

Synthesis, Characterization, Mechanism of Decomposition, and Antiproliferative Activity of a Class of PEGylated Benzopolysulfanes Structurally Similar to the Natural Product Varacin

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- S49 Figure 45: (A) LCMS extracted ion chromatograms of **6A-F**. (B) LCMS extracted ion chromatograms (overlaid) of **6A-F**.

S50 Figure 46: (A) Extracted ion chromatogram of norbornenetrithiolane **17** formed in the reaction of **6A-F** and norbornene in the presence of ethanethiol, Rt 16.75 min. (B) MS spectrum of norbornenetrithiolane **17**, Rt 16.75 min.

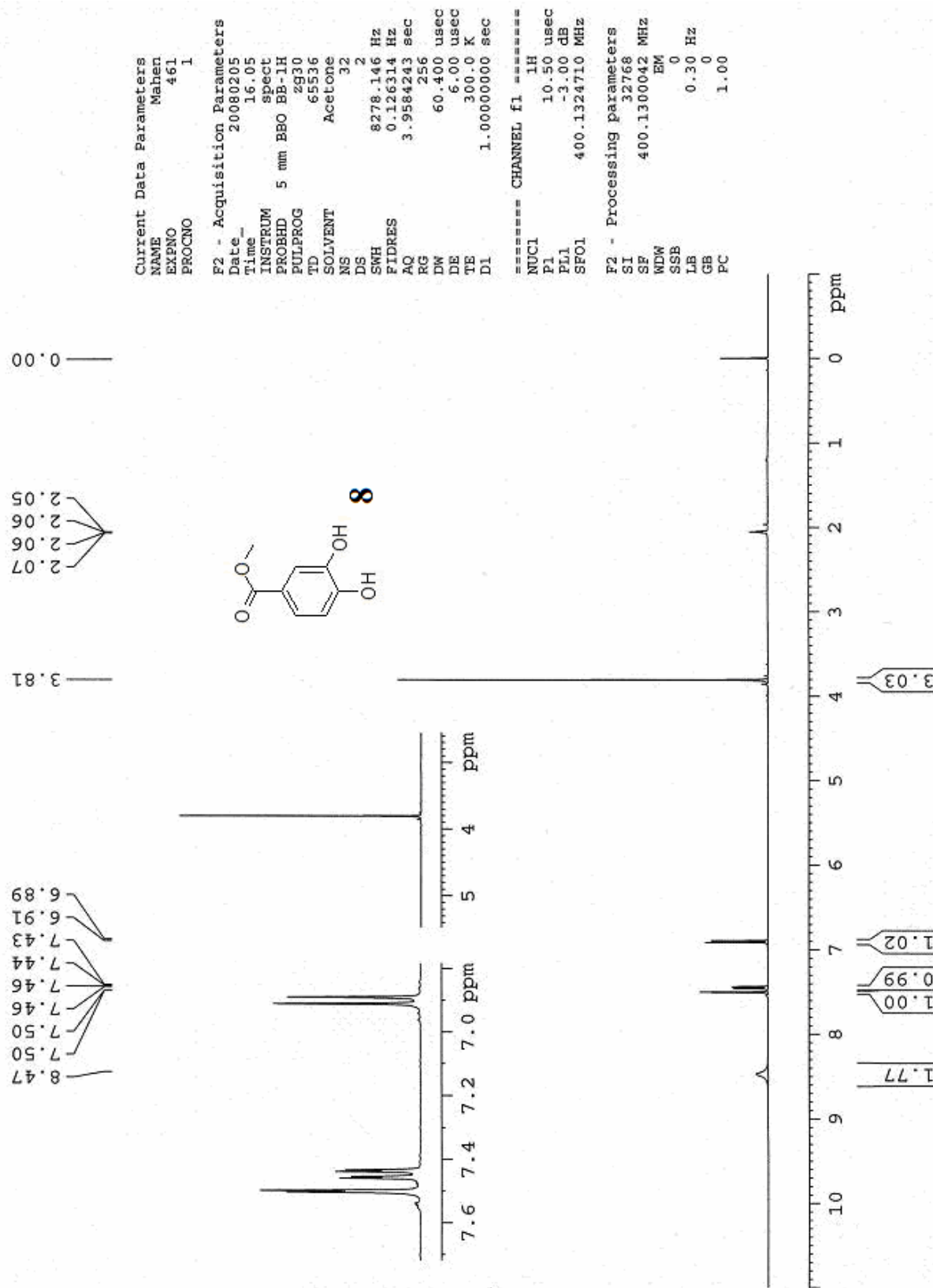


Figure 1. ^1H NMR of 3,4-dihydroxybenzoic acid methyl ester- $\text{acetone-}d_6$.

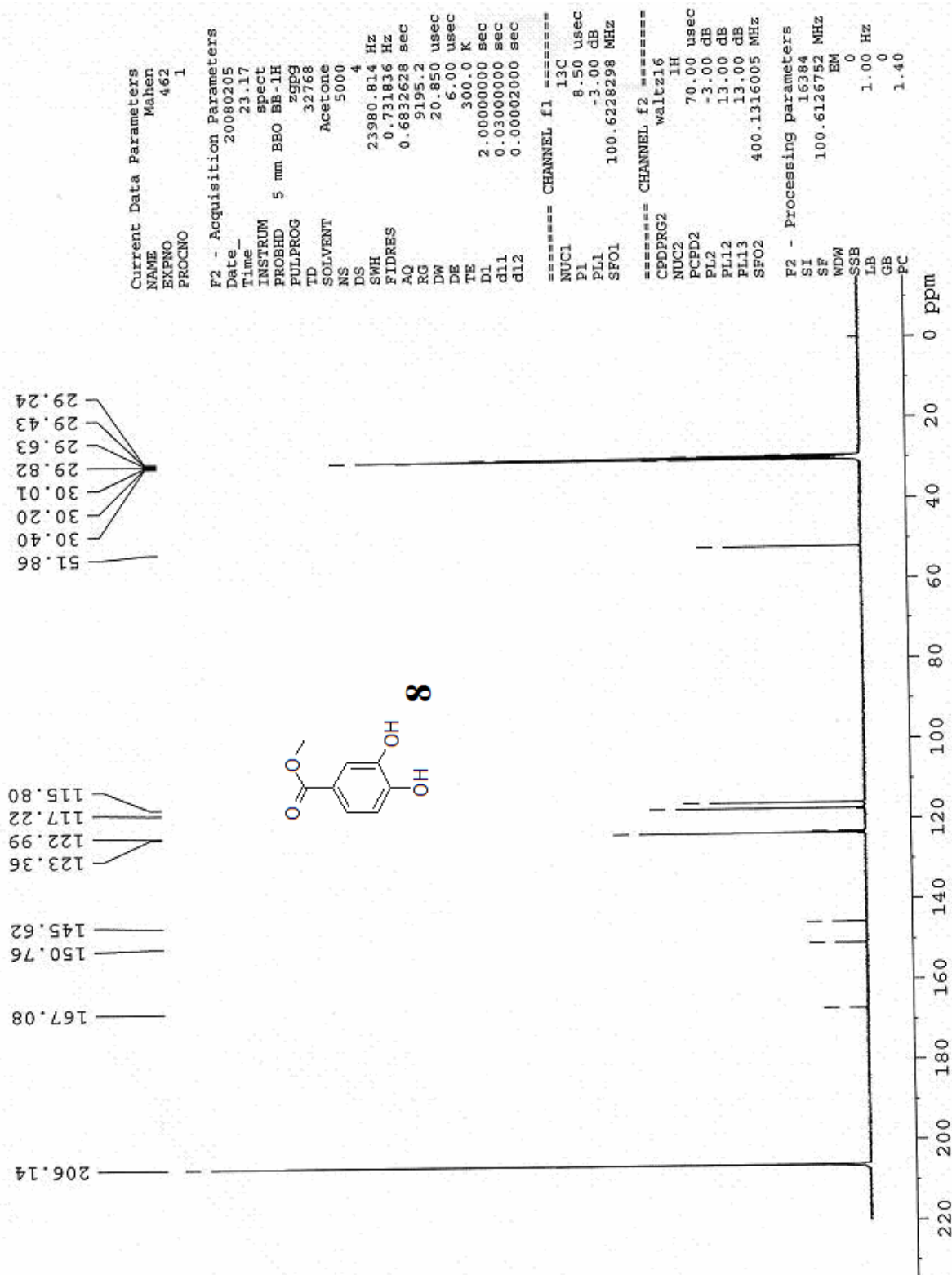
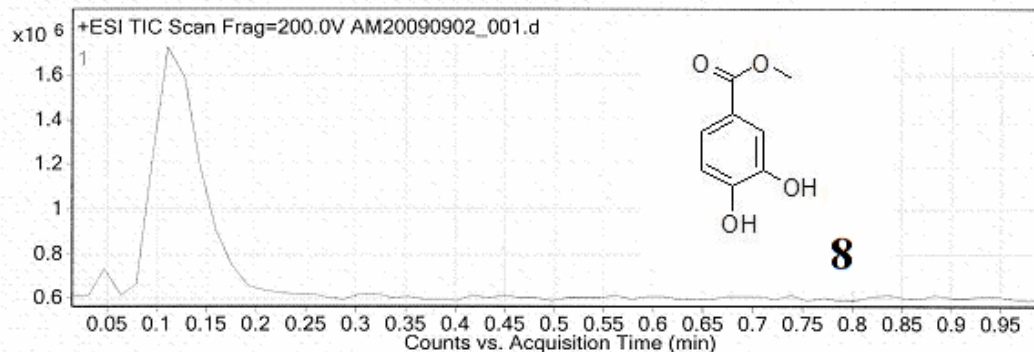


Figure 2. ^{13}C NMR of 3,4-dihydroxybenzoic acid methyl ester– acetone- d_6 .

Qualitative Compound Report

Data File	AM20090902_001.d	Sample Name	Sample 1
Sample Type	Sample	Position	P1-F1
Instrument Name	Instrument 1	User Name	Mahen
Acq Method		IRM Calibration Status	Success
DA Method	MahenMethod1.m	Comment	Methyl 3,4 dihydroxy benzo carboxylate

Fragmentor Voltage 200 Collision Energy 0 Ionization Mode Esi



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C8 H8 O4	0.112	168.0423	84872	C8 H8 O4	168.0423	0.31

Compound Label	RT	Algorithm	Mass
Cpd 1: C8 H8 O4	0.112	Find By Formula	168.0423

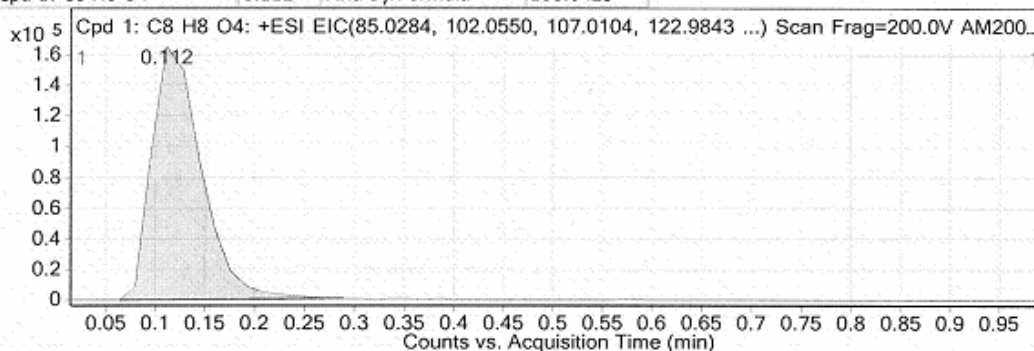
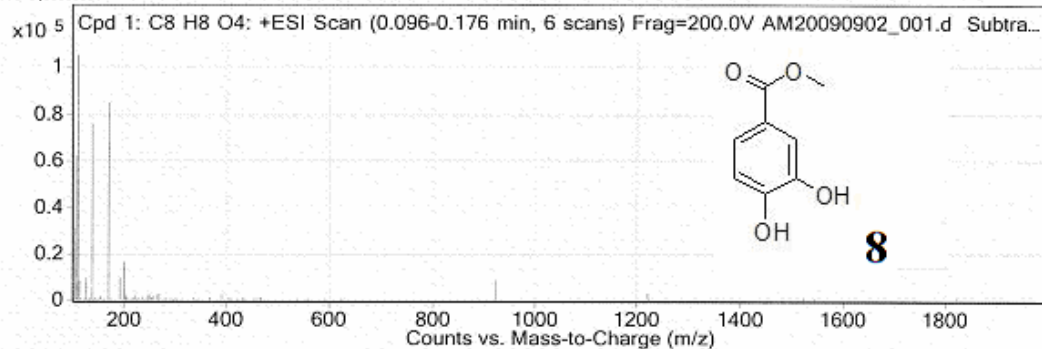


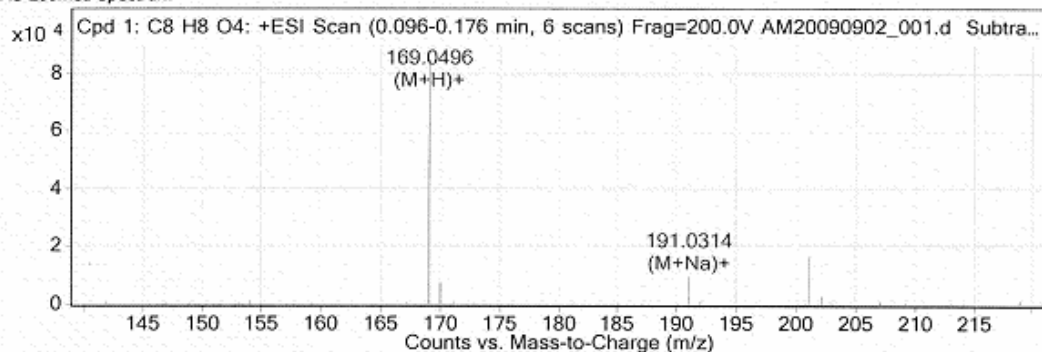
Figure 3. HRMS of 3,4-dihydroxybenzoic acid methyl ester.

Qualitative Compound Report

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
105.0449				31352		
106.0478				2441		
107.0493				61806		
108.0513				5545		
109.0296				7255		
110.0363				105208		
111.0411				8409		
169.0496	169.0495	0.31	1	84872	C ₈ H ₉ O ₄	(M+H) ⁺
170.053	170.0529	0.17	1	7472	C ₈ H ₉ O ₄	(M+H) ⁺
191.0314	191.0315	-0.47	1	9551	C ₈ H ₈ Na O ₄	(M+Na) ⁺

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Figure 4. HRMS of 3,4-dihydroxybenzoic acid methyl ester.

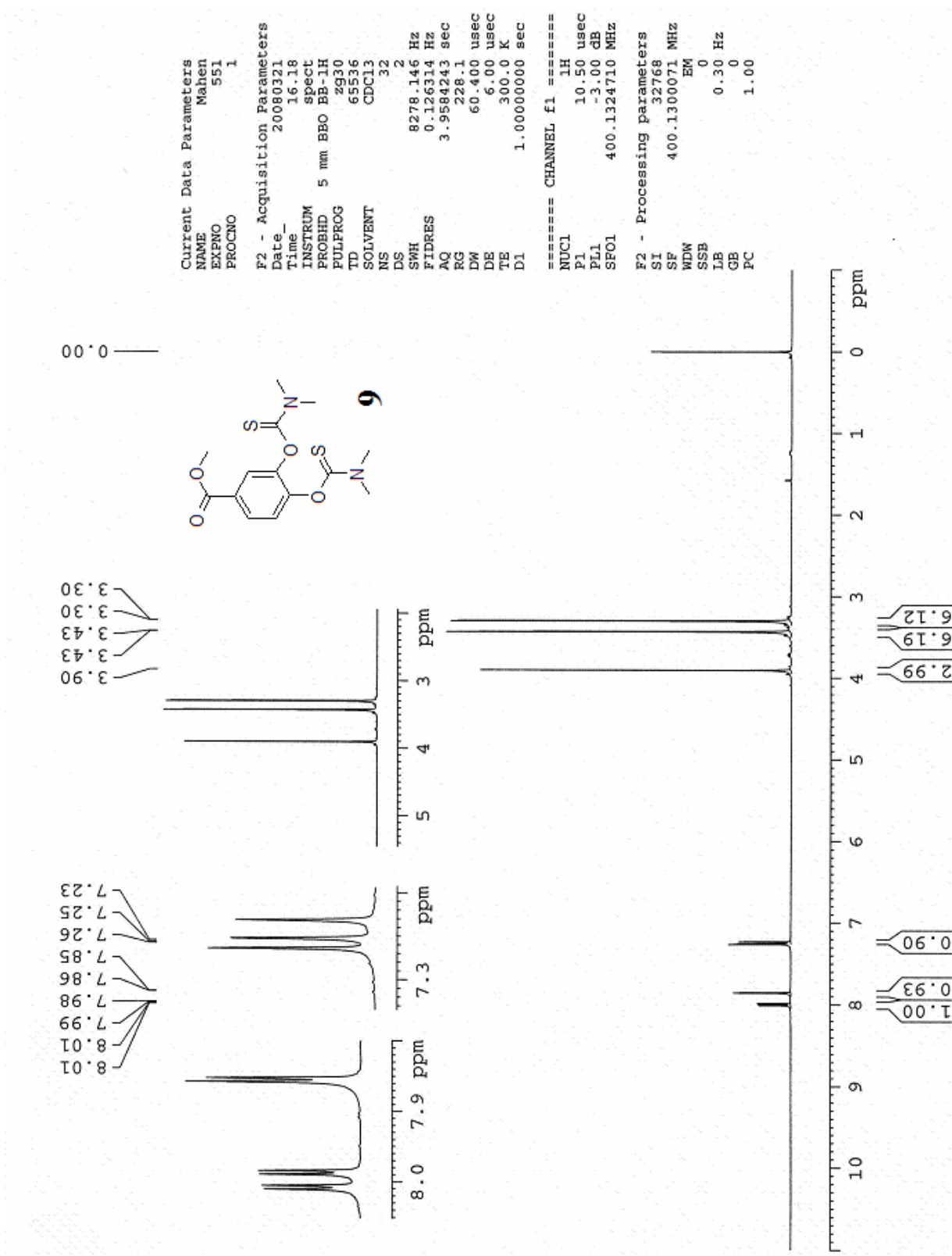


Figure 5. ¹H NMR of methyl 1-3,4-bis{[dimethylamino]carbothioyl}oxy}benzoate – CDCl₃.

