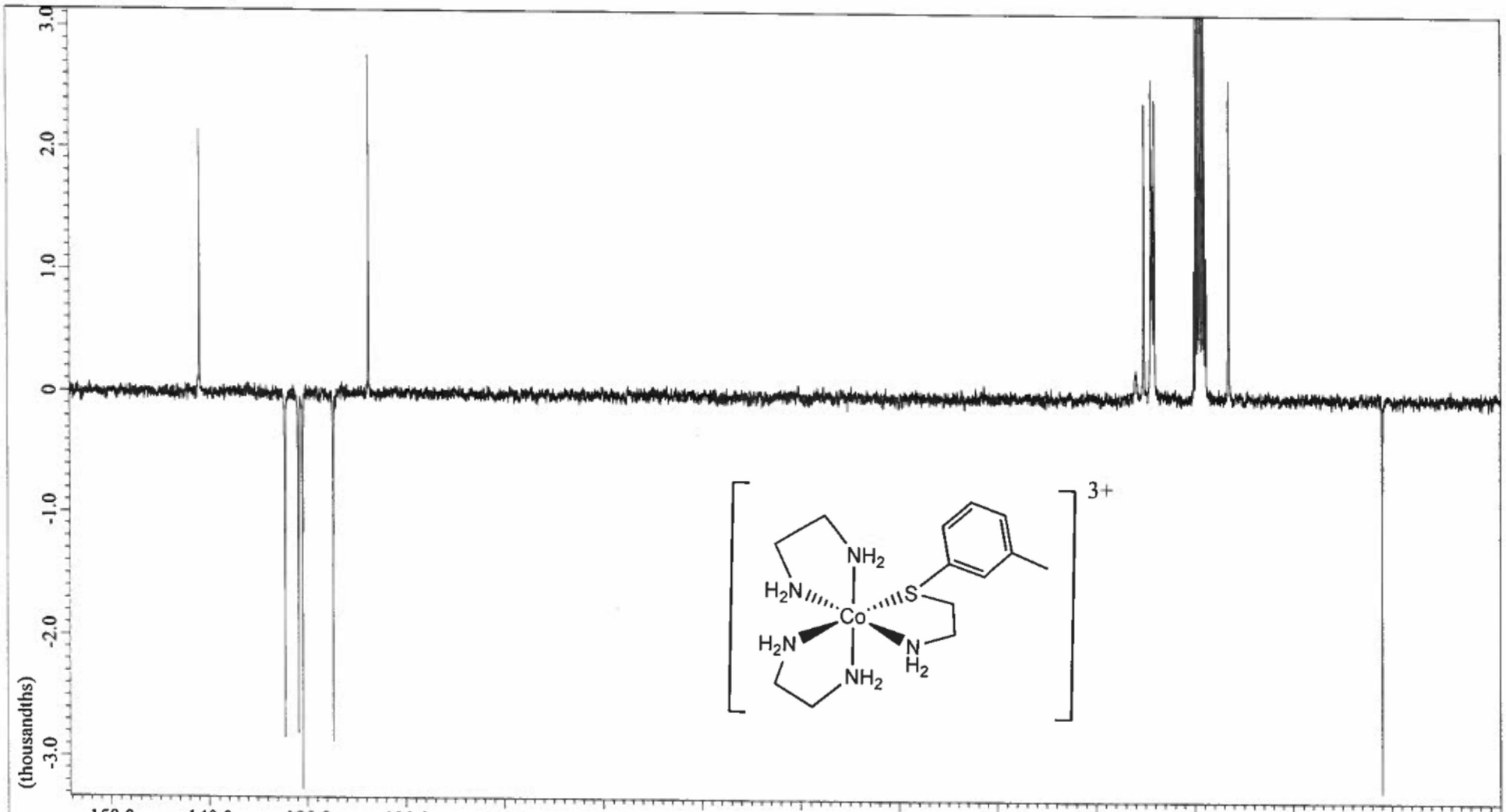
JEOL



2c

Filename	= LR 3 ME BIDEN p42_	Field_Strength	= 9.389766[T] (400[M	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]	sexp(2.0[Hz], 0.0[s])
Experiment	= carbon.jxp	X_Domain	= 13C	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= LR 3 ME BIDEN p42	X_Freq	= 100.52530333[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 100[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 25-JAN-2024 14:43:	X_Points	= 32768	machinephase
Revision_Time	= 14-MAY-2024 16:30:	X_Prescans	= 4	ppm
Comment	= single pulse decou	X_Resolution	= 0.96330739[Hz]	Derived from: LR 3 ME BIDEN p42_carbon-1-1.
Data_Format	= 1D COMPLEX	X_Sweep	= 31.56565657[kHz]	
Dim_Size	= 26214	X_Sweep_Clipped	= 25.25252525[kHz]	
Dim_Title	= Carbon13	Irr_Domain	= Proton	
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]	
Dimensions	= X	Irr_Offset	= 5[ppm]	
Site	= NMU ECZ400 NMR	Clipped	= TRUE	
Spectrometer	= DELTA2_NMR	Scans	= 4096	
		Total_Scans	= 4096	

JEOL

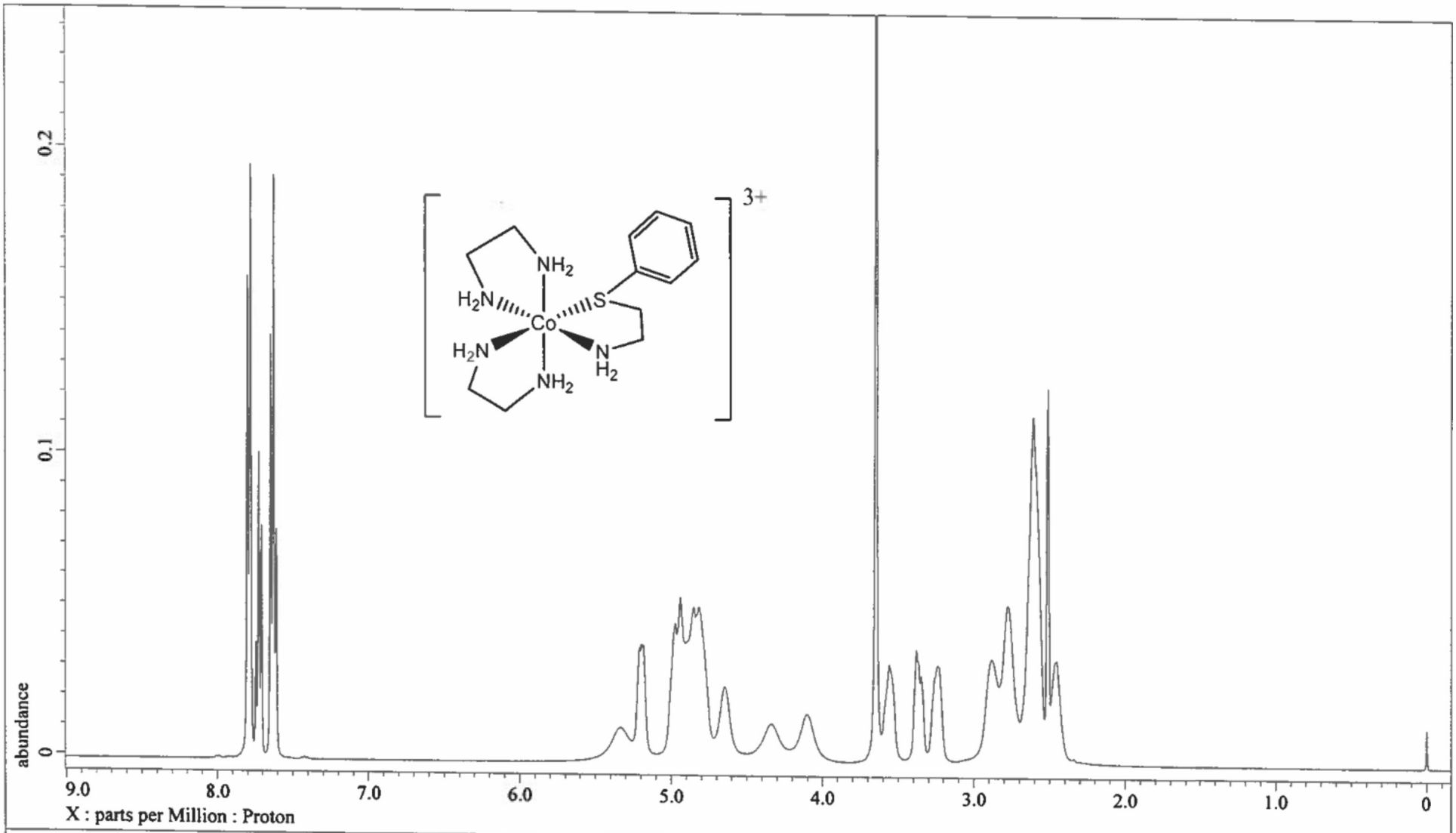


Filename	= LR 3 Me BIDEN APT_	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= apt.jxp	X_Domain	= 13C
Sample_Id	= LR 3 Me BIDEN APT	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 26-JAN-2024 12:42:	X_Points	= 32768
Revision_Time	= 26-JAN-2024 14:31:	X_Prescans	= 4
		X_Resolution	= 0.96330739[Hz]
Comment	= APT Experiment	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= TRUE
Site	= NMU EC2400 NMR	Scans	= 3366
Spectrometer	= DELTA2_NMR	Total_Scans	= 3366

