Electronic Supporting Information
Volume 2

A Simple Hückel Model-Driven Synthetic Strategy to Overcome Electronic Barriers to Retro-Brook Silylation Relevant to Aryne and Bisaryne Precursor Synthesis

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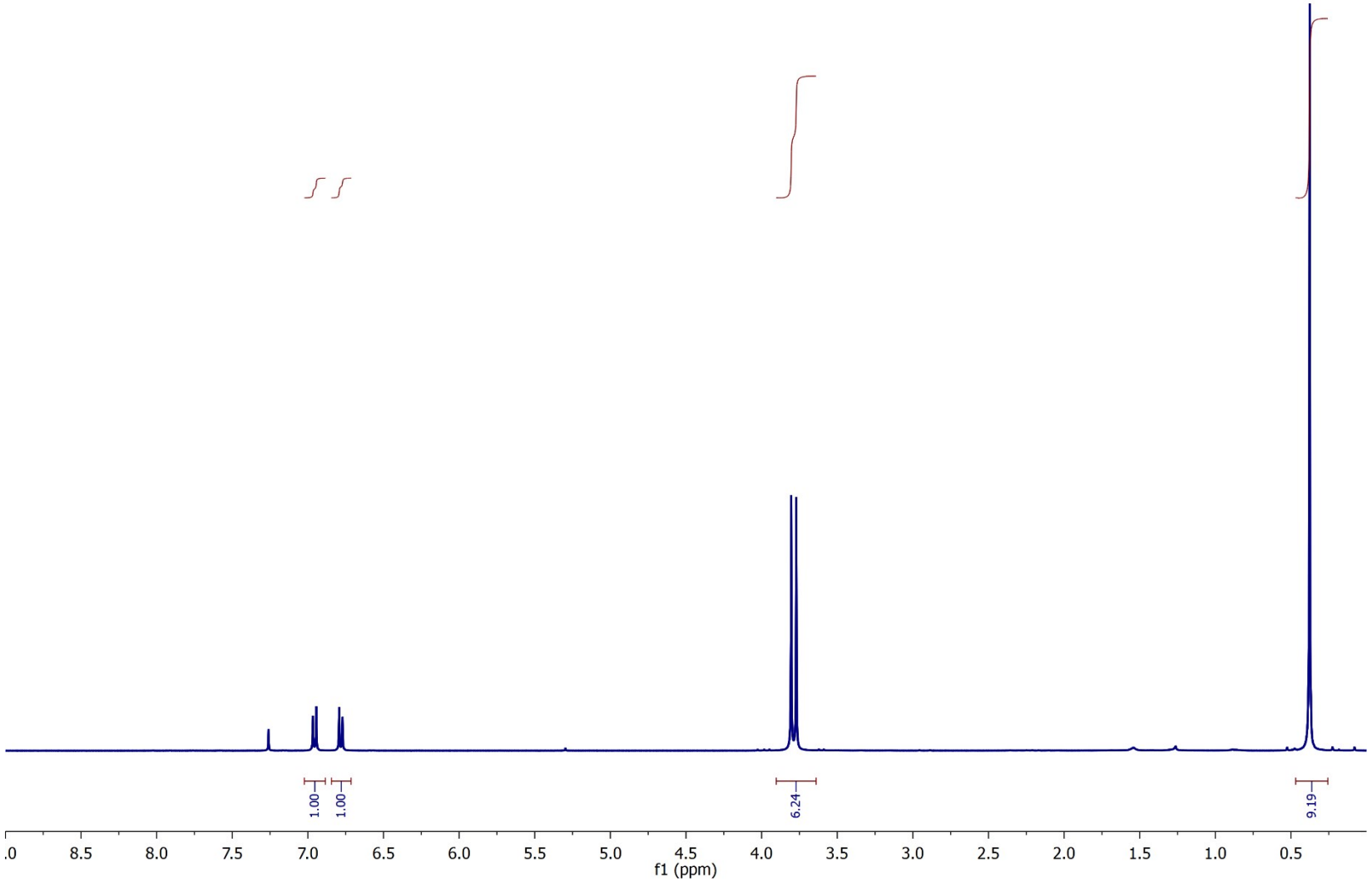
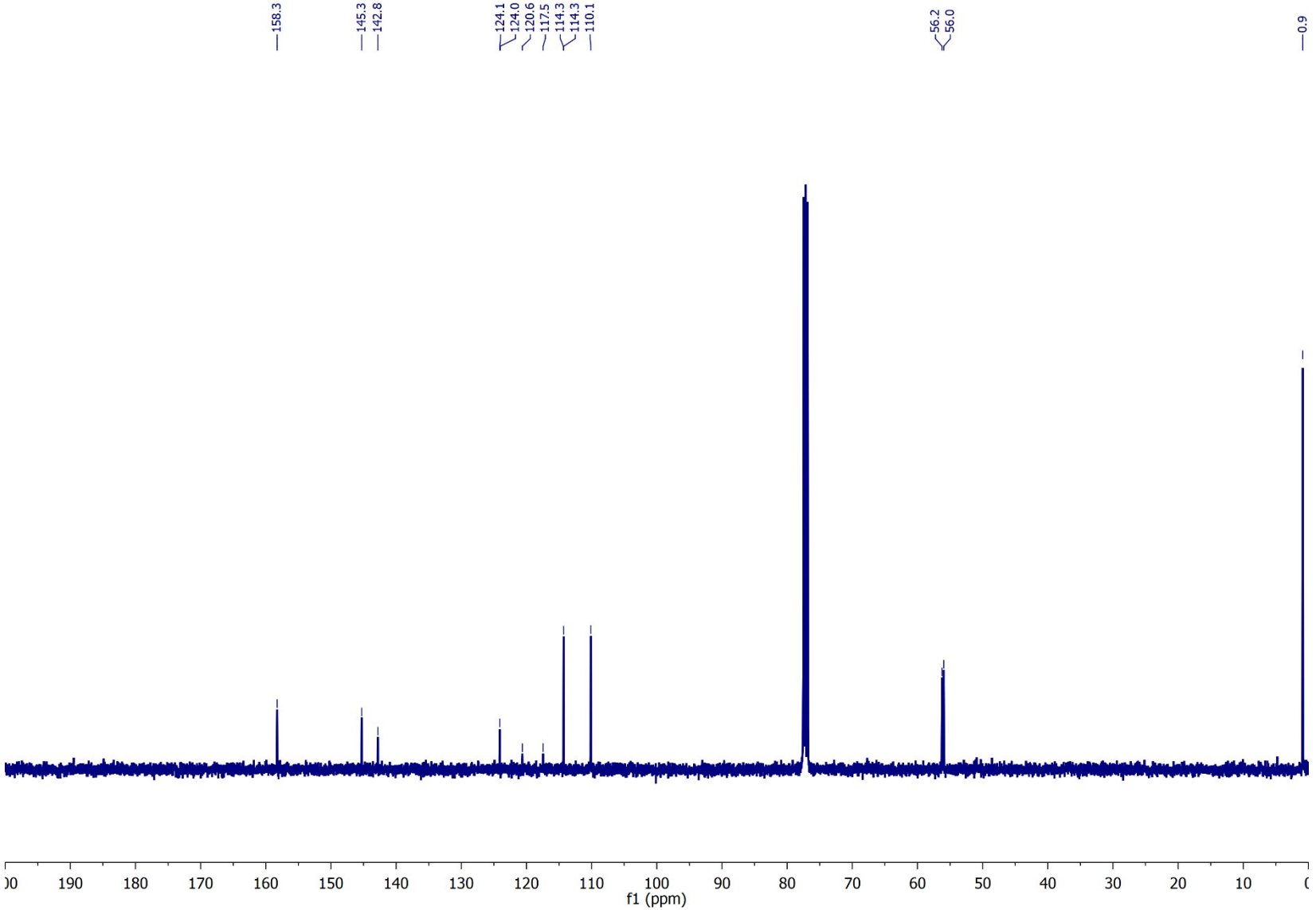