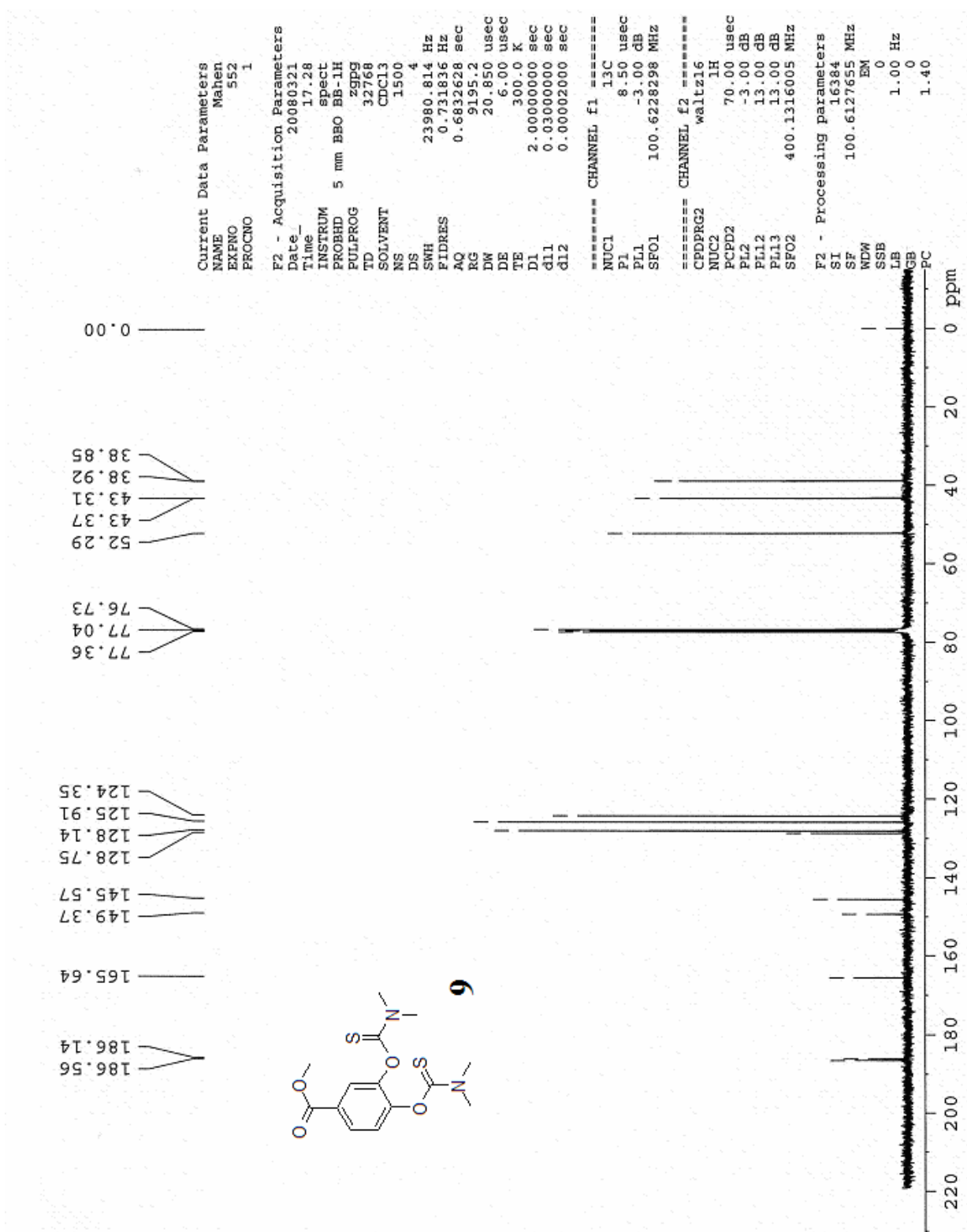
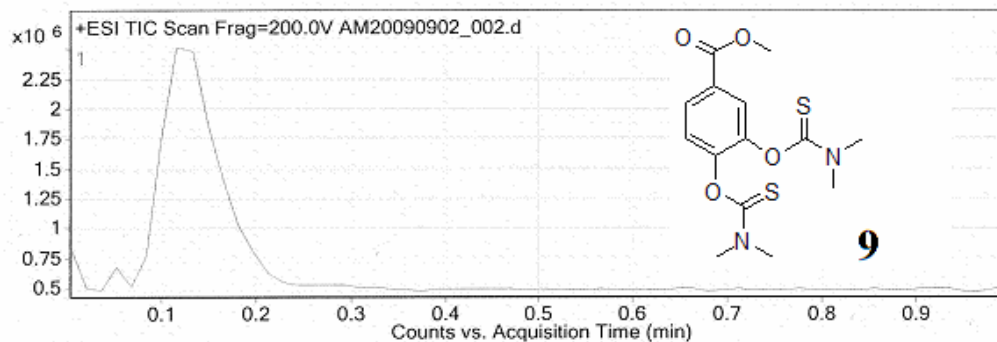


Figure 6. ¹³C NMR of methyl 1-3,4-bis{[dimethylamino]carbothioyl}oxy}benzoate - CDCl₃.

Qualitative Compound Report

Data File	AM20090902_002.d	Sample Name	Sample 2
Sample Type	Sample	Position	P1-F1
Instrument Name	Instrument 1	User Name	Mahen
Acq Method		IRM Calibration Status	Success
DA Method	MahenMethod1.m	Comment	

Fragmentor Voltage 200 Collision Energy 0 Ionization Mode Esi



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C14 H18 N2 O4 S2	0.117	342.0708	240448	C14 H18 N2 O4 S2	342.0708	-0.03

Compound Label	RT	Algorithm	Mass
Cpd 1: C14 H18 N2 O4 S2	0.117	Find By Formula	342.0708

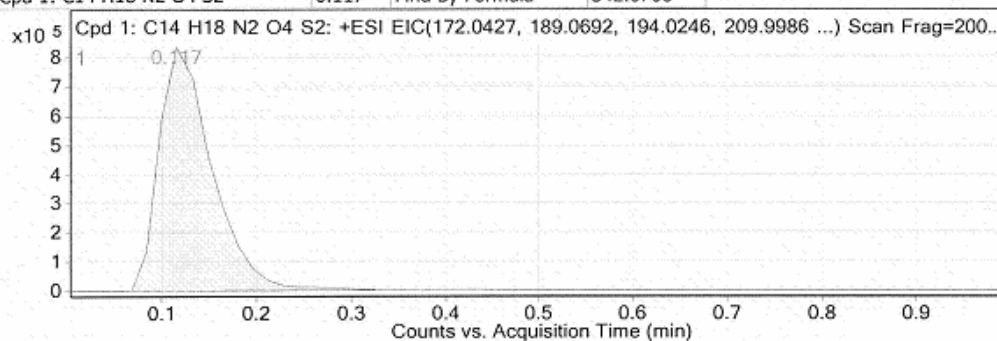


Figure 7. HRMS of methyl-3,4-bis[[dimethylamino)carbothioyl]oxy]benzoate.

Qualitative Compound Report

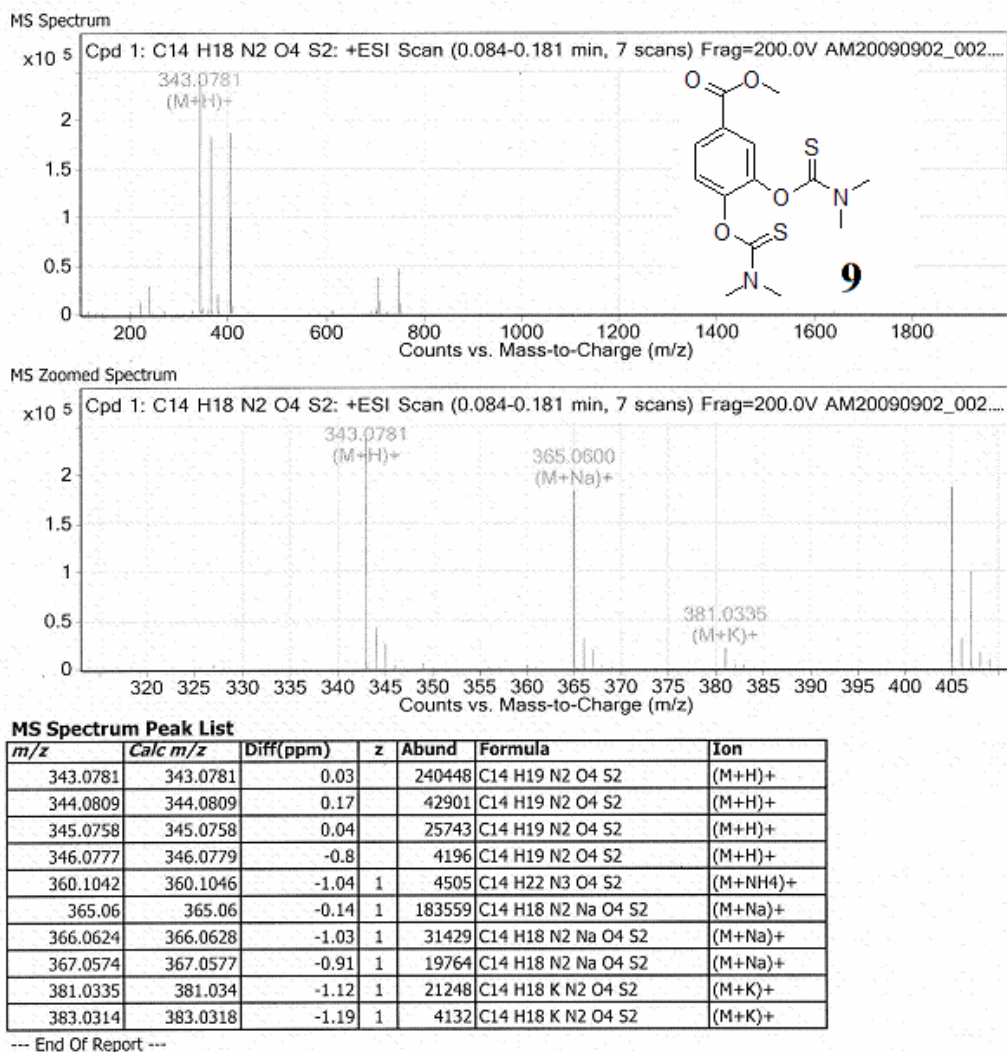


Figure 8. HRMS of methyl-3,4-bis{[dimethylamino)carbothioyl]oxy}benzoate.

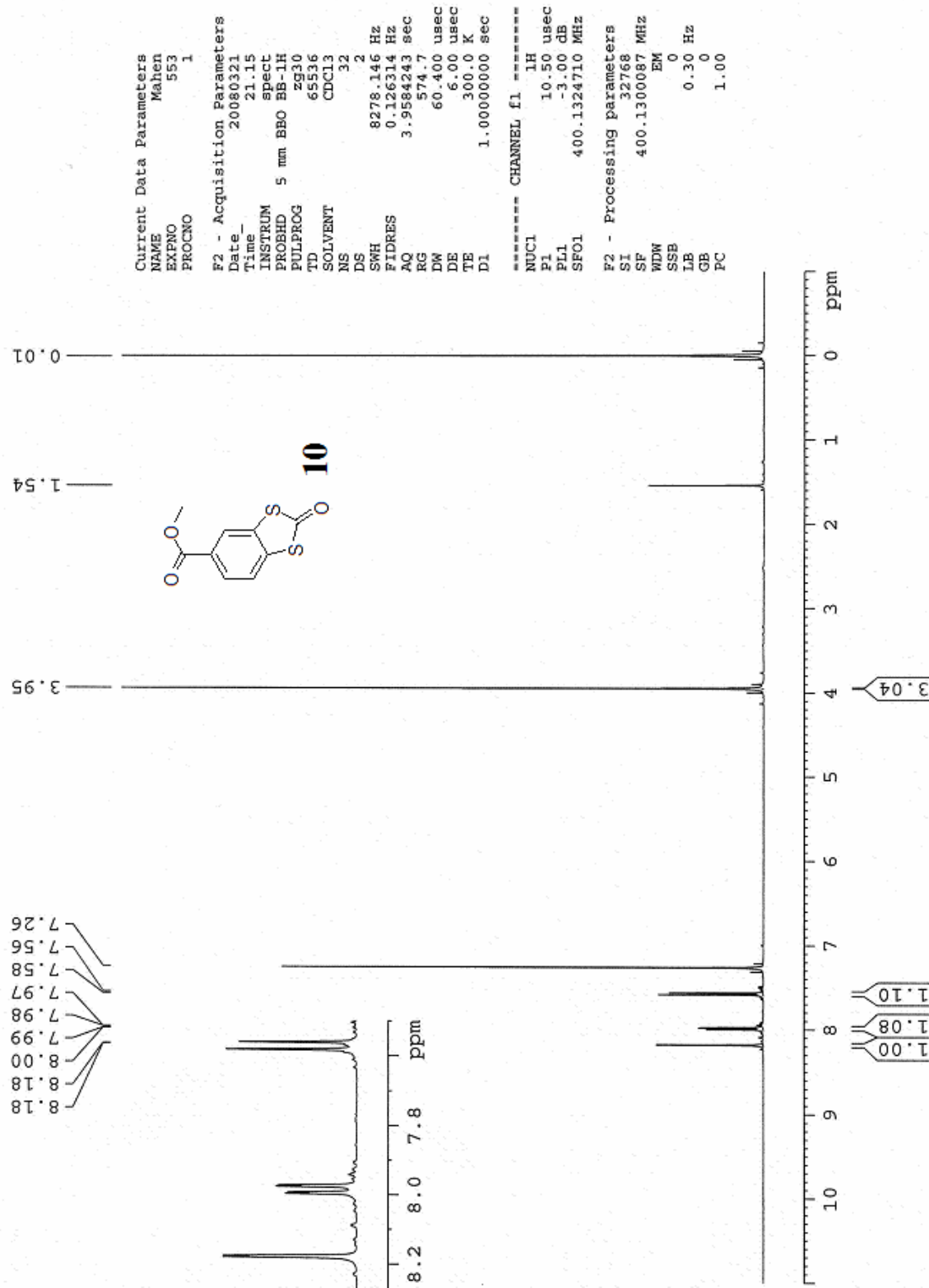


Figure 9. ^1H NMR of methyl-2-oxo-1,3-benzodithiole-5-carboxylate - CDCl_3 .

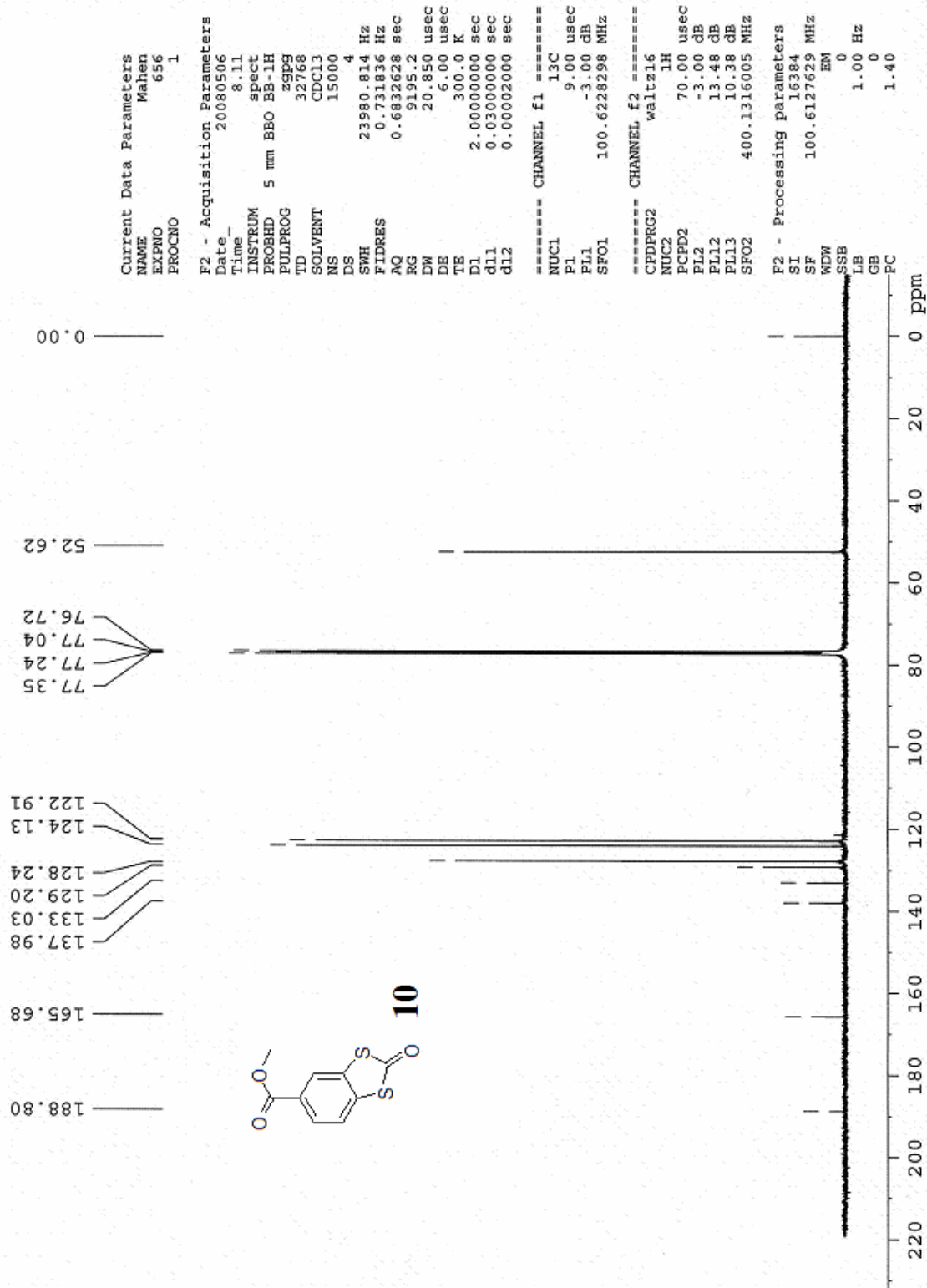


Figure 10. ^{13}C NMR of methyl-2-oxo-1,3-benzodithiole-5-carboxylate - CDCl_3 .

le : D:\MAHEN\Snapshot\20090817_2.D
 erator : am
 quired : 17 Aug 2009 16:55 using AcqMethod MAHEN_BISMERCAT
 trument : Instrumen
 mple Name: oxobenzothiol
 sc Info :
 al Number: 1

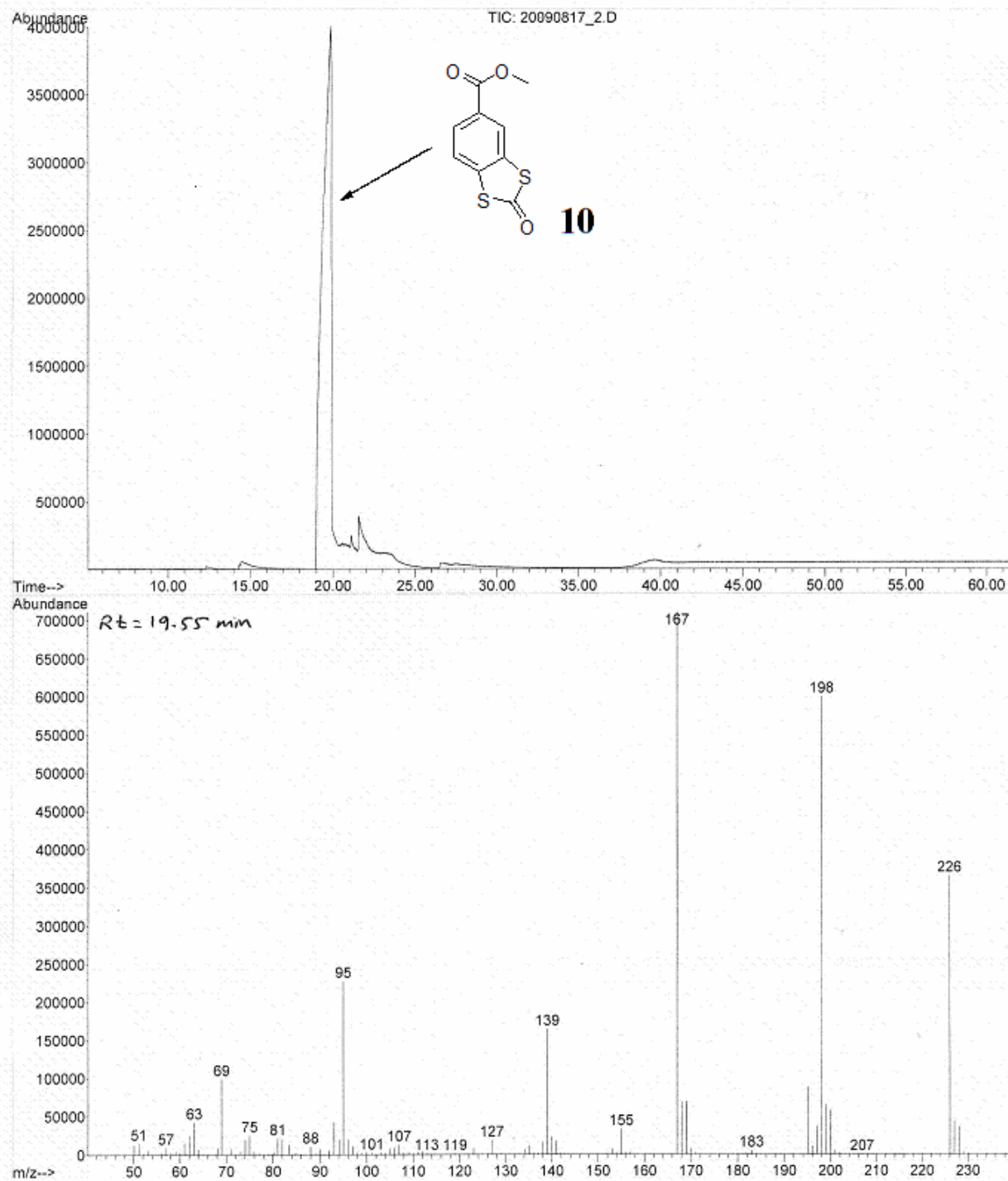
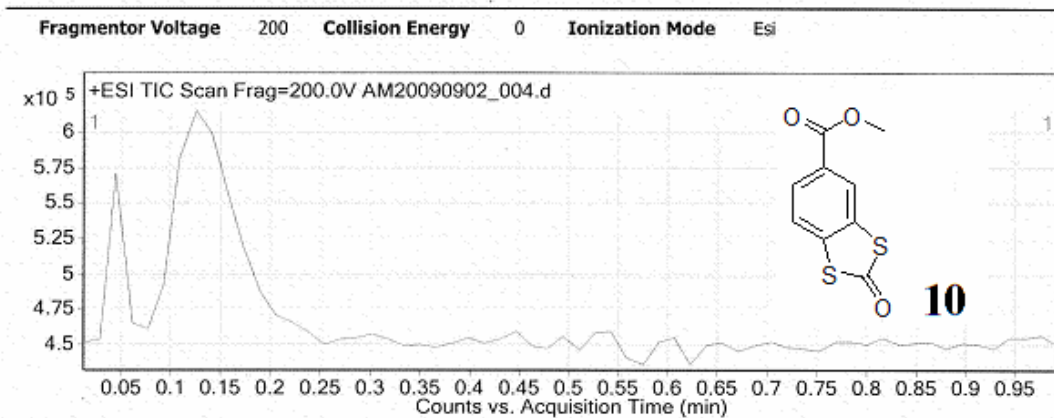


Figure 11. GC/MS of methyl-2-oxo-1,3-benzodithiole-5-carboxylate (Rt = 19.55 min).