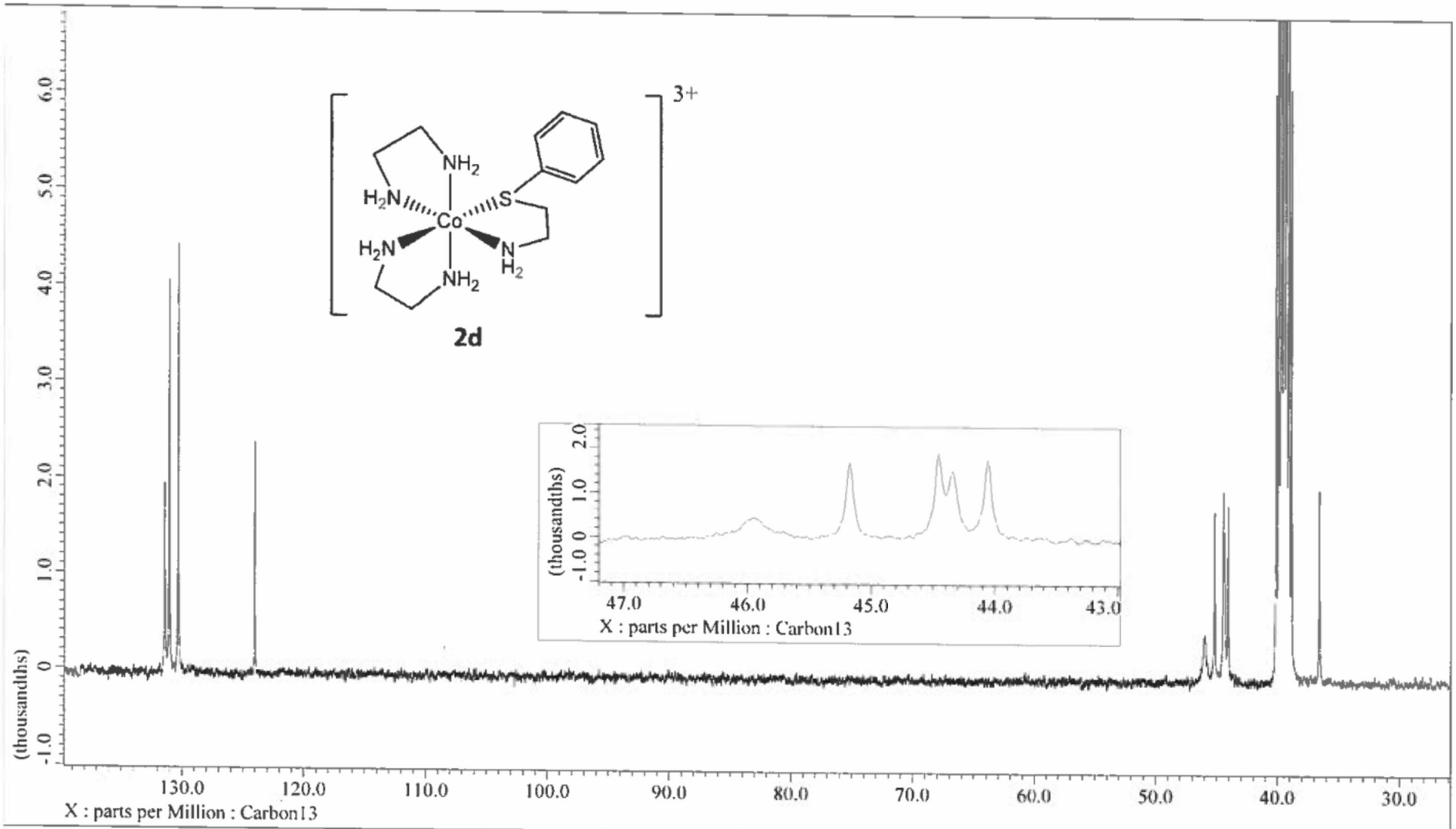
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: LR 3 Me BIDEN APT_apt-1-1.jdf
```

JEOL



Filename	= LR phenyl BIDEN REXTA	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR phenyl BIDEN REXTA	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 3-NOV-2023 07:44:44	X_Points	= 16384	machinephase	
Revision_Time	= 19-DEC-2023 15:25:13	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: LR phenyl BIDEN REXTAL_proton	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU EC2400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		

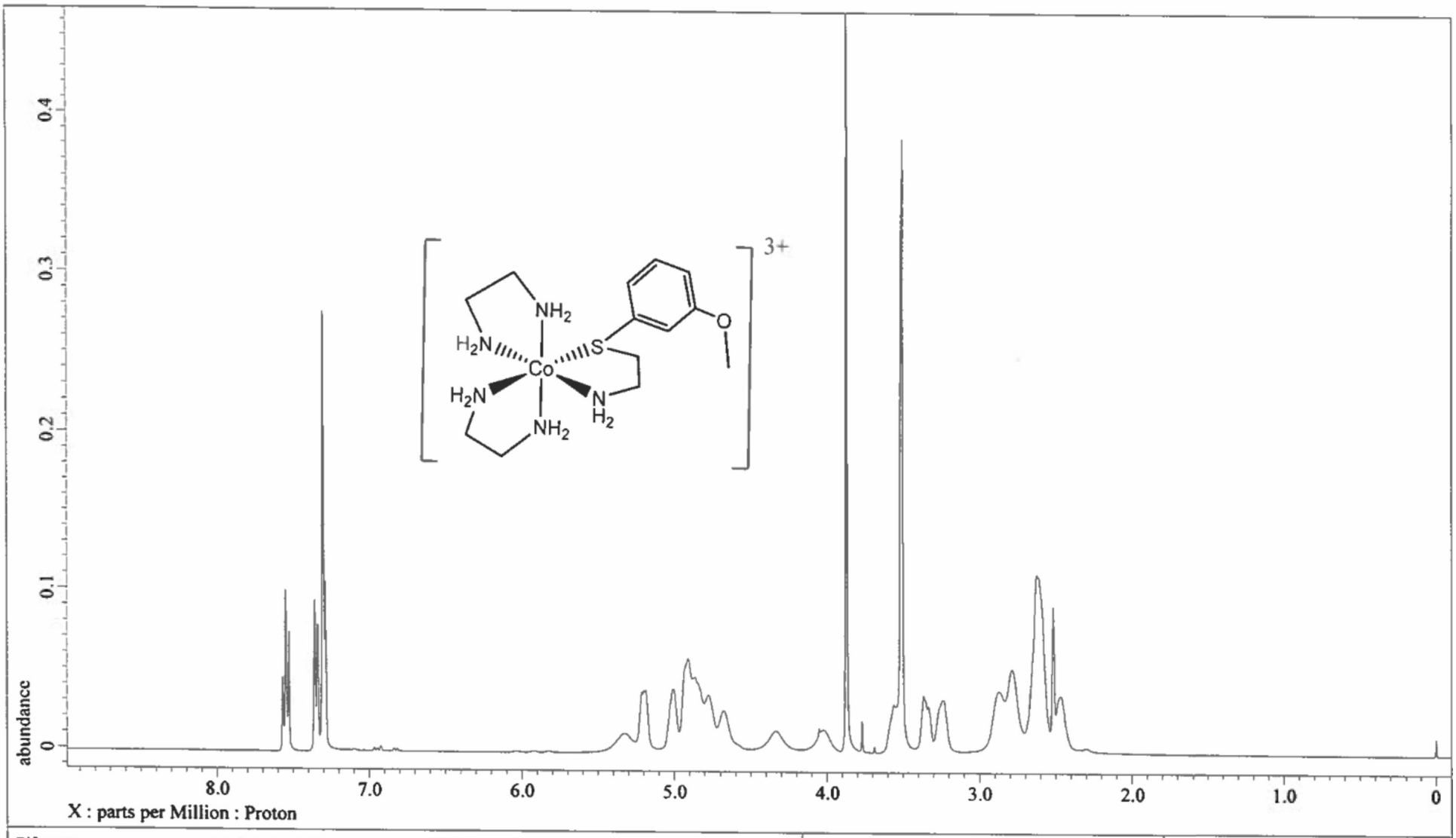


Filename	= LR phenyl BIDEN RE	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= carbon.jxp	X_Domain	= 13C
Sample_Id	= LR phenyl BIDEN RE	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 3-NOV-2023 07:48:	X_Points	= 32768
Revision_Time	= 15-MAY-2024 07:49:	X_Prescans	= 4
		X_Resolution	= 0.96330739[Hz]
Comment	= single pulse decou	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= TRUE
Site	= NMU ECZ400 NMR	Scans	= 3072
Spectrometer	= DELTA2_NMR	Total_Scans	= 3072

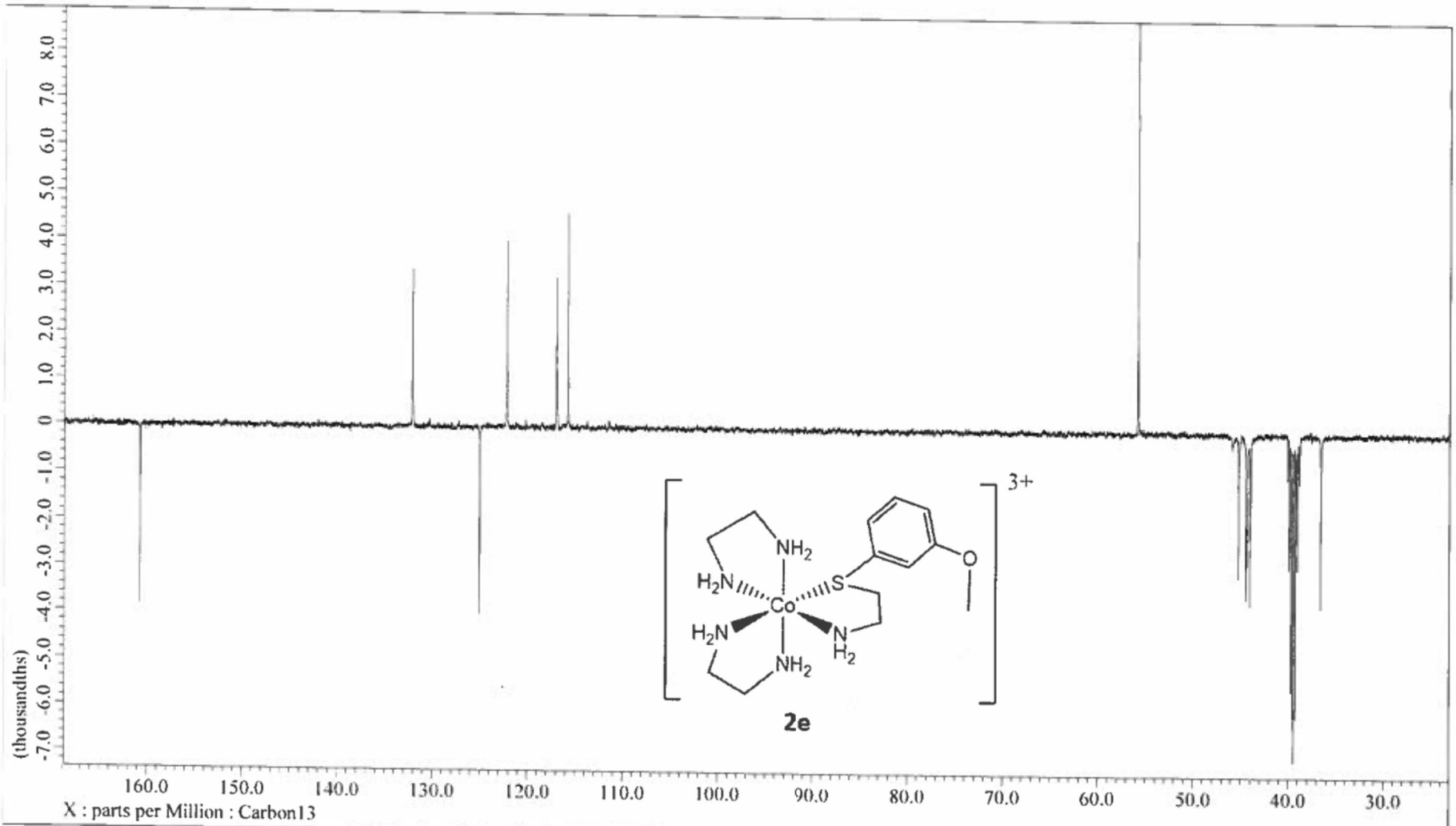
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: LR phenyl BIDEN REXTAL_carbon
```

