Electronic Supplementary Material (ESI) for RSC Advances.

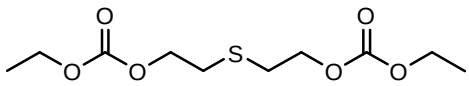
Supplementary Information

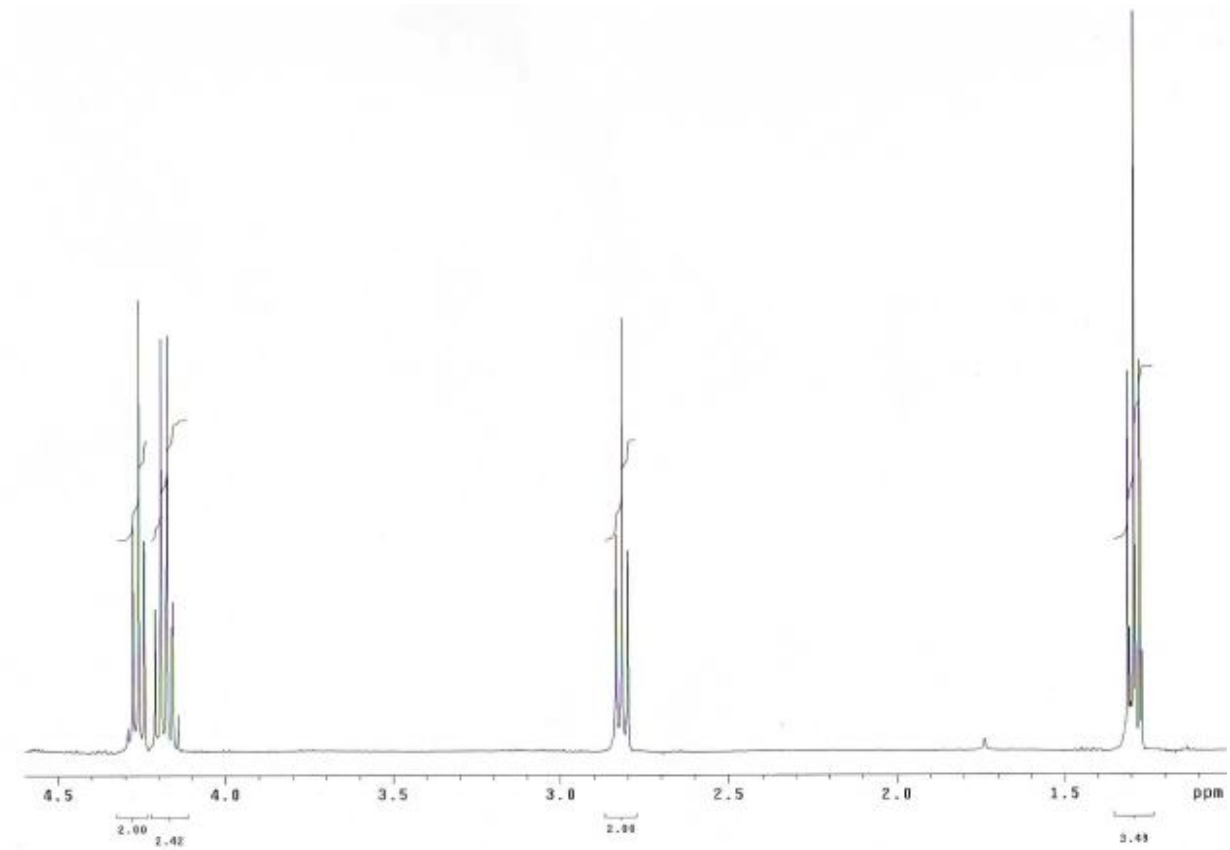
Behaviour of iprit carbonate analogues in solventless reactions

Fabio Aricò, Serena Evaristo, Pietro Tundo

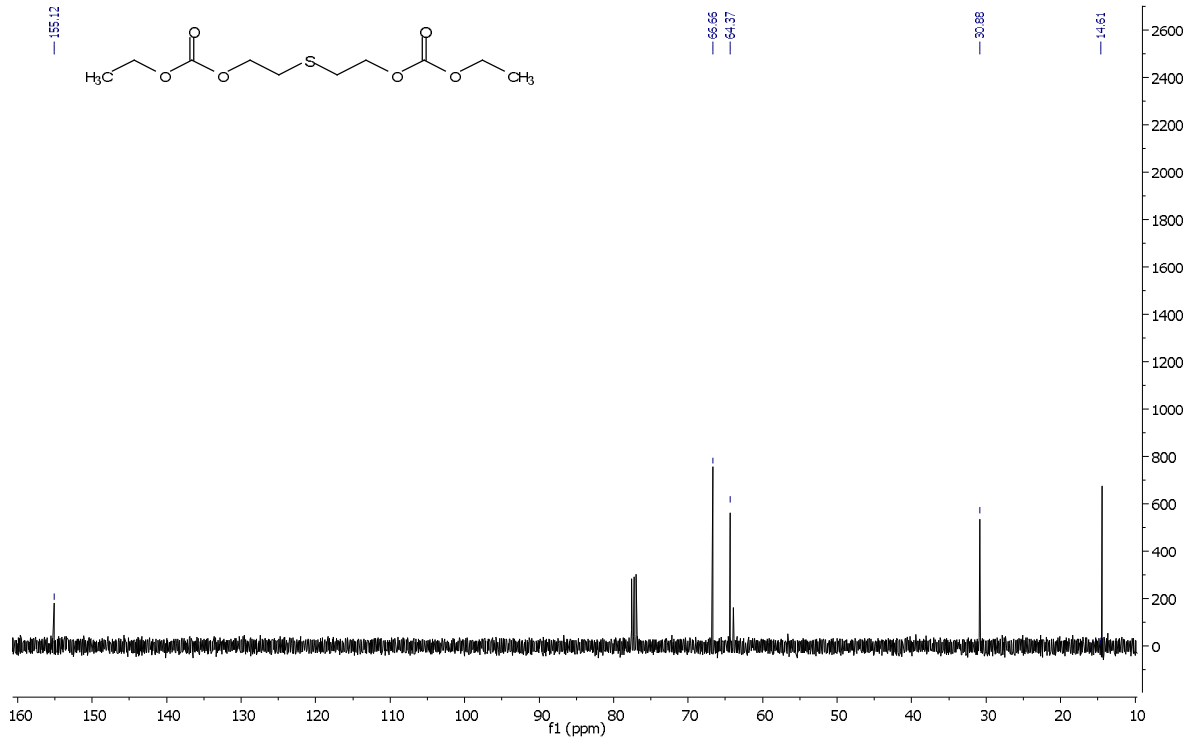
SUPPORTING INFORMATION

^{1}H NMR spectrum of Bis-(2-ethylcarbonate)ethyl sulfide **7**

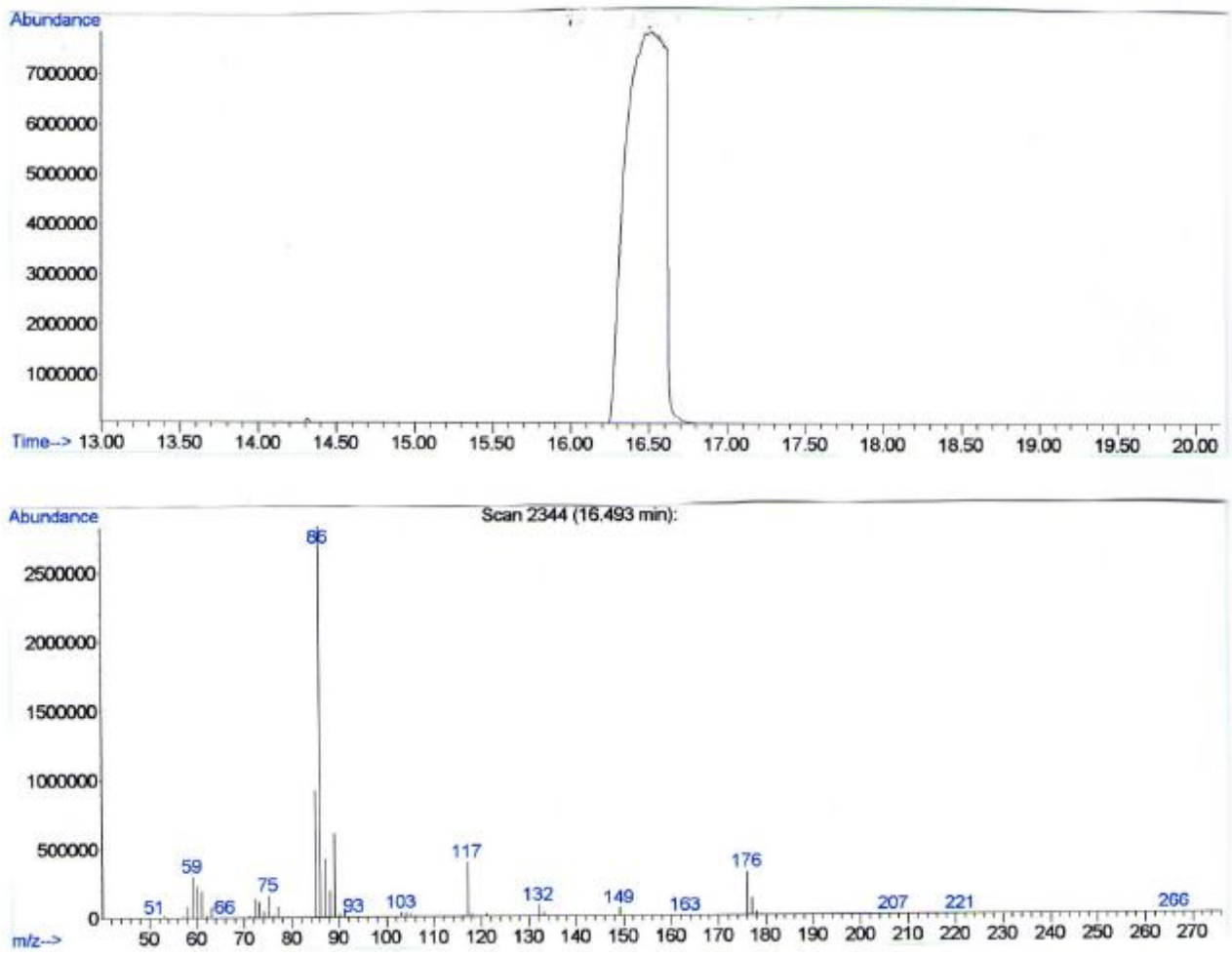




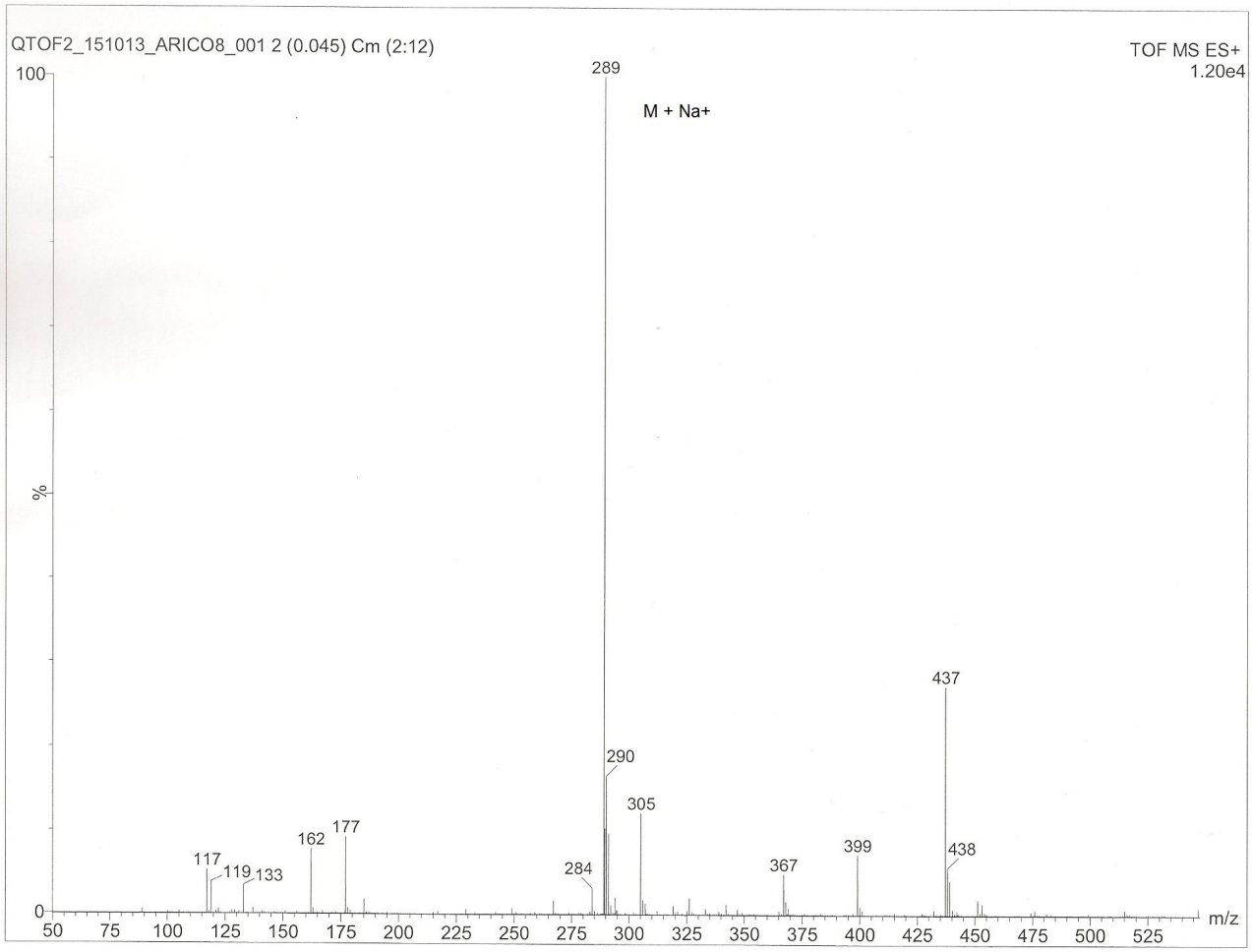
^{13}C NMR spectrum of Bis-(2-ethylcarbonate)ethyl sulfide **7**



GC-MS spectrum of Bis-(2-ethylcarbonate)ethyl sulfide **7**



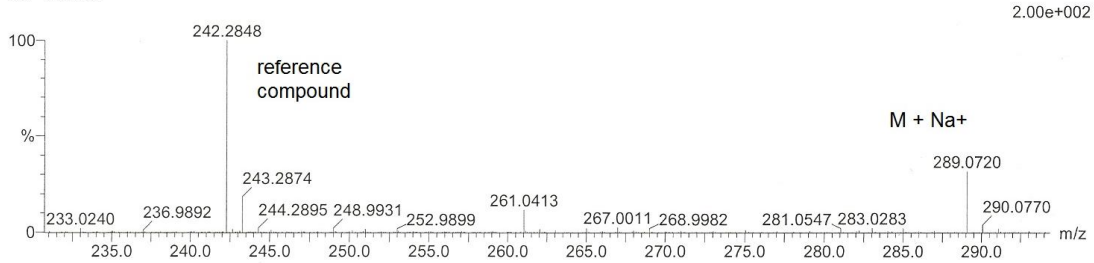
HRMS analysis of Bis-(2-ethylcarbonate)ethyl sulfide **7**



Elemental Composition Report **Page 1**

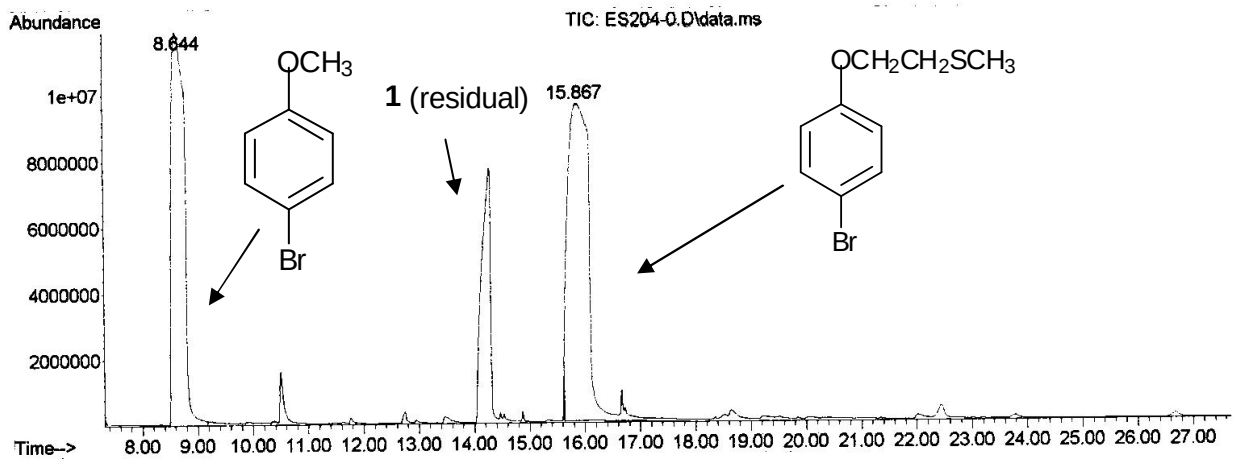
Single Mass Analysis
Tolerance = 100.0 mDa / DBE: min = -5.0, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

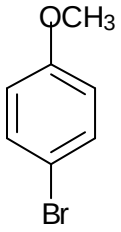
Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 2 results within limits (up to 40 best isotopic matches for each mass)
Elements Used:
C: 0-50 H: 0-100 O: 6-6 Na: 1-1 S: 1-1
QTOF2_151013_ARICO8_002 14 (0.270) AM (Cen,6, 80.00, Ht,9600.0,242.28,0.60); Sm (SG, 10x5.00); Cm (11:14)
TOF MS ES+



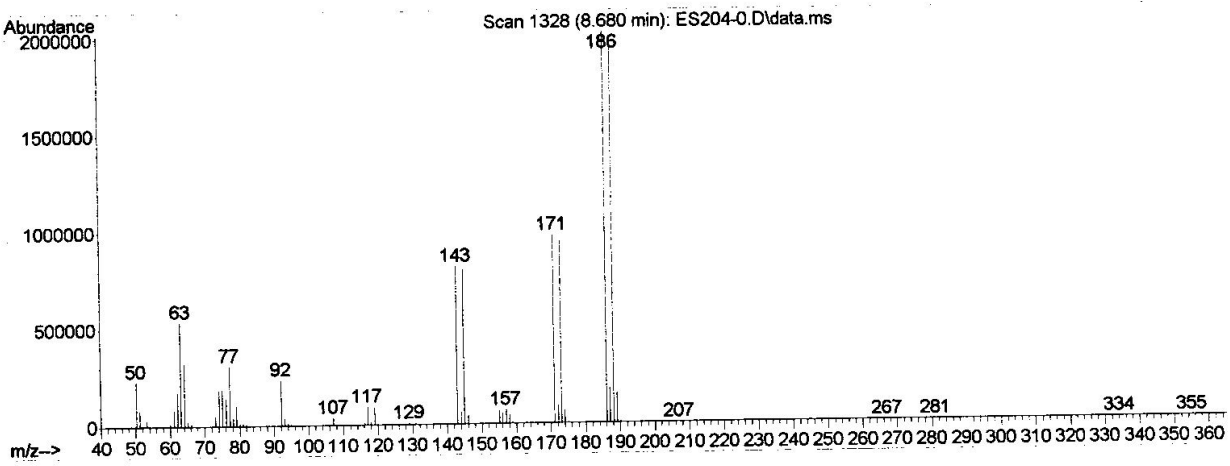
Minimum:				-5.0		
Maximum:		100.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
289.0720	289.0722	-0.2	-0.7	1.5	0.0	C10 H18 O6 Na S
	288.9783	93.7	324.1	8.5	20.8	C11 H6 O6 Na S

GC-MS spectrum of the reaction of 4-bromophenol with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **12** (entry 1, Table 2)





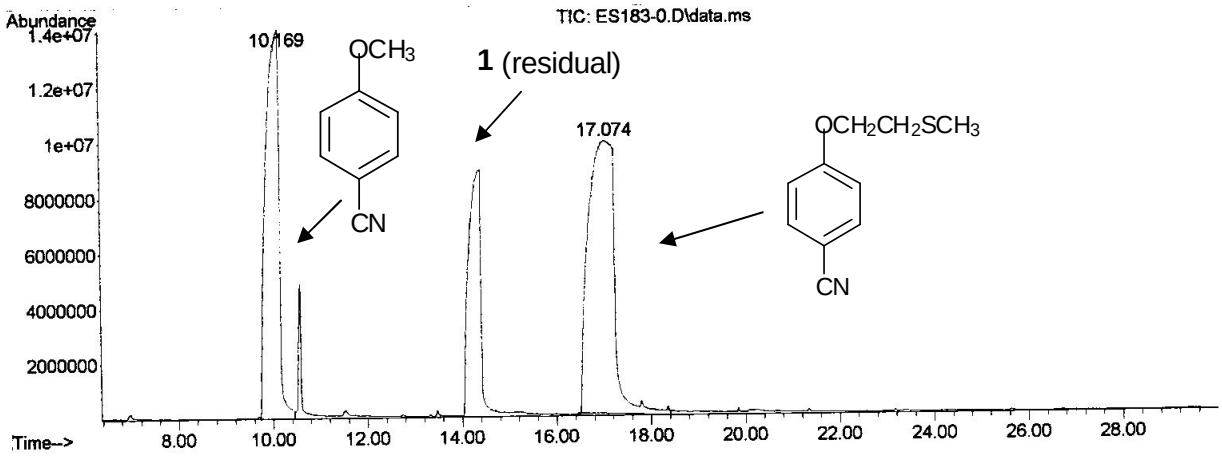
Chemical Formula: C_7H_7BrO
Exact Mass: 185,97
Molecular Weight: 187,03

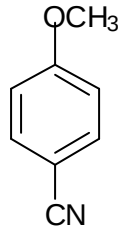


Signal : TIC: ES204-0.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	8.646	1262	1322	1414	M8	11888011	1943714622	74.00%	42.530%
2	15.867	2541	2584	2997	M	9654613	2626478485	100.00%	57.470%