Qualitative Compound Report

Data File	AM20090902_004.d	Sample Name	Sample 3
Sample Type	Sample	Position	P1-F1
Instrument Name	Instrument 1	User Name	Mahen
Acq Method		IRM Calibration Status	Success
DA Method	MahenMethod1.m	Comment	



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C9 H6 O3 S2	0.125	225.9757	1949	C9 H6 O3 S2	225.9758	-0.7

Compound Label	RT	Algorithm	Mass
Cpd 1: C9 H6 O3 S2	0.125	Find By Formula	225.9757

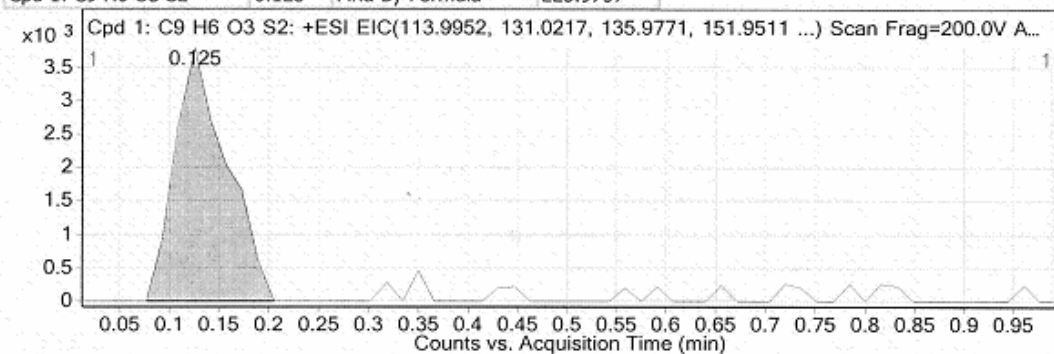


Figure 12. HRMS of methyl-2-oxo-1,3-benzodithiole-5-carboxylate.

Qualitative Compound Report

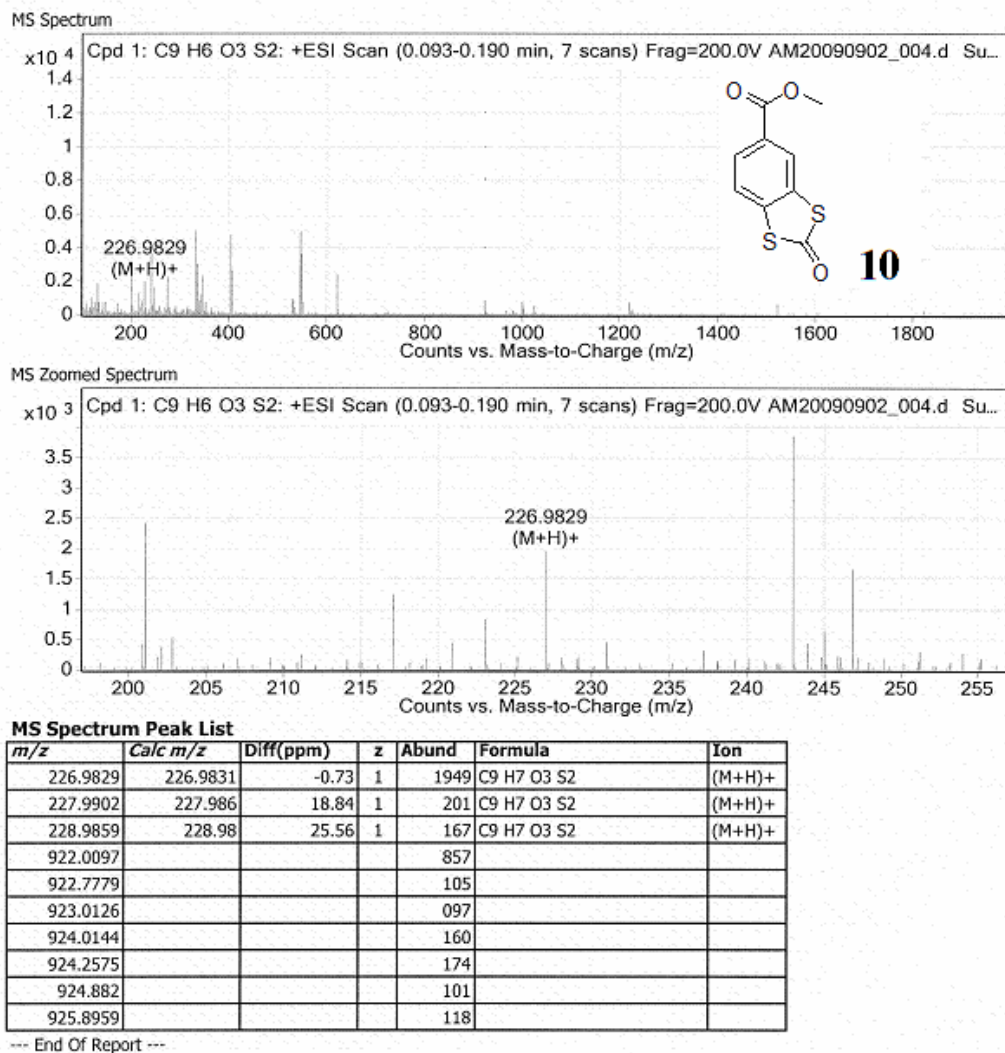


Figure 13. HRMS of methyl-2-oxo-1,3-benzodithiole-5-carboxylate.

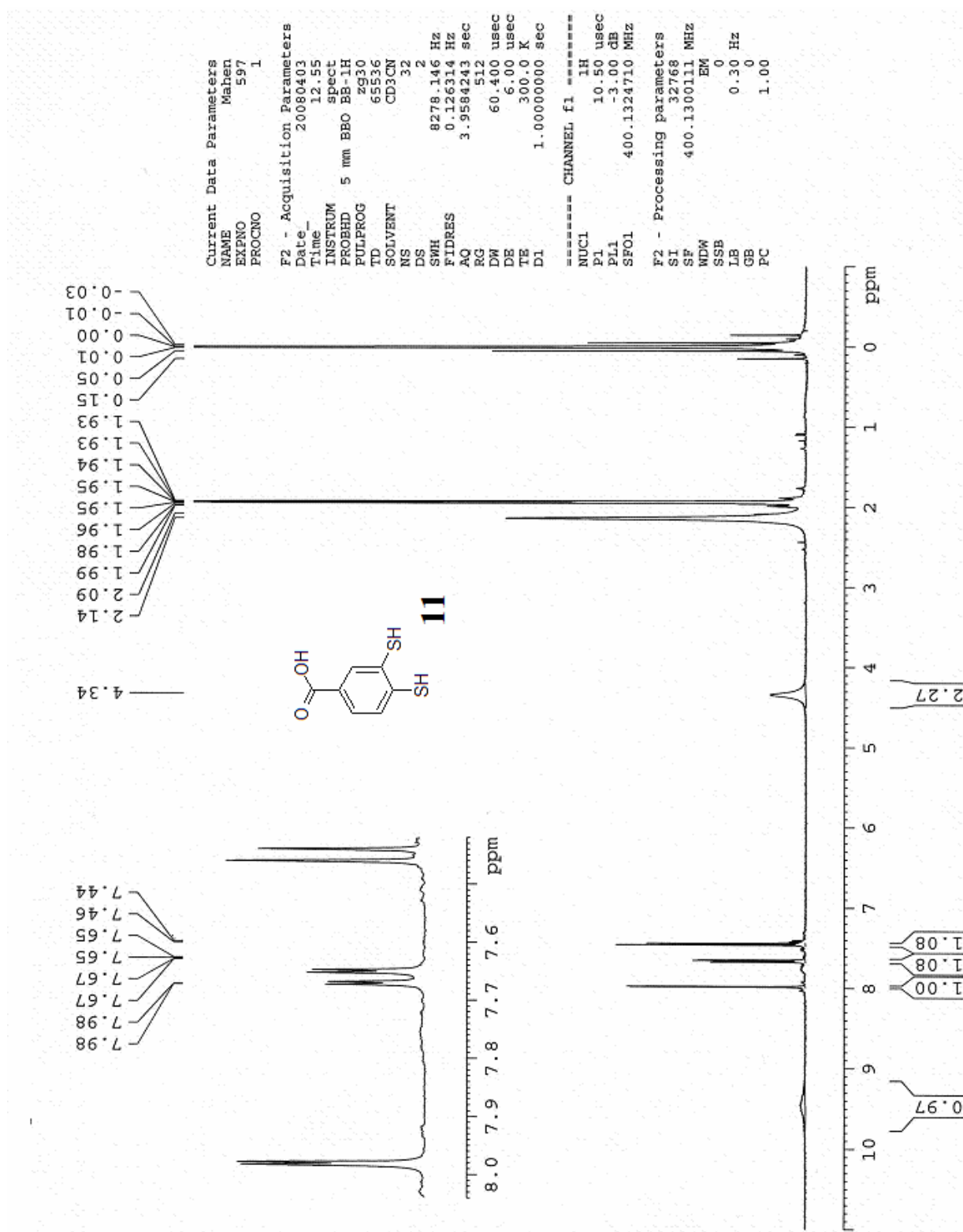


Figure 14. ^1H NMR of 3,4-disulfanylbenzoic acid - CD_3CN .

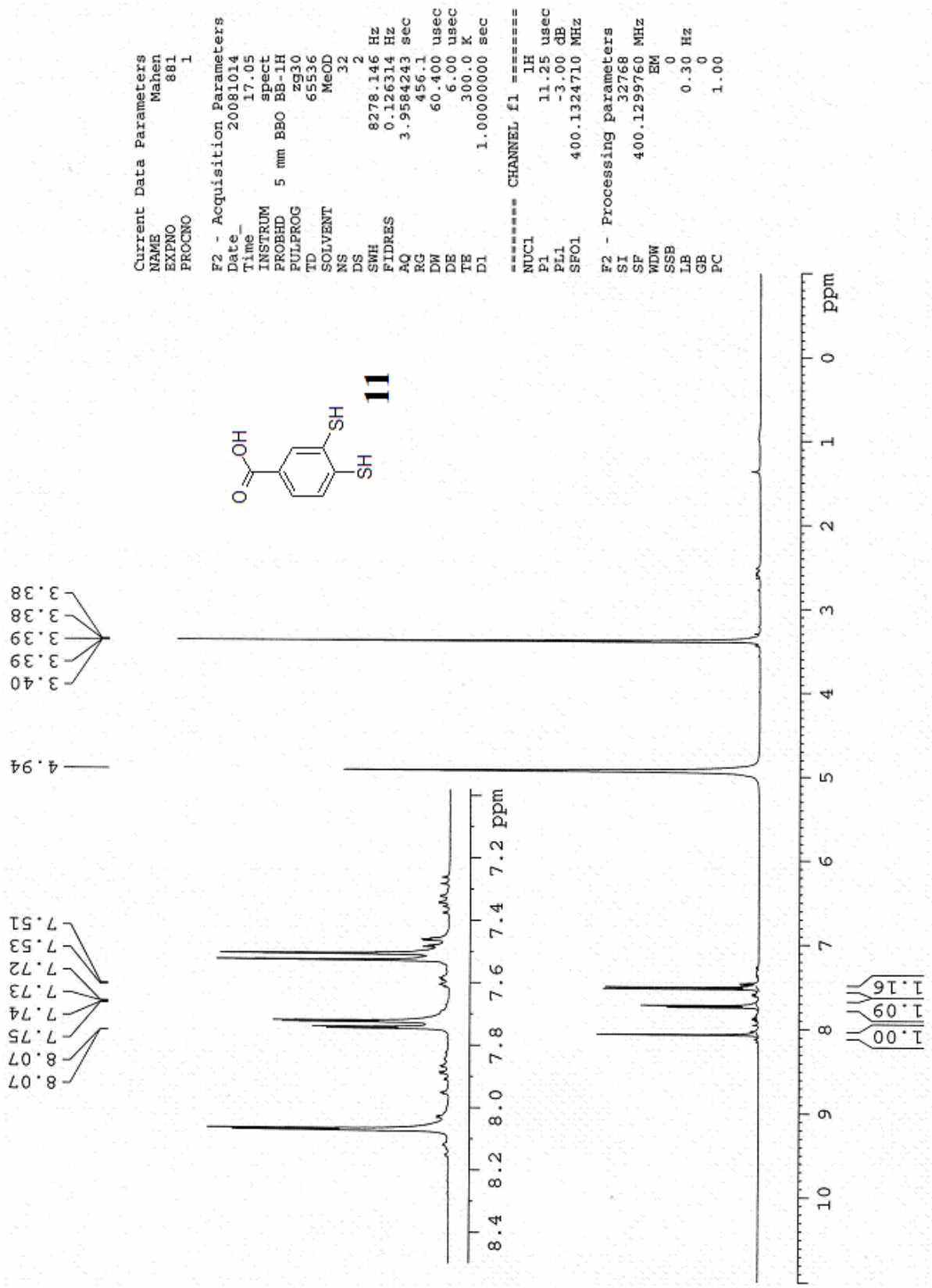


Figure 15. ¹H NMR of 3,4- disulfanylbenzoic acid - CD₃OD.

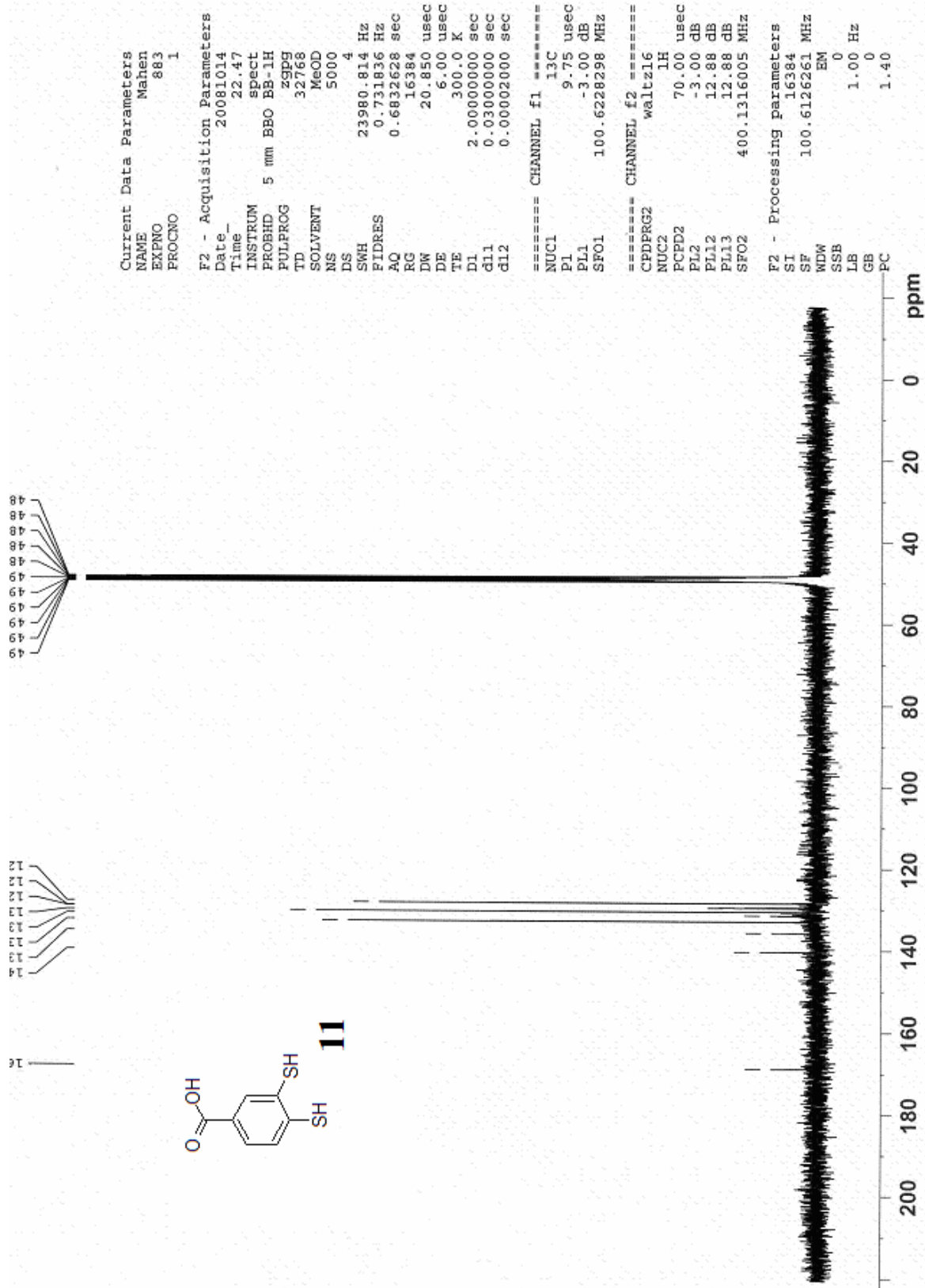
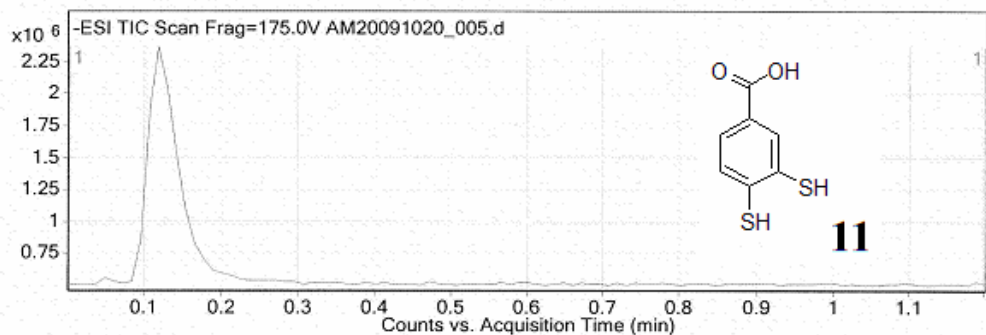


Figure 16. ^{13}C NMR of 3,4- disulfanylbenzoic acid - CD_3OD .