JEOL



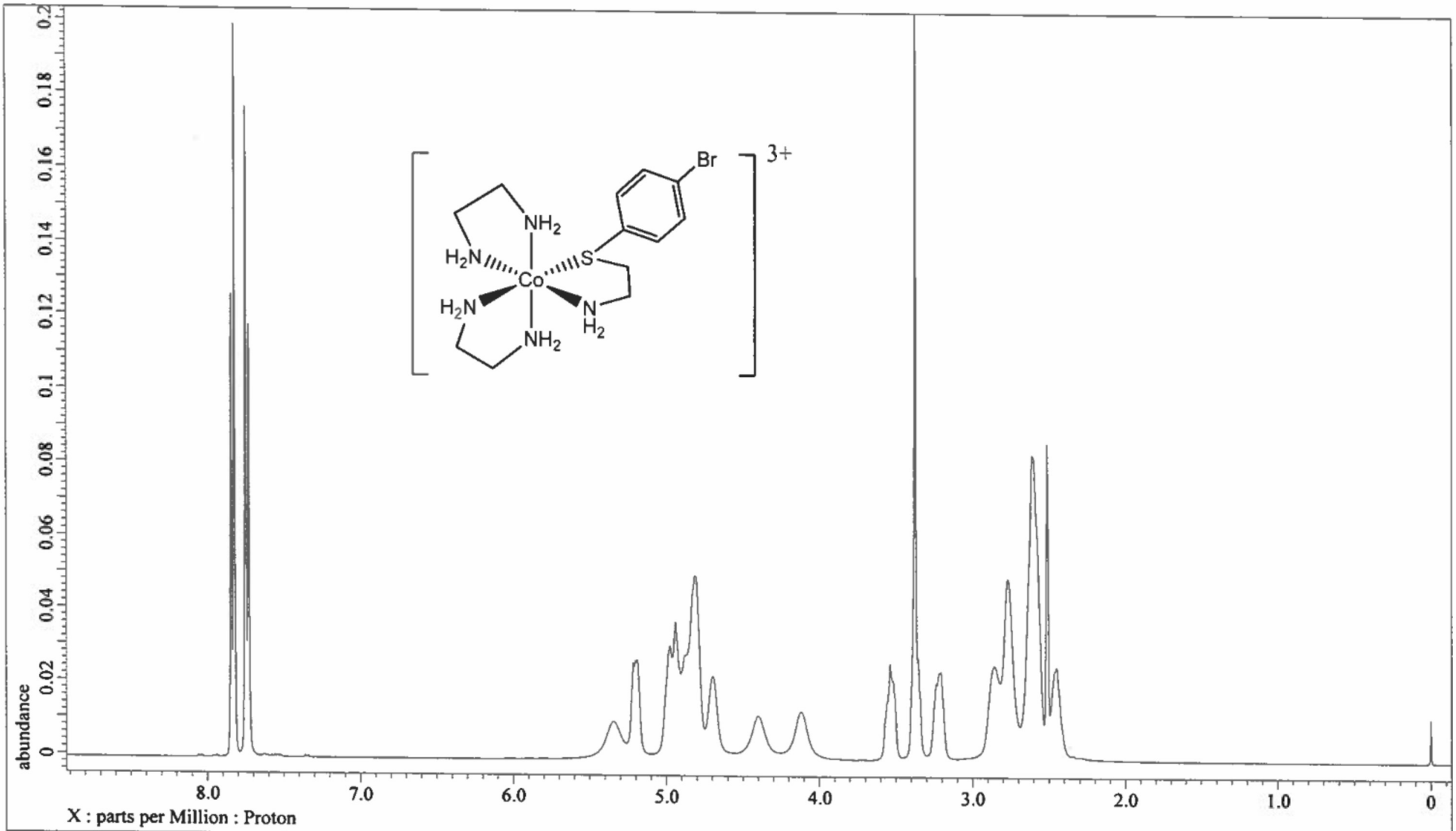
Filename	= LR 3 MeO BIDEN_proton	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])
Sample_Id	= LR 3 MeO BIDEN	X_Freq	= 399.78219838[MHz]	zerofill(1)
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)
Actual_Start_Time	= 8-NOV-2023 16:06:55	X_Points	= 16384	machinephase
Revision_Time	= 19-DEC-2023 15:30:36	X_Prescans	= 1	ppm
		X_Resolution	= 0.45739775[Hz]	
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: LR 3 MeO BIDEN_proton-2-1.jdf
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]	
Dim_Size	= 13107	Irr_Domain	= Proton	
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]	
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]	
Dimensions	= X	Tri_Domain	= Proton	
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]	
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]	
		Clipped	= FALSE	