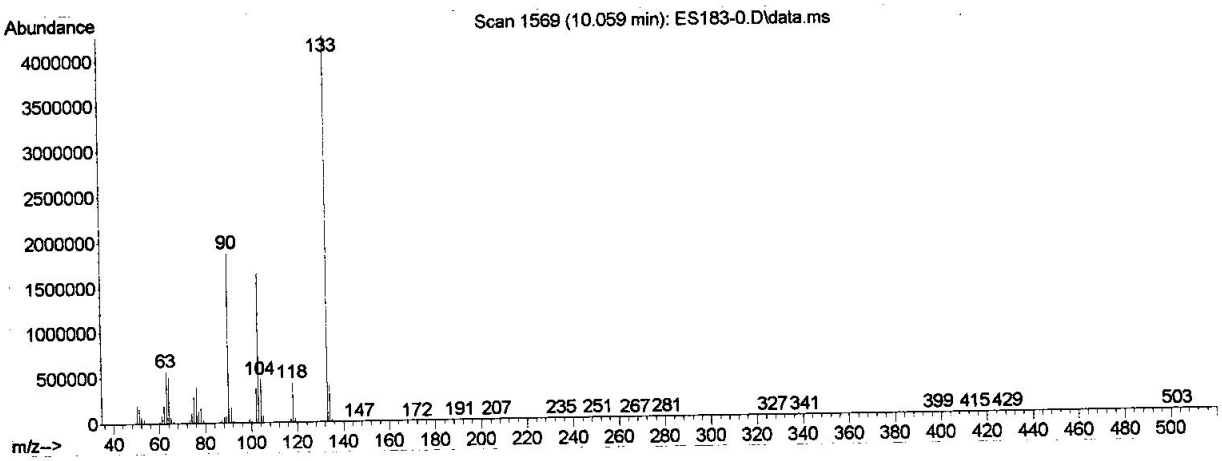
GC-MS spectrum of the reaction of *p*-cyanophenol with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **13** (entry 2, Table 2)





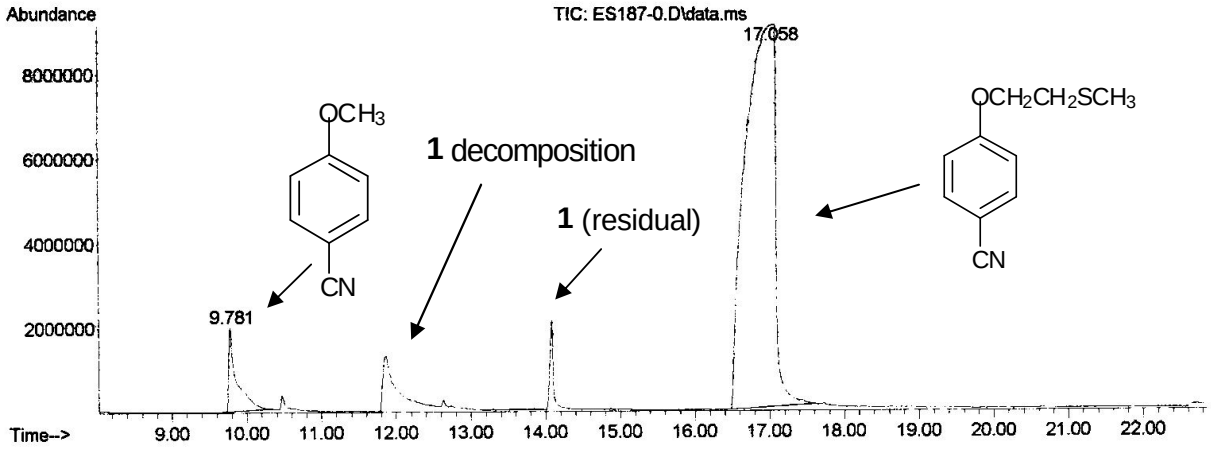
Chemical Formula: C_8H_7NO
Exact Mass: 133,05
Molecular Weight: 133,15

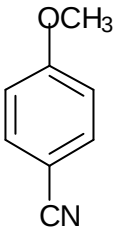
1-bromo-4-methoxybenzene



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	10.168	1511	1588	1625	M3	14073898	2709078218	70.69%	41.414%
2	17.074	2669	2795	3101	M	9990055	3832401815	100.00%	58.586%

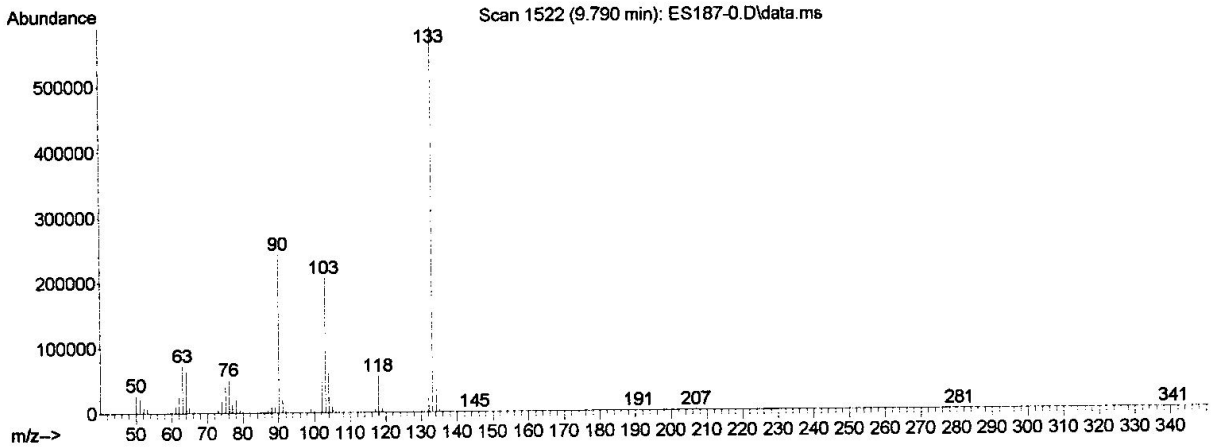
GC-MS spectrum of the reaction of *p*-cyanophenol with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **13** (entry 3, Table 2)





Chemical Formula: C_8H_7NO
Exact Mass: 133,05
Molecular Weight: 133,15

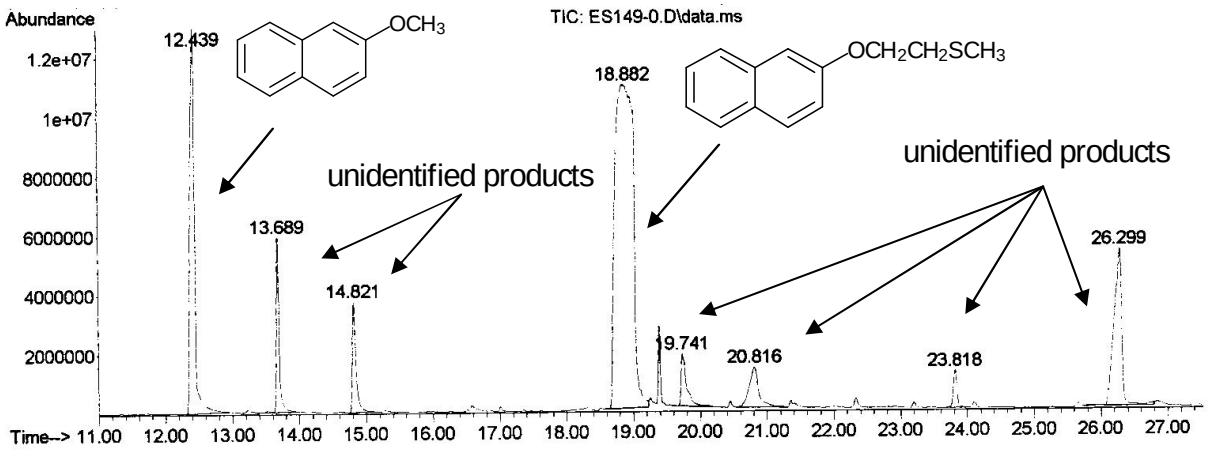
1-bromo-4-methoxybenzene

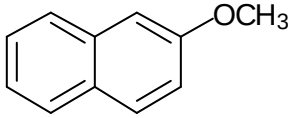


Signal : TIC: ES187-0.D\data.ms

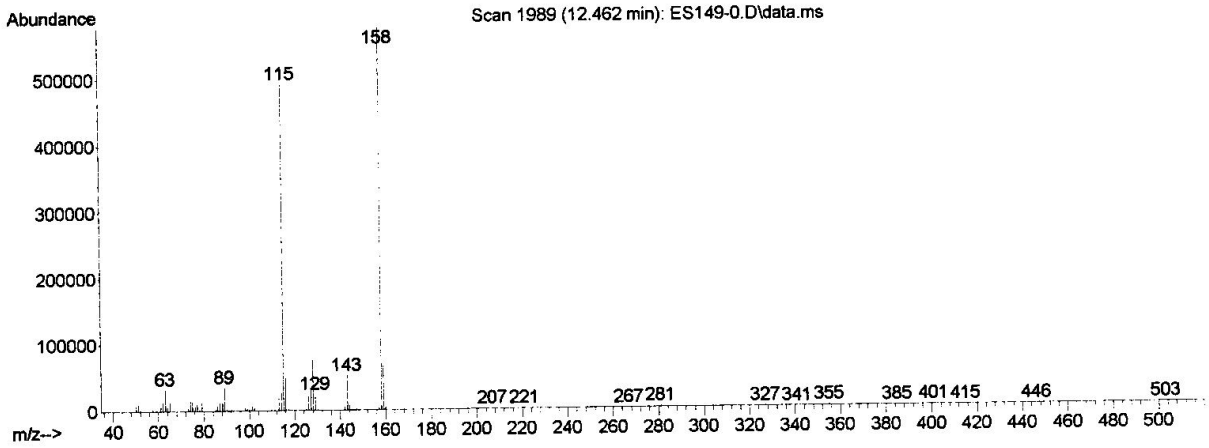
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	9.784	1509	1521	1610	BB	1976464	149465356	5.89%	5.567%
2	17.057	2685	2792	2887	BB	9057850	2535562192	100.00%	94.433%

GC-MS spectrum of the reaction of *β*-naphtol with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **14** (entry 4, Table 2)



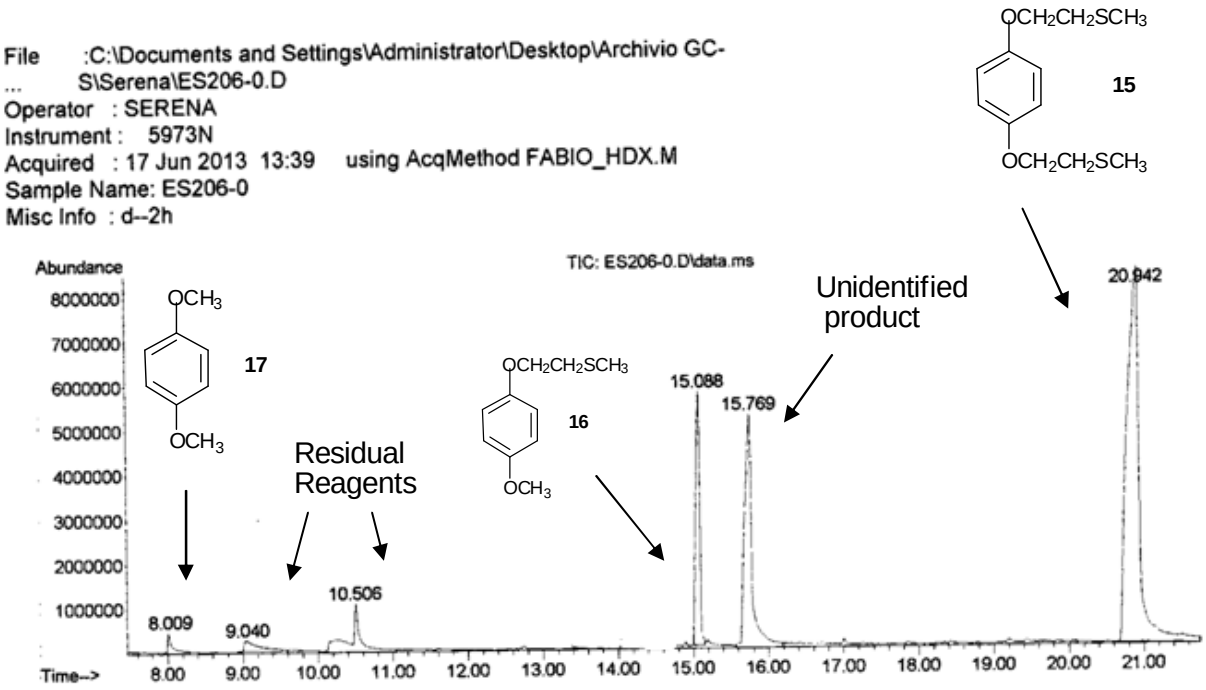


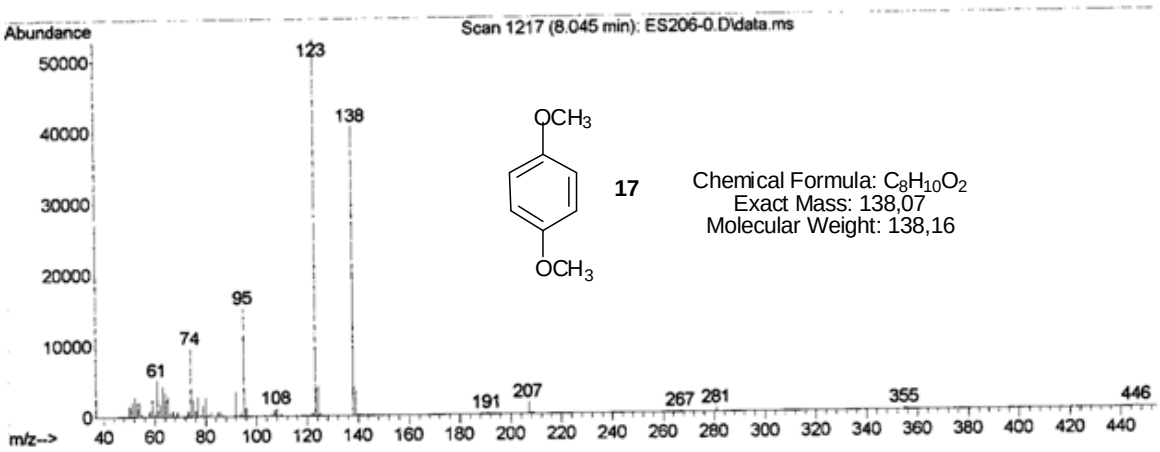
Chemical Formula: $C_{11}H_{10}O$
Exact Mass: 158,07
Molecular Weight: 158,20



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	12.439	1957	1985	2072	BB	13170727	639533690	31.04%	17.105%
2	13.692	2159	2204	2254	BB	5924094	171629765	8.33%	4.590%
3	14.820	2387	2401	2457	BB	3639239	141678671	6.88%	3.789%
4	18.882	3056	3111	3170	VV 3	10930743	2060610972	100.00%	55.114%
5	19.740	3249	3261	3344	BB 2	1758140	102890625	4.99%	2.752%
6	20.816	3402	3449	3534	BV	1348183	135322582	6.57%	3.619%
7	23.820	3945	3974	4006	BBA2	1267098	50139413	2.43%	1.341%
8	26.298	4308	4407	4493	M	5346086	437017659	21.21%	11.689%

GC-MS spectrum of the reaction of hydroquinone with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **15, 16, 17** (entry 5, Table 2)





Signal : TIC: ES206-0.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	8.010	1194	1211	1286	M	474178	27003383	2.73%	1.722%
2	15.088	2389	2448	2510	M	5770193	240304759	24.31%	15.328%
3	15.769	2542	2567	2610	M	5129329	312086566	31.57%	19.906%
4	20.942	3409	3471	3699	M2	8446973	988400978	100.00%	63.044%

GC-MS spectrum of the reaction of biphenyl-2,2'-diol with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **18**, **19**, **20** (entry 6, Table 2)

File :C:\Documents and Settings\Administrator\Desktop\Archivio GC-...S\Serena\ES205-0.D
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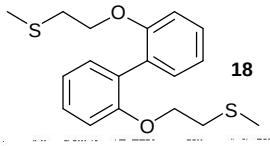
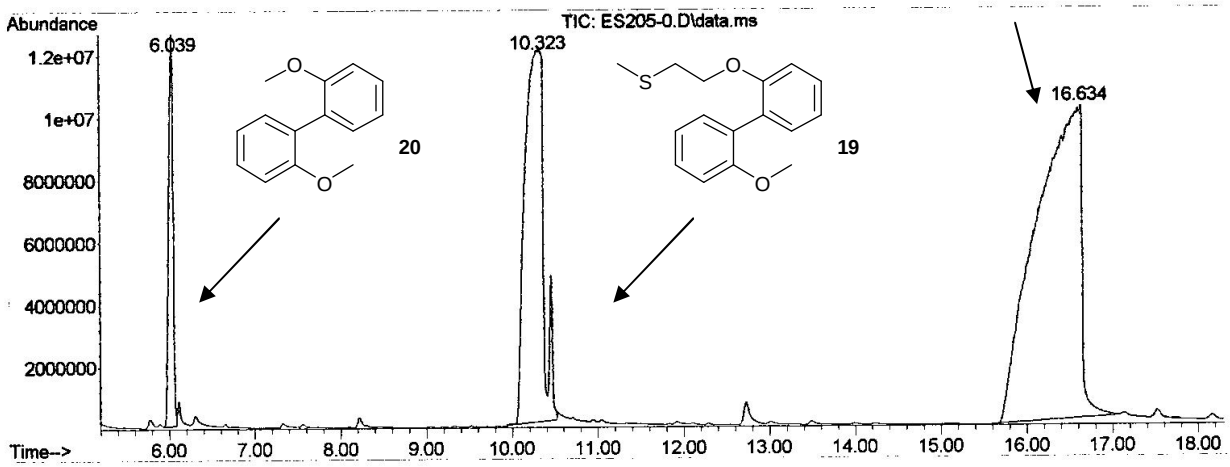
Instrument : 5973N
Acquired : 13 Jun 2013 13:03 using AcqMethod FABIO_HDX.M
Sample Name: ES205-0
Misc Info : d=2h

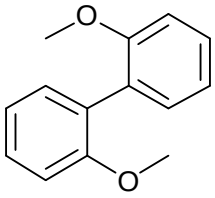


18



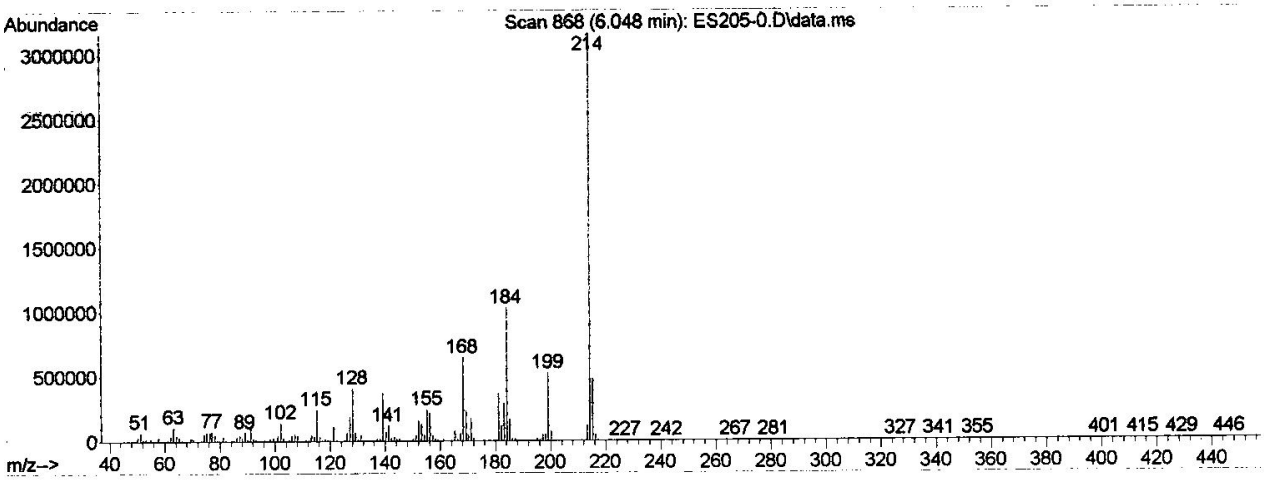
20

19



20

Chemical Formula: $C_{14}H_{14}O_2$
Exact Mass: 214,10
Molecular Weight: 214,26



Signal : TIC: ES205-0.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	6.042	821	867	935	M	12722215	523990521	13.68%	8.654%
2	10.322	1547	1615	1624	M2	12172956	1701582162	44.44%	28.103%
3	16.645	2526	2720	2860	M	10251764	3829332278	100.00%	63.243%

GC-MS spectrum of the reaction of phenylsulfonyl)acetonitrile with 2-(methylthio)ethyl methyl carbonate **1** – Product identification **21**, **22**, **23** (entry 7, Table 2)

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S\Serena\ES189-0.D
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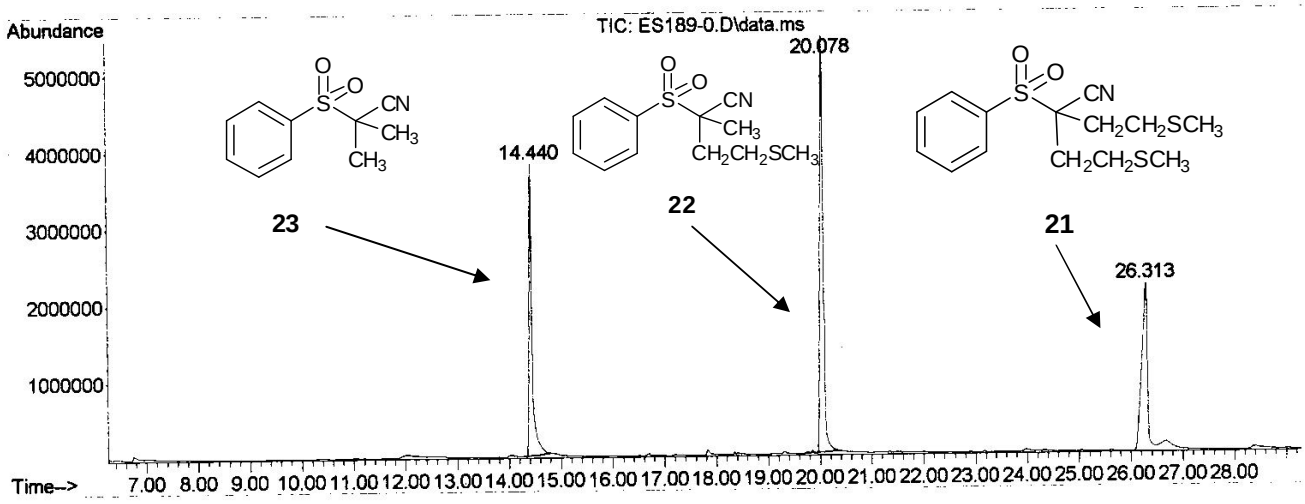
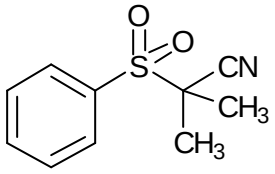
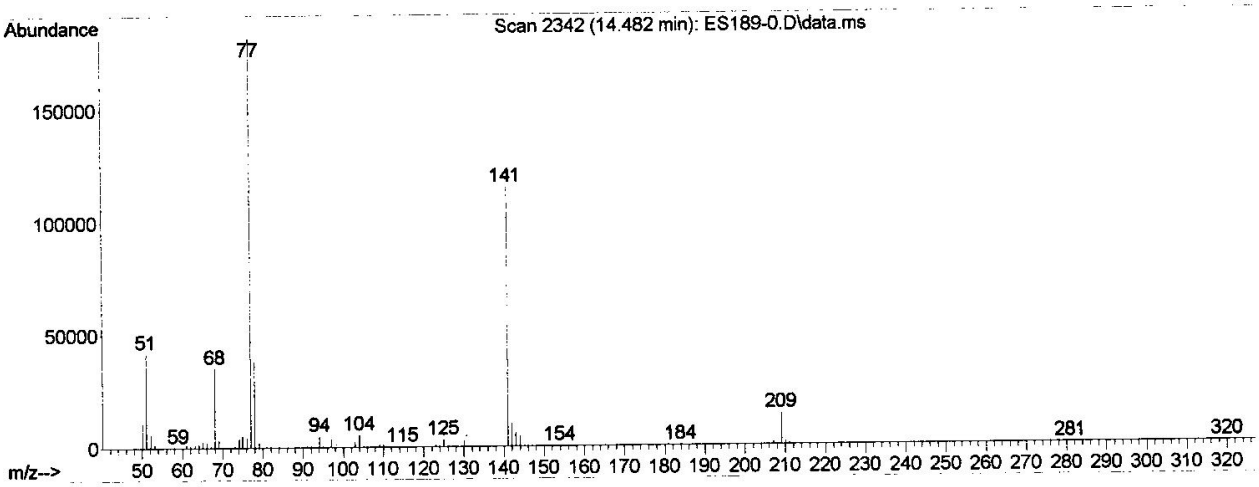
Instrument : 5973N
Acquired : 3 Jun ... 15:52 using AcqMethod FABIO_HDX.M
Sample Name: ES189-0
Misc Info : d=5h