Qualitative Compound Report

Data File	AM20091020_005.d	Sample Name	Sample 1
Sample Type	Sample	Position	P1-F5
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	Success
DA Method	MahenMethod1.m	Comment	EM=185.9809, CF=C7H6O2S2

Fragmentor Voltage 175 **Collision Energy** 0 **Ionization Mode** Esi



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C7 H6 O2 S2	0.119	185.9811	35053	C7 H6 O2 S2	185.9809	0.98

Compound Label	RT	Algorithm	Mass
Cpd 1: C7 H6 O2 S2	0.119	Find By Formula	185.9811

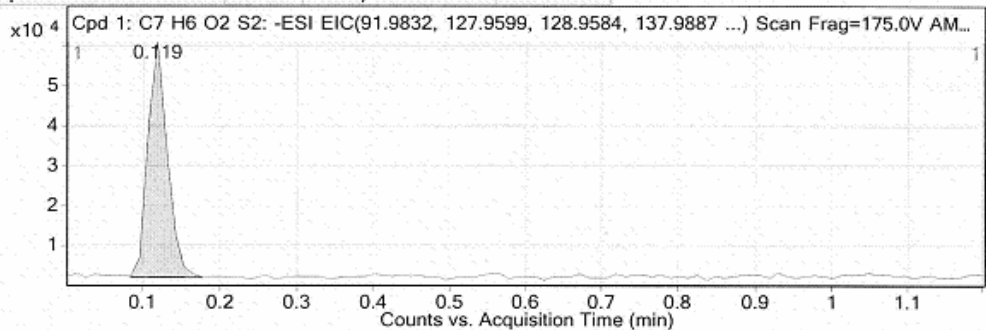
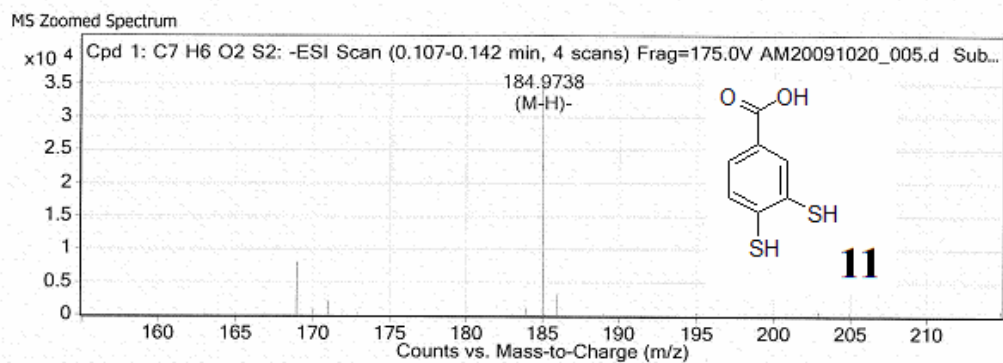


Figure 17. HRMS of 3,4- disulfanylbzoic acid.

Qualitative Compound Report



MS Spectrum Peak List

<i>m/z</i>	<i>Calc m/z</i>	Diff(ppm)	<i>z</i>	Abund	Formula	Ion
184.9738	184.9736	0.99	1	35053	C7 H5 O2 S2	(M-H)-
425.8635				15324		
430.861				505097		
431.0516				7314		
431.1046				4824		
431.8634				87070		
432.859				329559		
433.8614				55297		
434.8569				56000		
435.8594				10457		

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Figure 18. HRMS of 3,4- disulfanylbenzoic acid.

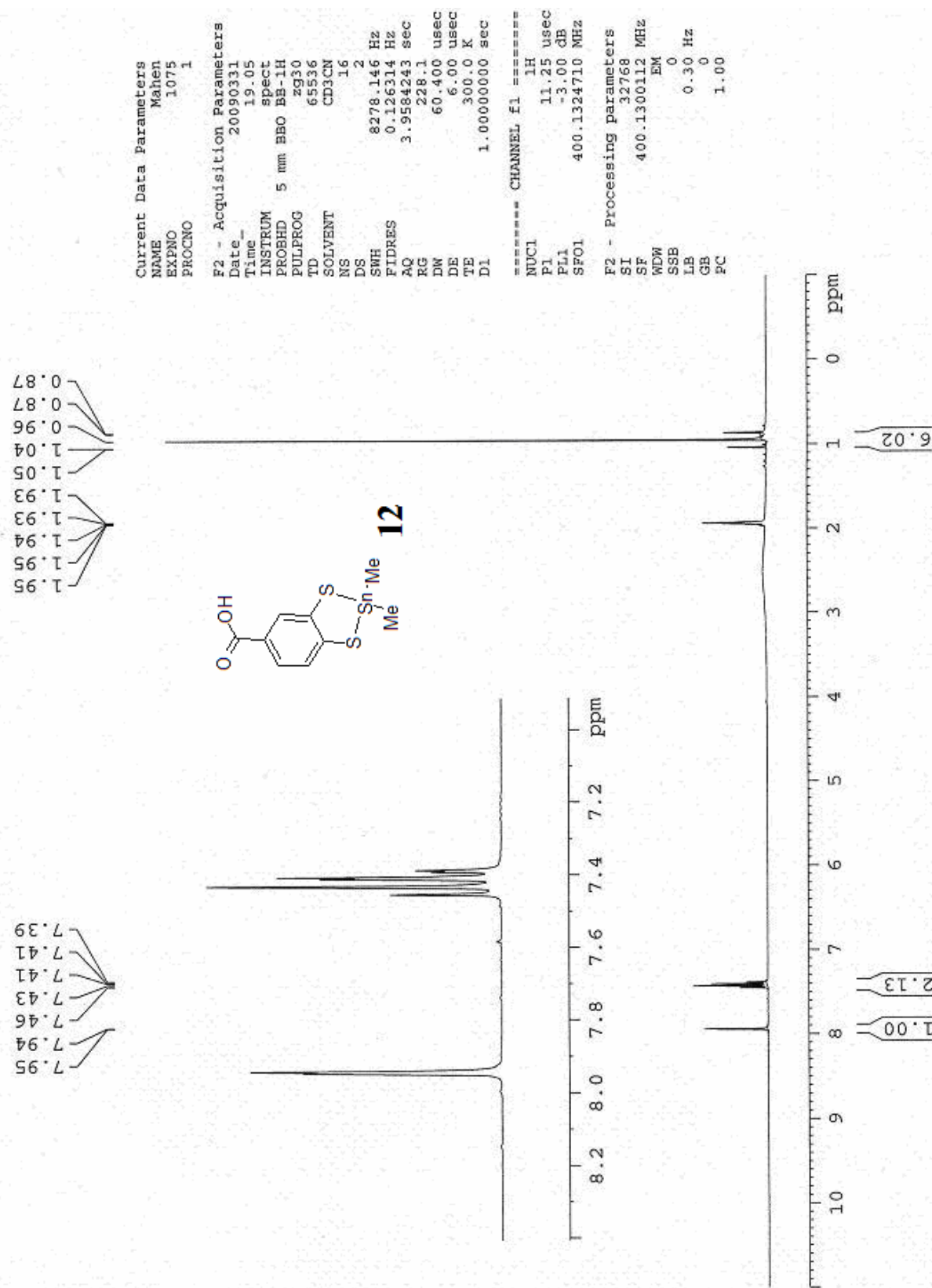


Figure 19. ^1H NMR of 2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylic acid - CD_3CN .

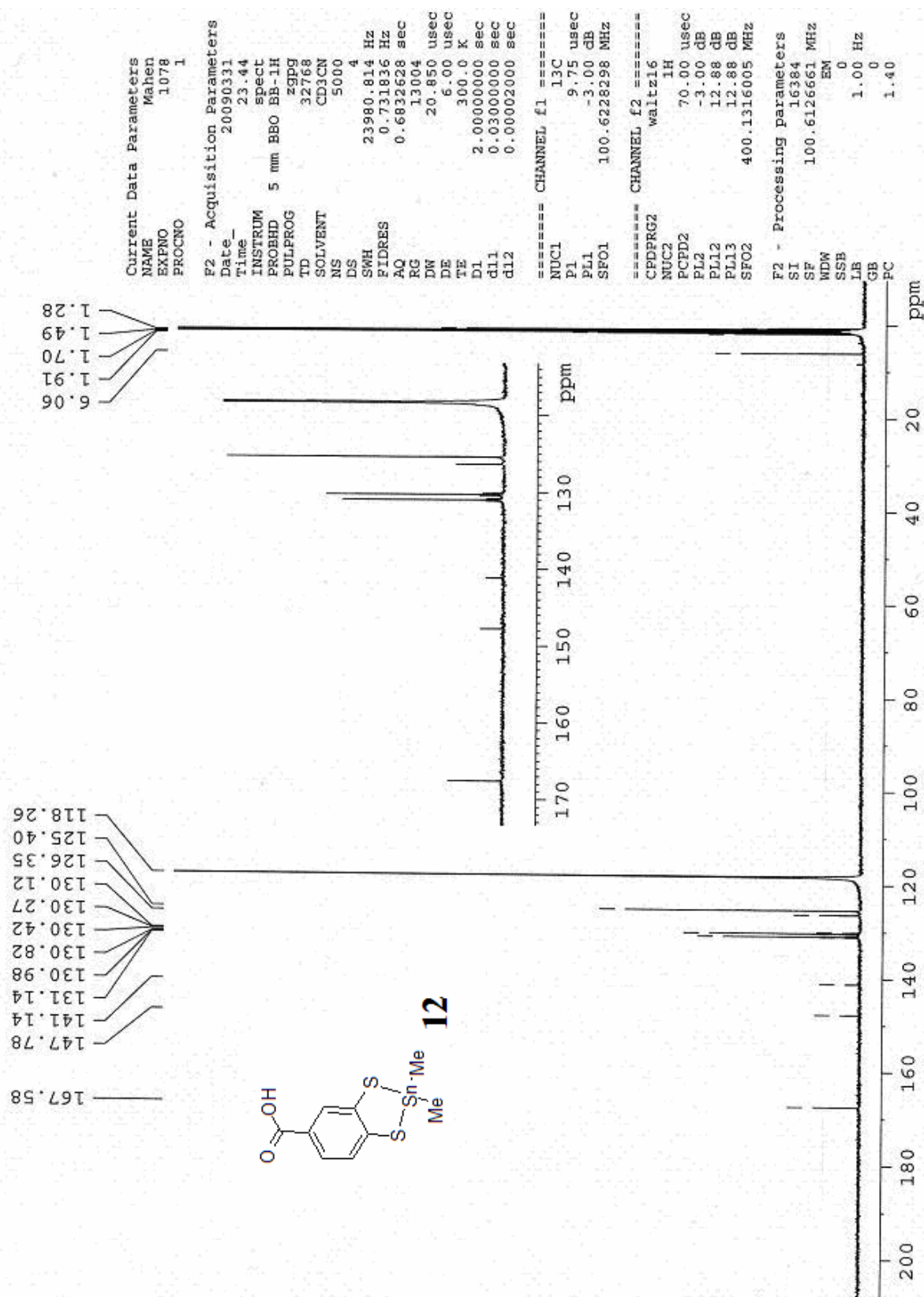
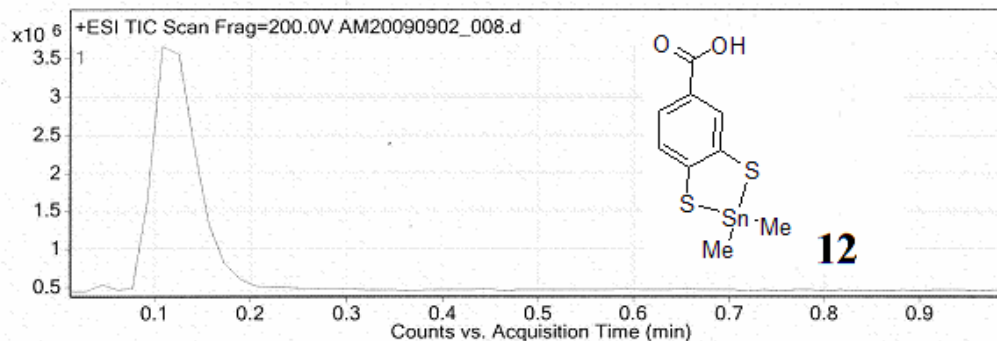


Figure 20. ^{13}C NMR of 2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylic acid - CD_3CN .

Qualitative Compound Report

Data File	AM20090902_008.d	Sample Name	Sample 5
Sample Type	Sample	Position	P1-F1
Instrument Name	Instrument 1	User Name	Mahen
Acq Method		IRM Calibration Status	Success
DA Method	MahenMethod1.m	Comment	

Fragmentor Voltage 200 Collision Energy 0 Ionization Mode Esi



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C9 H10 O2 S2 Sn	0.11	325.9171	116190	C9 H10 O2 S2 Sn	325.917	0.03

Compound Label	RT	Algorithm	Mass
Cpd 1: C9 H10 O2 S2 Sn	0.11	Find By Formula	325.9171

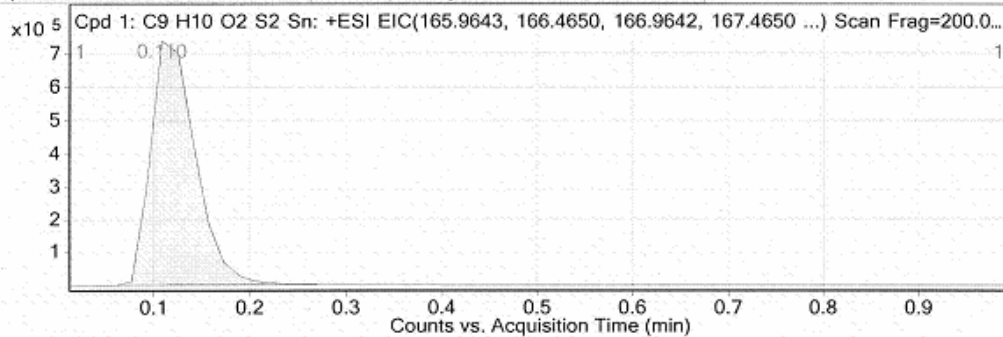


Figure 21. HRMS of 2,2-dimethylbenzo[d][1,3]dithiastannole-5-carboxylic acid.

Qualitative Compound Report

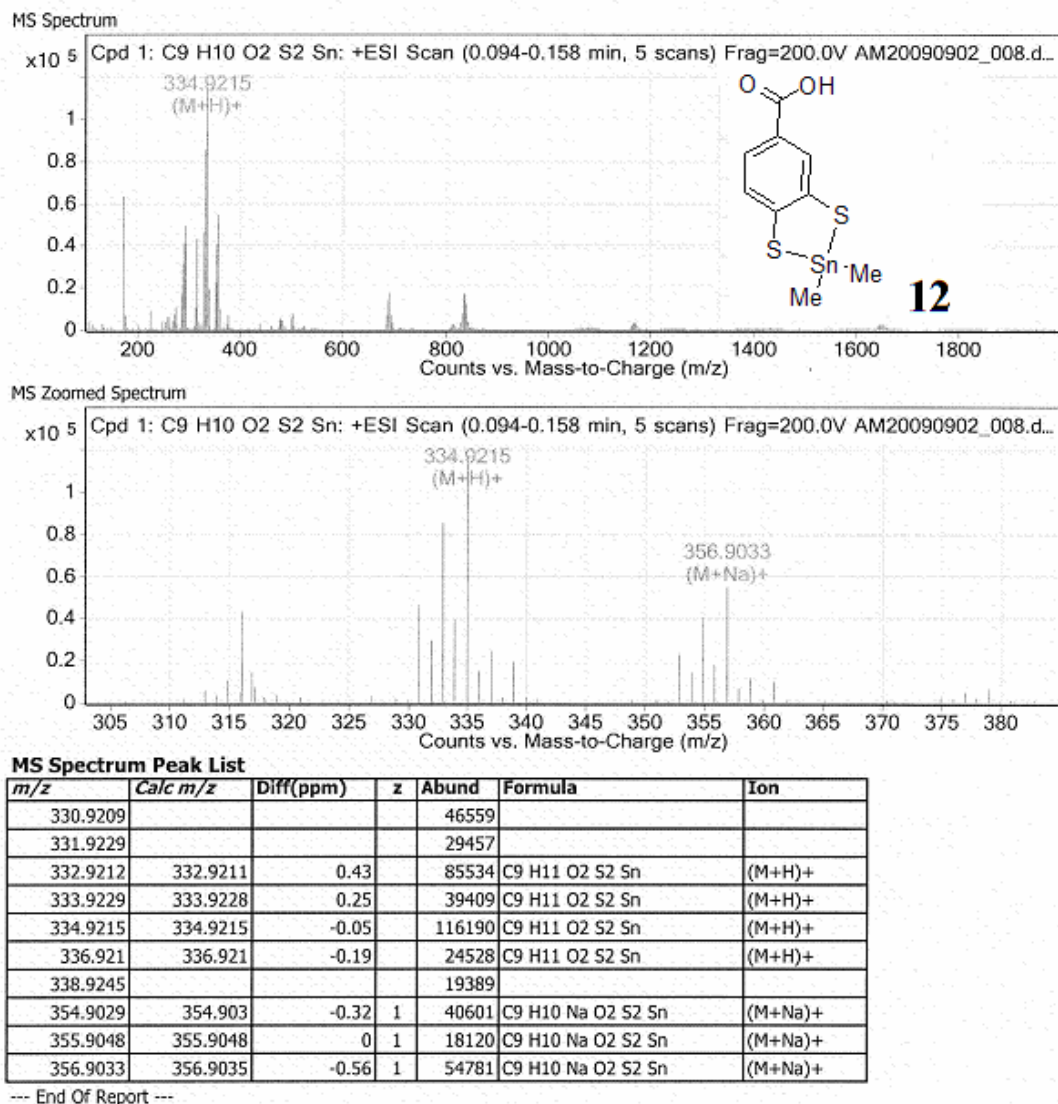


Figure 22. HRMS of 2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylic acid.

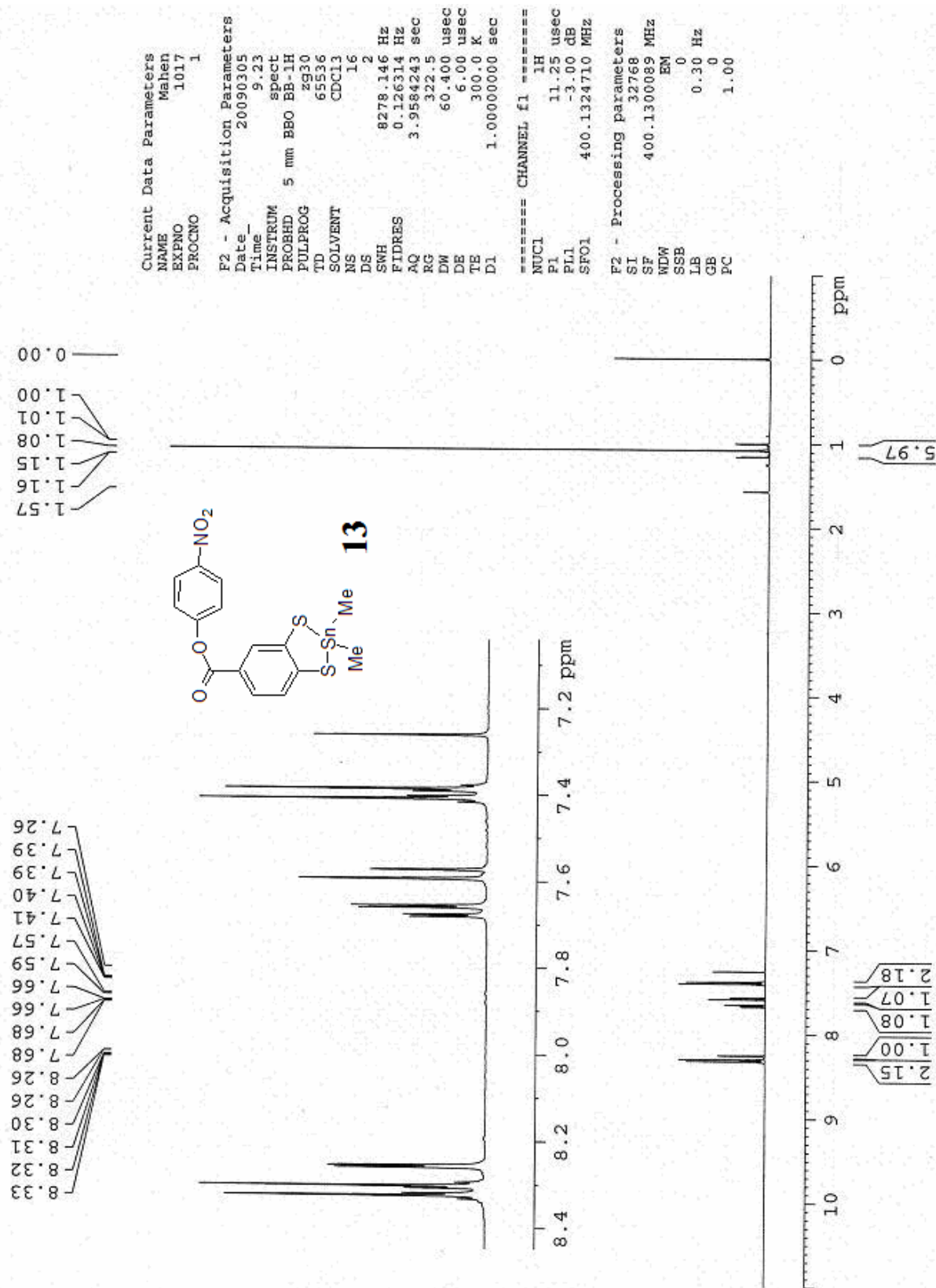


Figure 23. ^1H NMR of 4-nitrophenyl-2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylate – CDCl_3 .