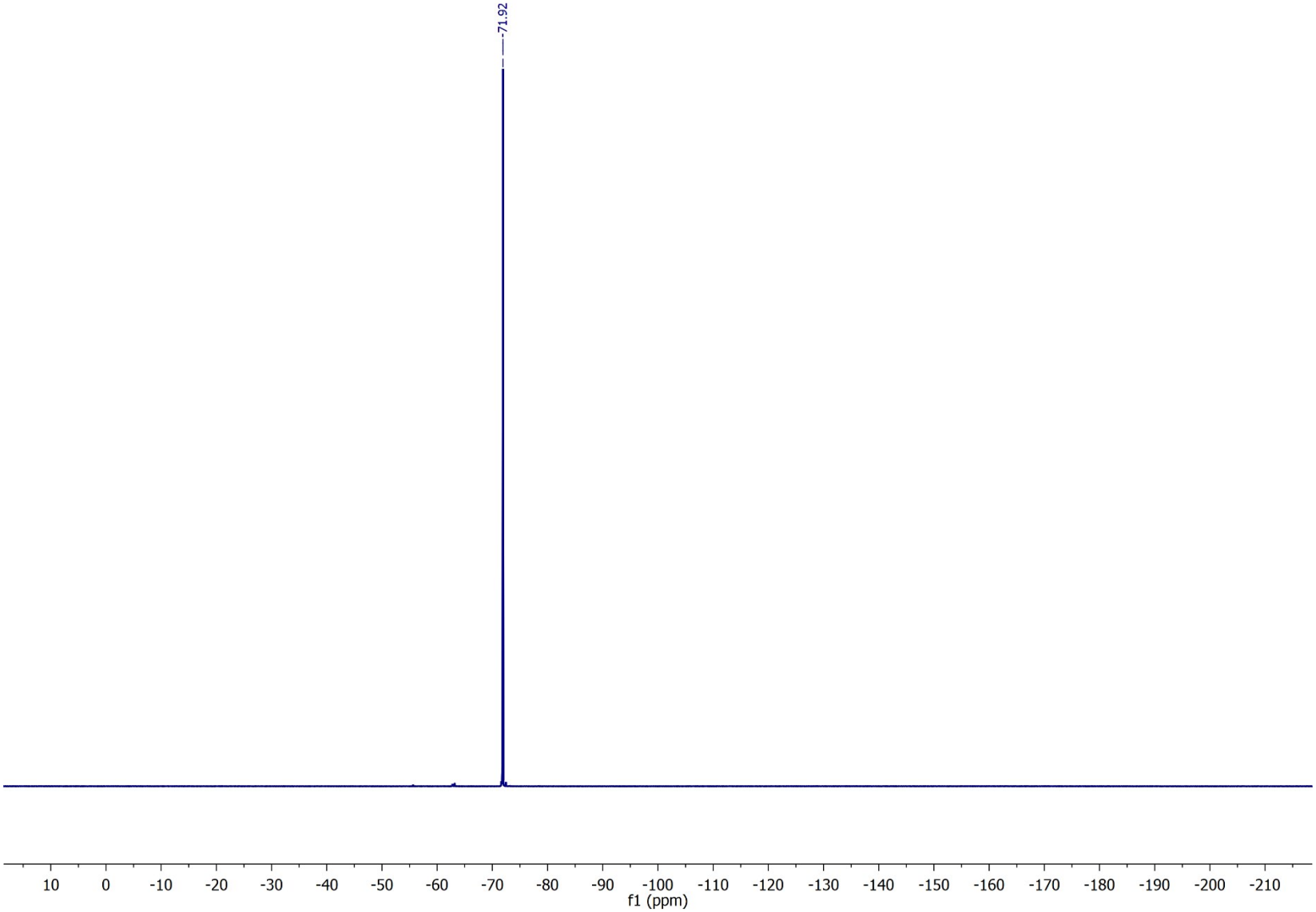
*3,6-Dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**13z**), ^{1}H NMR, 400 MHz, 298 K*



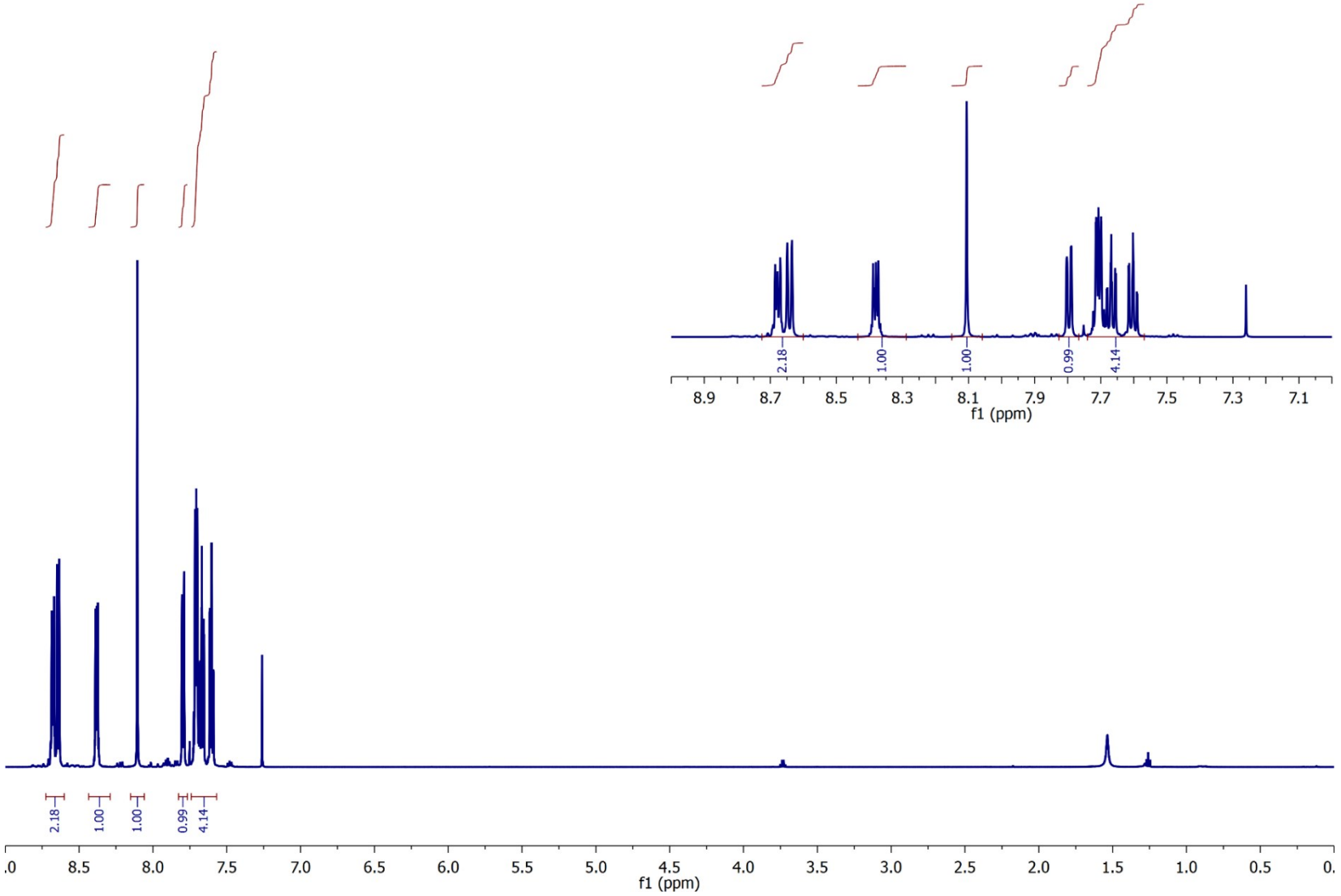