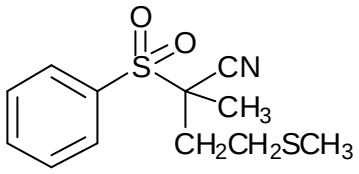


Chemical Formula: $C_{10}H_{11}NO_2S$
Exact Mass: 209,05
Molecular Weight: 209,26

23

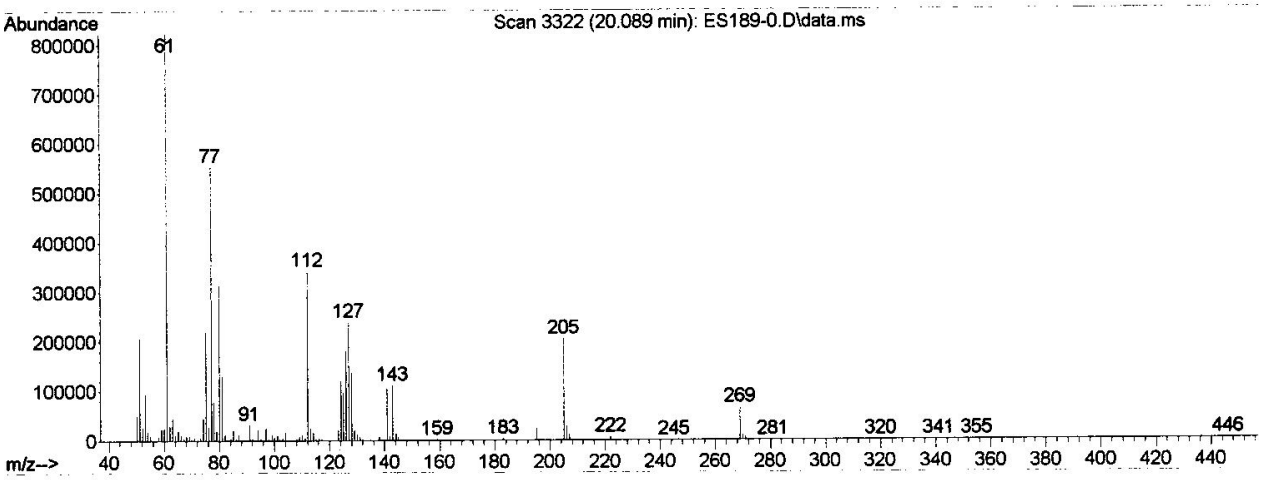


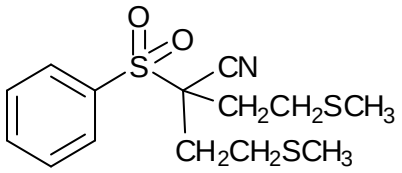
GC-MS spectrum of the reaction of phenylsulfonyl)acetonitrile with 2-(methylthio)ethyl methyl carbonate **1**



Chemical Formula: $C_{12}H_{15}NO_2S_2$
Exact Mass: 269,05
Molecular Weight: 269,38

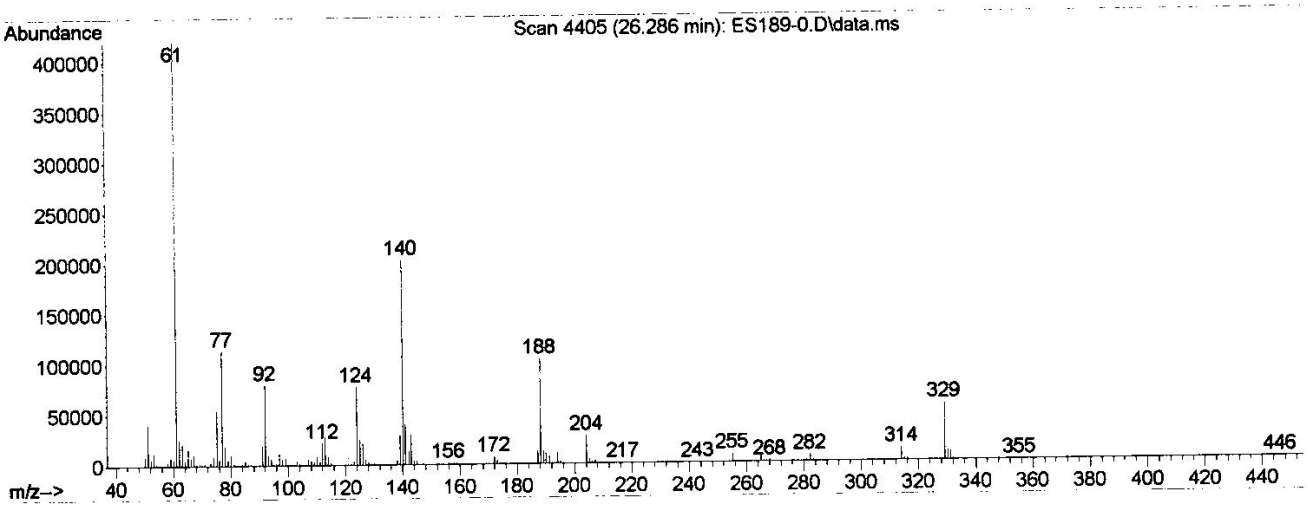
22





Chemical Formula: $C_{14}H_{19}NO_2S_3$
Exact Mass: 329,06
Molecular Weight: 329,50

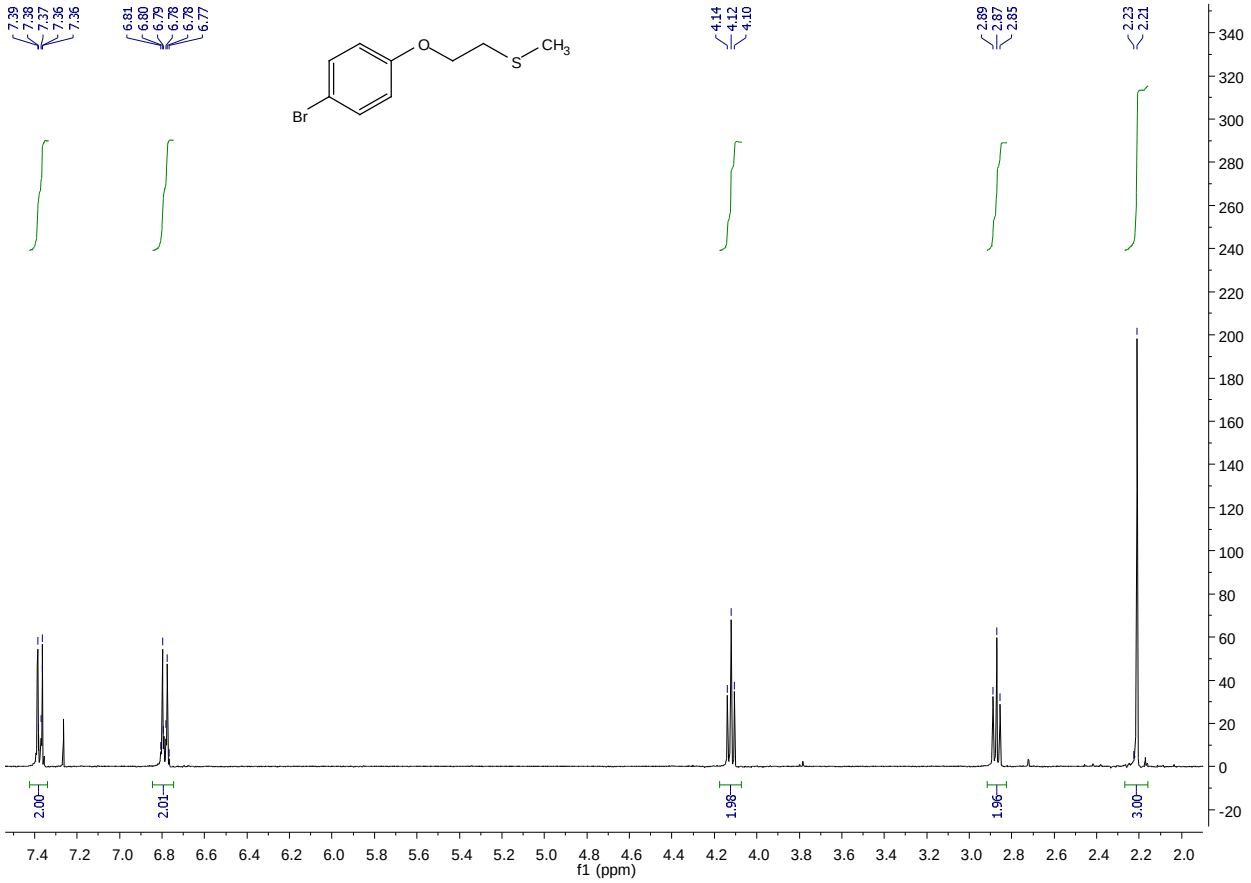
21



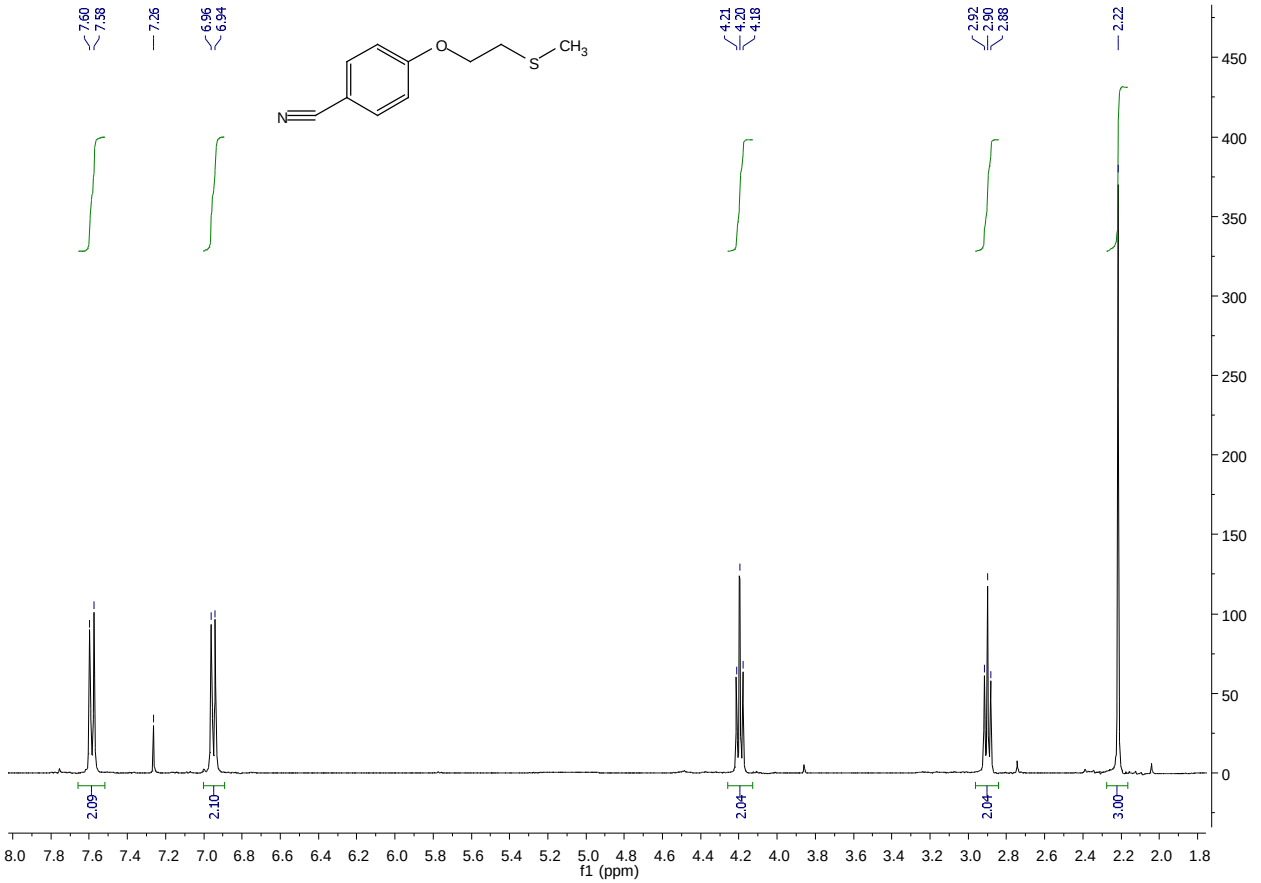
Signal : TIC: ES189-0.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	14.442	2254	2335	2439	M	3800142	163957400	58.84%	25.532%
2	20.084	3240	3321	3445	M	5486738	278666335	100.00%	43.395%
3	26.315	4321	4410	4568	M	2192638	199536475	71.60%	31.073%

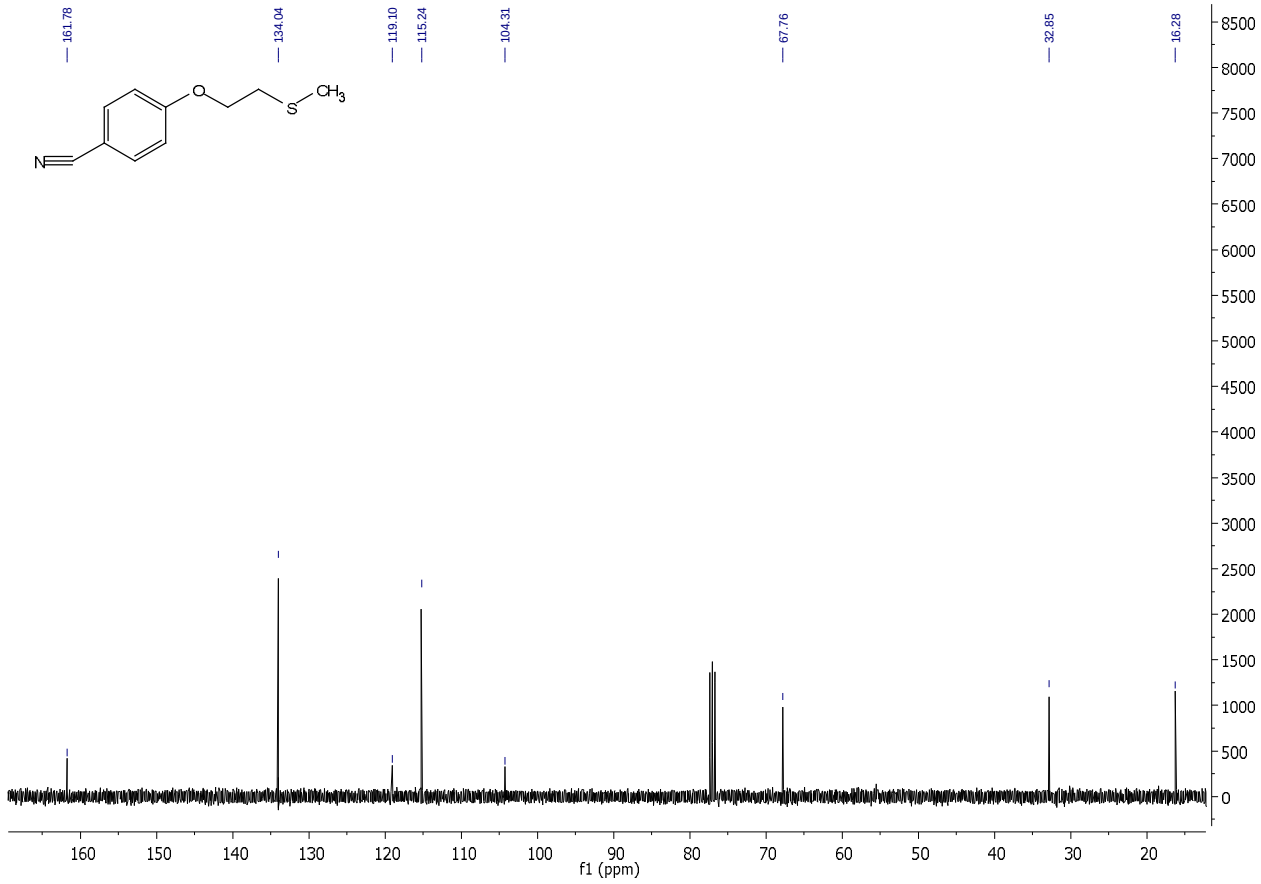
^{1}H NMR spectrum of methyl 2-(4-bromophenoxy)ethyl sulfide **12**



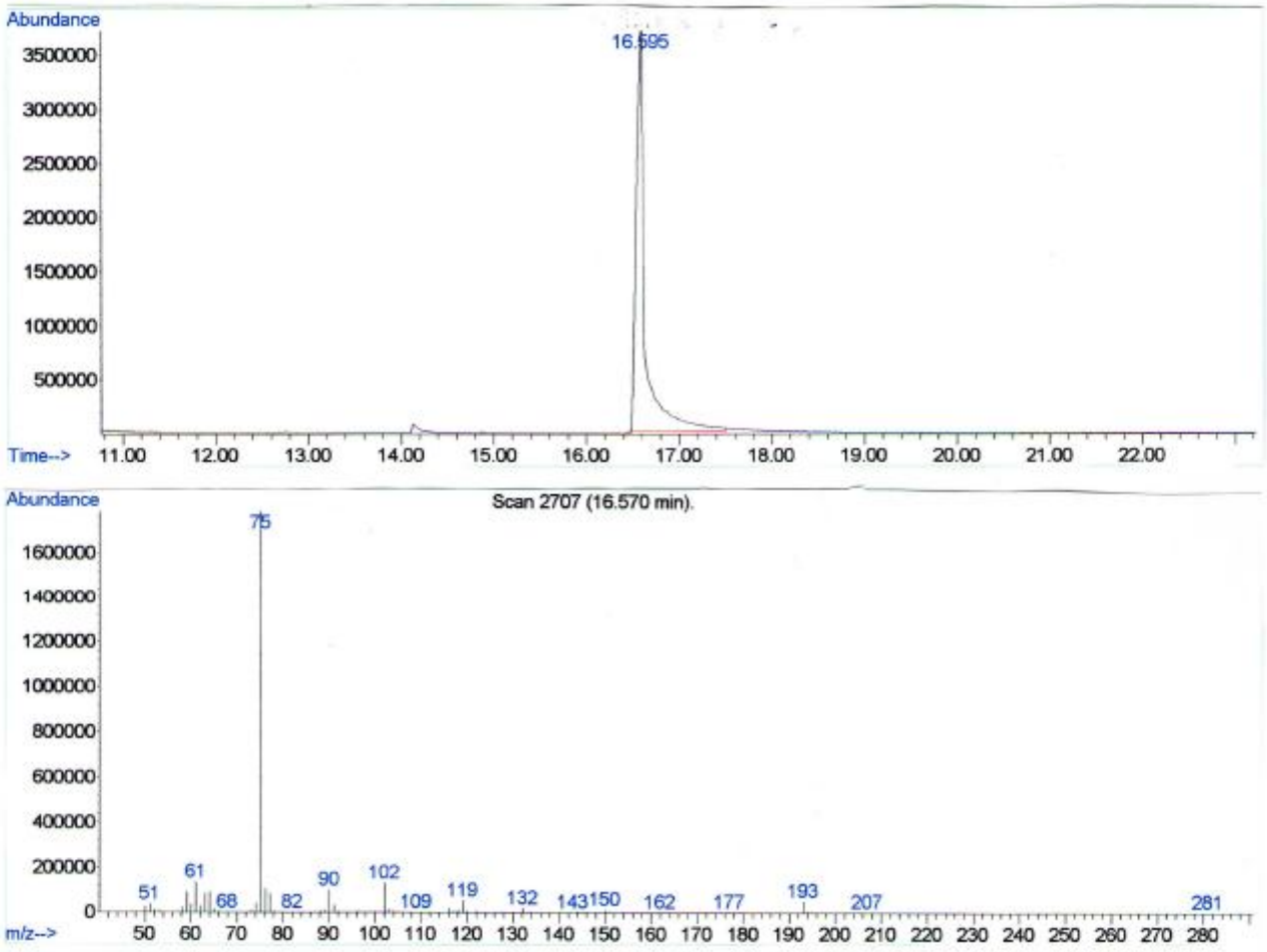
^{1}H NMR spectrum of 4-[2-(methylthio)ethoxy]benzonitrile **13**



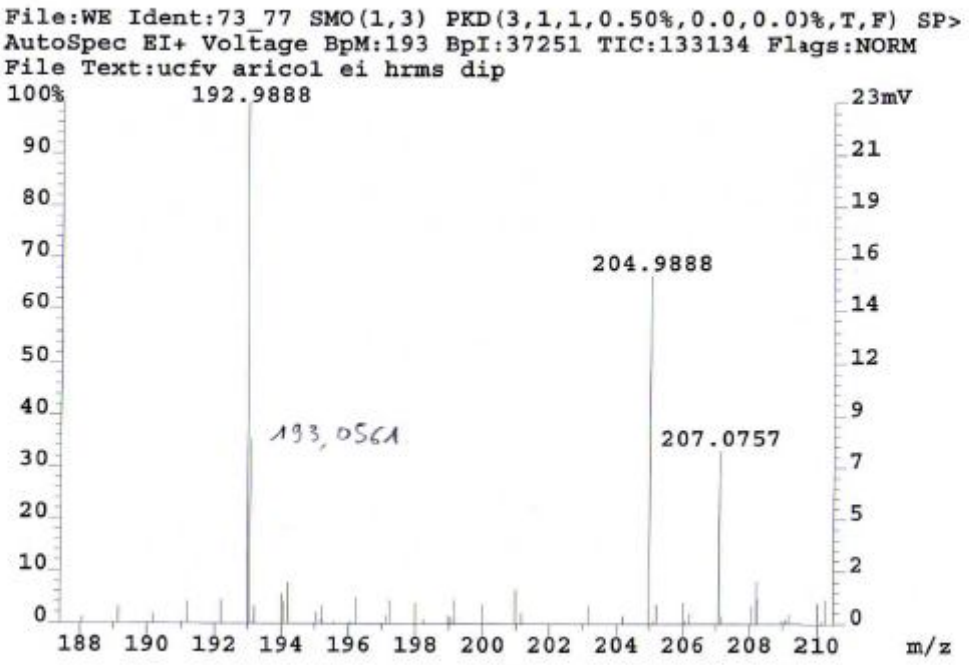
^{13}C NMR spectrum of 4-[2-(methylthio)ethoxy]benzonitrile **13**