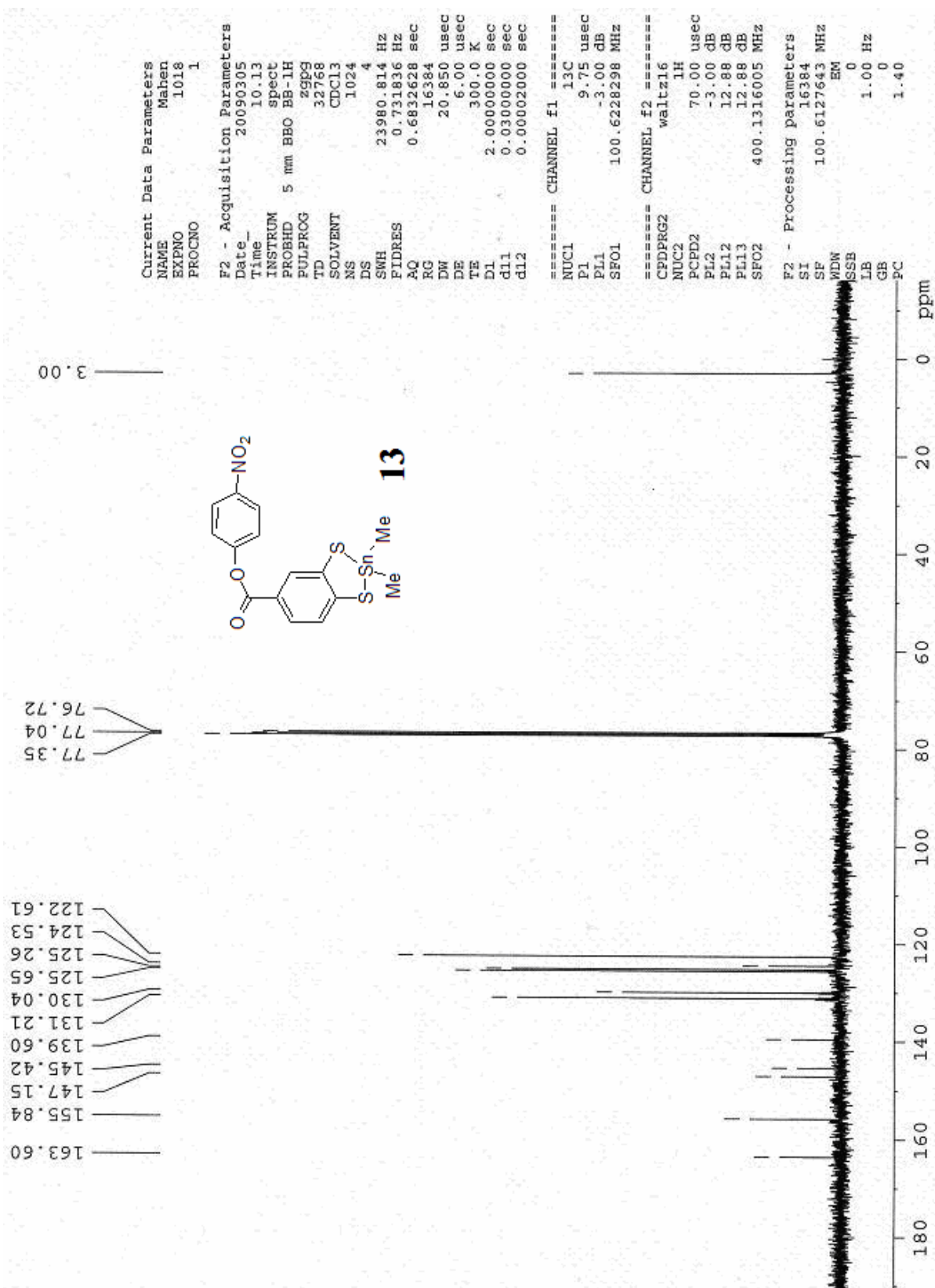


Figure 24. ¹³C NMR of 4-nitrophenyl-2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylate – CDCl₃.

Qualitative Compound Report

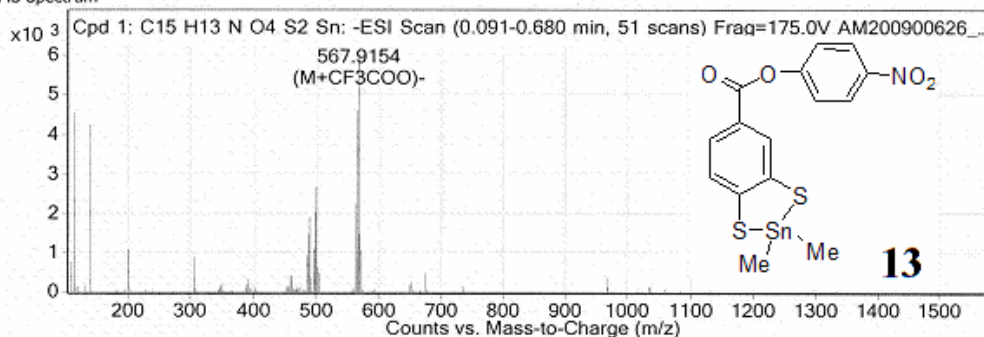
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Sample Type	Sample	Position	P1-F3
Instrument Name	Instrument 1	User Name	Mahen
Acq Method		IRM Calibration Status	Success
DA Method	HCEmpirical1.m	Comment	FI

Compound Table

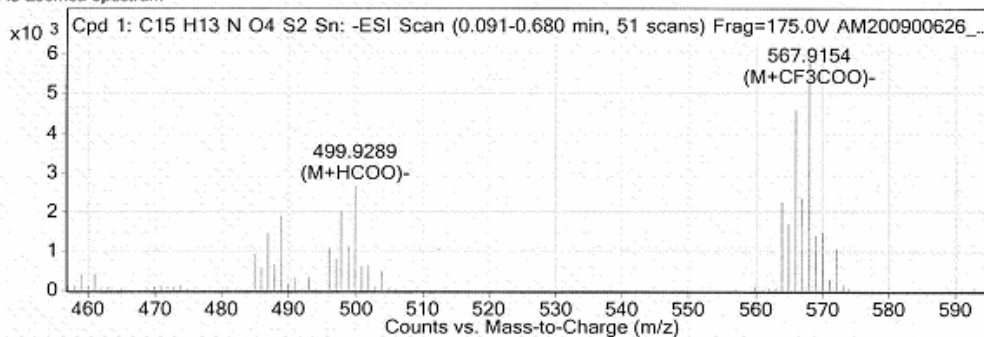
Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C15 H13 N O4 S2 Sn	0.115	446.9324	5940	C15 H13 N O4 S2 Sn	446.9334	-2.34

Compound Label	RT	Algorithm	Mass
Cpd 1: C15 H13 N O4 S2 Sn	0.115	Find By Formula	446.9324

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
486.9047	486.9014	6.94	1	1491	C15 H13 Cl N O4 S2 Sn	(M+Cl) ⁻
487.907	487.8993	15.79	1	688	C15 H13 Cl N O4 S2 Sn	(M+Cl) ⁻
488.905	488.9009	8.38	1	1882	C15 H13 Cl N O4 S2 Sn	(M+Cl) ⁻
489.9082	489.8995	17.65	1	174	C15 H13 Cl N O4 S2 Sn	(M+Cl) ⁻

Figure 25. HRMS of 4-nitrophenyl-2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylate.

Qualitative Compound Report

<i>m/z</i>	<i>Calc m/z</i>	<i>Diff(ppm)</i>	<i>z</i>	<i>Abund</i>	<i>Formula</i>	<i>Ion</i>
490.907	490.9009	12.29	1	309	C15 H13 Cl N O4 S2 Sn	(M+Cl)-
491.9263	491.8983	56.82	1	37	C15 H13 Cl N O4 S2 Sn	(M+Cl)-
497.9285	497.9285	0	1	2017	C16 H14 N O6 S2 Sn	(M+HCOO)-
498.9304	498.9304	0.18	1	1134	C16 H14 N O6 S2 Sn	(M+HCOO)-
499.9289	499.929	-0.27	1	2675	C16 H14 N O6 S2 Sn	(M+HCOO)-
500.9315	500.9313	0.4	1	603	C16 H14 N O6 S2 Sn	(M+HCOO)-
501.9287	501.9288	-0.34	1	637	C16 H14 N O6 S2 Sn	(M+HCOO)-
502.9311	502.9315	-0.66	1	106	C16 H14 N O6 S2 Sn	(M+HCOO)-
562.9158				59		
563.9157				2238		
564.9176				1698		
565.914	565.9159	-3.48		4588	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
566.1206				10		
566.917	566.9178	-1.32		2344	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
567.0853				5		
567.9154	567.9164	-1.81		5940	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
568.0776				10		
568.2491				5		
568.2786				5		
568.9174	568.9187	-2.2		1429	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
569.1225				10		
569.9155	569.9163	-1.38		1484	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
570.9175	570.9189	-2.44		293	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
571.9193	571.919	0.54		1048	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
572.9221	572.922	0.14	1	160	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-
573.9193	573.9177	2.75	1	68	C17 H13 F3 N O6 S2 Sn	(M+CF3COO)-

--- End Of Report ---

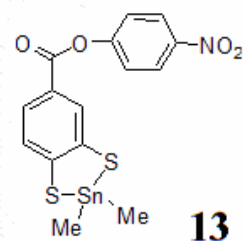


Figure 26. HRMS of 4-nitrophenyl-2,2-dimethylbenzo[d][1,3,2]dithiastannole-5-carboxylate.

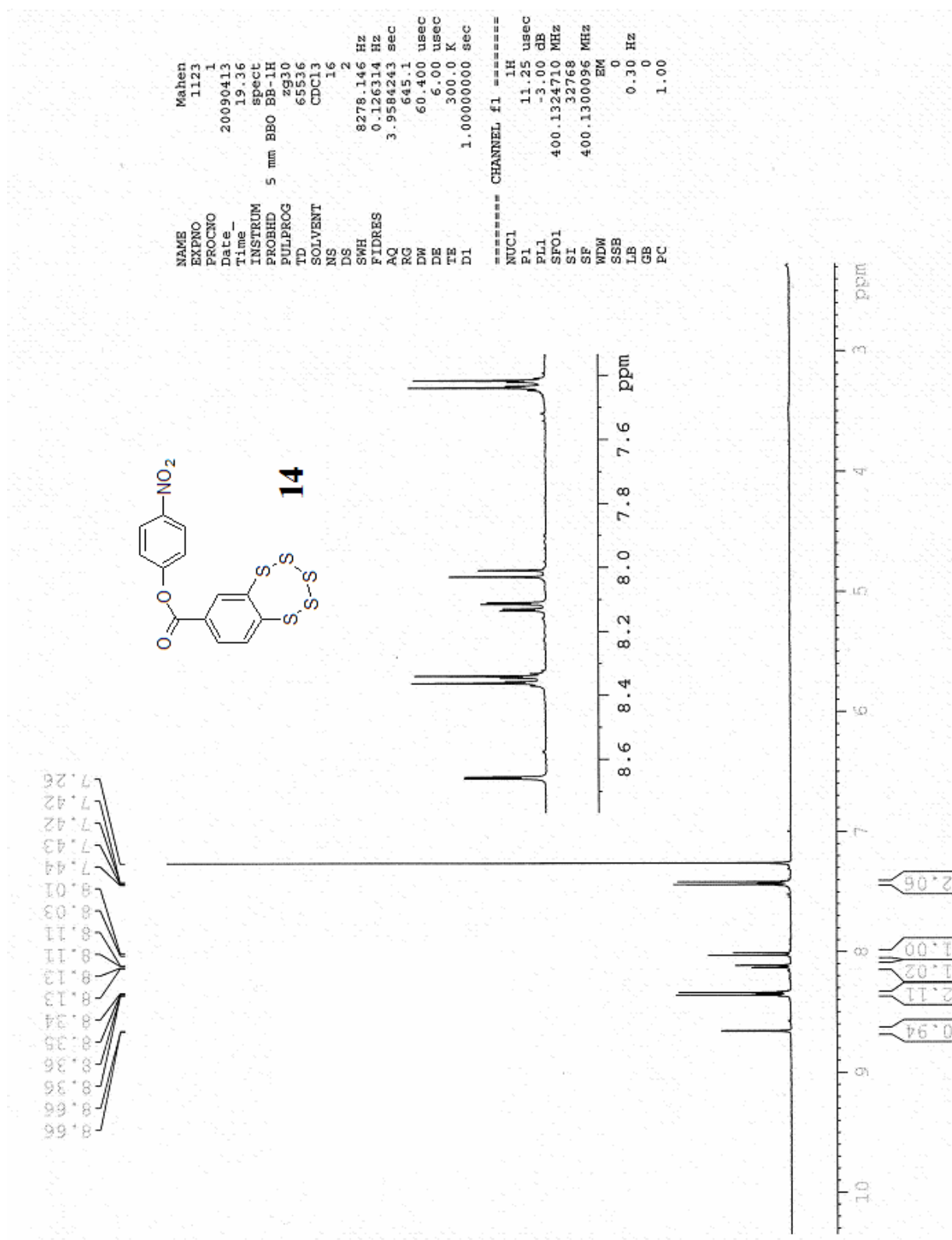


Figure 27. ¹H of NMR 4-nitrophenylbenzo[f][1,2,3,4,5]pentathiepine-7-carboxylate - CDCl₃.

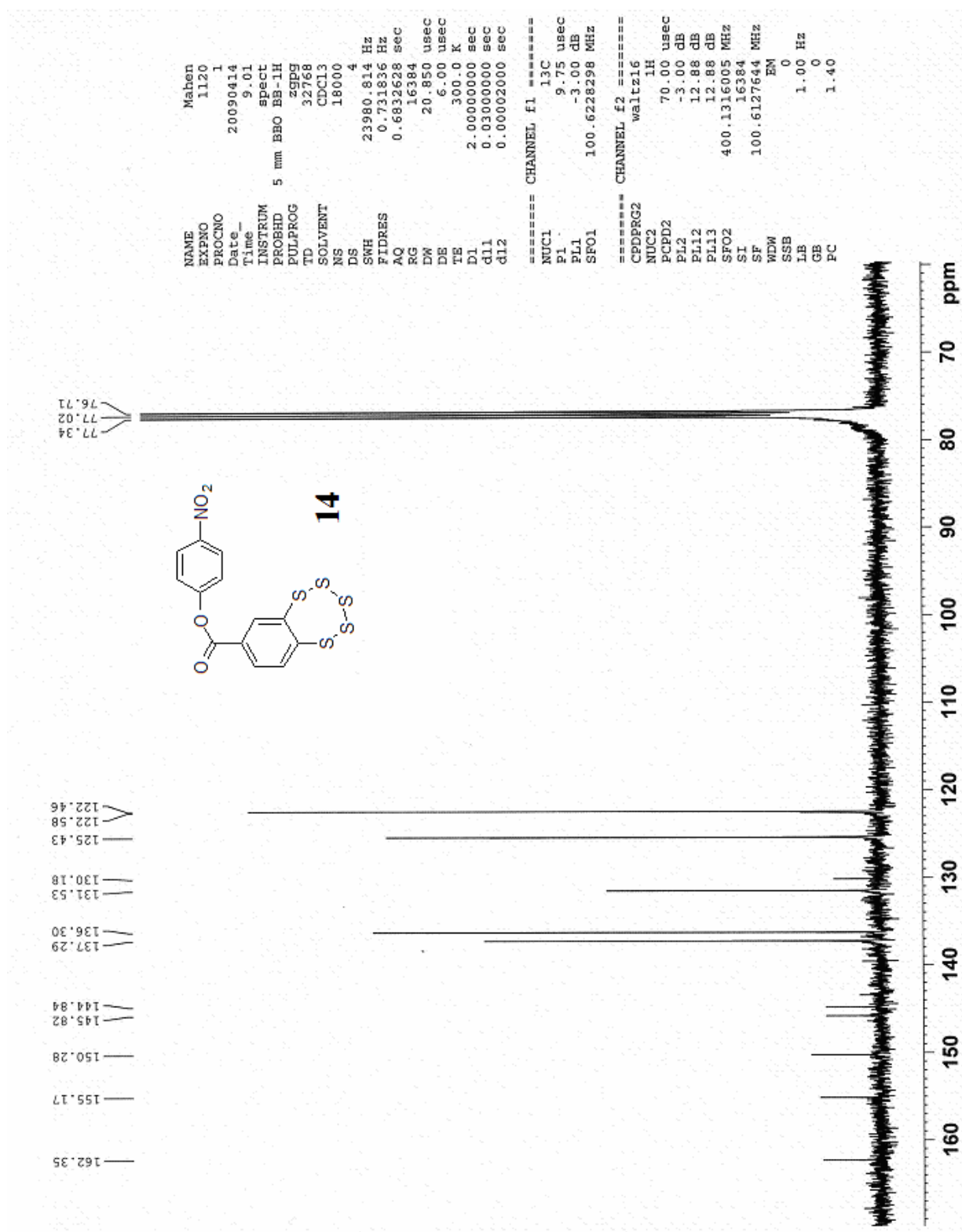


Figure 28. ¹³C NMR of 4-nitrophenylbenzo[f][1,2,3,4,5]pentathiepine-7-carboxylate - CDCl₃.