*3,6-Dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**13z**), ^{13}C NMR, 100 MHz, 298 K*



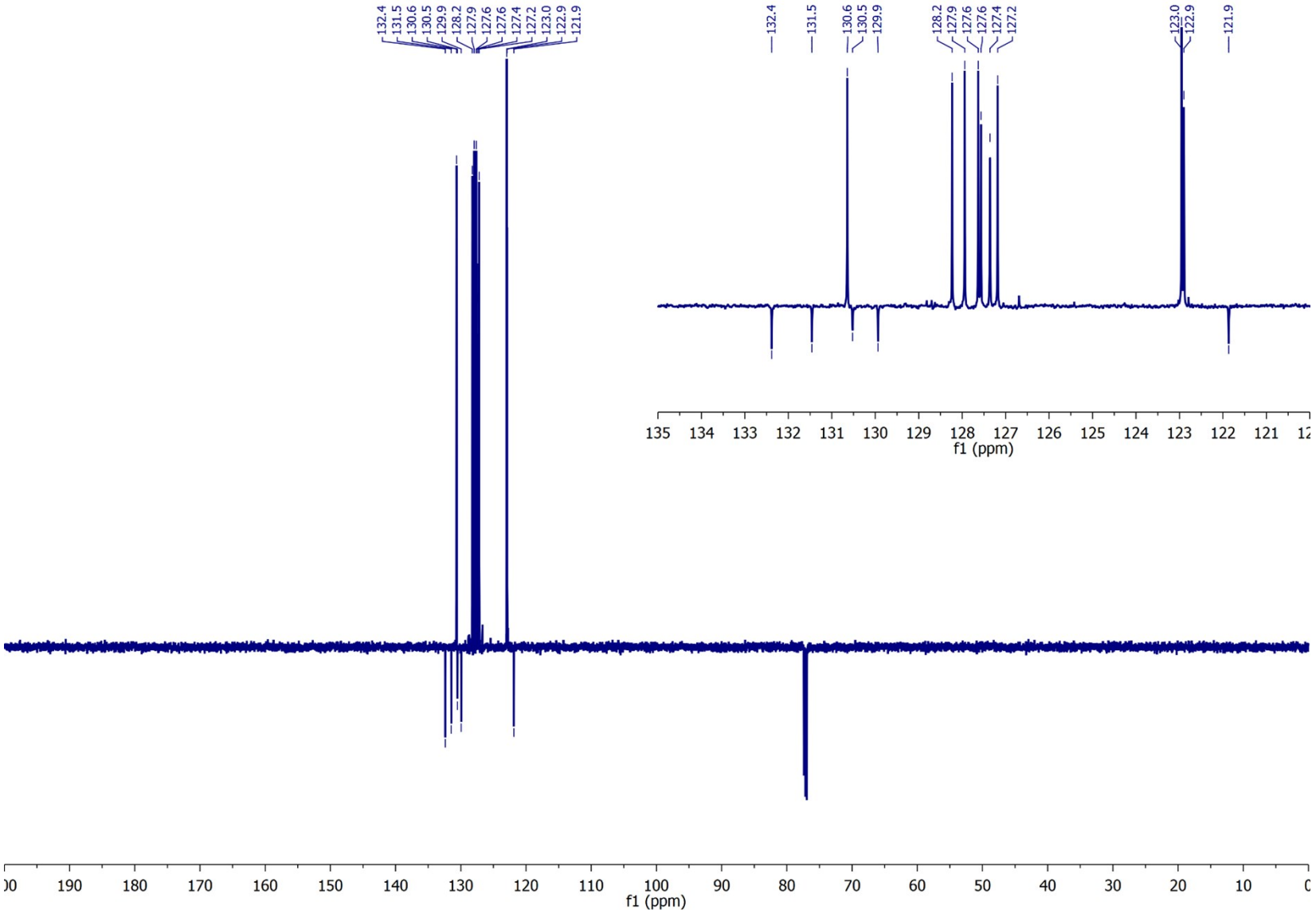