GC-MS spectrum of 4-[2-(methylthio)ethoxy]benzonitrile **13**



HRMS analysis of 4-[2-(methylthio)ethoxy]benzonitrile **13**



Elemental Composition Date : 7-OCT-2013

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AutoSpec EI+ Voltage BpM:193 BpI:37251 TIC:133134 Flags:NORM
File Text:ucfv aricol ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

				-0.5	0	0	1	1	1
193.056077		10.0		20.0	200	400	1	1	1

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
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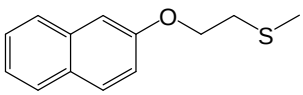
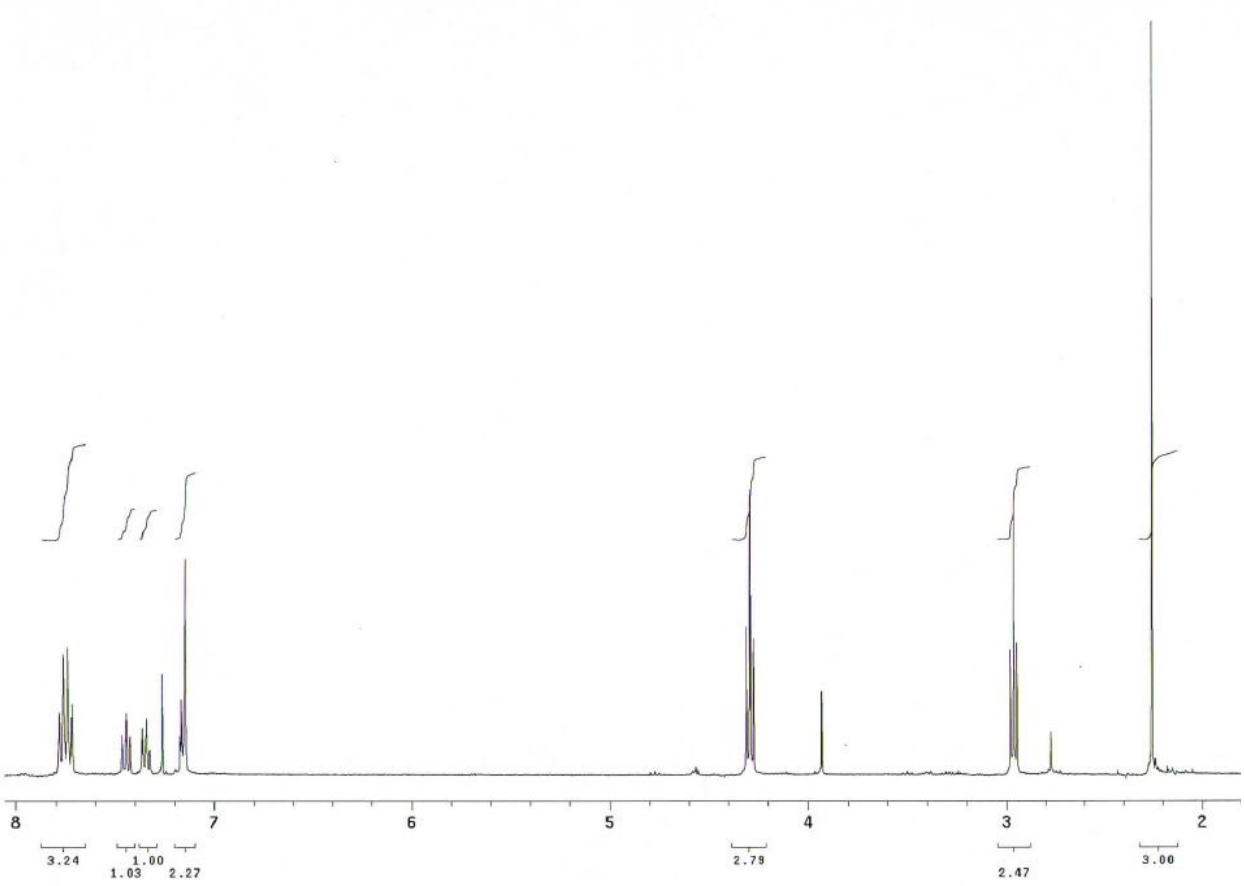
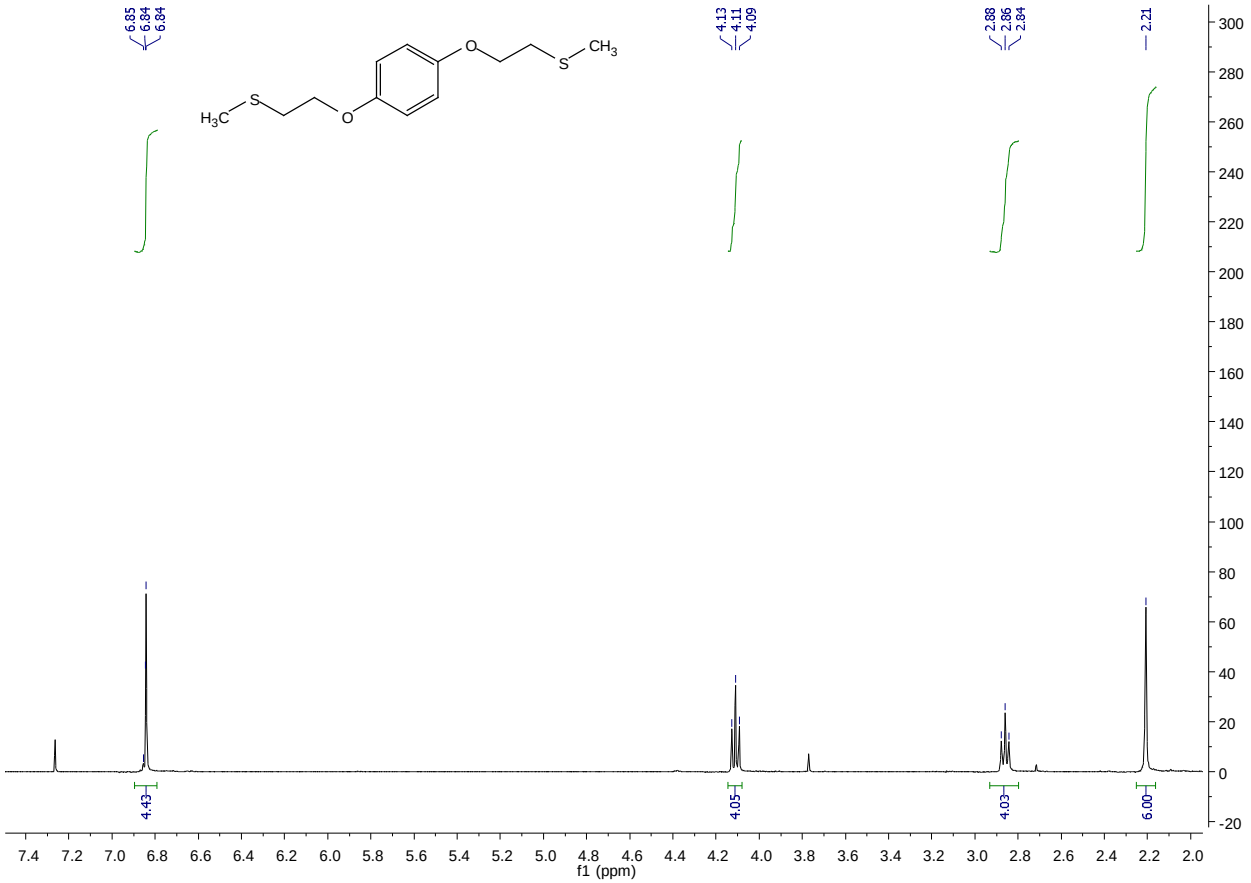
^{1}H NMR spectrum of methyl 2-(naphthalen-2-yloxy)ethyl sulfide **14**

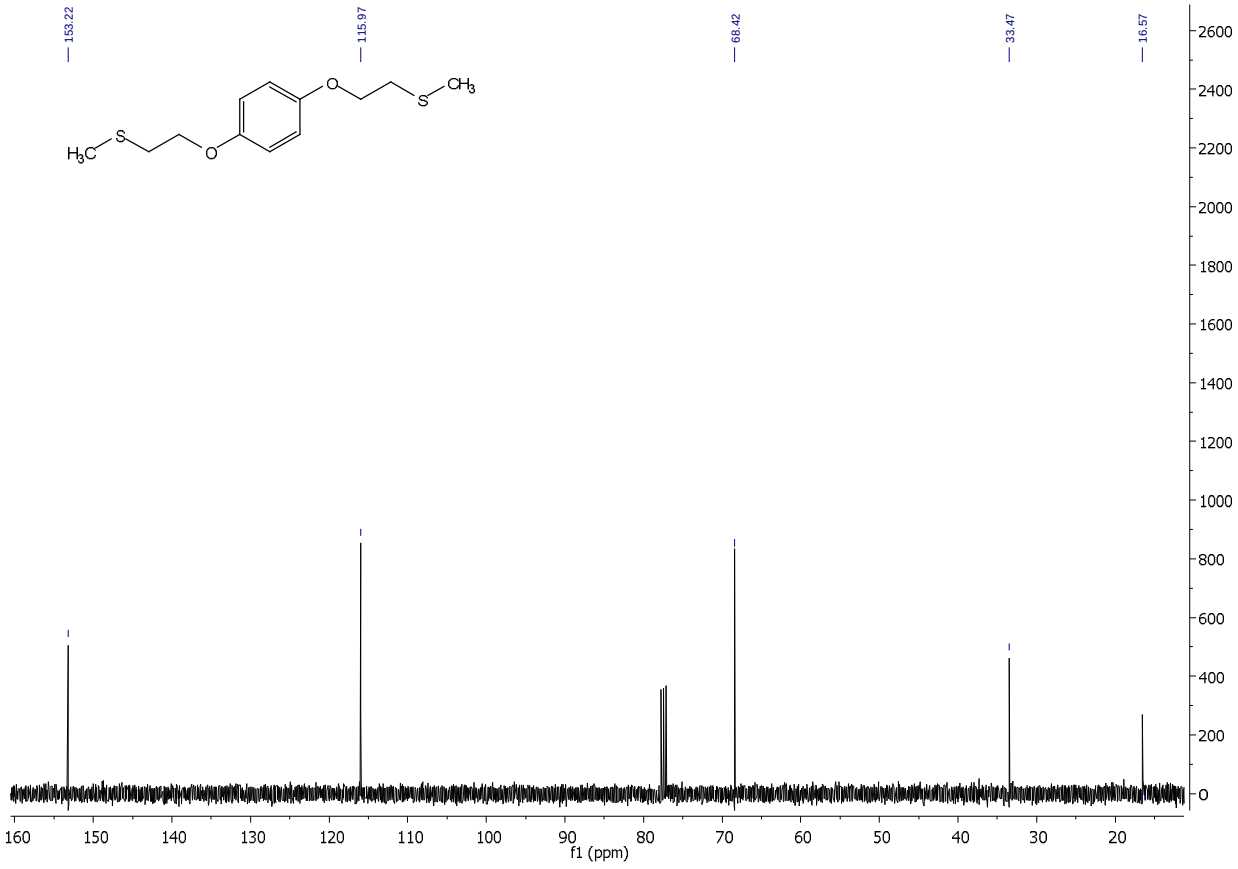




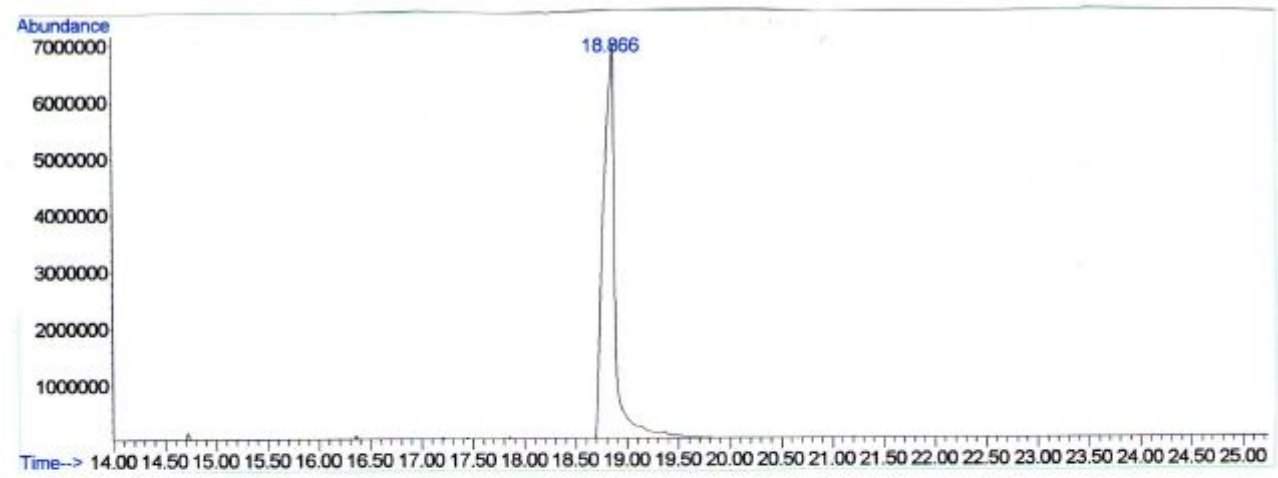
^{1}H NMR spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene **15**

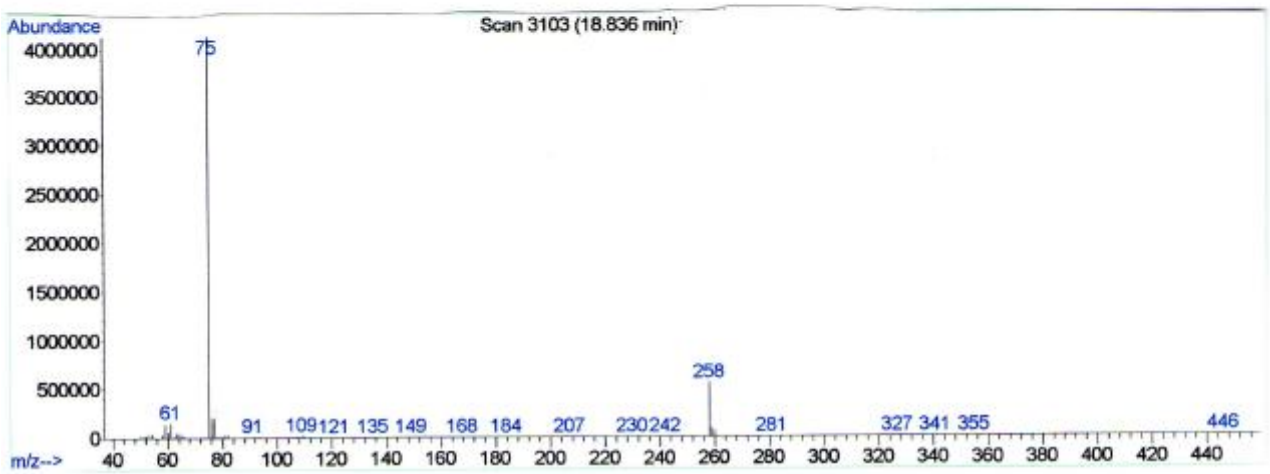


^{13}C NMR spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene **15**

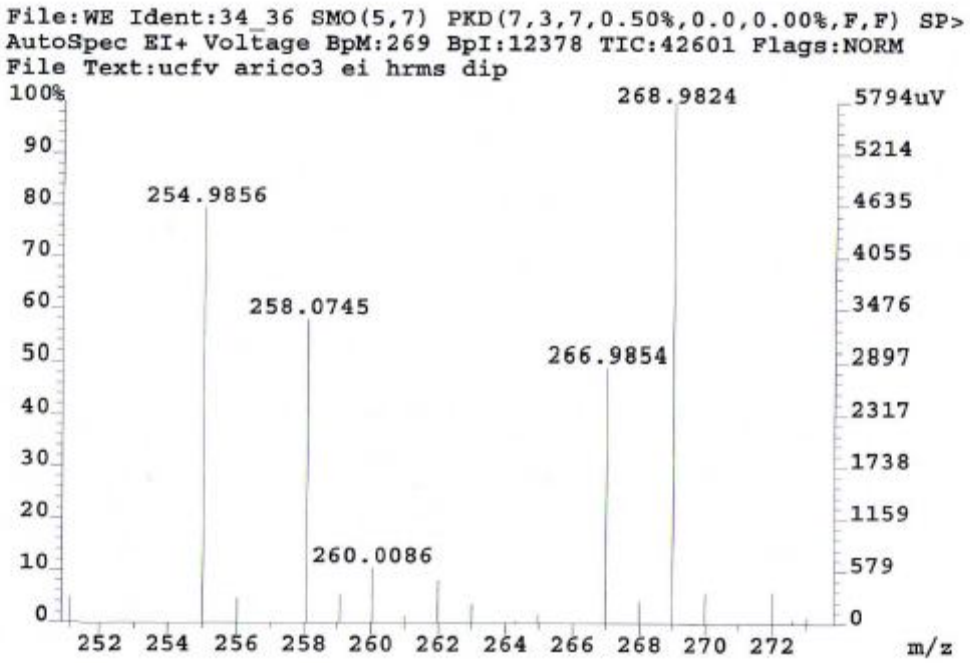


GC-MS spectrum of 1,4-bis-[2-(methylthio)ethoxy]benzene **15**





HRMS analysis of 1,4-bis-[2-(methylthio)ethoxy]benzene **15**



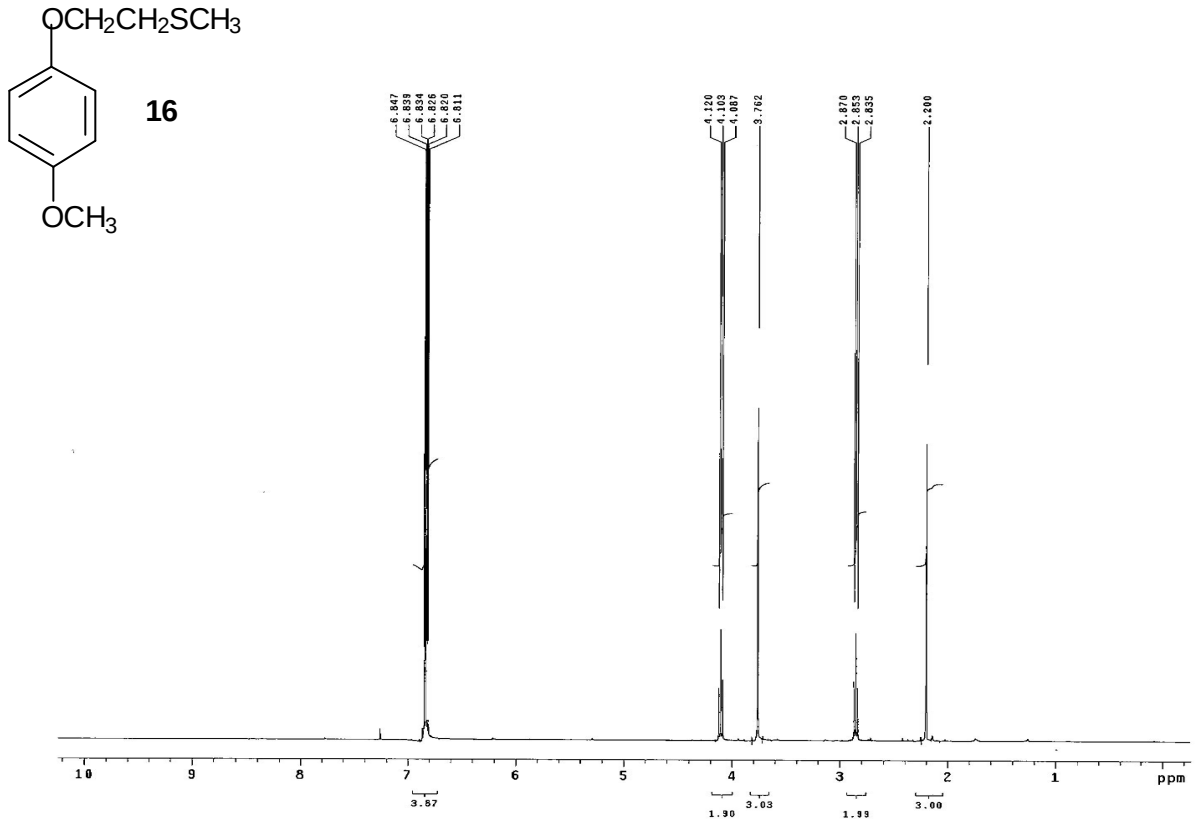
Elemental Composition Date : 1-OCT-2013

File:WE Ident:34_36 SMO(5,7) PKD(7,3,7,0.50%,0.0,0.00%,F,F)
AutoSpec EI+ Voltage BpM:269 BpI:12378 TIC:42601 Flags:NORM
File Text:ucfv arico3 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

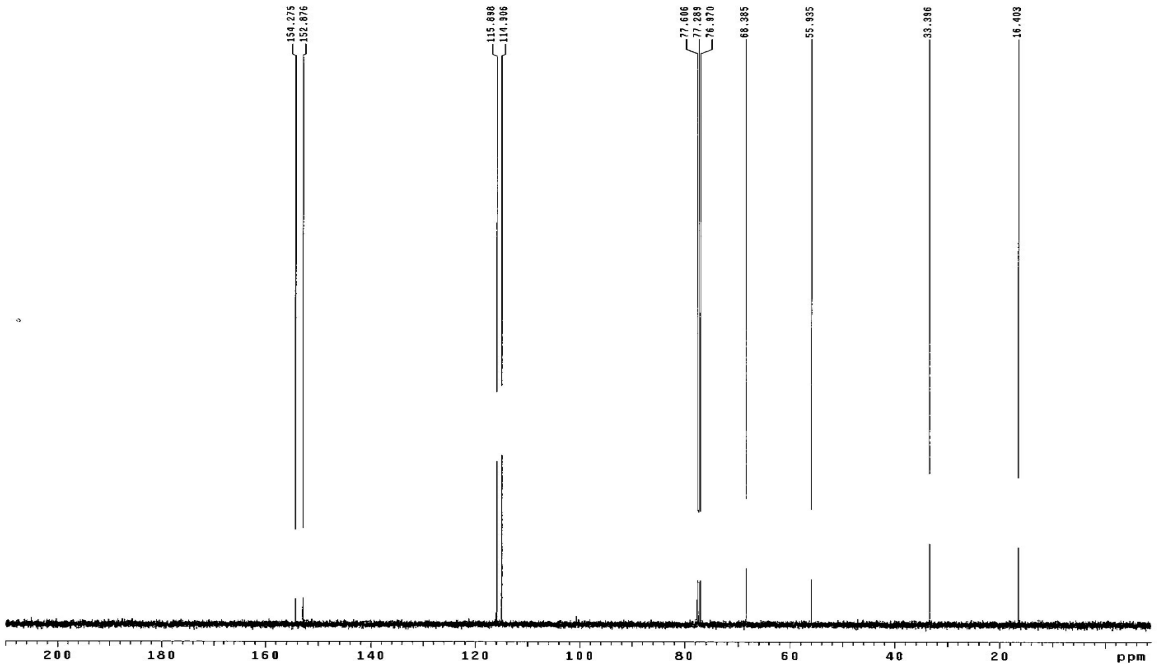
			-0.5	0	0	2	2	
258.074480	10.0		20.0	200	400	2	2	