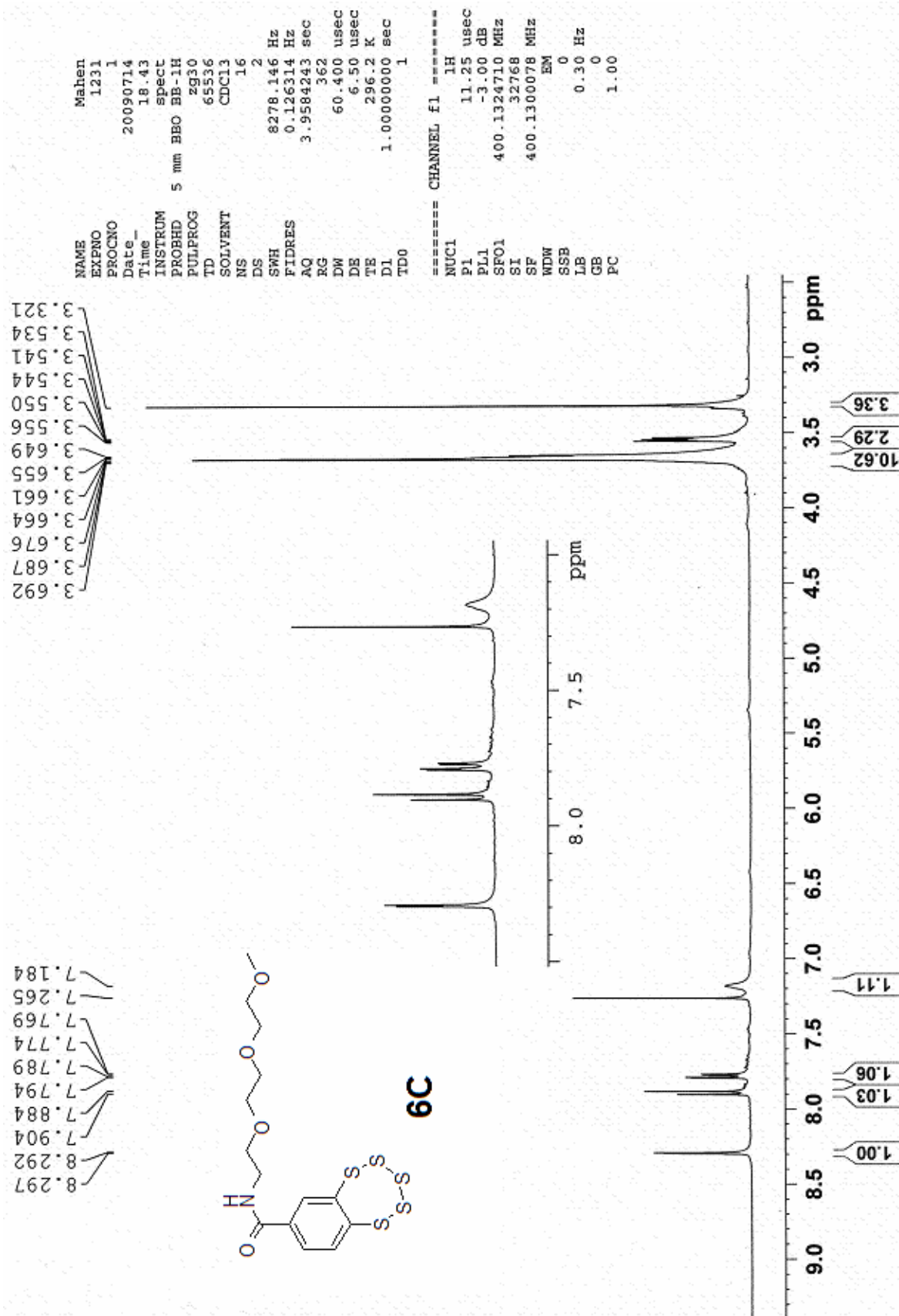


Figure 29. ^1H NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDCl_3 .

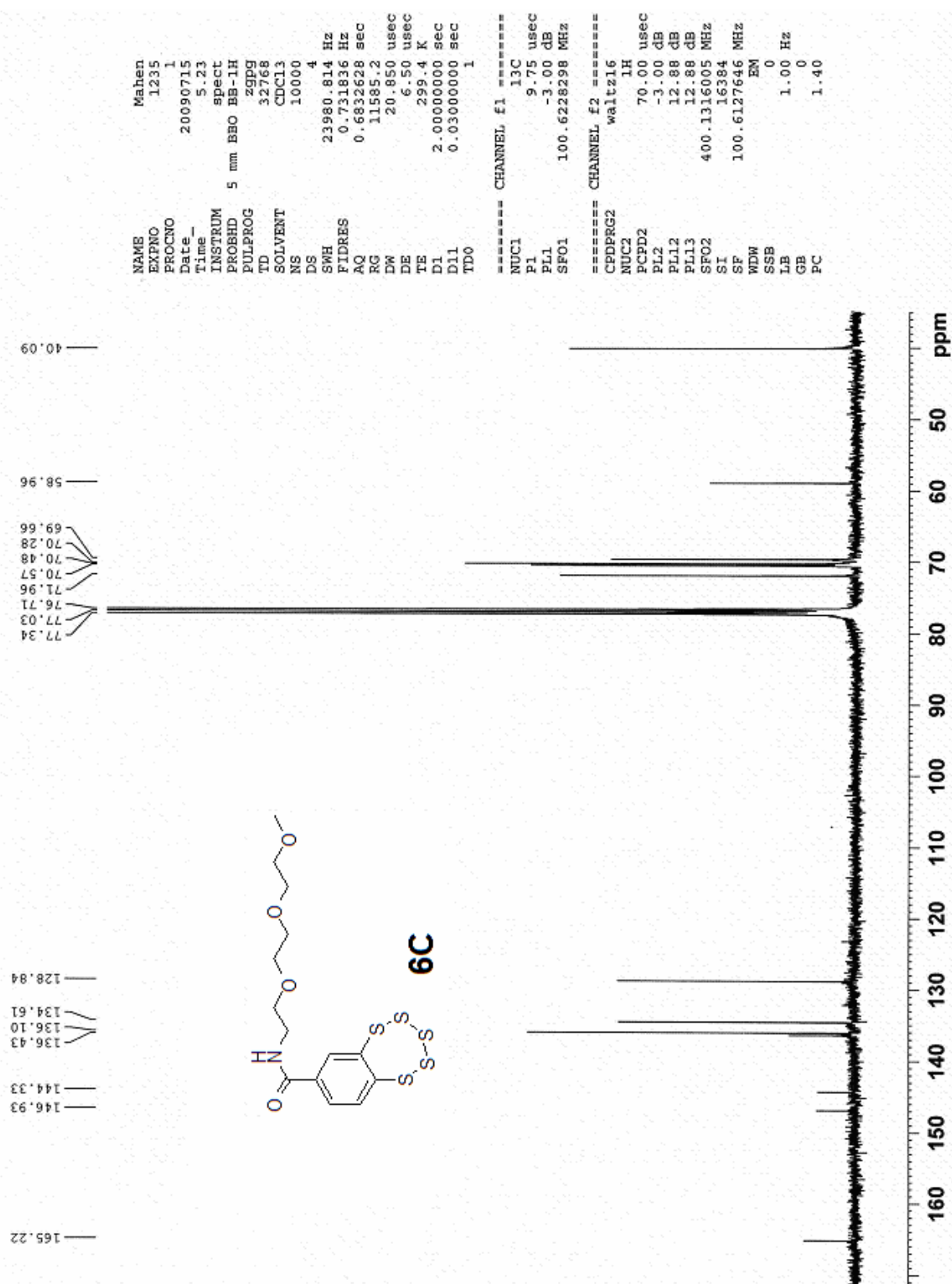


Figure 30. ¹³C NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDCl₃.

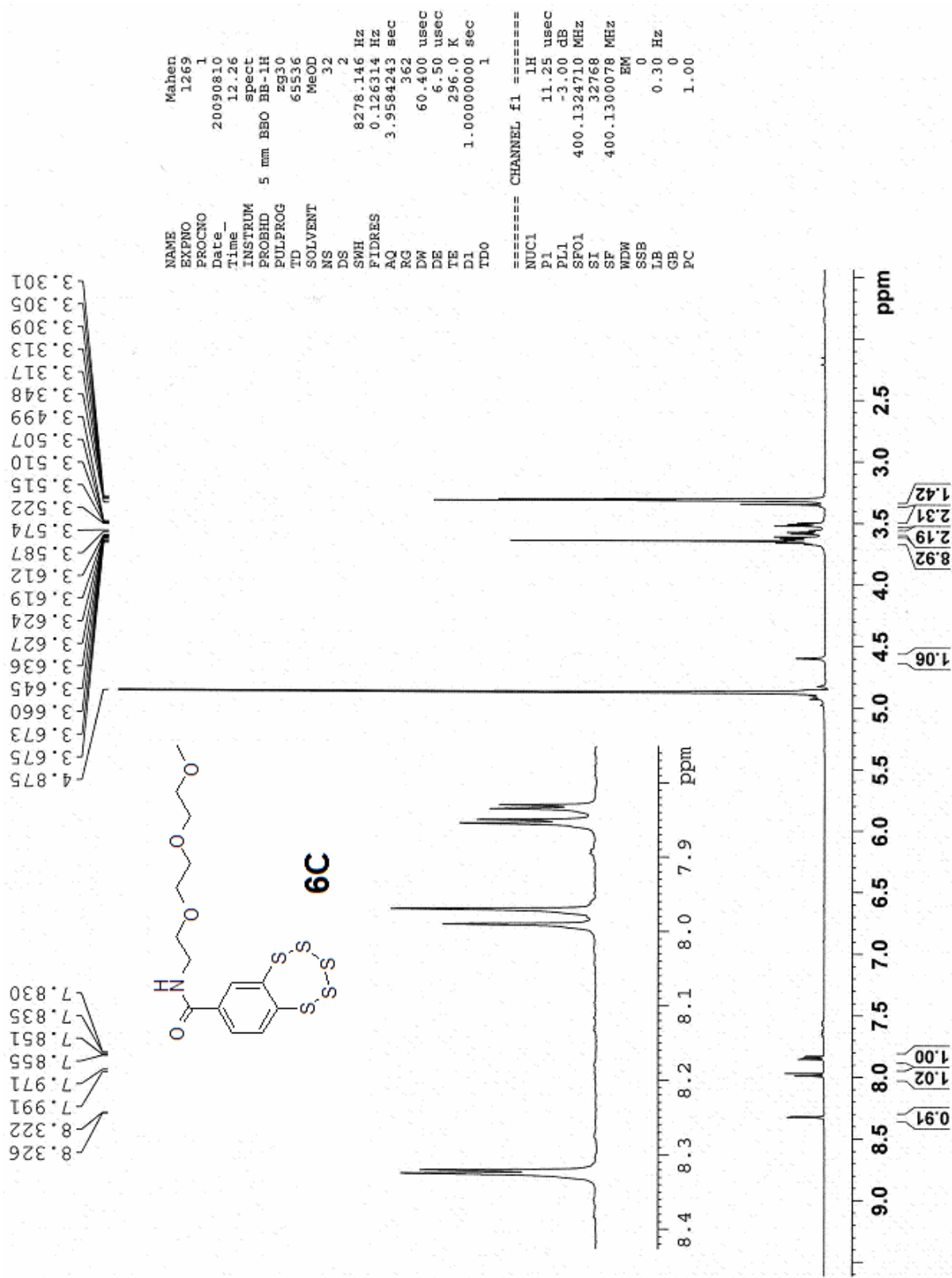


Figure 31. ¹H NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide – CD₃OD.

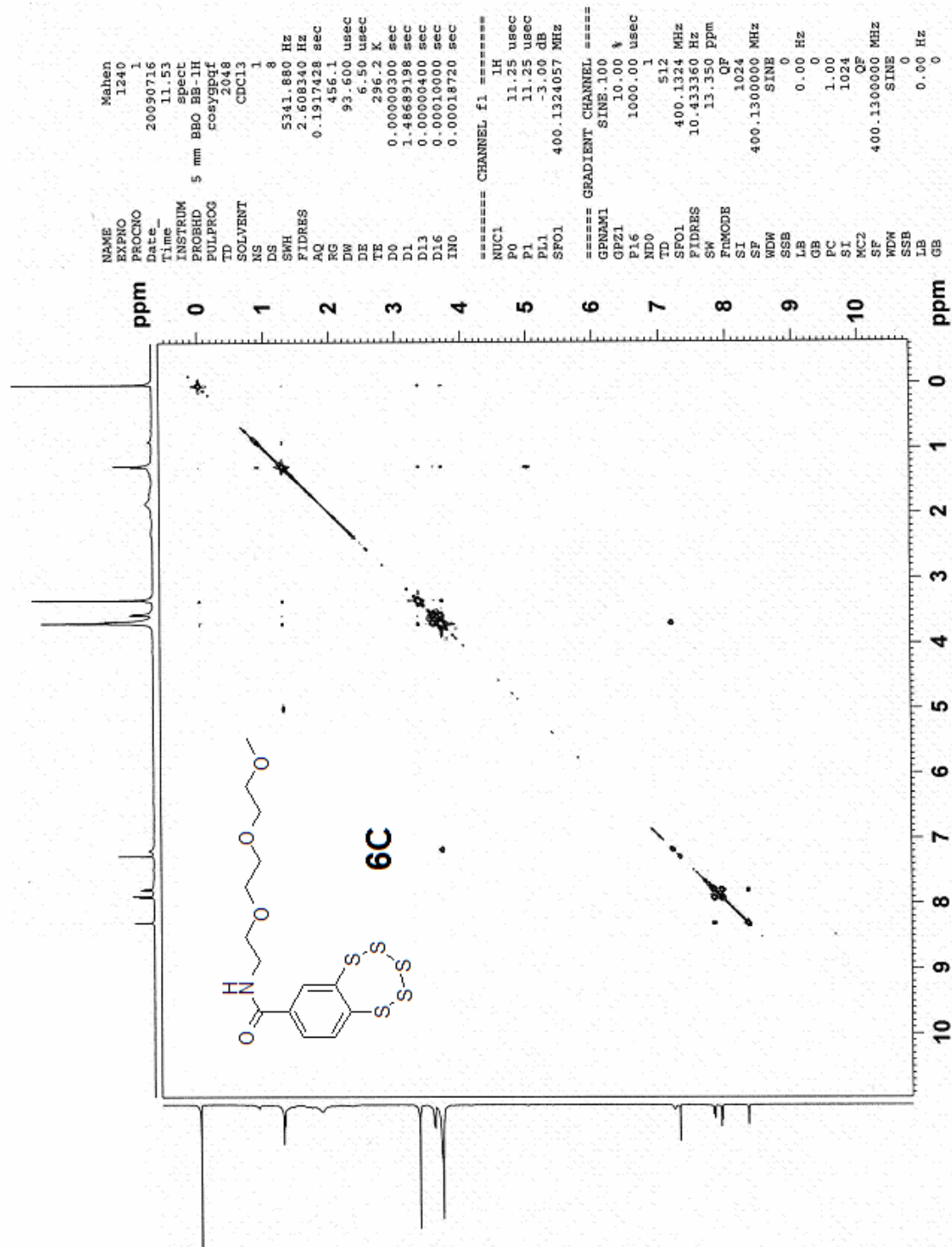


Figure 32. COSY NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDCl₃

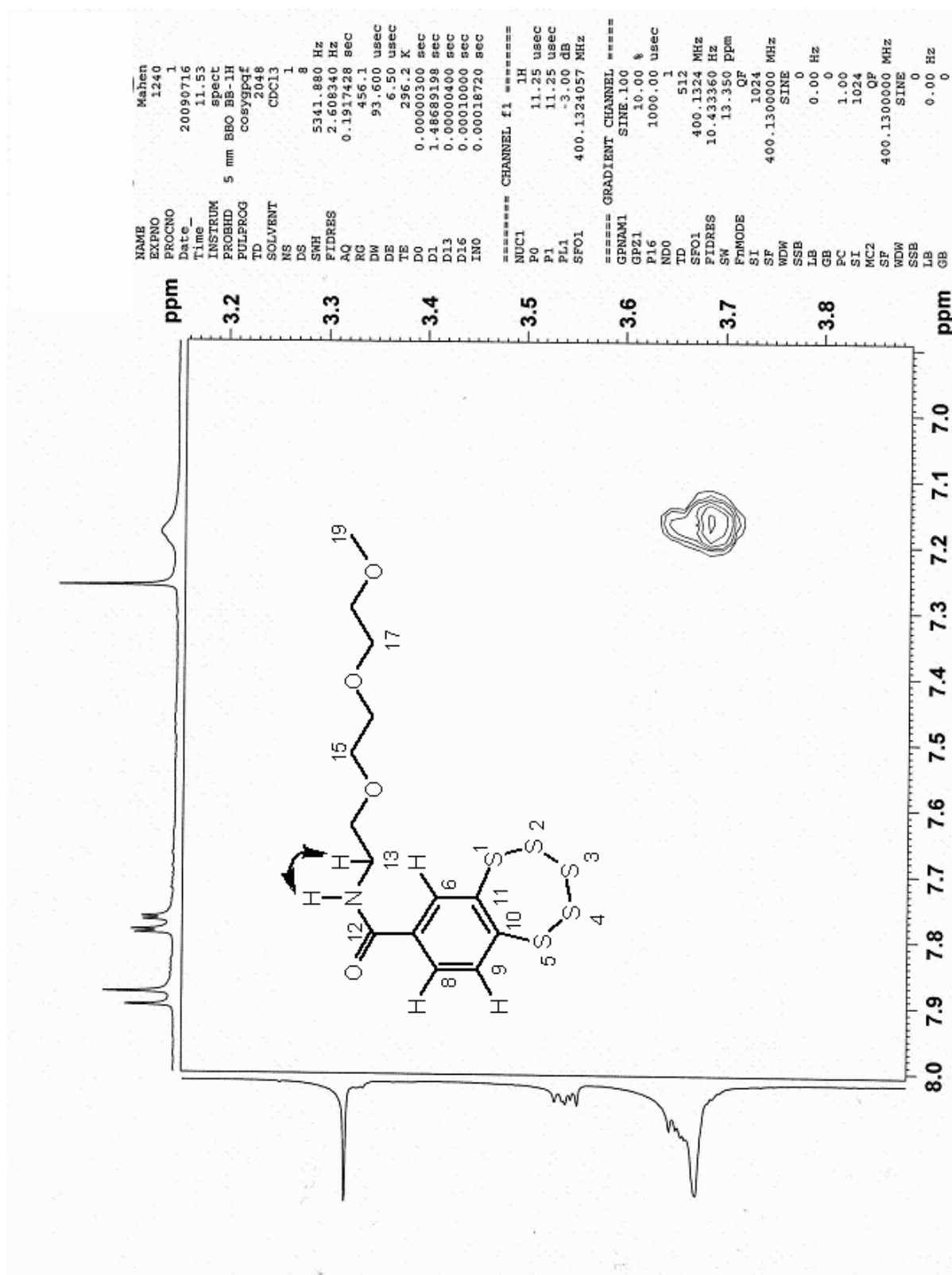
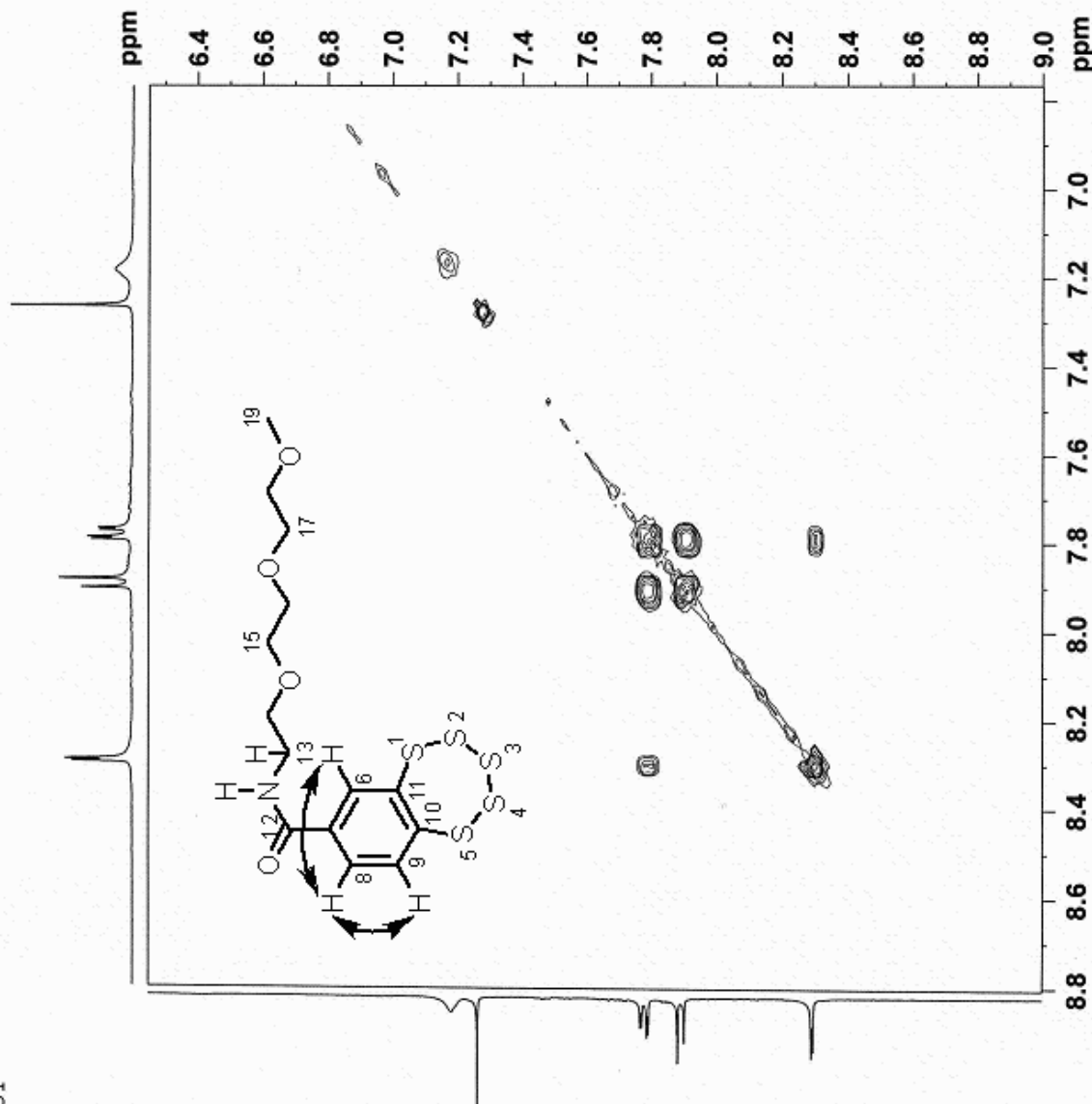


Figure 33. COSY NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDCl₃.