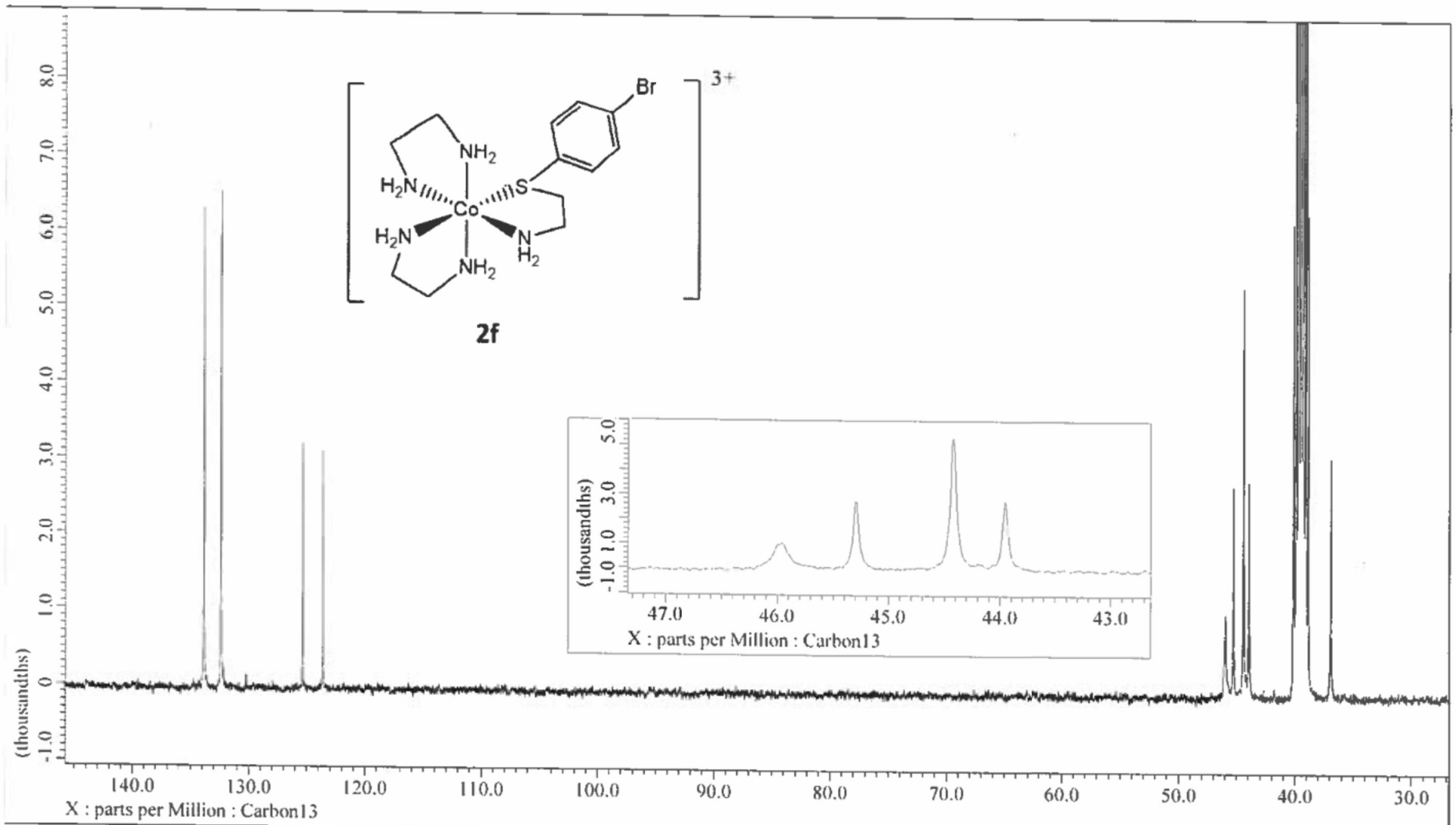
2e

Filename	= LR 3 MeO BIDEN_apt	Field_Strength	= 9.389766[T] (400[M	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]	sexp(2.0[Hz], 0.0[s])	
Experiment	= apt.jxp	X_Domain	= 13C	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR 3 MeO BIDEN	X_Freq	= 100.52530333[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 100[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 8-NOV-2023 16:51:	X_Points	= 32768	machinephase	
Revision_Time	= 14-MAY-2024 16:32:	X_Prescans	= 4	ppm	
		X_Resolution	= 0.96330739[Hz]	reference(39.95458[ppm], 39.51[ppm])	
Comment	= APT Experiment	X_Sweep	= 31.56565657[kHz]	phase(0, 0, 50[%])	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]		
Dim_Size	= 26214	Irr_Domain	= Proton		
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Clipped	= TRUE		
Site	= NMU ECZ400 NMR	Scans	= 2000		
Spectrometer	= DELTA2_NMR	Total_Scans	= 2000		

JEOL



Filename	= Lr 4 Br BIDEN REXTAL_	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= Lr 4 Br BIDEN REXTAL	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 13-OCT-2023 16:47:57	X_Points	= 16384	machinephase	
Revision_Time	= 19-DEC-2023 15:32:37	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: Lr 4 Br BIDEN REXTAL_proton-2	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU EC2400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		