Mass	PPM	mDa	Calc. Mass	DBE	C	H	O	S
258.074480	1.3	0.3	258.074824	4.0	12	18	2	2

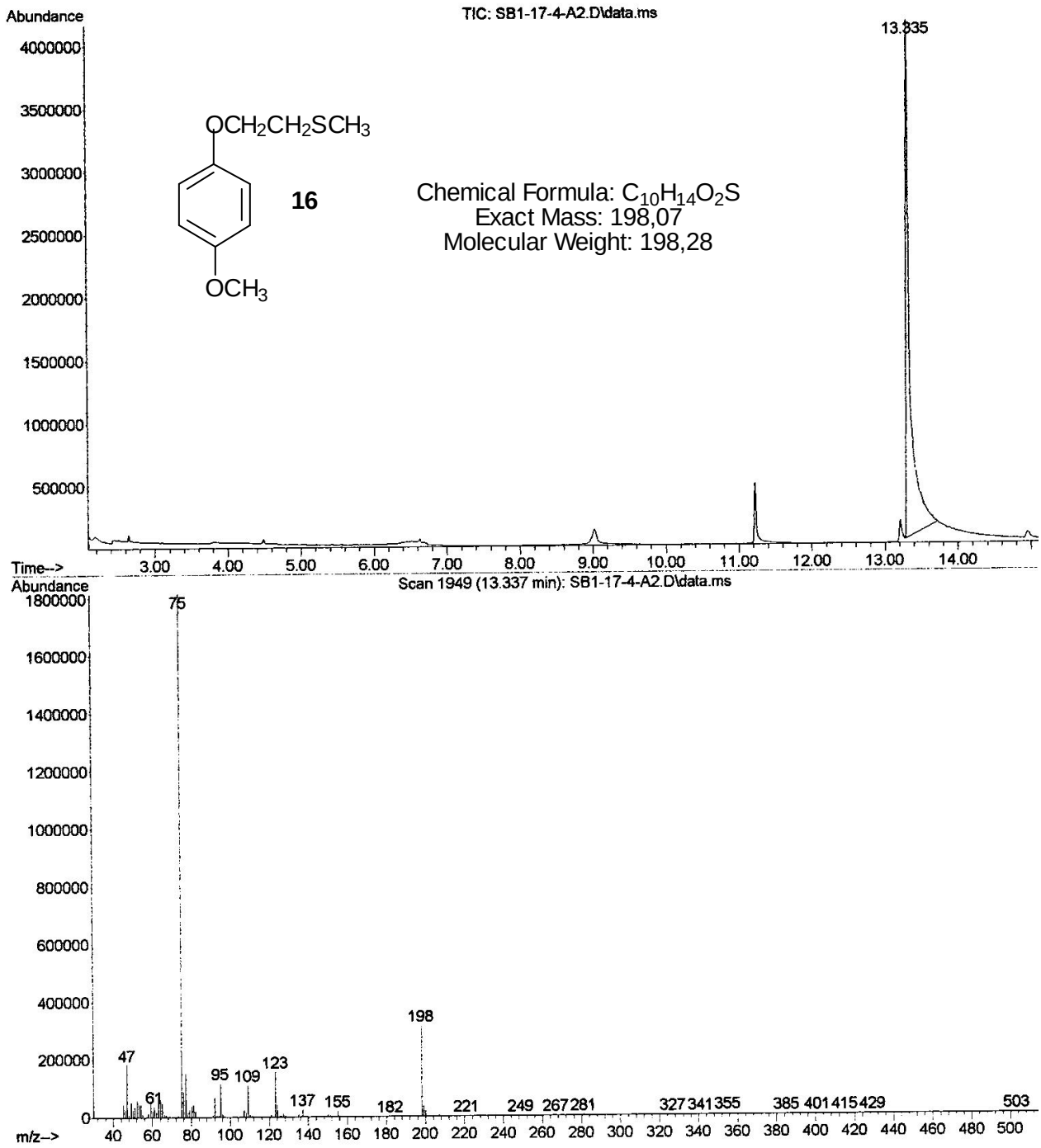
^{1}H NMR spectrum of 4-[2-(methylthio)ethoxy]anisole **16**



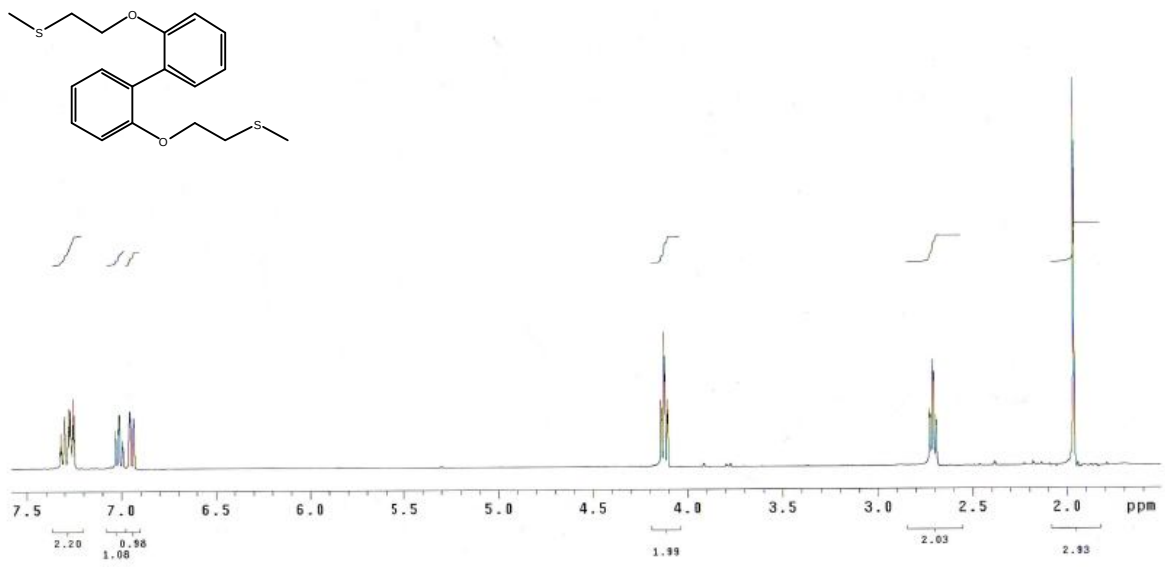
^{13C} NMR spectrum of 4-[2-(methylthio)ethoxy]anisole **16**



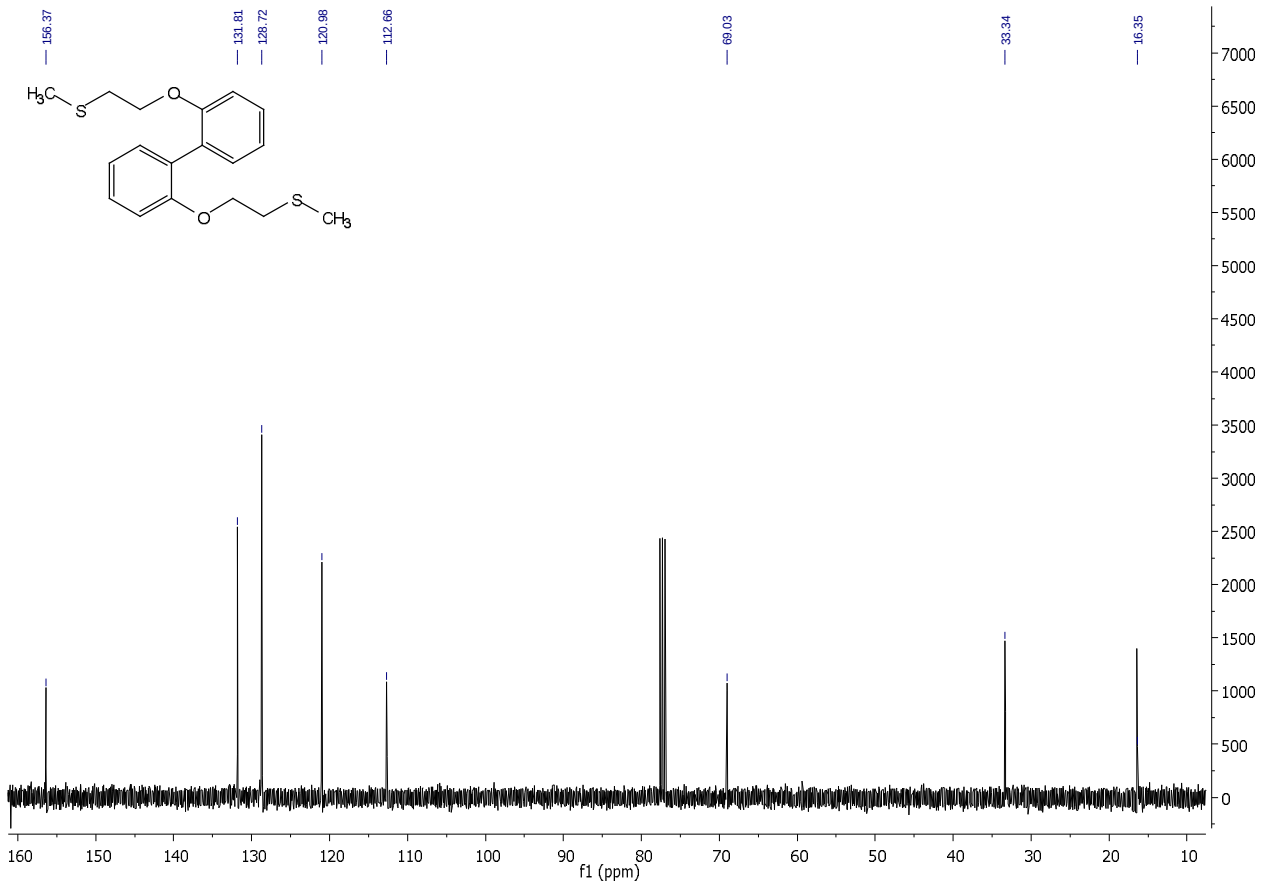
GC-MS spectrum of 4-[2-(methylthio)ethoxy]anisole **16**



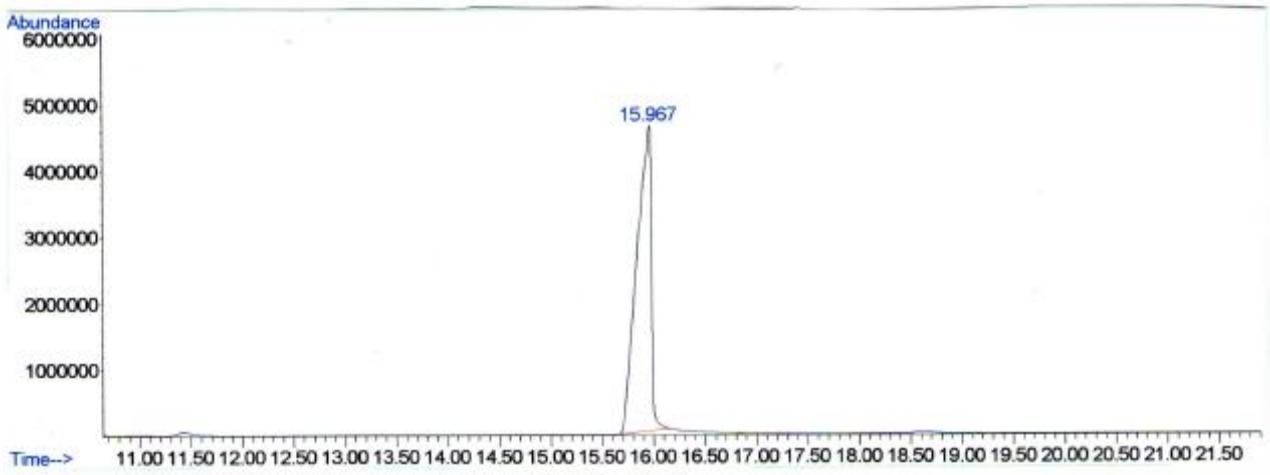
^{1}H NMR spectrum of 2,2'-[2-(methylthio)ethoxy]biphenyl **18**



^{13}C NMR spectrum of 2,2'-[2-(methylthio)ethoxy]biphenyl **18**



GC-MS spectrum of 2,2'-[2-(methylthio)ethoxy]biphenyl **18**


Abundance
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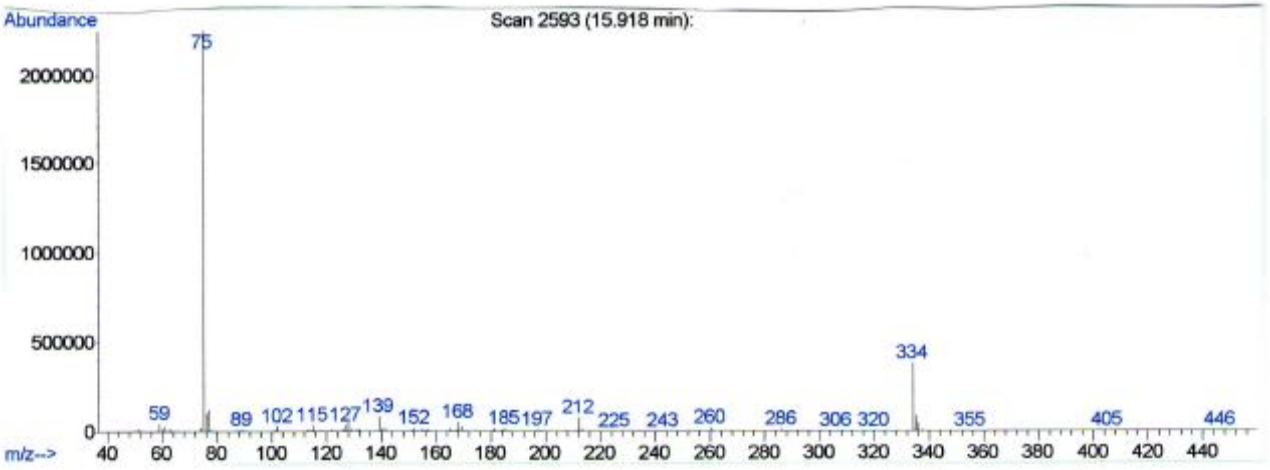
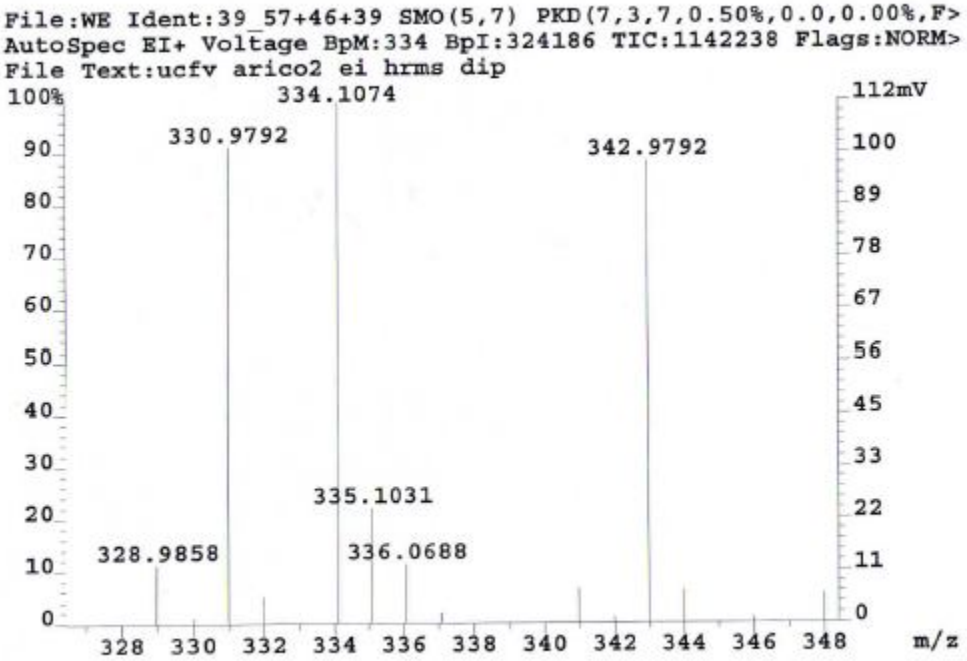
4000000
3000000
2000000
1000000
15.967
Time-->
11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00 15.50 16.00 16.50 17.00 17.50 18.00 18.50 19.00 19.50 20.00 20.50 21.00 21.50


Abundance
Scan 2593 (15.918 min):
75
2000000
1500000
1000000
500000
334
0
59
89 102 115 127 139 152 168 185 197 212 225 243 260 286 306 320 355 405 446
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440

HRMS analysis of 2,2'-[2-(methylthio)ethoxy]biphenyl **18**



Elemental Composition Date : 1-OCT-2013

File:WE Ident:39_57+46+39 SMO(5,7) PKD(7,3,7,0.50%,0.0,0.00%,F,F)
AutoSpec EI+ Voltage BpM:334 BpI:324186 TIC:1142238 Flags:NORM
File Text:ucfv arico2 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

				-0.5	0	0	2	2
334.107396		10.0		20.0	200	400	2	2

Mass	PPM	mDa	Calc. Mass	DBE	C	H	O	S
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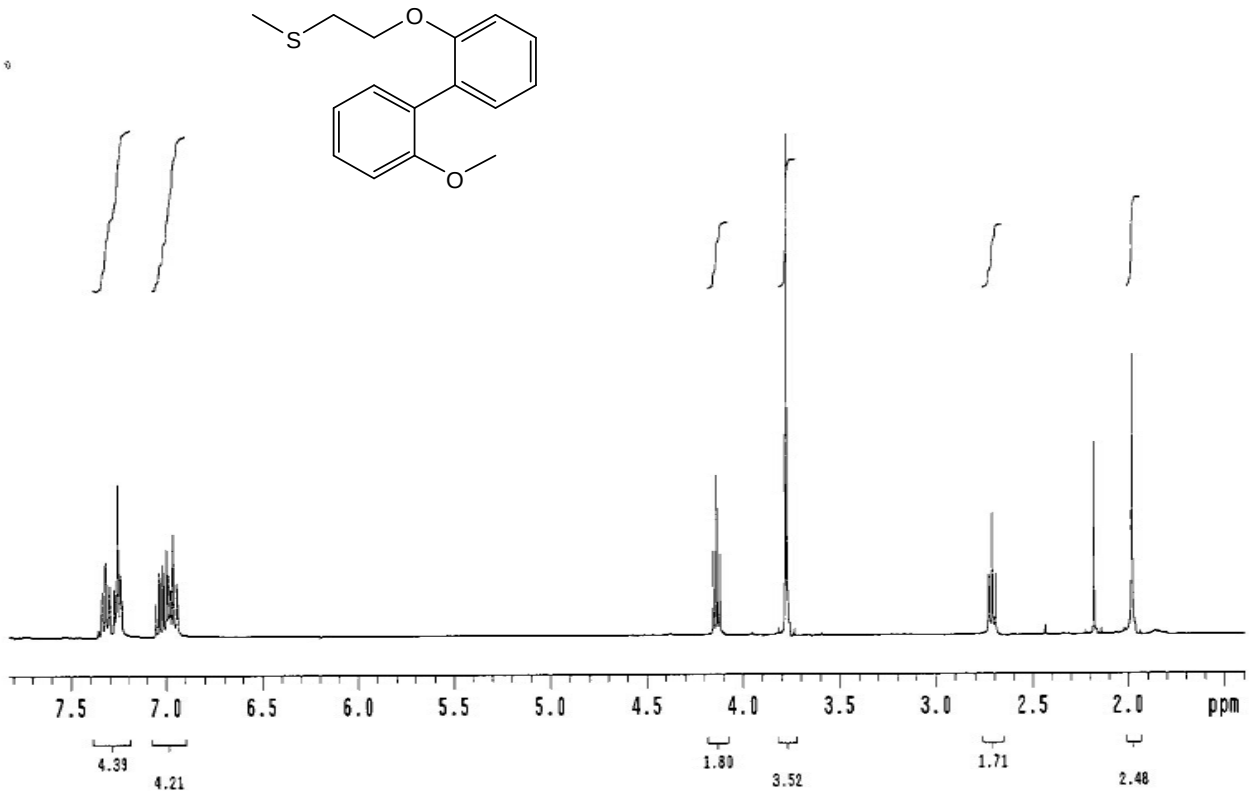
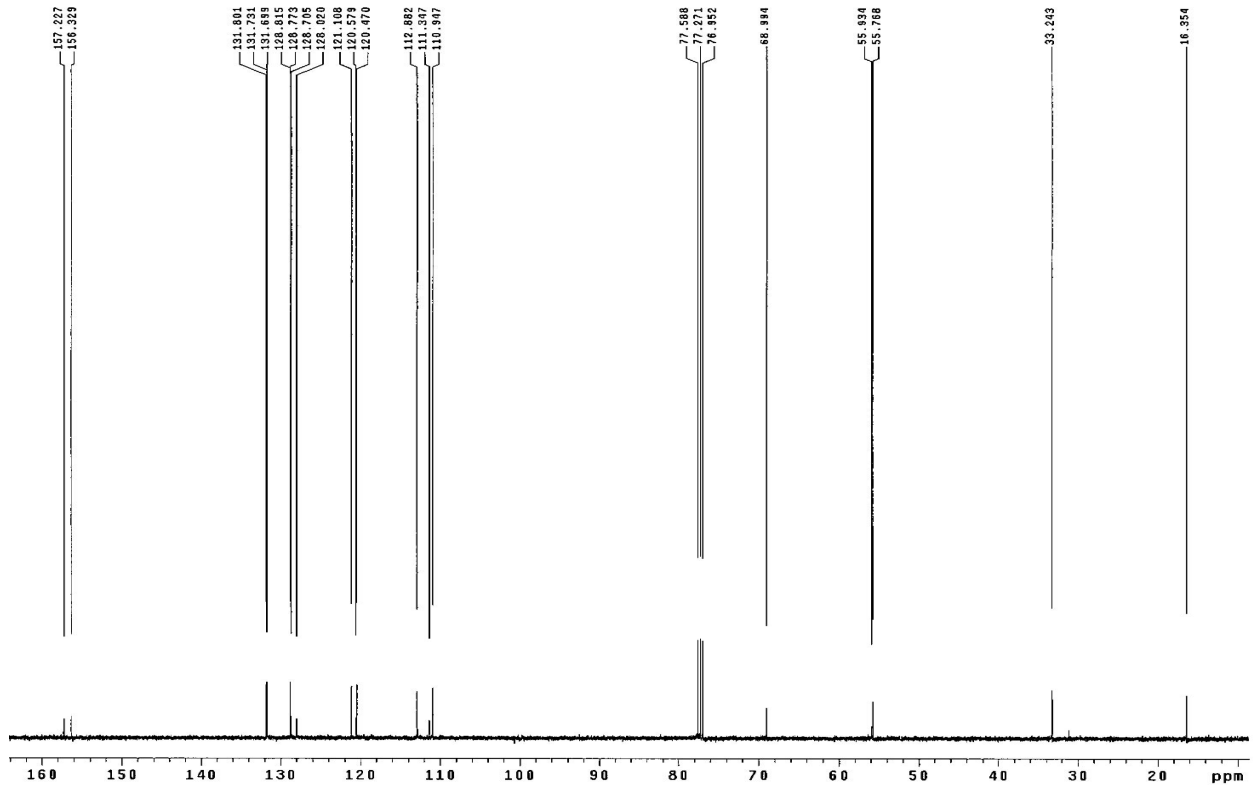
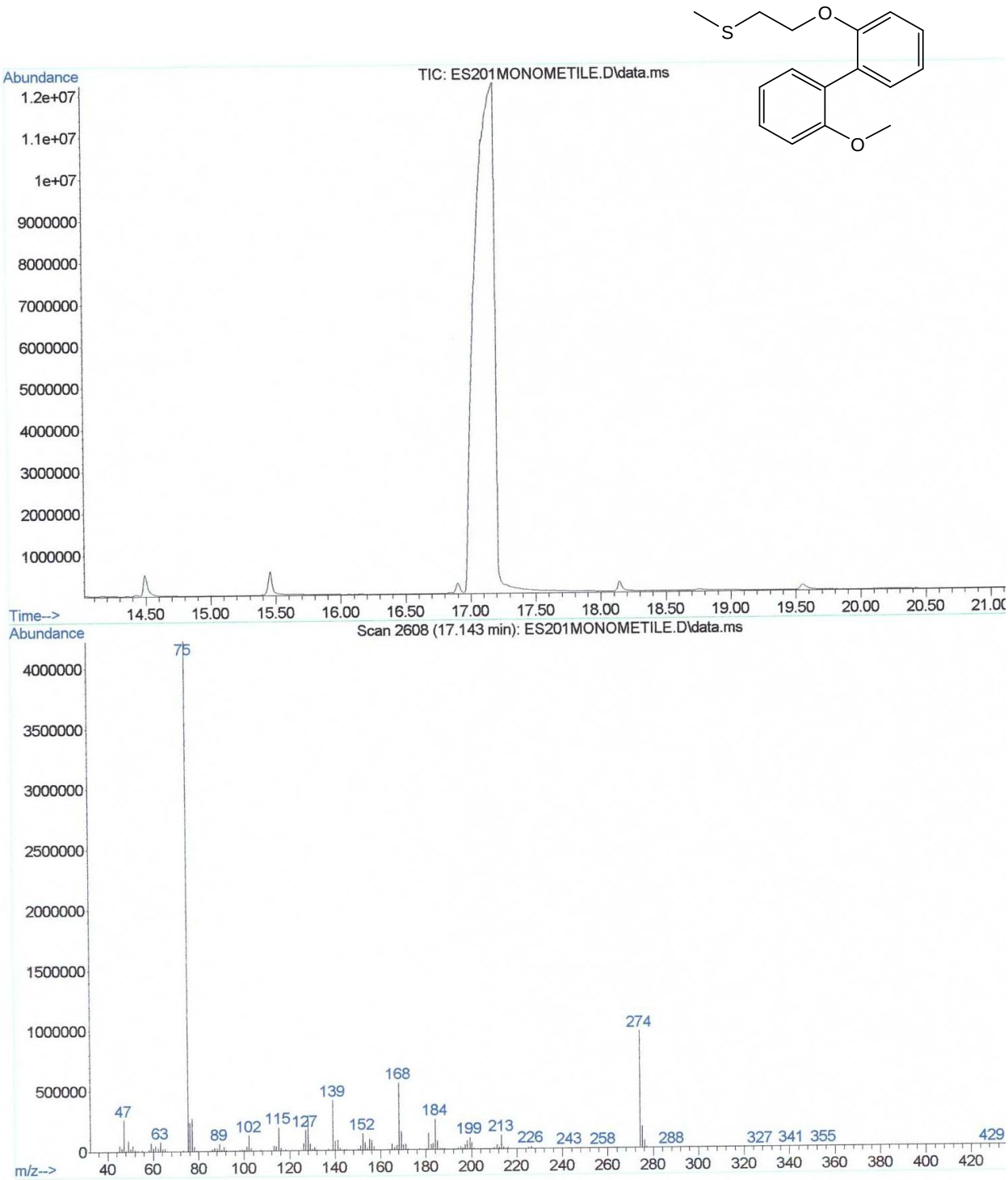
^{1}H NMR spectrum of 2-[2-(methylthio)ethoxy]-2'-methoxybiphenyl **19**