COSY



```

NAME          Mahan
EXPNO         1240
PROCNO        1
Date_         20090716
Time_         11.53
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       cosy3pqr
TD            2048
SOLVENT       CDCl3
NS            1
DS            8
SMH           5341.880 Hz
FIDRES        2.608340 Hz
AQ            0.1917428 sec
RG            456.1
DM            93.600 usec
DE            6.50 usec
TE            296.2 K
D0            0.00000300 sec
D1            1.48689198 sec
D13           0.00000400 sec
D16           0.00010000 sec
IN0           0.00018720 sec

===== CHANNEL f1 =====
NUC1          1H
P0            11.25 usec
PL            11.25 usec
PL1          -3.00 dB
SFO1         400.1324057 MHz

===== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPZ1          10.00 %
P16           1000.00 usec
ND0           1
TD            512
SFO1         400.1324 MHz
FIDRES        10.433360 Hz
SW            13.350 ppm
PnMODE        QF
SI            1024
SF           400.1300000 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
SI            1024
MC2           QF
SF           400.1300000 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
  
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Figure 34. COSY NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDCl₃.

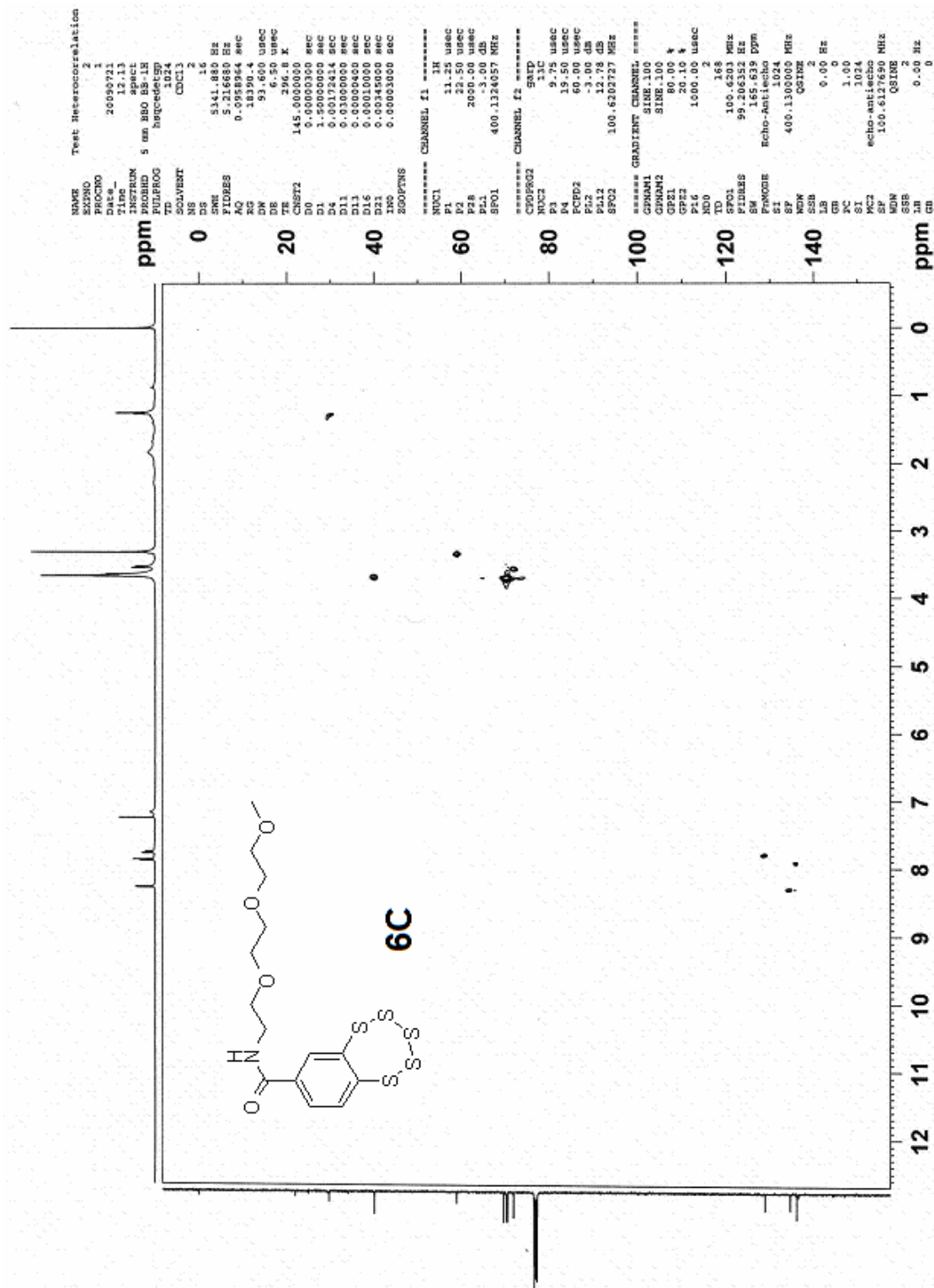


Figure 35. HSQC NMR of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide - CDC1₃.

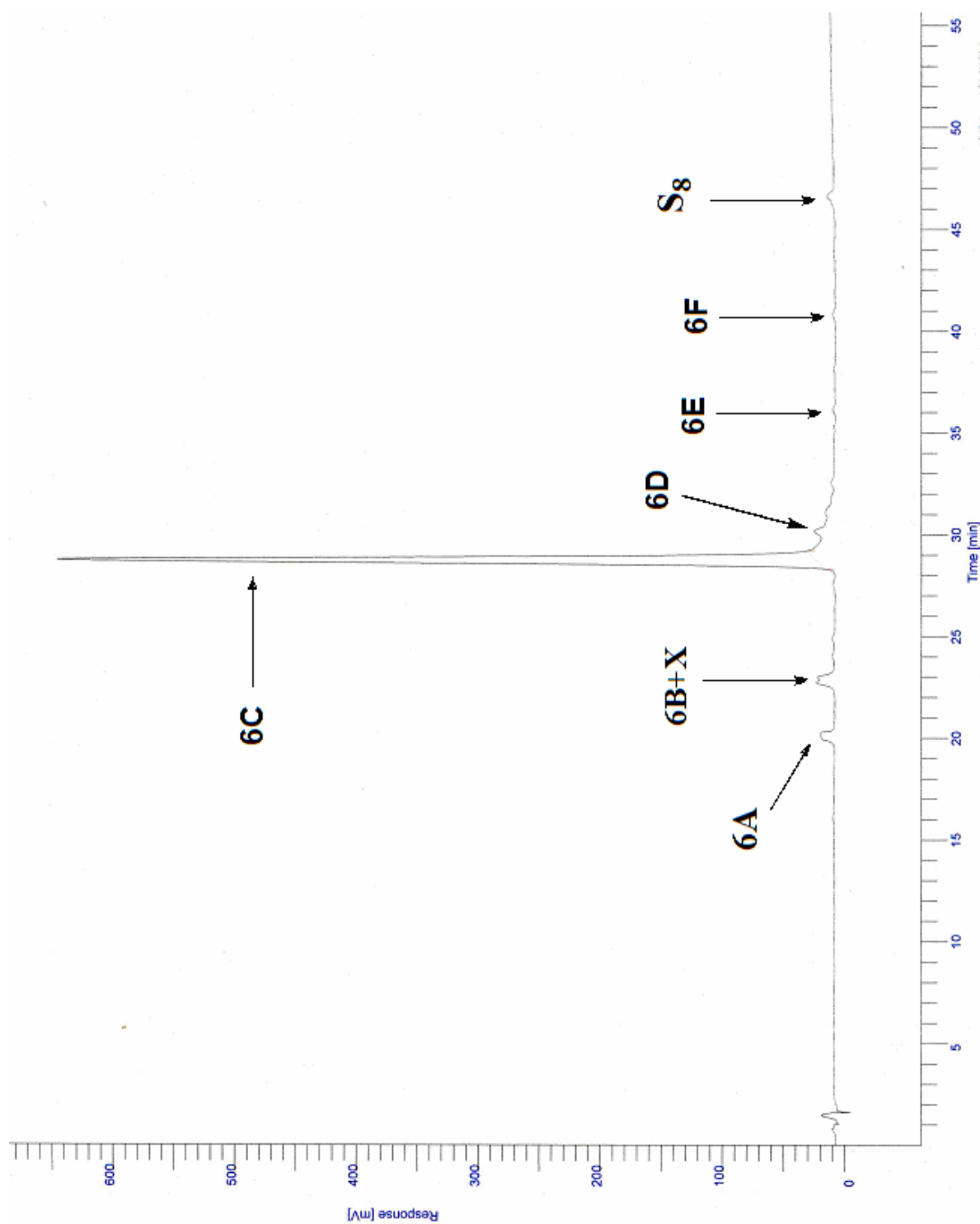
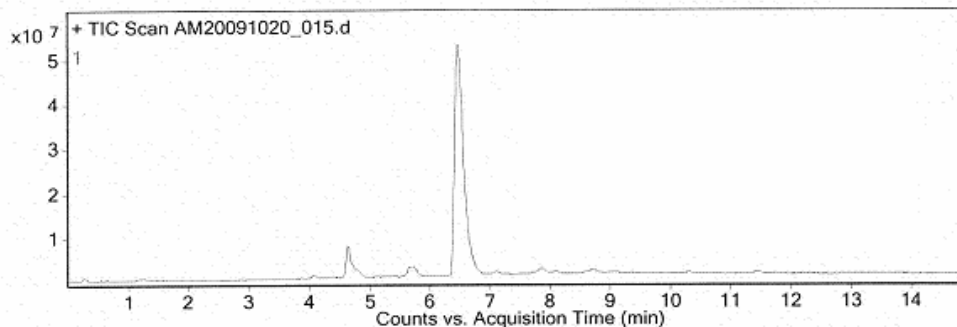


Figure 37. HPLC of N-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5]pentathiepine-7-carboxamide.

Qualitative Compound Report

Data File	AM20091020_015.d	Sample Name	Sample 1
Sample Type	Sample	Position	P1-F9
Instrument Name	Instrument 1	User Name	
Acq Method		IRM Calibration Status	Success
DA Method	Default.m	Comment	PEG-BPT

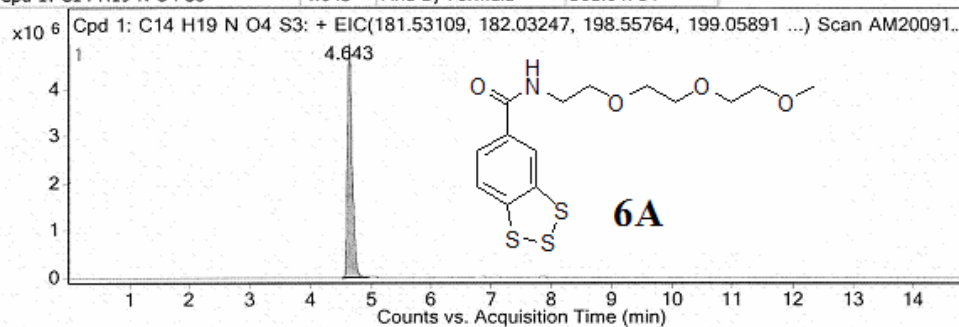
Fragmentor Voltage 175 Collision Energy 0 Ionization Mode ESI



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C14 H19 N O4 S3	4.643	361.0478	1949056	C14 H19 N O4 S3	361.0476	0.62
Cpd 2: C14 H19 N O4 S4	5.644	393.0193	129810	C14 H19 N O4 S4	393.0197	-1
Cpd 3: C14 H19 N O4 S5	6.456	424.9926	1446643	C14 H19 N O4 S5	424.9918	1.96
Cpd 4: C14 H19 N O4 S6	7.116	456.9636	171847	C14 H19 N O4 S6	456.9638	-0.6
Cpd 5: C14 H19 N O4 S7	7.822	488.9354	38501	C14 H19 N O4 S7	488.9359	-1.07
Cpd 6: C14 H19 N O4 S9	9.152	552.8788	6126	C14 H19 N O4 S9	552.88	-2.17

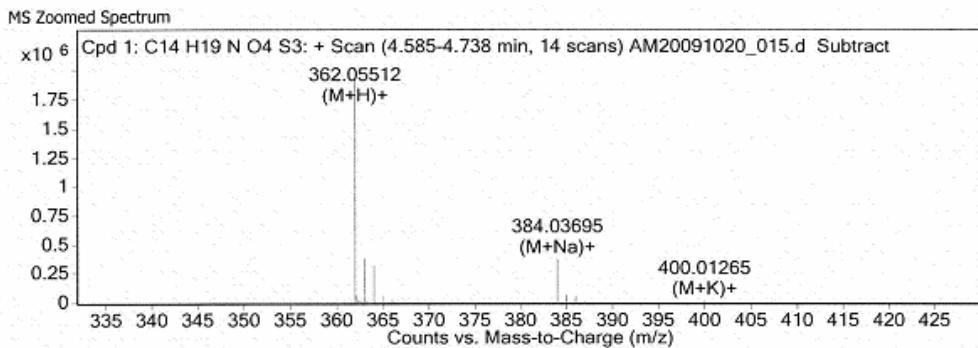
Compound Label	RT	Algorithm	Mass
Cpd 1: C14 H19 N O4 S3	4.643	Find By Formula	361.04784



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Figure 38. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[d][1,2,3]trithiole-5-carboxamide.

Qualitative Compound Report



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
362.05512	362.0549	0.62		1949056	C ₁₄ H ₂₀ N O ₄ S ₃	(M+H)+
362.22313				59205		
362.30833				21866		
363.05794	363.05765	0.79		380735	C ₁₄ H ₂₀ N O ₄ S ₃	(M+H)+
364.05233	364.0521	0.63		317984	C ₁₄ H ₂₀ N O ₄ S ₃	(M+H)+