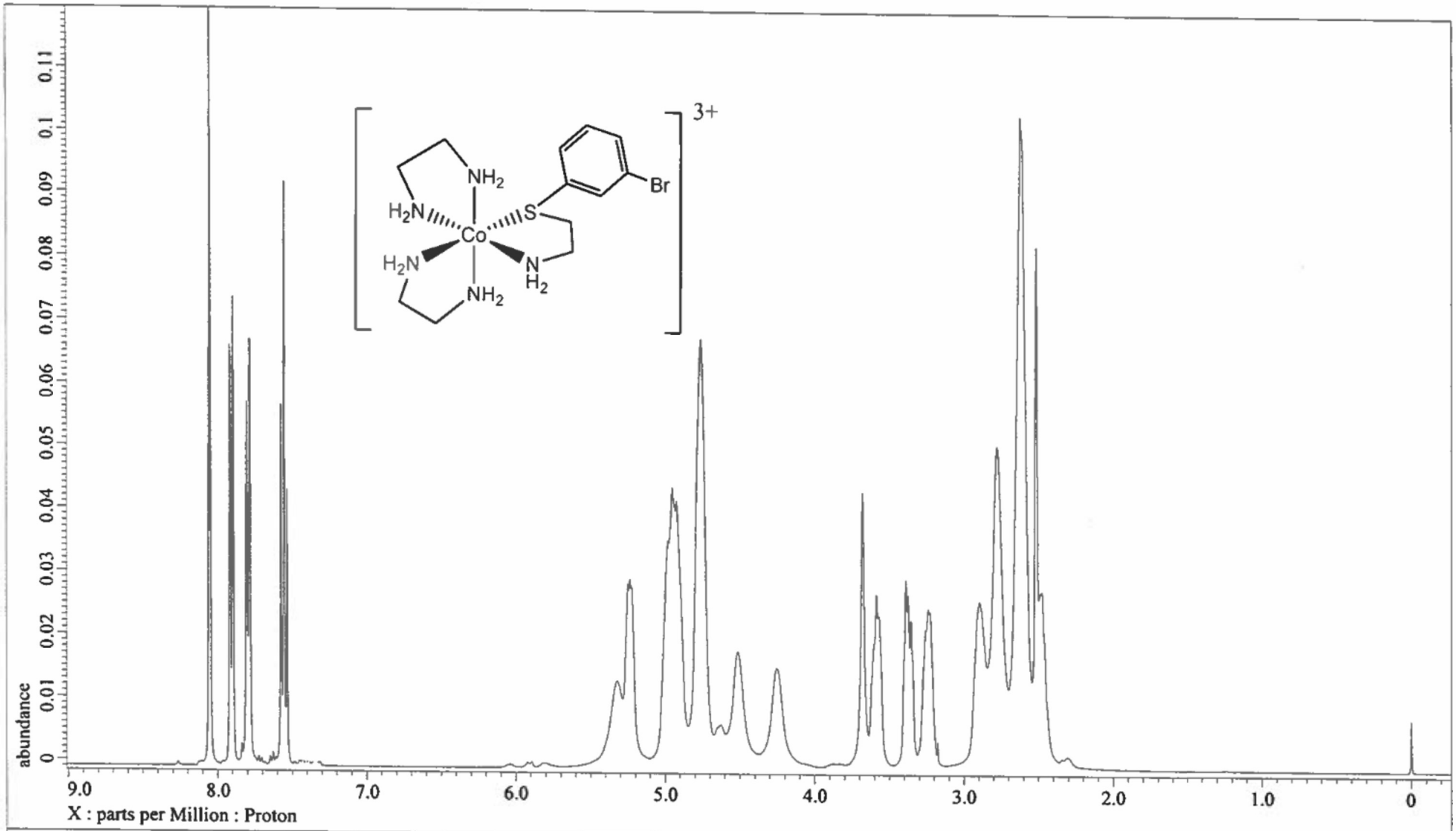


Filename	= LR 4-Br BIDENTATE	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= carbon.jxp	X_Domain	= 13C
Sample_Id	= LR 4-Br BIDENTATE	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 21-SEP-2023 07:28:	X_Points	= 32768
Revision_Time	= 14-MAY-2024 16:21:	X_Prescans	= 4
		X_Resolution.	= 0.96330739[Hz]
Comment	= single pulse decou	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= FALSE
Site	= NMU EC2400 NMR	Scans	= 3072
Spectrometer	= DELTA2_NMR	Total_Scans	= 3072

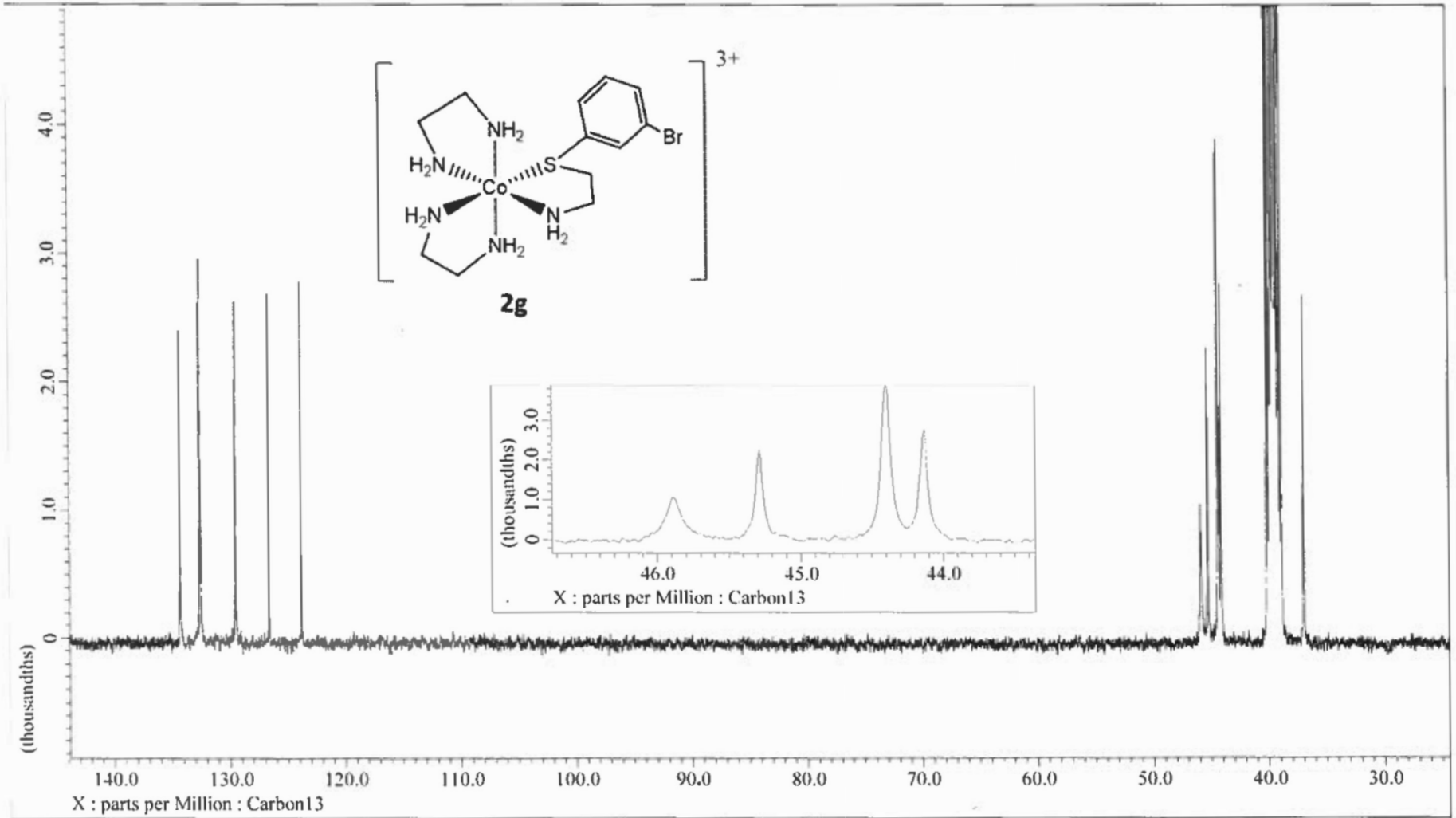
```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: LR 4-Br BIDENTATE REXTL_carbo
```

JEOL



Filename	= LR 3Br BIDEN p34_prot	Field_Strength	= 9.389766[T] (400[MHz]	---- PROCESSING PARAMETERS ----	
Author	= Lee_Roecker	X_Acq_Duration	= 2.18628096[s]	sexp(0.2[Hz], 0.0[s])	
Experiment	= proton.jxp	X_Domain	= 1H	trapezoid(0[%], 0[%], 80[%], 100[%])	
Sample_Id	= LR 3Br BIDEN p34	X_Freq	= 399.78219838[MHz]	zerofill(1)	
Solvent	= DMSO-D6	X_Offset	= 5[ppm]	fft(1, TRUE, TRUE)	
Actual_Start_Time	= 10-OCT-2023 07:28:08	X_Points	= 16384	machinephase	
Revision_Time	= 19-DEC-2023 15:46:04	X_Prescans	= 1	ppm	
		X_Resolution	= 0.45739775[Hz]		
Comment	= single_pulse	X_Sweep	= 7.4940048[kHz]	Derived from: LR 3Br BIDEN p34_proton-2-1.j	
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 5.99520384[kHz]		
Dim_Size	= 13107	Irr_Domain	= Proton		
Dim_Title	= Proton	Irr_Freq	= 399.78219838[MHz]		
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]		
Dimensions	= X	Tri_Domain	= Proton		
Site	= NMU ECZ400 NMR	Tri_Freq	= 399.78219838[MHz]		
Spectrometer	= DELTA2_NMR	Tri_Offset	= 5[ppm]		
		Clipped	= FALSE		