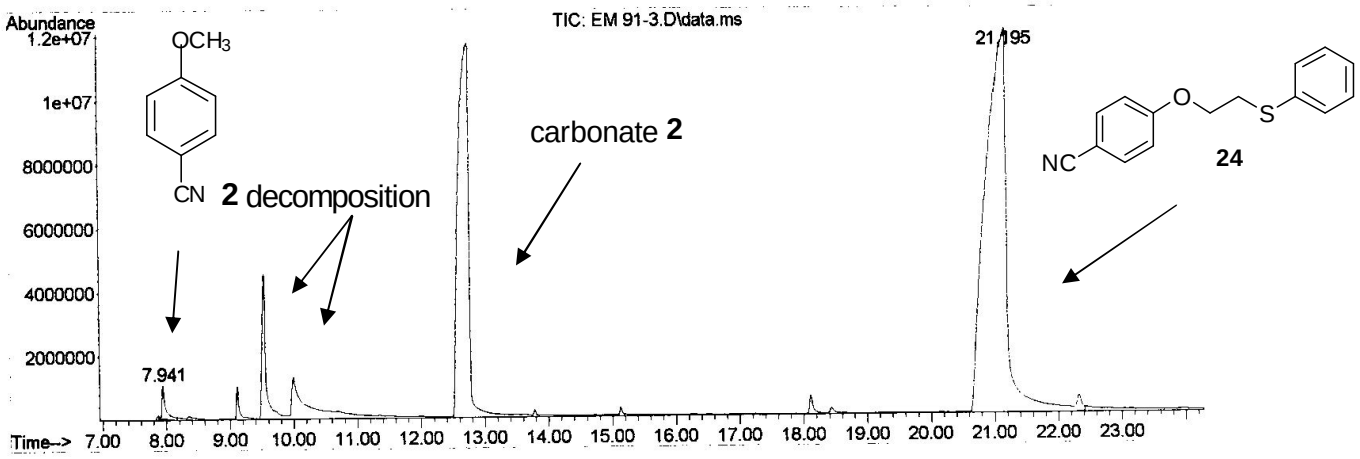
^{13}C NMR spectrum of 2-[2-(methylthio)ethoxy]-2'-methoxybiphenyl **19**

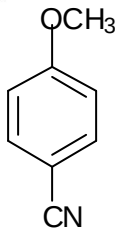


GC-MS spectrum of 2-[2-(methylthio)ethoxy]-2'-methoxybiphenyl **19**

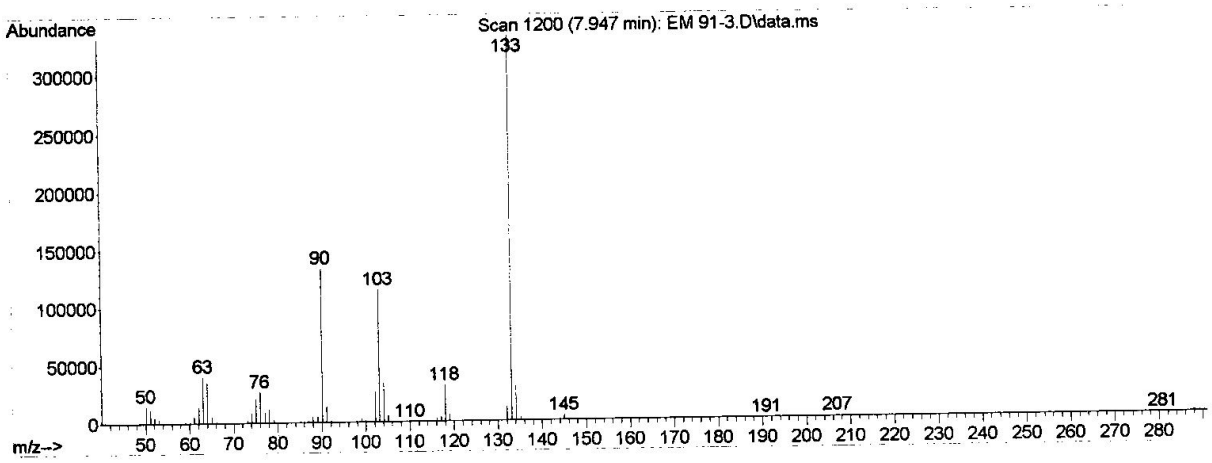


GC-MS spectrum of the reaction of *p*-cyanophenol with 2-(phenylthio)ethyl carbonate **2** – Product identification **24** (entry 1, Table 3)



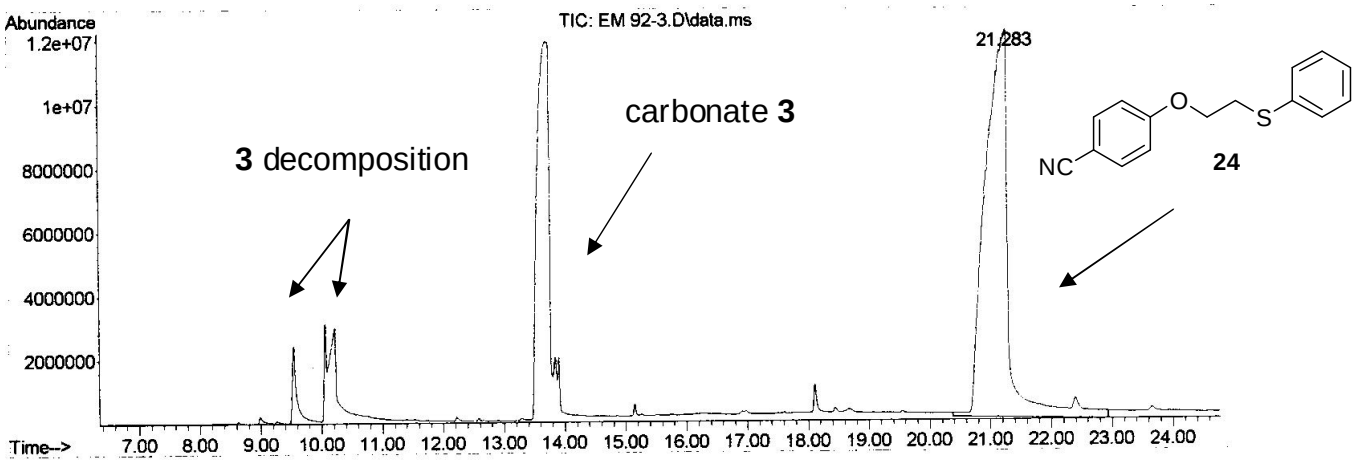


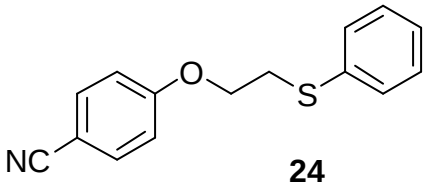
Chemical Formula: C_8H_7NO
Exact Mass: 133,05
Molecular Weight: 133,15



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	7.942	1187	1199	1238	M	1061127	43760416	1.53%	1.509%
2	21.194	3405	3515	3727	M	12139028	2856199181	100.00%	98.491%

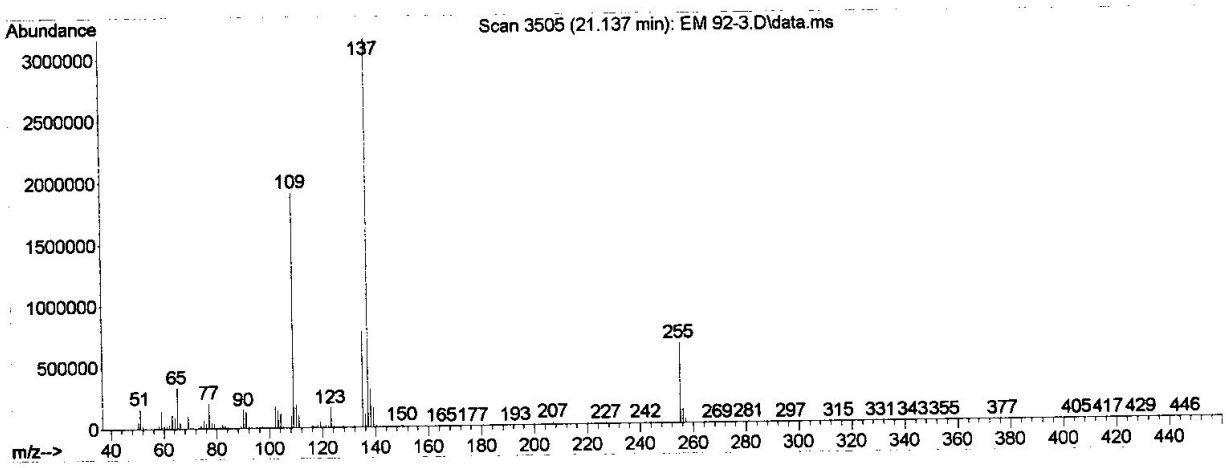
GC-MS spectrum of the reaction of *p*-cyanophenol with ethyl 2-(phenylthio)ethyl carbonate **3** – Product identification **24** (entry 2, Table 3)





24

Chemical Formula: $C_{15}H_{13}NOS$
Exact Mass: 255,07
Molecular Weight: 255,33

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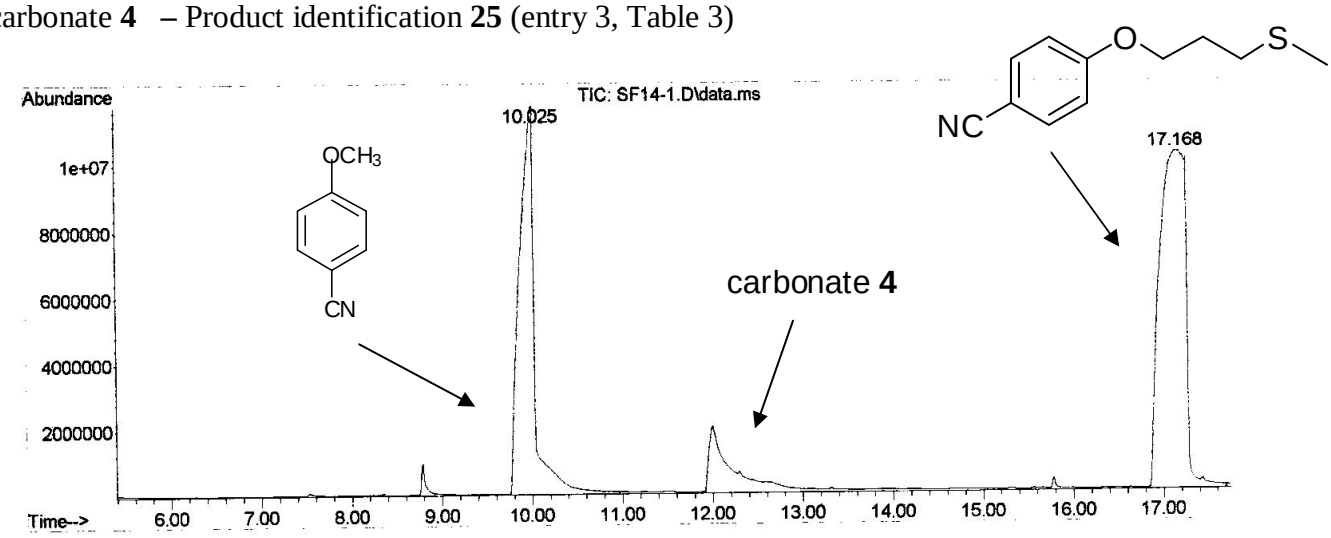
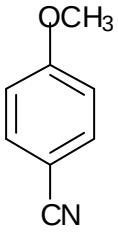
Method     : D:\msdchem\1\METHODS\SERENA 1.M
Title      :