365.05446	365.0544	0.17		50422	C ₁₄ H ₂₀ N O ₄ S ₃	(M+H)+
384.03695	384.03684	0.29	1	374101	C ₁₄ H ₁₉ N Na O ₄ S ₃	(M+Na)+
385.03935	385.0396	-0.64	1	65545	C ₁₄ H ₁₉ N Na O ₄ S ₃	(M+Na)+
386.03369	386.03404	-0.9	1	54866	C ₁₄ H ₁₉ N Na O ₄ S ₃	(M+Na)+
400.01265	400.01078	4.68	1	6284	C ₁₄ H ₁₉ K N O ₄ S ₃	(M+K)+

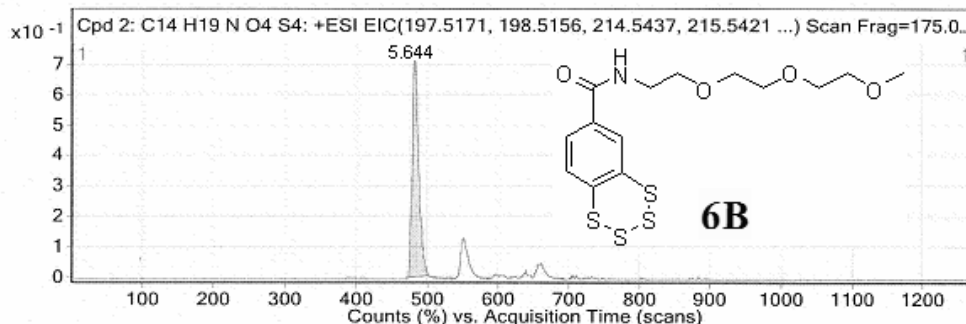


Agilent Technologies

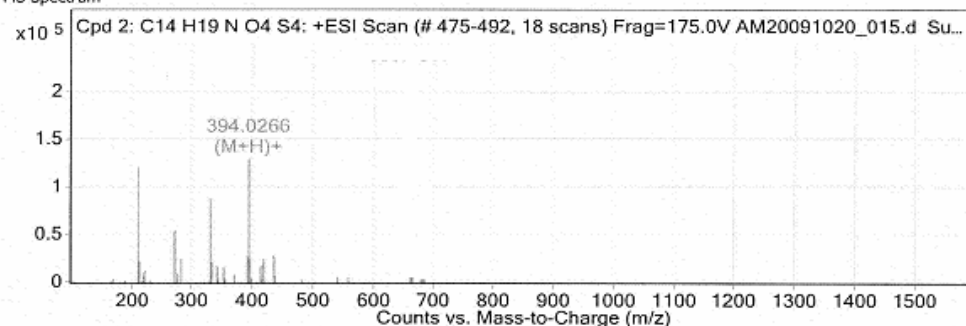
Figure 39. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[d][1,2,3]trithiole-5-carboxamide.

Qualitative Compound Report

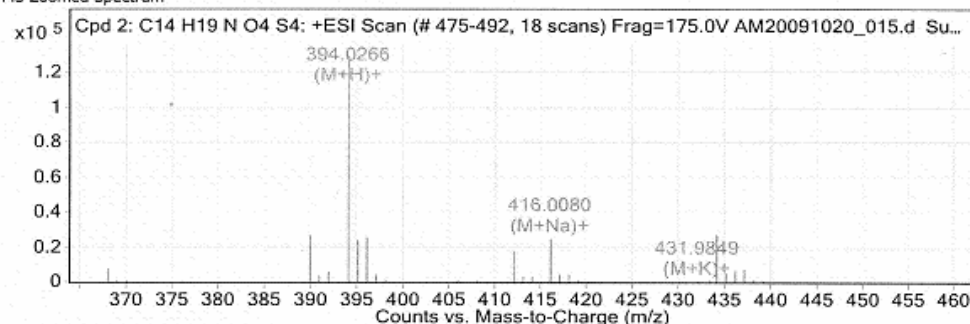
Compound Label	RT	Algorithm	Mass
Cpd 2: C14 H19 N O4 S4	5.644	Find By Formula	393.0193



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
394.0266	394.027	-0.99	1	129810	C14 H20 N O4 S4	(M+H)+
395.0293	395.0296	-0.71	1	24666	C14 H20 N O4 S4	(M+H)+
396.0233	396.0239	-1.38	1	25885	C14 H20 N O4 S4	(M+H)+
411.0528	411.0535	-1.82	1	261	C14 H23 N2 O4 S4	(M+NH4)+
416.008	416.0089	-2.24	1	25332	C14 H19 N Na O4 S4	(M+Na)+
431.9849	431.9828	4.66	1	484	C14 H19 K N O4 S4	(M+K)+

Figure 40. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[e][1,2,3,4]tetrathine-6-carboxamide

Qualitative Compound Report

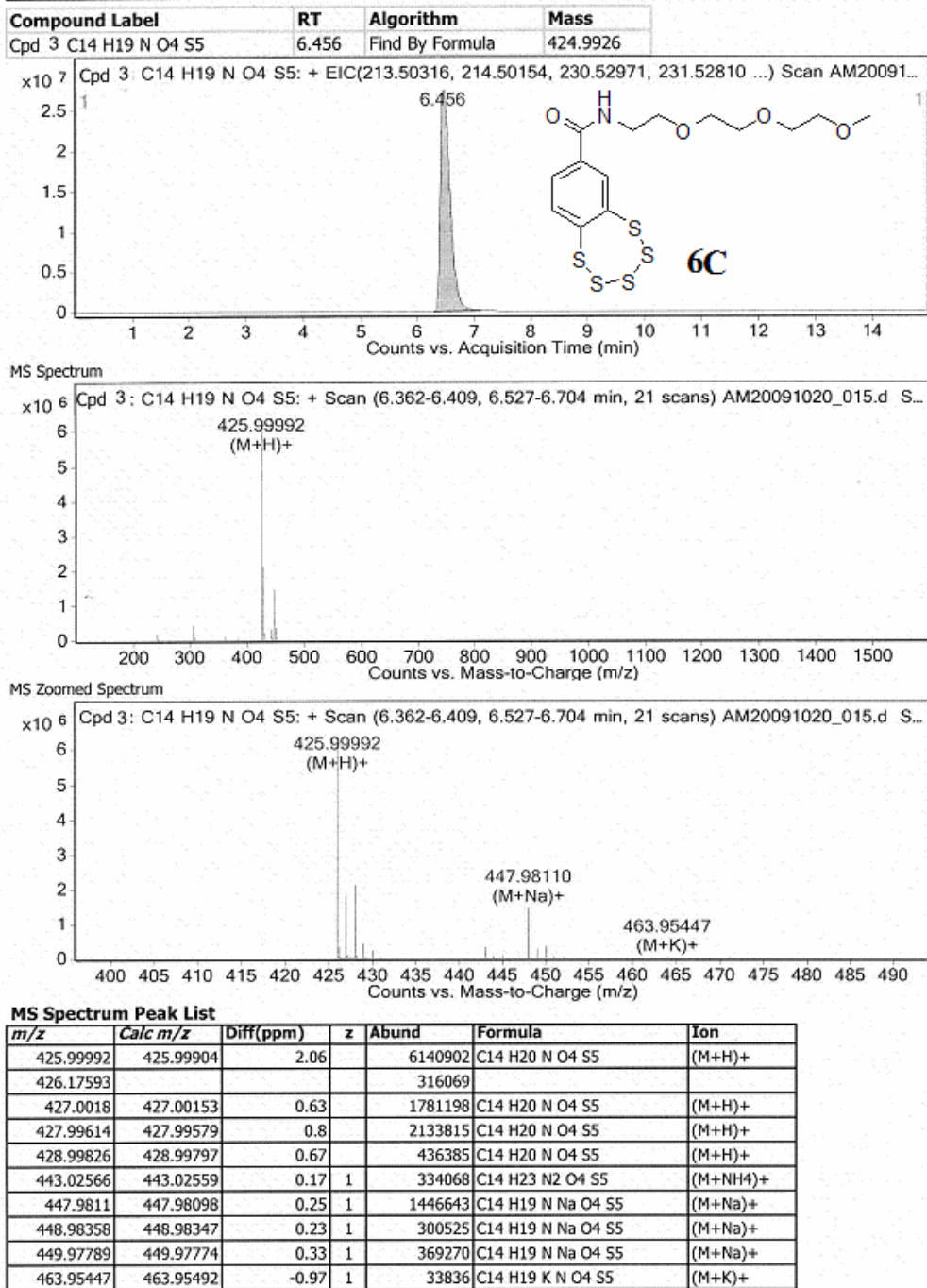


Figure 41. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[f][1,2,3,4,5] pentathiepine-7-carboxamide

Qualitative Compound Report

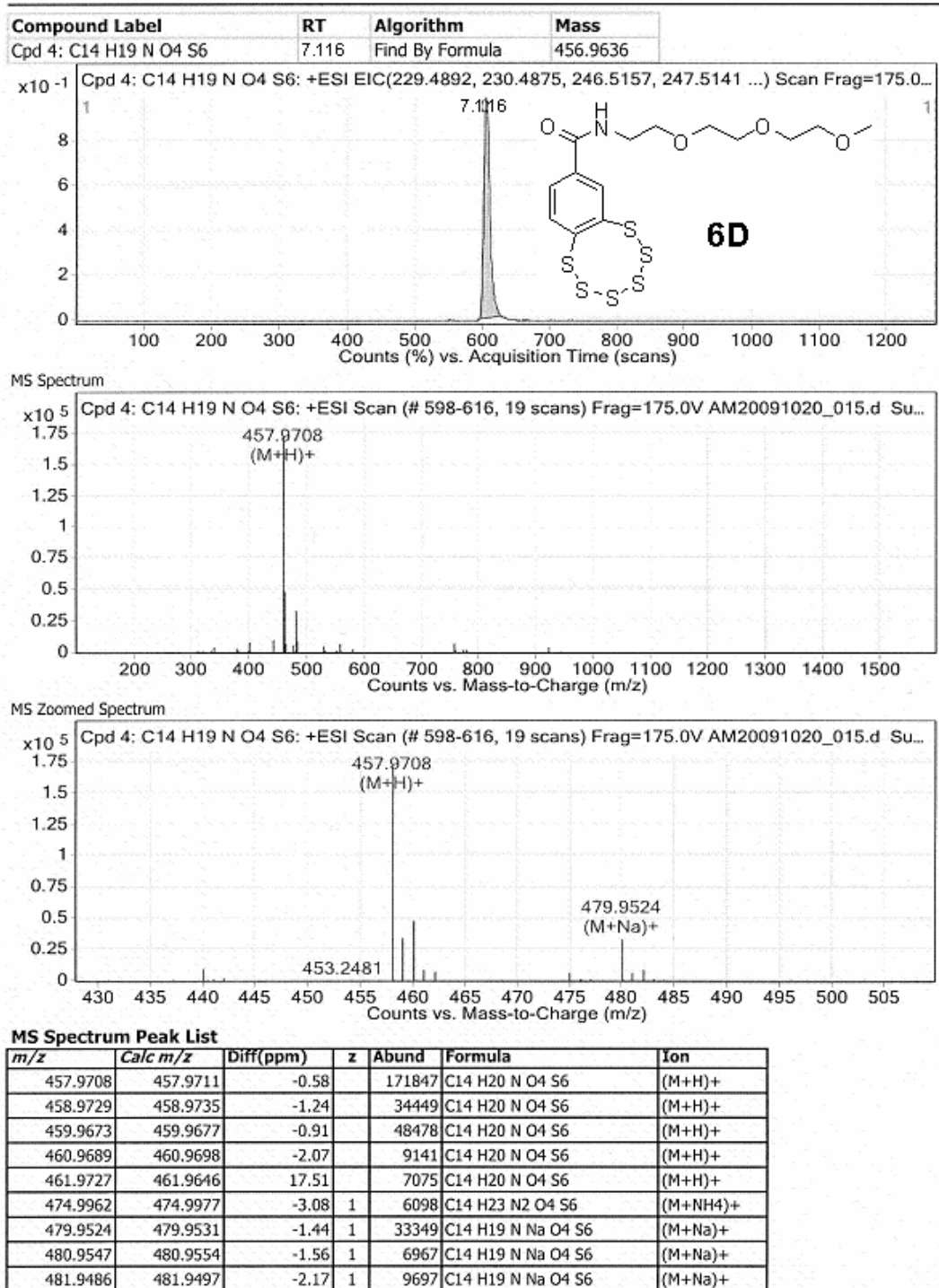


Figure 42. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[g][1,2,3,4,5,6] hexathiocine-8-carboxamide

Qualitative Compound Report

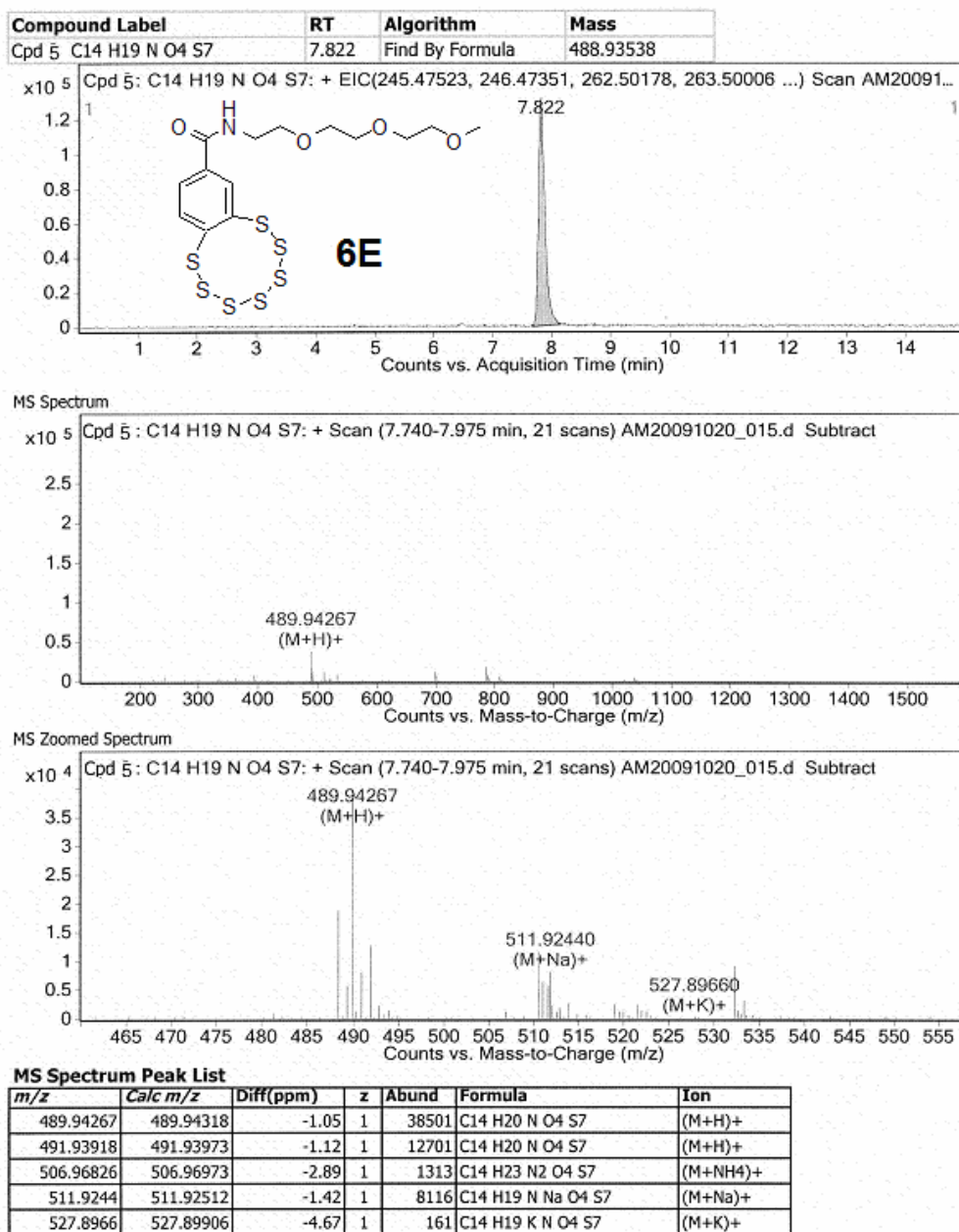
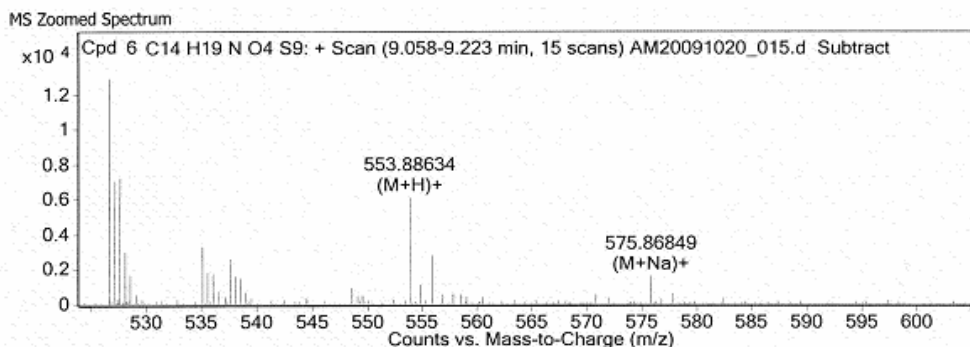
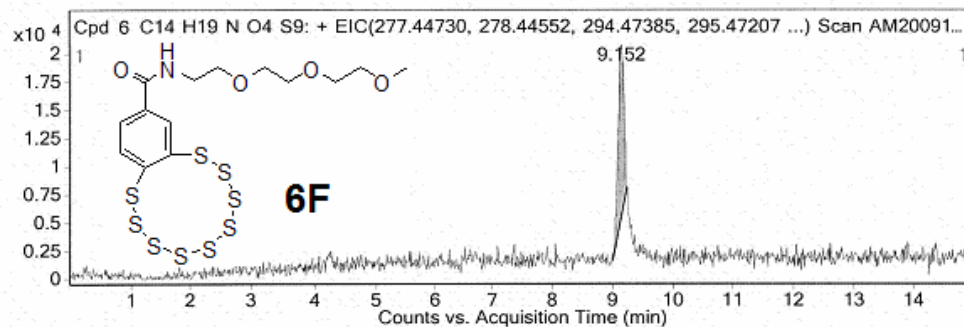


Figure 43. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[h][1,2,3,4,5,6,7]heptathionine-9-carboxamide.

Qualitative Compound Report



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Formula	Ion
526.59251				12948		
527.09367				7088		
527.59195				7242		
528.09262				3021		
528.59104				1677		
553.88634	553.88732	-1.77	1	6126	C14 H20 N O4 S9	(M+H) ⁺
554.87626	554.88938	-23.65	1	1144	C14 H20 N O4 S9	(M+H) ⁺
555.88118	555.88376	-4.63	1	2828	C14 H20 N O4 S9	(M+H) ⁺
575.86849	575.86927	-1.34	1	1619	C14 H19 N Na O4 S9	(M+Na) ⁺
577.86307	577.8657	-4.55	1	640	C14 H19 N Na O4 S9	(M+Na) ⁺

--- End Of Report ---

Figure 44. HRMS of N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzo[j][1,2,3,4,5,6,7,8,9]nonathiacycloundecine-11-carboxamide.

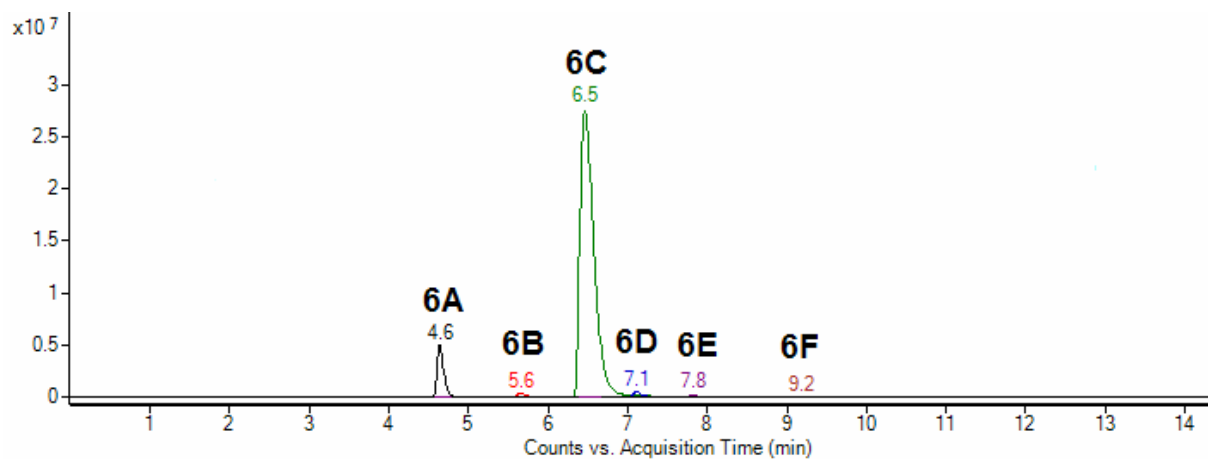
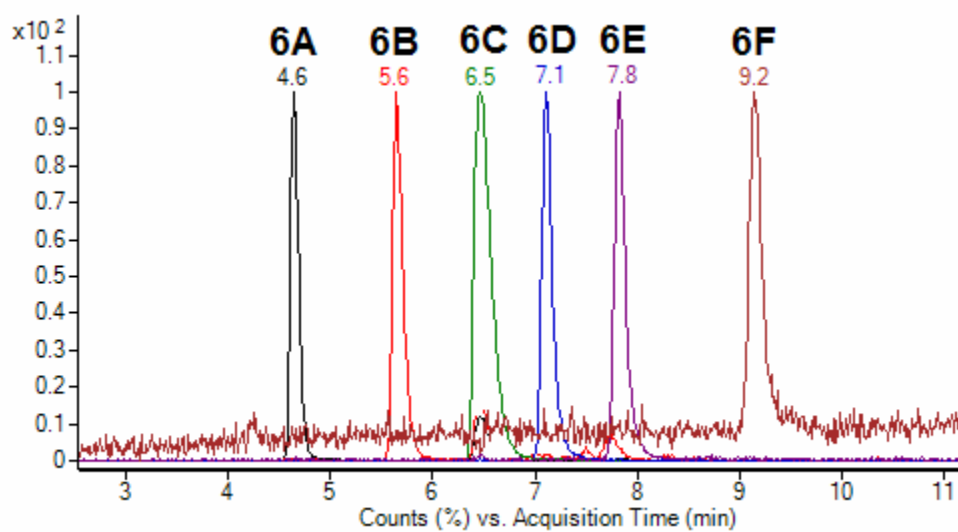
A**B**

Figure 45. (A) LCMS extracted ion chromatograms of **6A-F**. (B) LCMS extracted ion normalized chromatograms (overlaid) of **6A-F**.

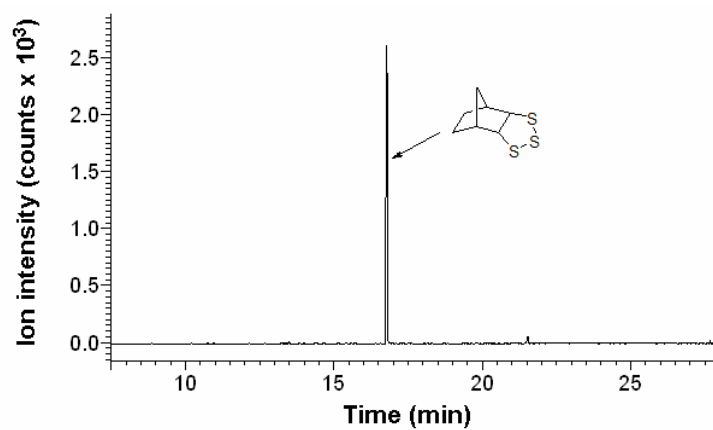
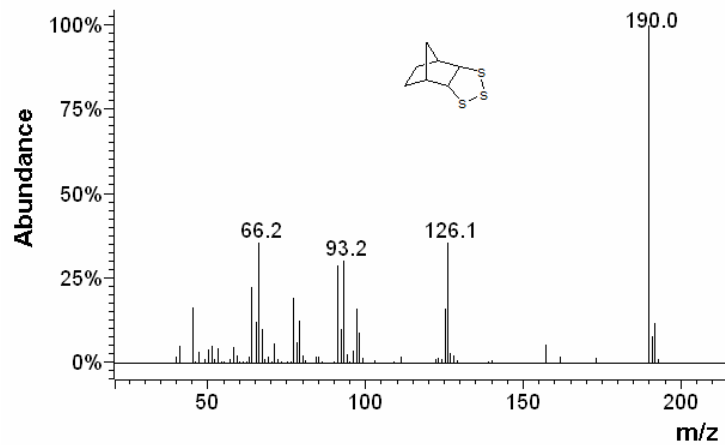
A**B**

Figure 46. (A) Extracted ion chromatogram of norbornenetritiolane **17** formed in the reaction of **6A-F** and norbornene in the presence of ethanethiol, Rt 16.75 min. (B) MS spectrum of norbornenetritiolane **17**, Rt 16.75 min.