Filename	= LR 3Br BIDEN p34_c	Field_Strength	= 9.389766[T] (400[M
Author	= Lee_Roecker	X_Acq_Duration	= 1.03809024[s]
Experiment	= carbon.jxp	X_Domain	= 13C
Sample_Id	= LR 3Br BIDEN p34	X_Freq	= 100.52530333[MHz]
Solvent	= DMSO-D6	X_Offset	= 100[ppm]
Actual_Start_Time	= 10-OCT-2023 07:31:	X_Points	= 32768
Revision_Time	= 15-MAY-2024 07:53:	X_Prescans	= 4
		X_Resolution	= 0.96330739[Hz]
Comment	= single pulse decou	X_Sweep	= 31.56565657[kHz]
Data_Format	= 1D COMPLEX	X_Sweep_Clipped	= 25.25252525[kHz]
Dim_Size	= 26214	Irr_Domain	= Proton
Dim_Title	= Carbon13	Irr_Freq	= 399.78219838[MHz]
Dim_Units	= [ppm]	Irr_Offset	= 5[ppm]
Dimensions	= X	Clipped	= FALSE
Site	= NMU EC2400 NMR	Scans	= 3072
Spectrometer	= DELTA2_NMR	Total_Scans	= 3072

```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: LR 3Br BIDEN p34_carbon-1-1.j
```

JEOL

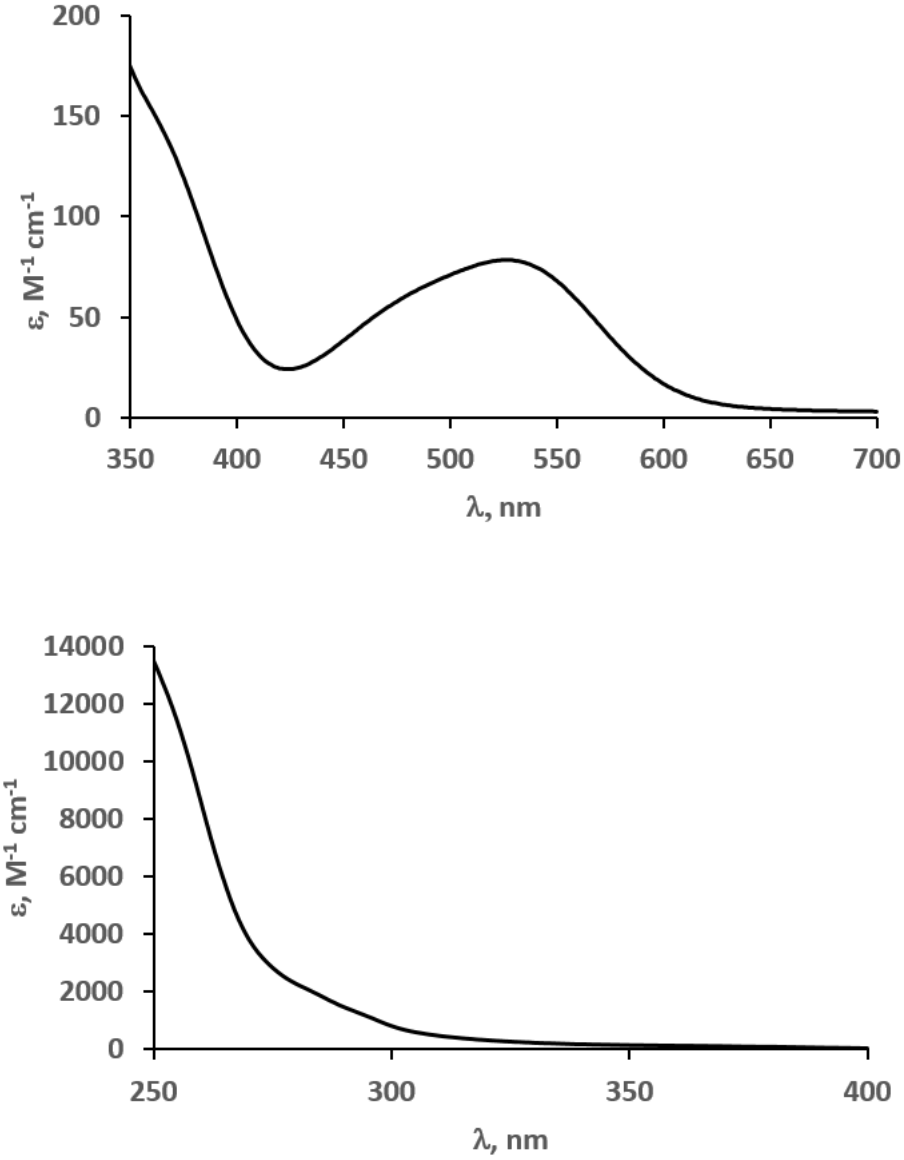
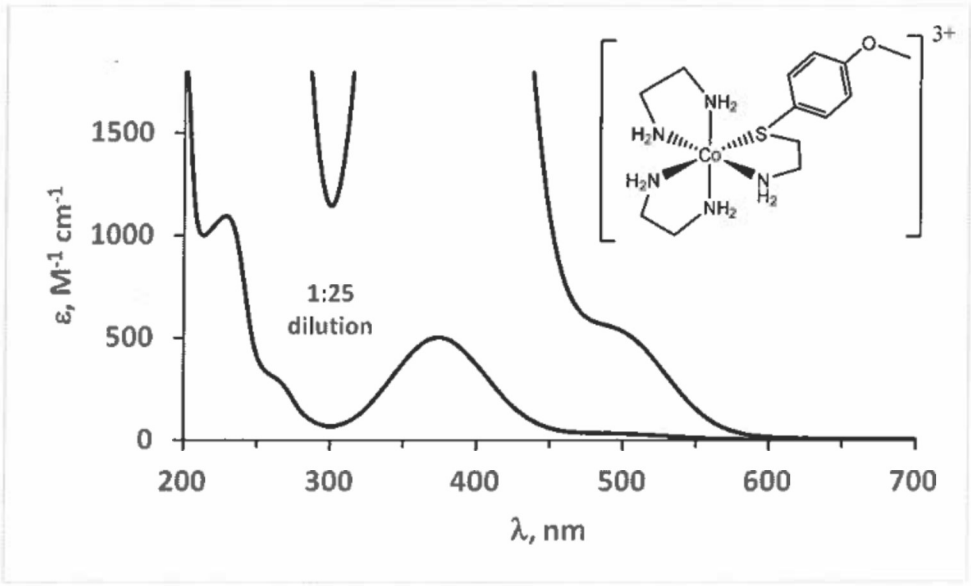
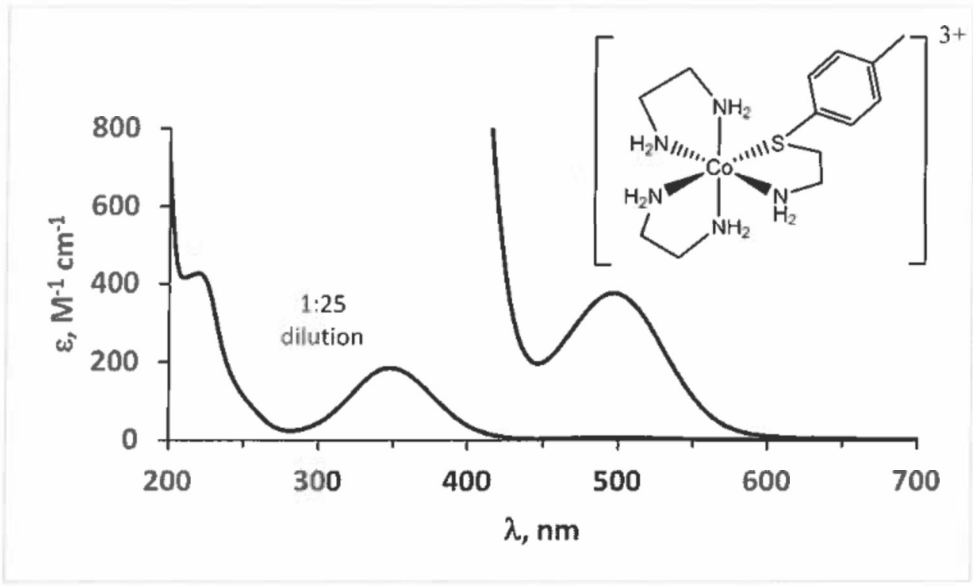