Signal     : TIC: EM 92-3.D\data.ms

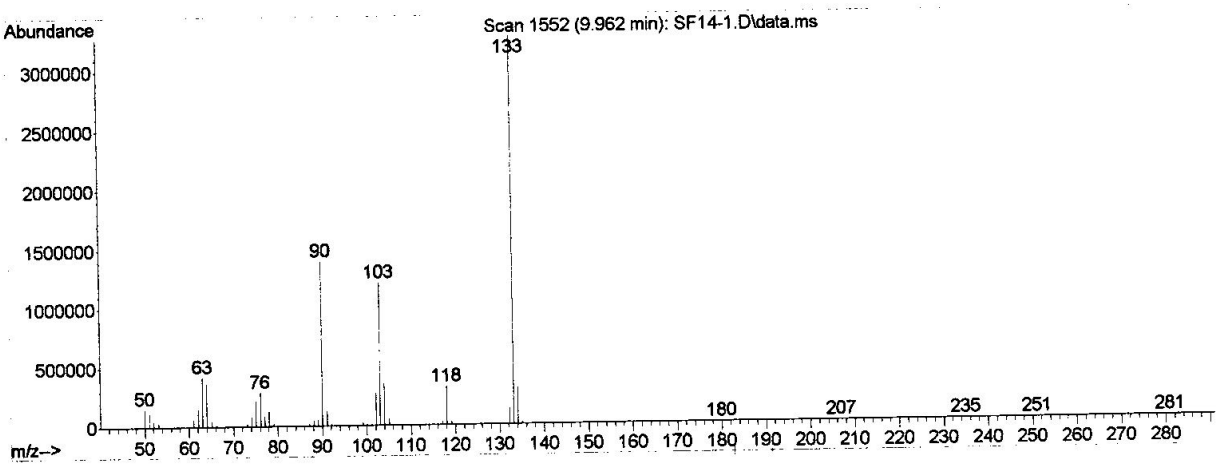
peak  R.T. first  max last  PK   peak      corr.      corr.     % of
  #   min   scan scan scan  TY  height     area      % max.    total
---  ----- ----- ---- ---- ---  -------   -------   ------   -------
 1  21.285  3371 3531 3818   M2 12222914 3289012753 100.00% 100.000%
```

GC-MS spectrum of the reaction of *p*-cyanophenol with ethyl 3-(Methylthio)propyl methyl carbonate **4** – Product identification **25** (entry 3, Table 3)



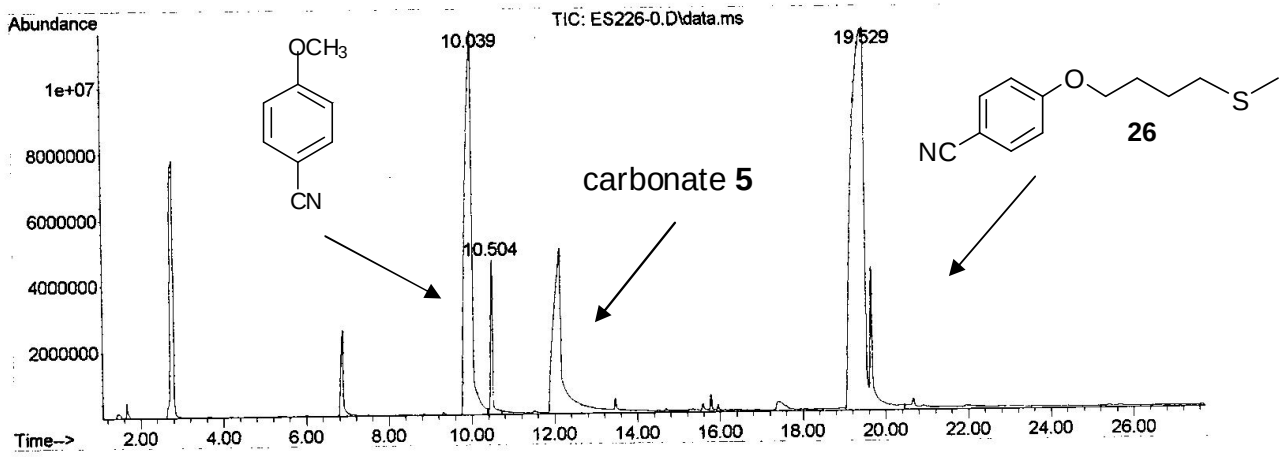


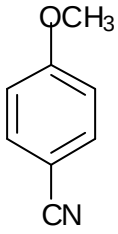
Chemical Formula: C_8H_7NO
Exact Mass: 133,05
Molecular Weight: 133,15



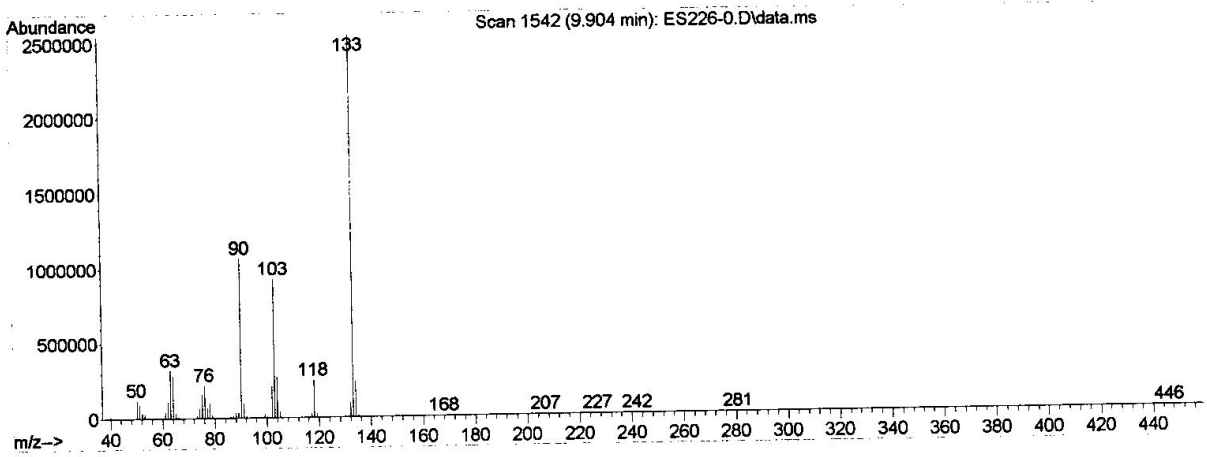
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	10.025	1483	1563	1727	M	11859911	1398999201	67.56%	40.321%
2	17.166	2753	2811	2903	M4	10287850	2070631842	100.00%	59.679%

GC-MS spectrum of the reaction of *p*-cyanophenol with ethyl 4-(methylthio)butyl methyl carbonate **5** – Product identification **26** (entry 4, Table 3)





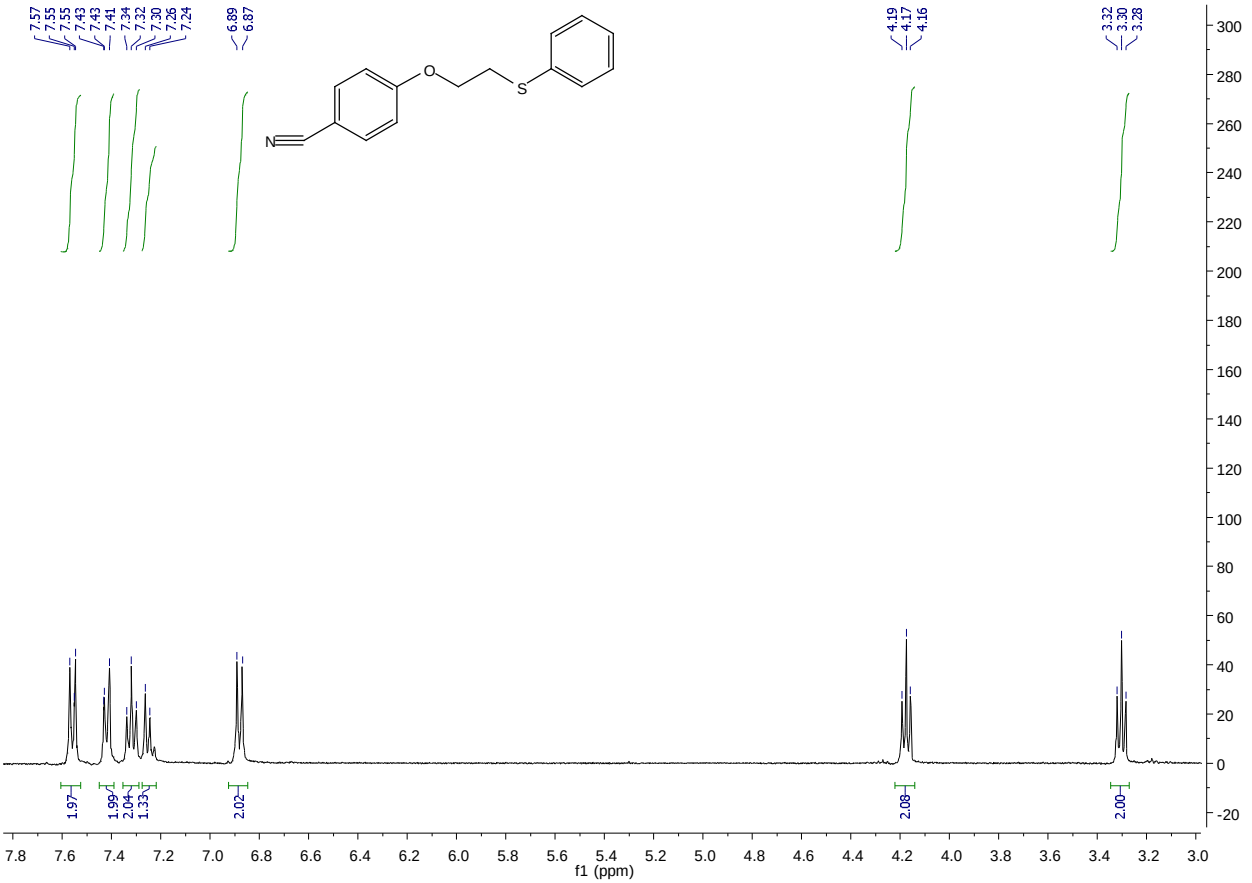
Chemical Formula: C_8H_7NO
Exact Mass: 133,05
Molecular Weight: 133,15



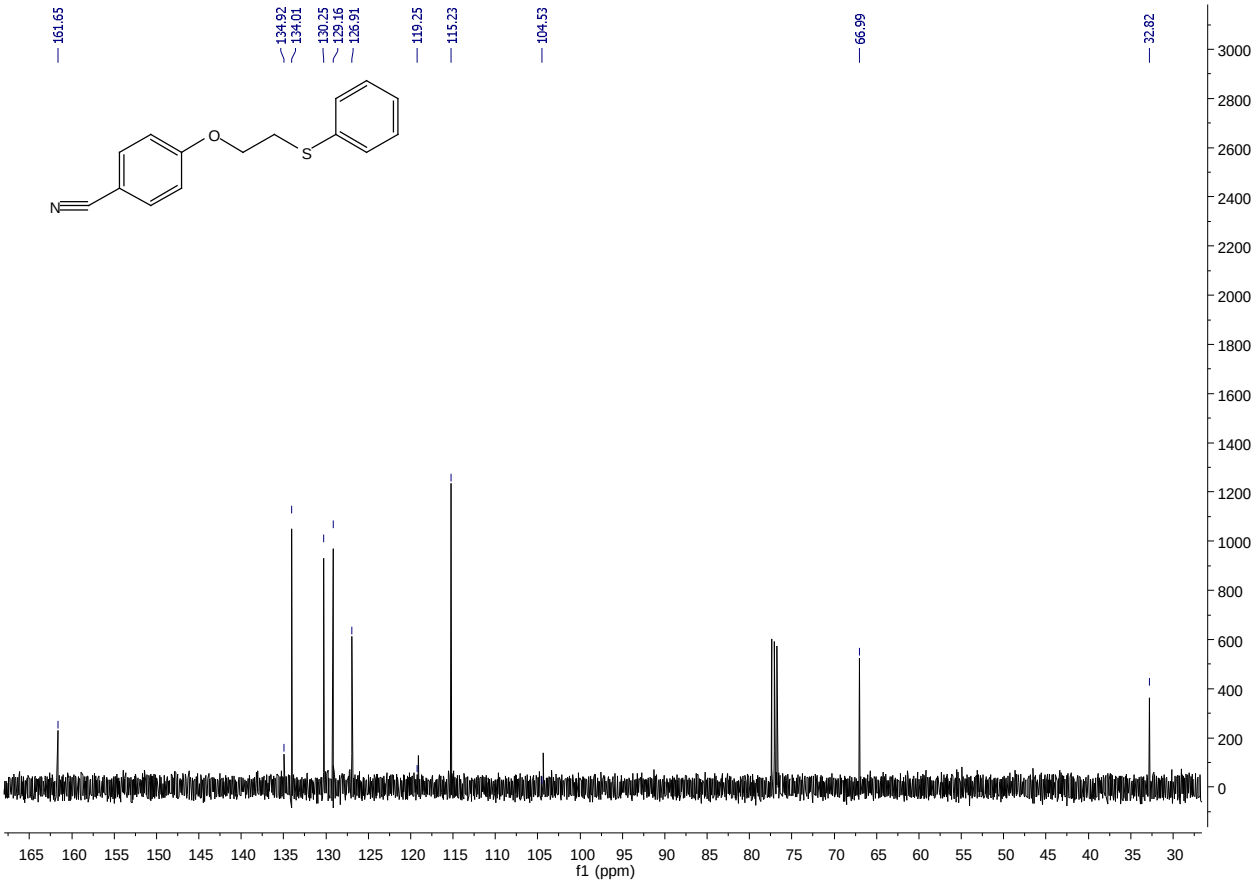
Signal : TIC: ES226-0.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	10.042	1514	1566	1621	M	11846952	1343629796	49.06%	31.591%
2	10.505	1628	1647	1684	M	4733019	171111804	6.25%	4.023%
3	19.529	3040	3224	3387	M3	11655220	2738500348	100.00%	64.386%

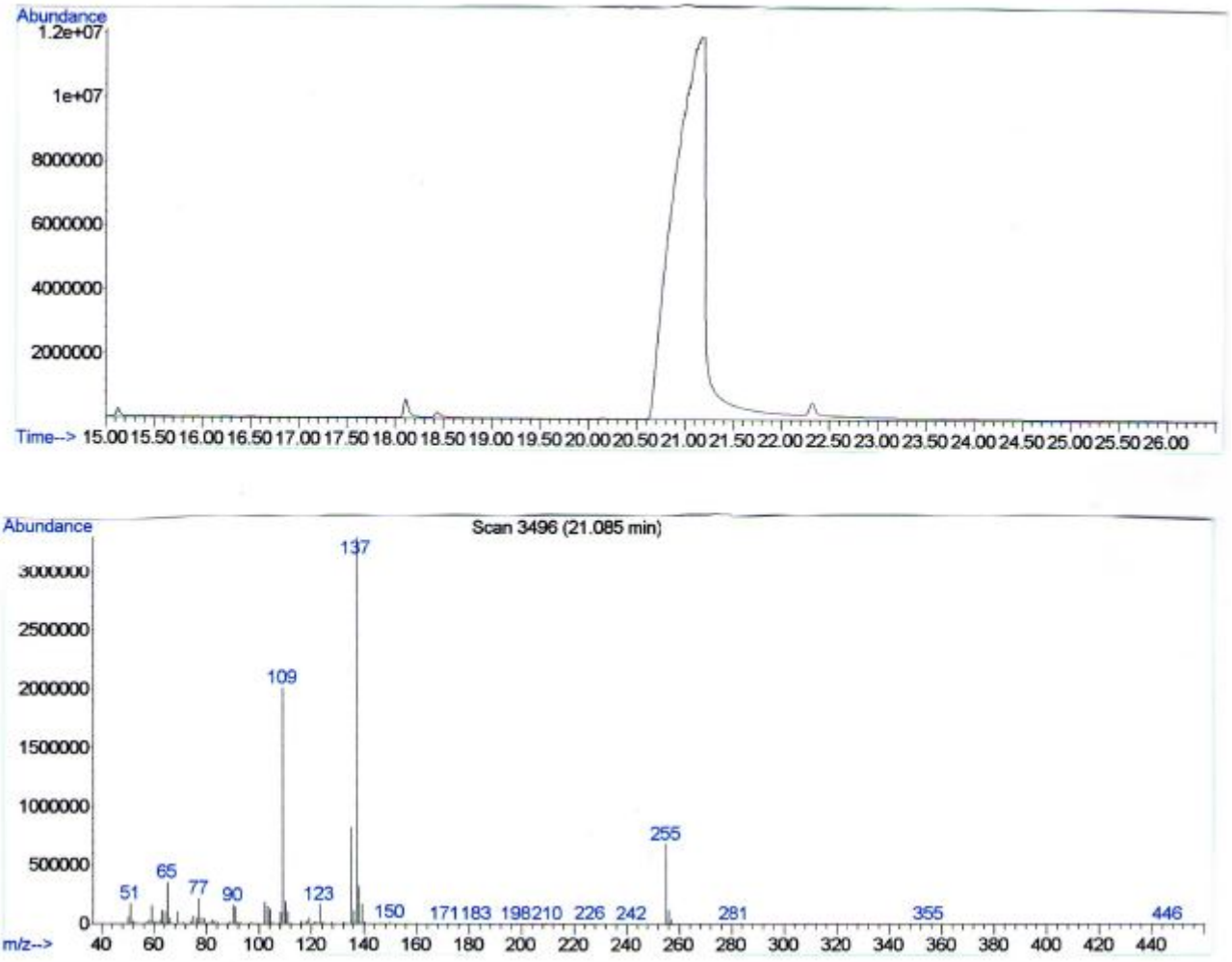
^{1}H NMR spectrum of 4-[2-(phenylthio)ethoxy]benzonitrile **24**



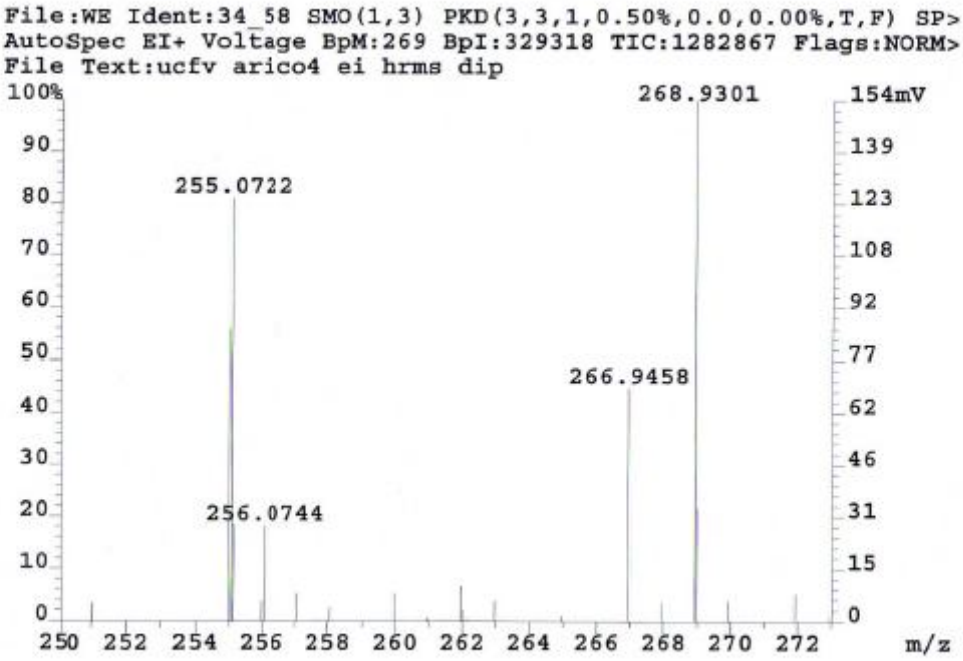
^{13}C NMR spectrum of 4-[2-(phenylthio)ethoxy]benzonitrile **24**



GC-MS spectrum of 4-[2-(phenylthio)ethoxy]benzonitrile **24**



HRMS analysis of 4-[2-(phenylthio)ethoxy]benzonitrile **24**



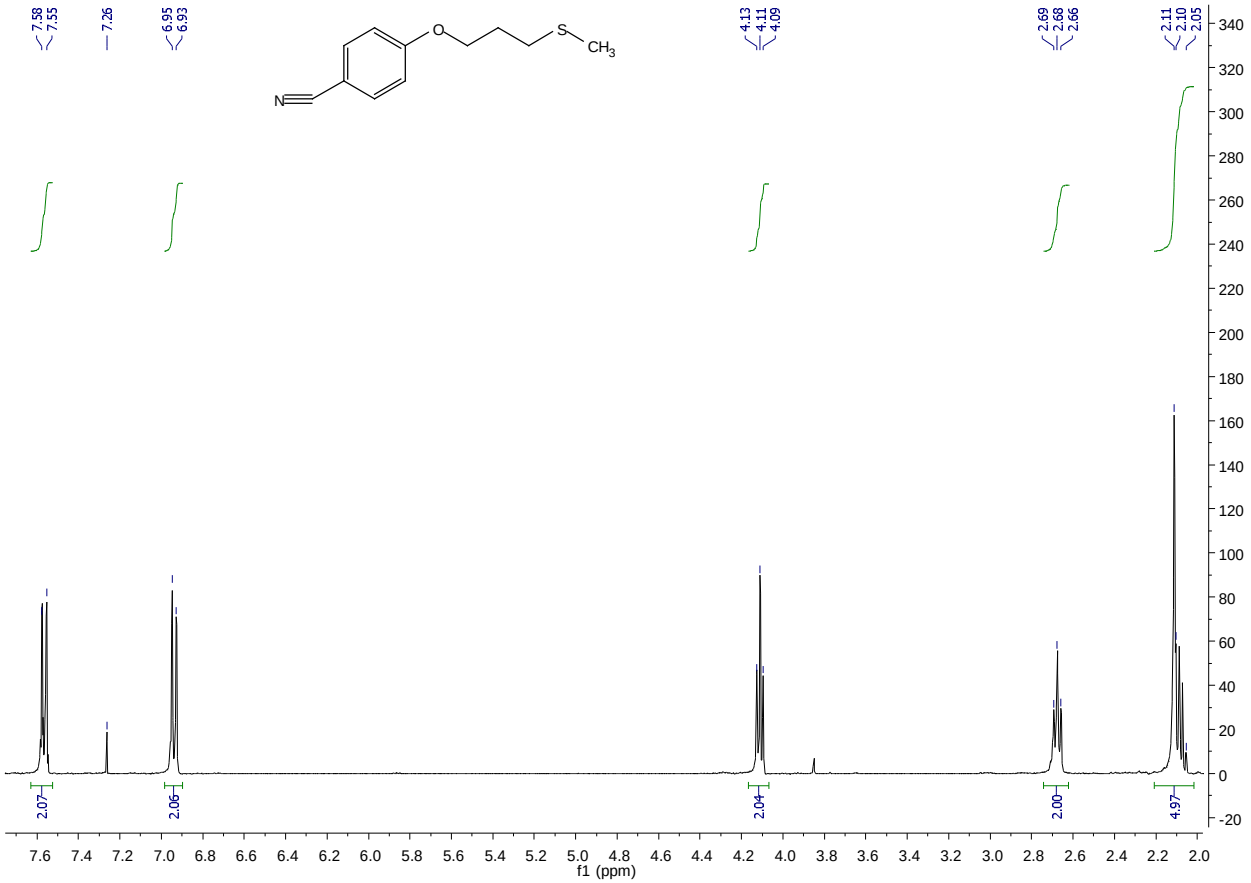
Elemental Composition Date : 1-OCT-2013

File:WE Ident:34_58 SMO(1,3) PKD(3,3,1,0.50%,0.0,0.00%,T,F)
AutoSpec EI+ Voltage BpM:269 BpI:329318 TIC:1282867 Flags:NORM
File Text:ucfv arico4 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

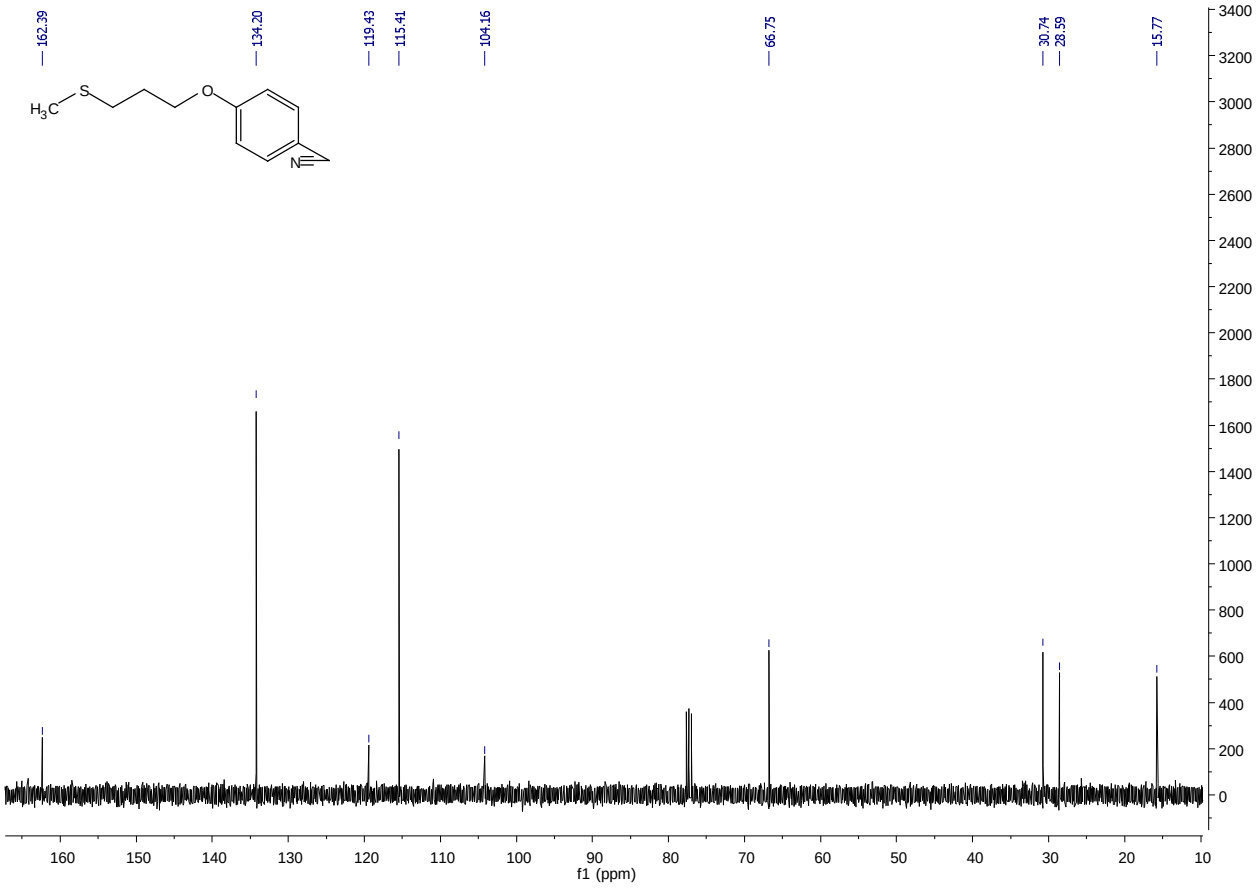
				-0.5	0	0	1	1	1
255.072174		10.0		20.0	200	400	1	1	1

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
255.072174	-1.5	-0.4	255.071786	10.0	15	13	1	1	1

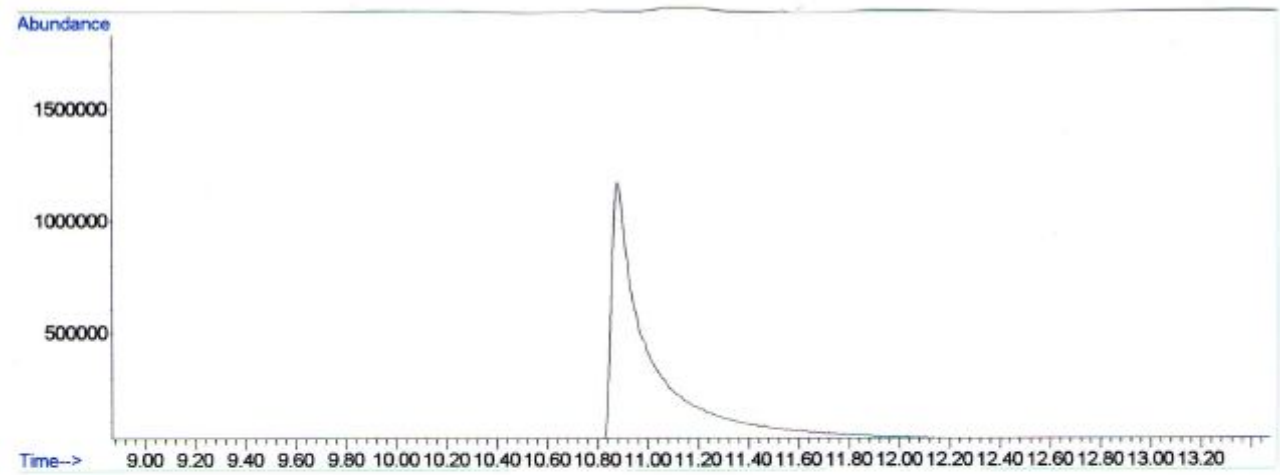