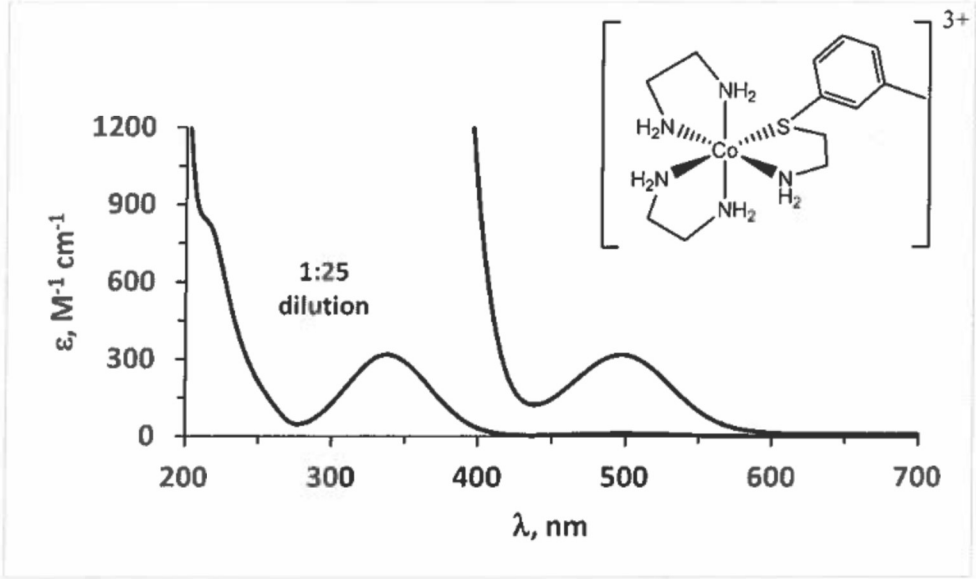
Figure S4. UV (lower) and visible (upper) spectra of **1g** in 0.01 M HCl. The lower spectrum was recorded after a 1:25 dilution.



2a

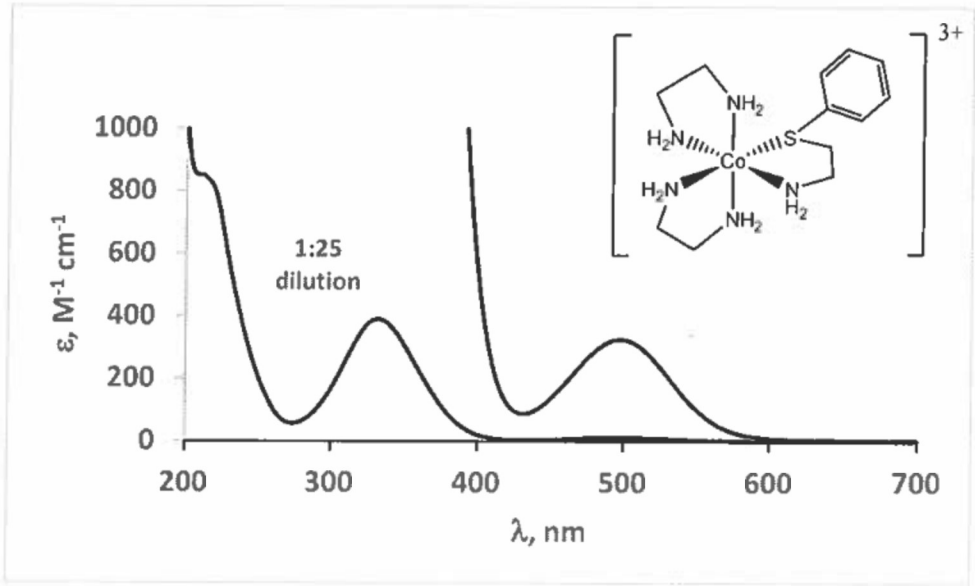


2b

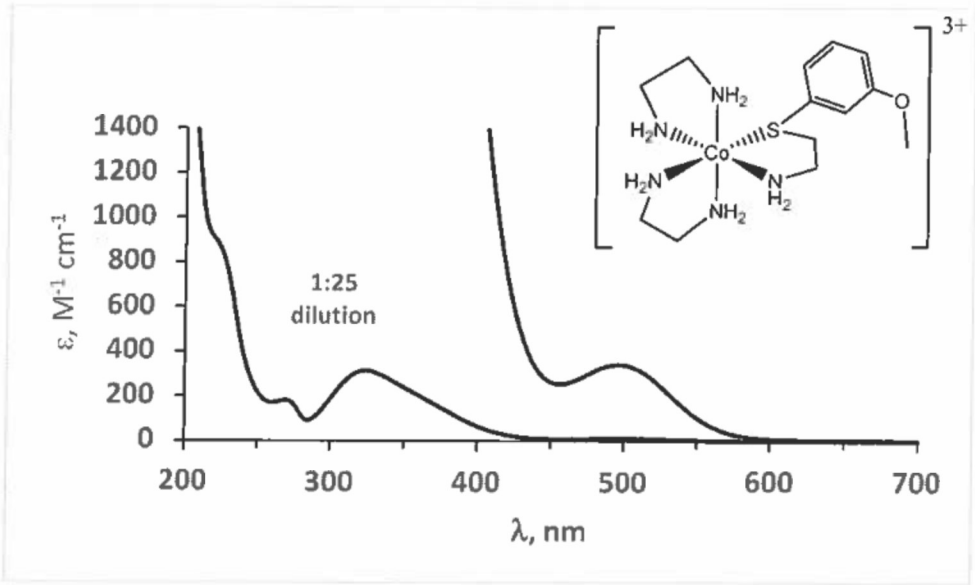


2c

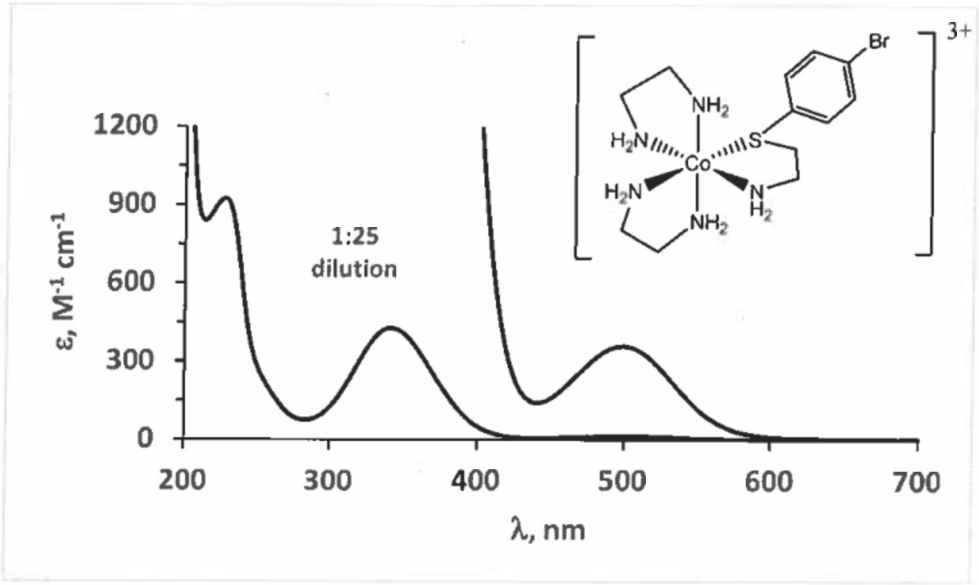
Figure S5. Visible-UV spectra of the κ^2N,S complexes (**2a - 2g**) in 0.01 M $HClO_4$.