^{1}H NMR spectrum of 4-[3-(methylthio)propoxy]benzonitrile **25**

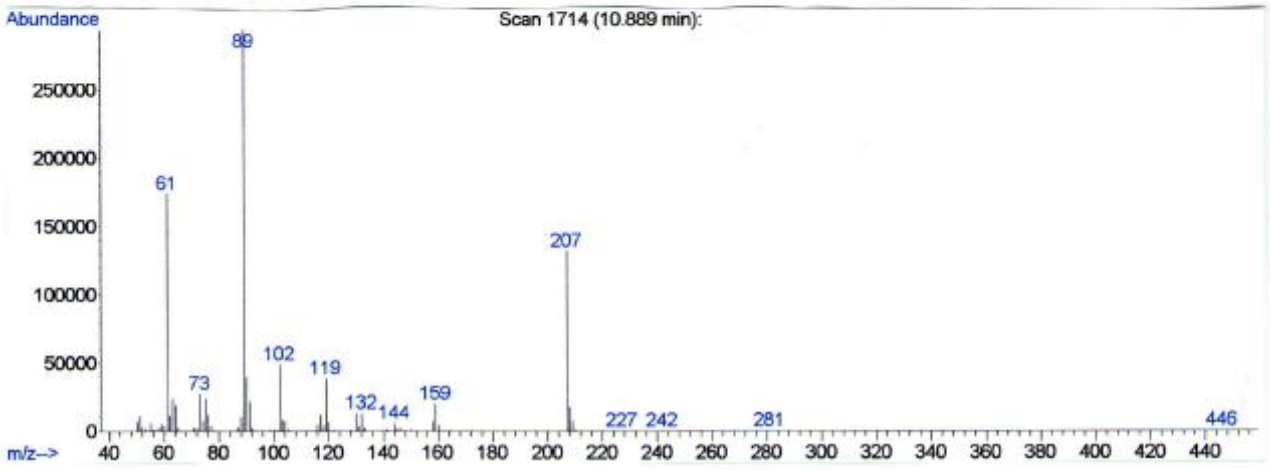


^{13}C NMR spectrum of 4-[3-(methylthio)propoxy]benzonitrile **25**

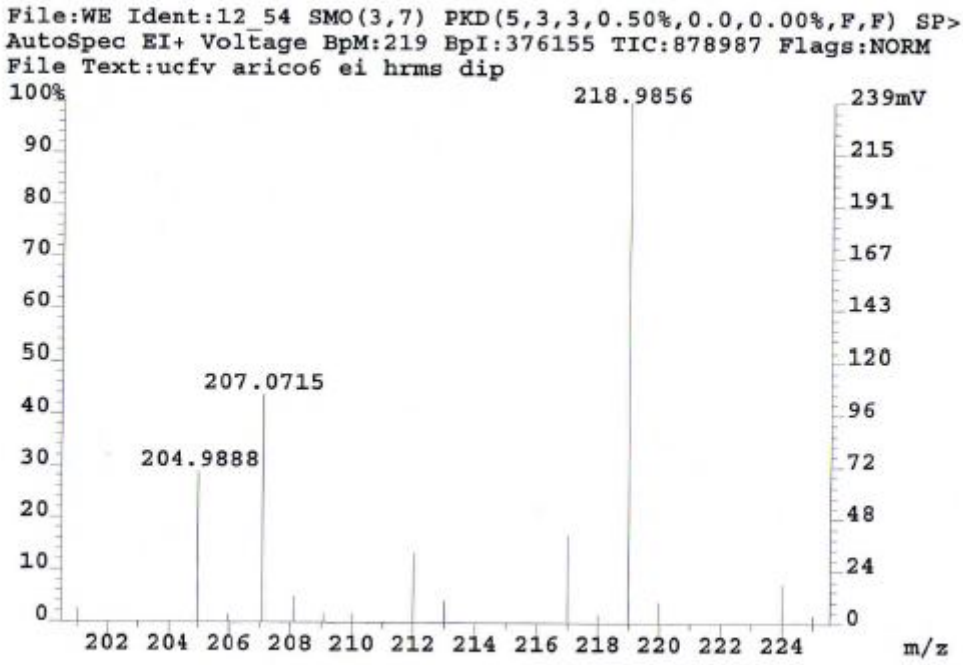


GC-MS spectrum of 4-[3-(methylthio)propoxy]benzonitrile **25**





HRMS analysis of 4-[3-(methylthio)propoxy]benzonitrile **25**



Elemental Composition Date : 7-OCT-2013

File:WE Ident:12_54 SMO(3,7) PKD(5,3,3,0.50%,0.0,0.00%,F,F)
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File Text:ucfv arico6 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

				-0.5	0	0	1	1	1
207.071494		10.0		20.0	200	400	1	1	1

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
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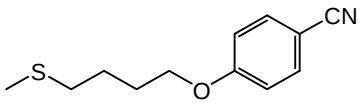
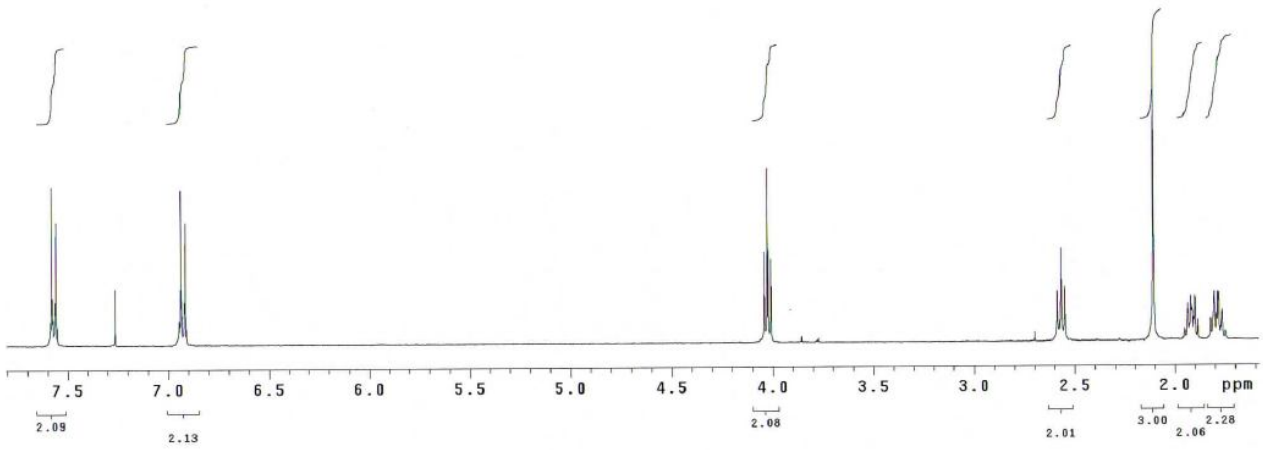
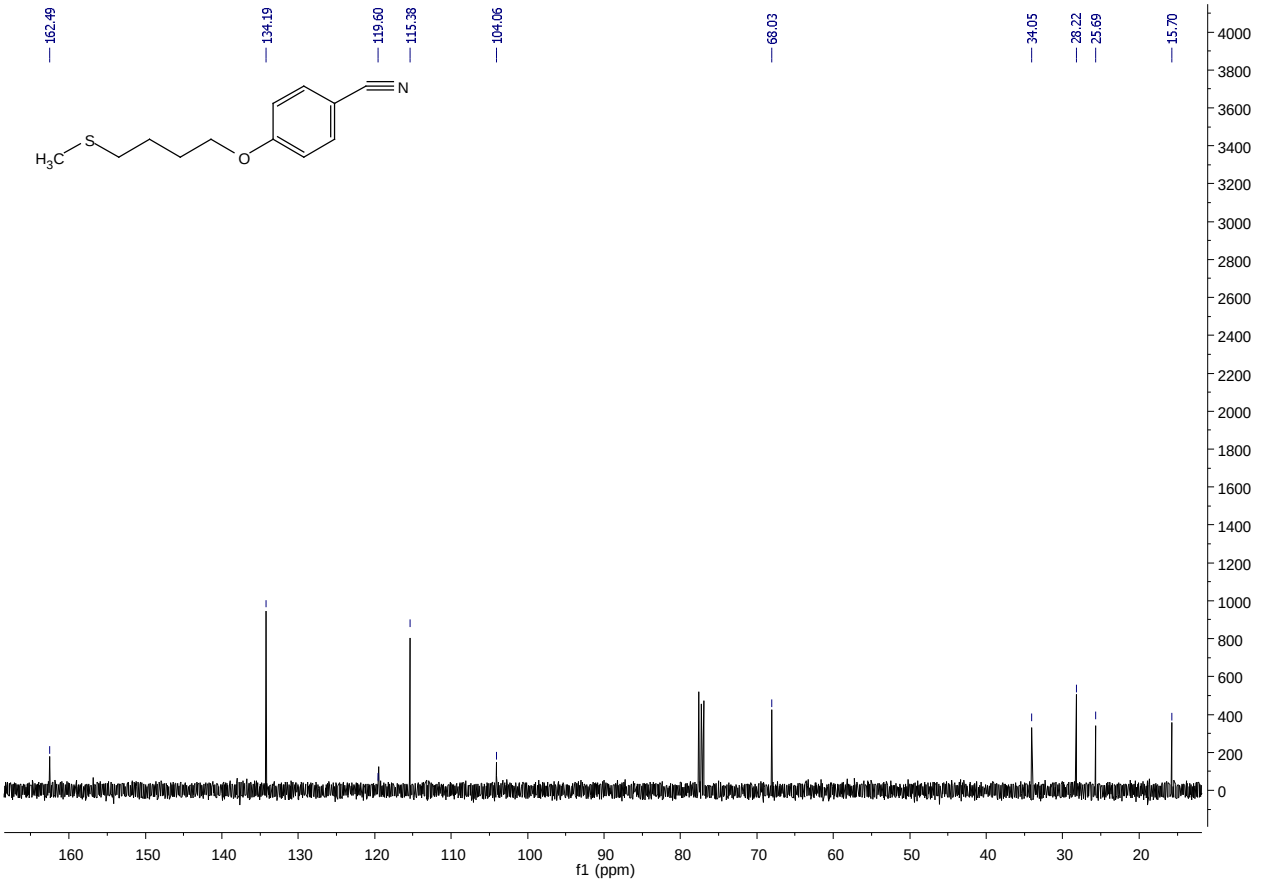
^{1}H NMR spectrum of 4-[4-(methylthio)butoxy]benzonitrile **26**

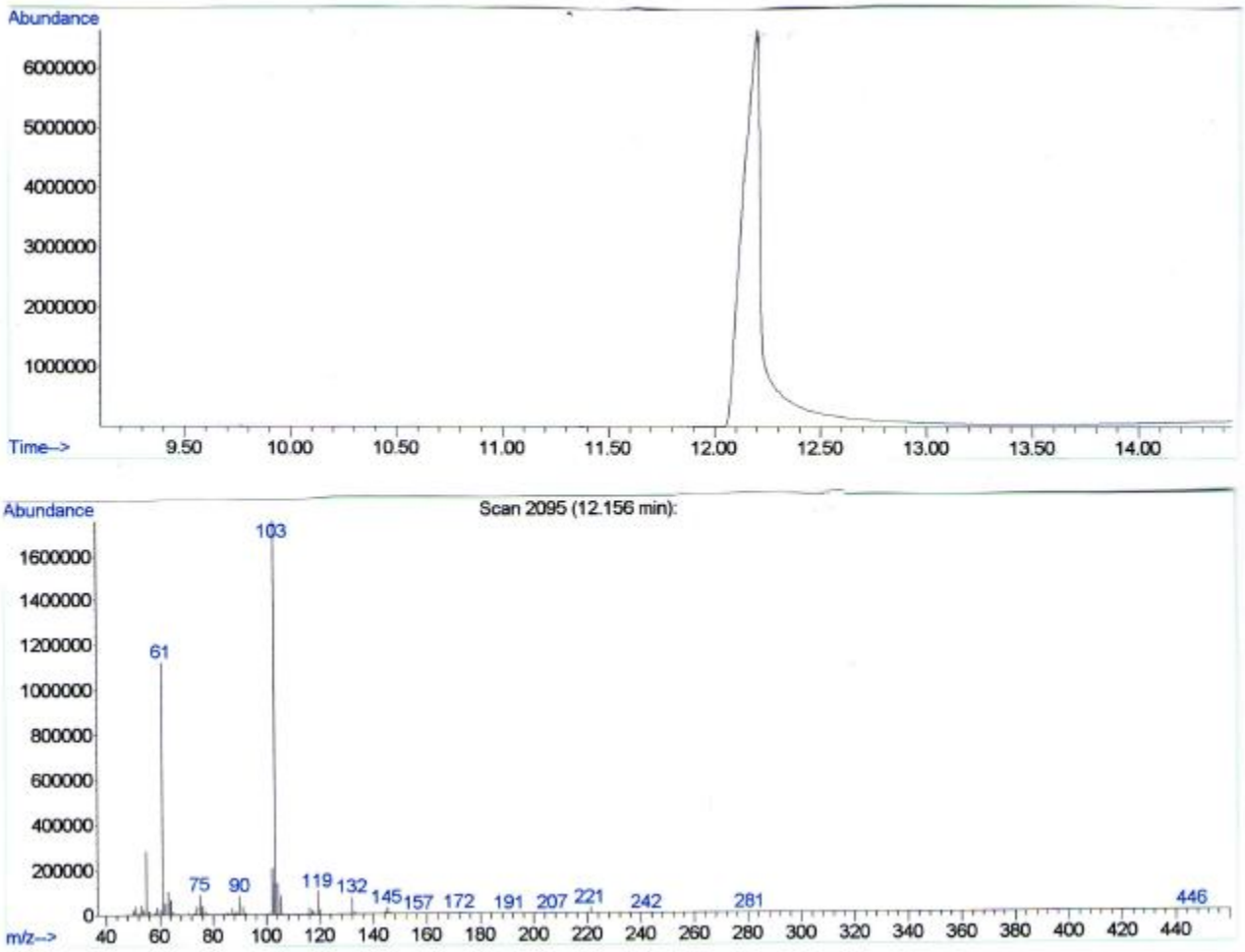




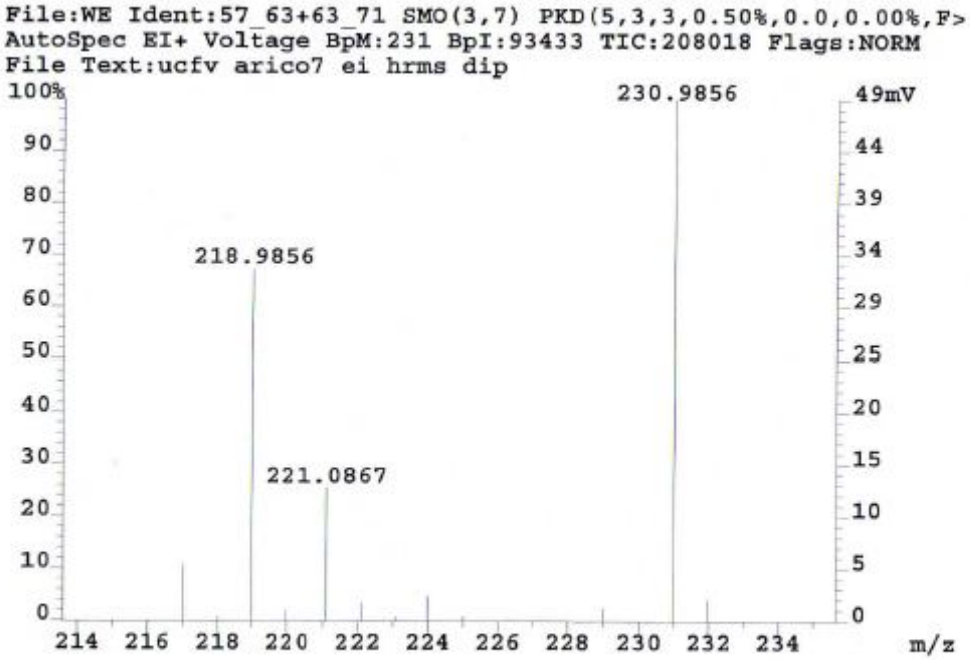
^{13}C NMR spectrum of 4-[4-(methylthio)butoxy]benzonitrile **26**



GC-MS spectrum of 4-[4-(methylthio)butoxy]benzonitrile **26**



HRMS analysis of 4-[4-(methylthio)butoxy]benzonitrile **26**



Elemental Composition Date : 7-OCT-2013

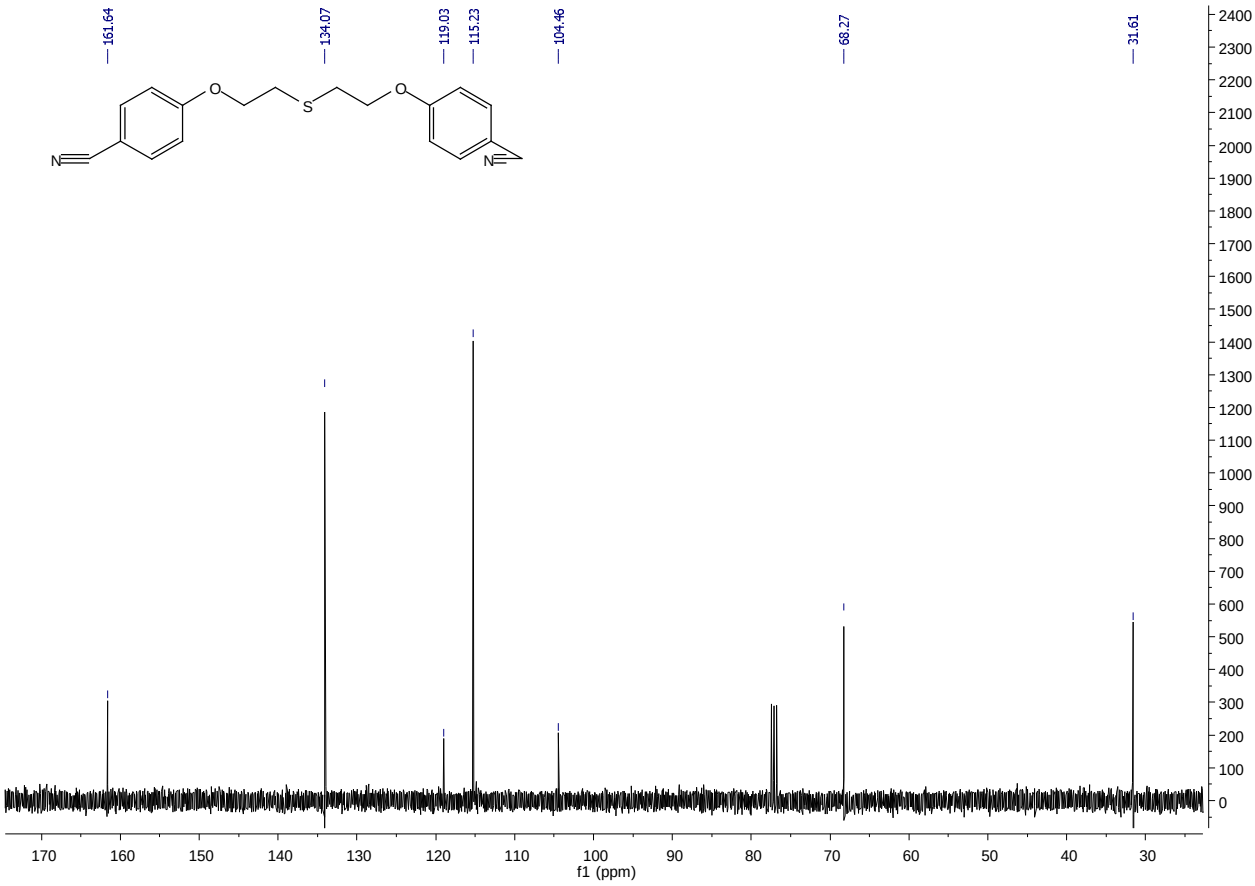
File:WE Ident:57_63+63_71 SMO(3,7) PKD(5,3,3,0.50%,0.0,0.00%,F,F)
AutoSpec EI+ Voltage BpM:231 BpI:93433 TIC:208018 Flags:NORM
File Text:ucfv arico7 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

				-0.5	0	0	1	1	1
221.086698		10.0		20.0	200	400	1	1	1

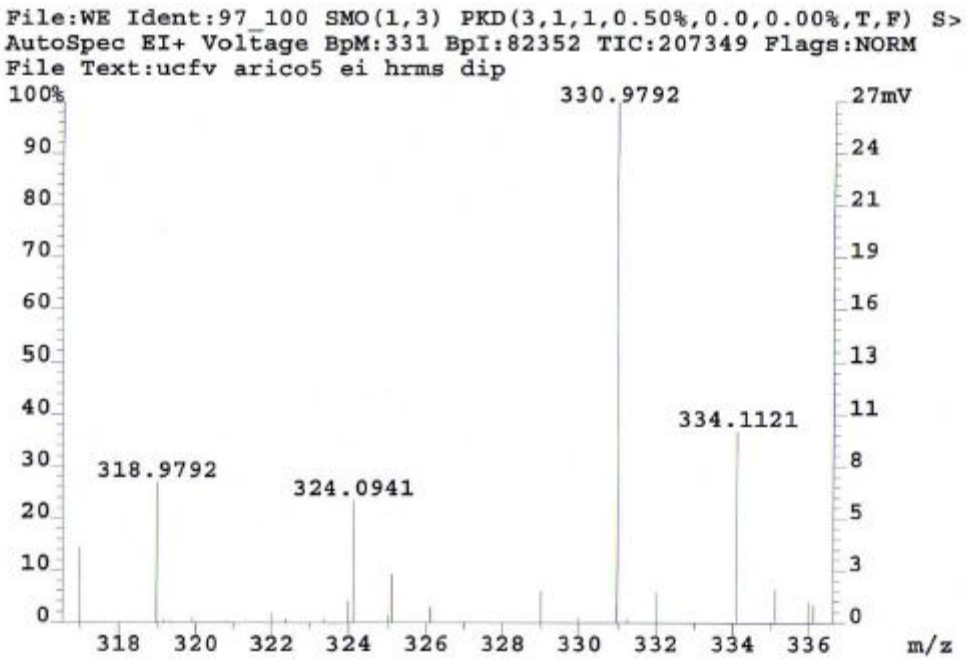
Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
221.086698	3.3	0.7	221.087436	6.0	12	15	1	1	1

^{1}H NMR spectrum of Bis[2-(4-cyanophenoxy)ethyl]sulfide **27**

^{13}C NMR spectrum of Bis[2-(4-cyanophenoxy)ethyl]sulfide **27**



HRMS analysis of Bis[2-(4-cyanophenoxy)ethyl]sulfide **27**



Elemental Composition Date : 7-OCT-2013

File:WE Ident:97_100 SMO(1,3) PKD(3,1,1,0.50%,0.0,0.00%,T,F)
AutoSpec EI+ Voltage BpM:331 BpI:82352 TIC:207349 Flags:NORM
File Text:ucfv arico5 ei hrms dip
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

				-0.5	0	0	2	2	1
324.094090		10.0		20.0	200	400	2	2	1

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
324.094090	-2.6	-0.8	324.093250	12.0	18	16	2	2	1