2d

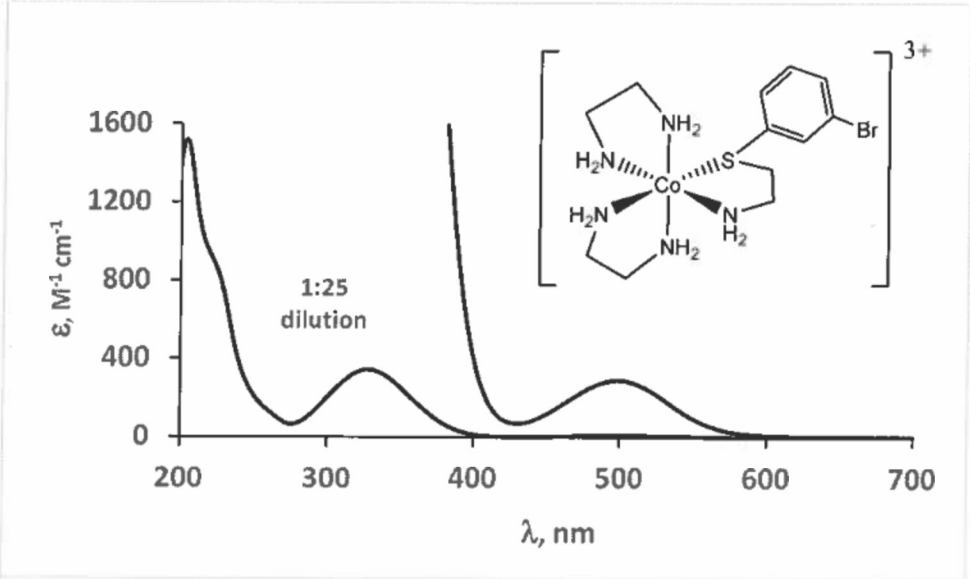


2e



2f

Figure S5. (*Cont.*)



2d

Figure S5. (*Cont*.)

(*a*)

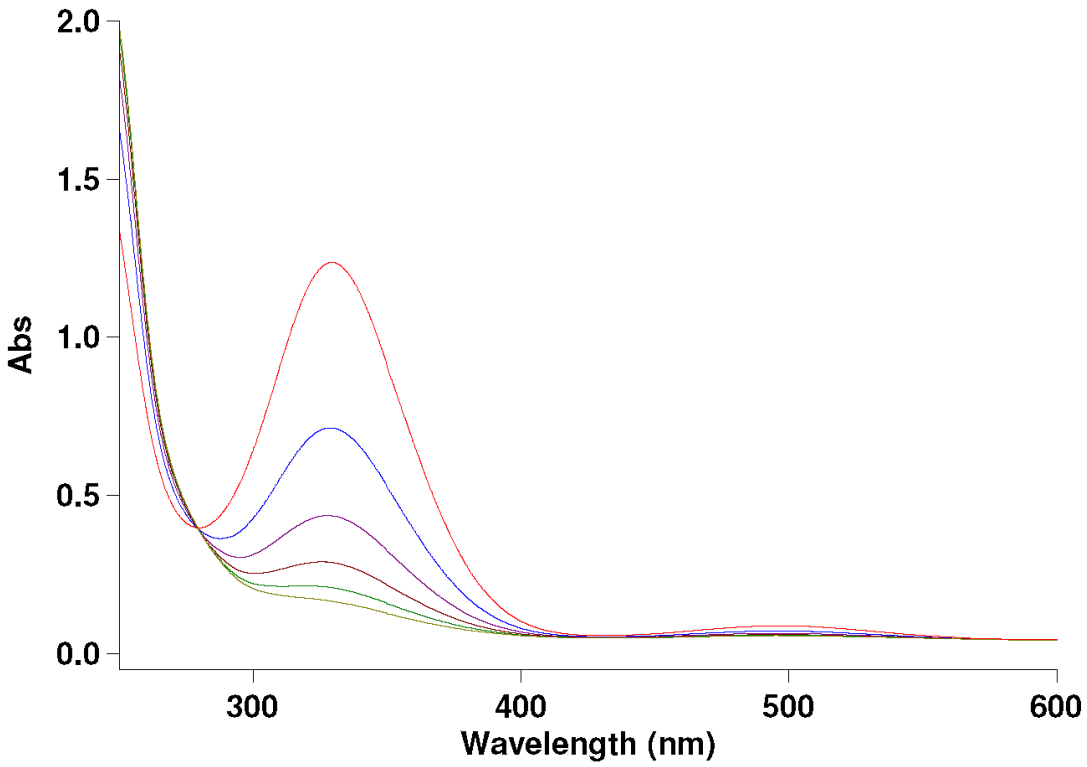
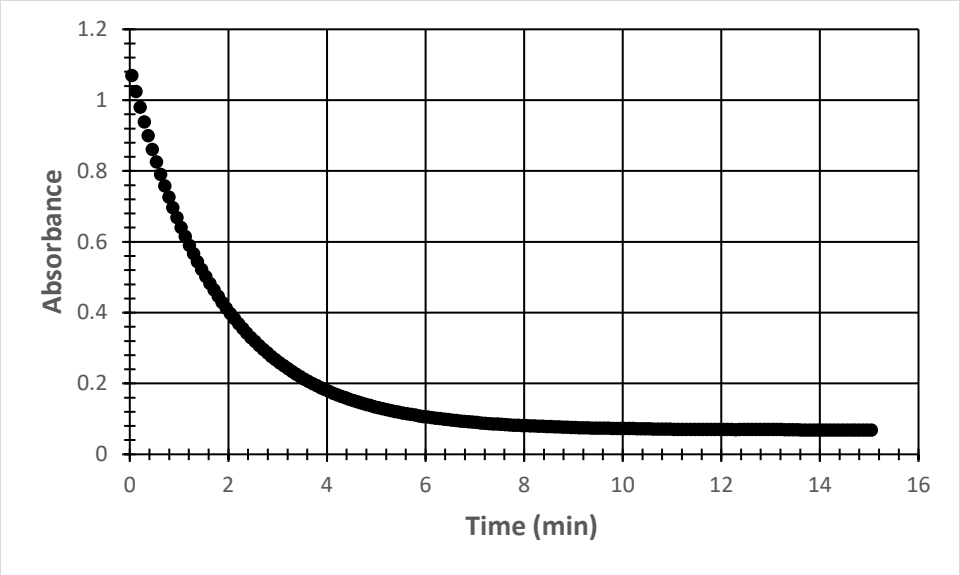


Figure S6. Representative kinetic plots. These data were collected on a CARY 100 Bio UV-visible spectrophotometer. (*a*) Repetitive scans for the base hydrolysis of **2d** at pH ~10.7. This is a lower pH than was used in the study in order to make a good figure given the instrument that was available. The isosbestic behavior is consistent with the formation of a single product. (*b*) Typical decay curve monitored at 332 nm for the base hydrolysis of 2d. In this example, 200 data points were collected. (*c*) Plot of ln|At – Ainf| *v*. time for the data collected in Figure S1*b*. Consistent with first-order behavior, this plot is linear for at least 5 half-lives.

(*b*)



(*c*)

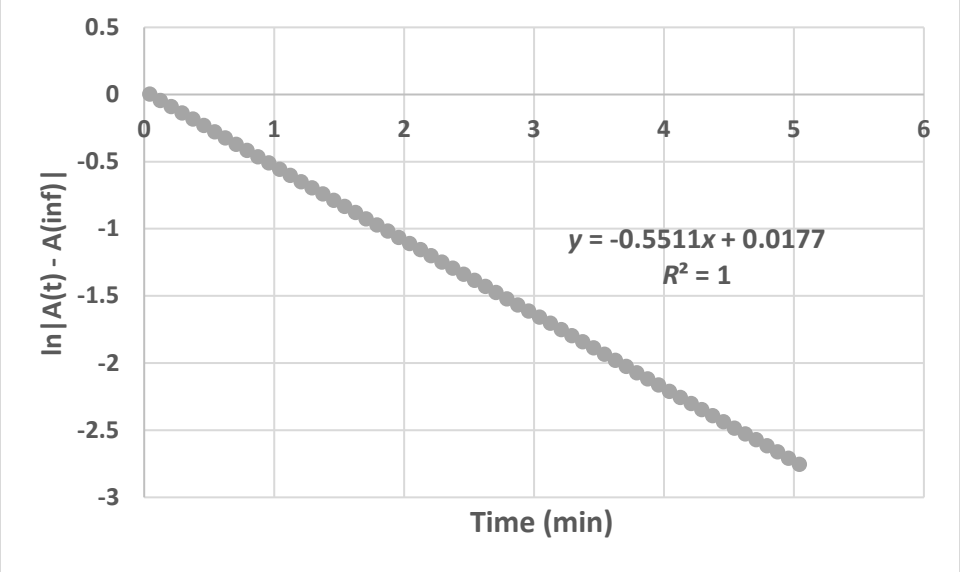


Figure Sb. (*Cont*.)