*3,6-Dimethoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (**13z**), ^{19}F NMR, 376 MHz, 298 K*



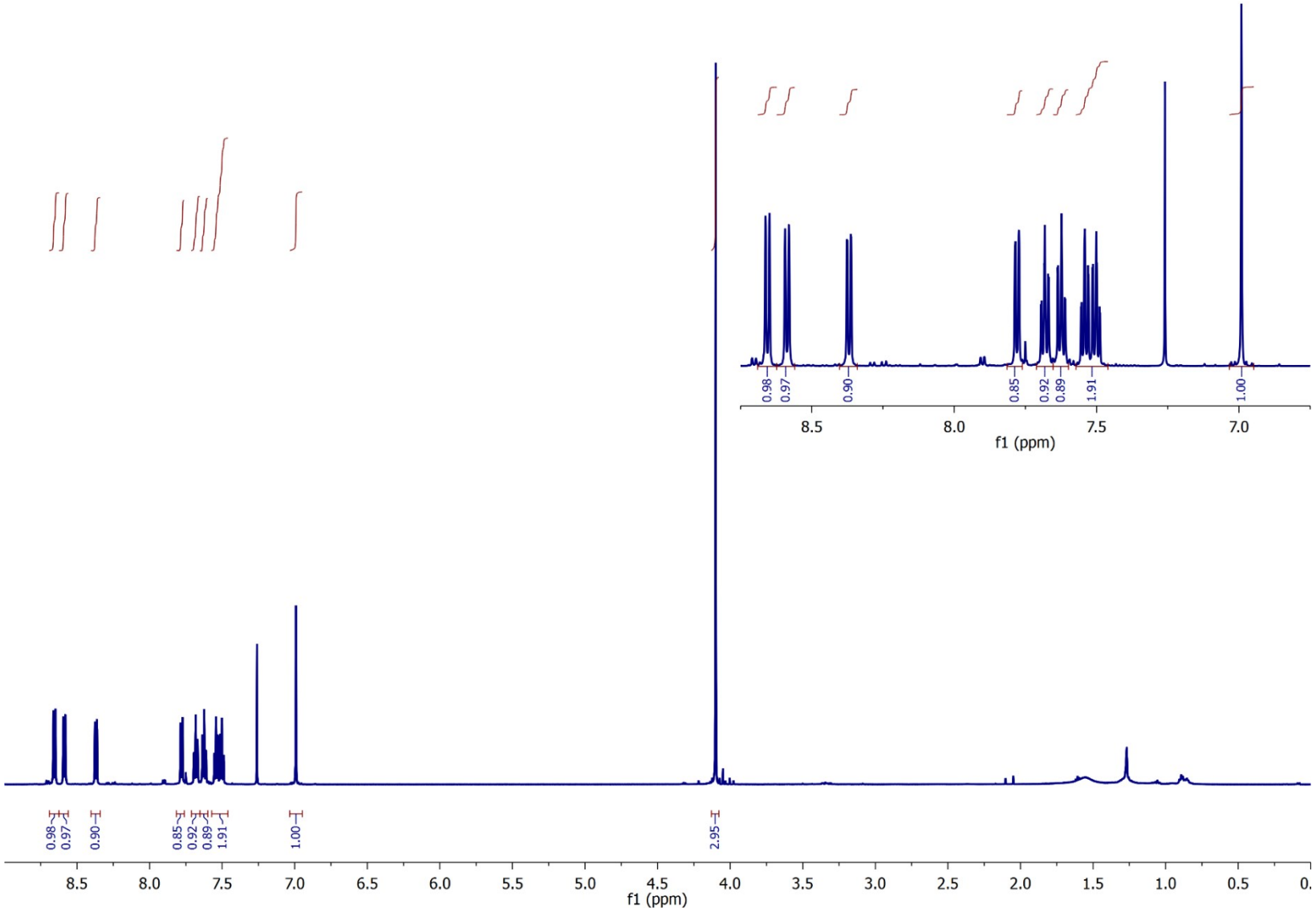
*9-Bromophenanthrene (**17**), ^{1}H NMR, 600 MHz, 298 K*



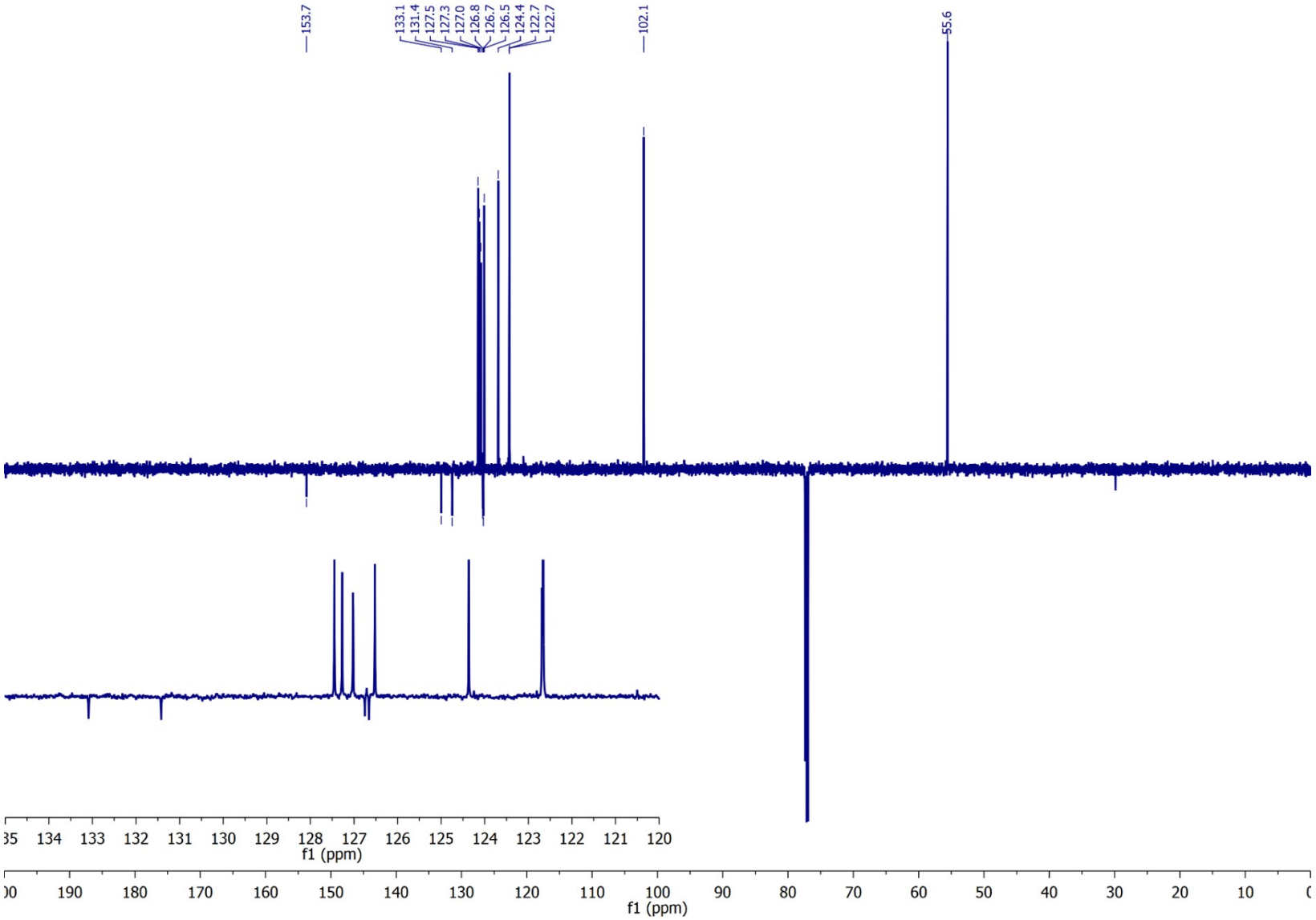
*9-Bromophenanthrene (**17**), ^{13}C DEPTQ135 NMR, 150 MHz, 298 K*



*9-Methoxyphenanthrene (**18**), ^{1}H NMR, 600 MHz, 298 K*



*9-Methoxyphenanthrene (**18**), ^{13}C DEPTQ135 NMR, 150 MHz, 298 K*



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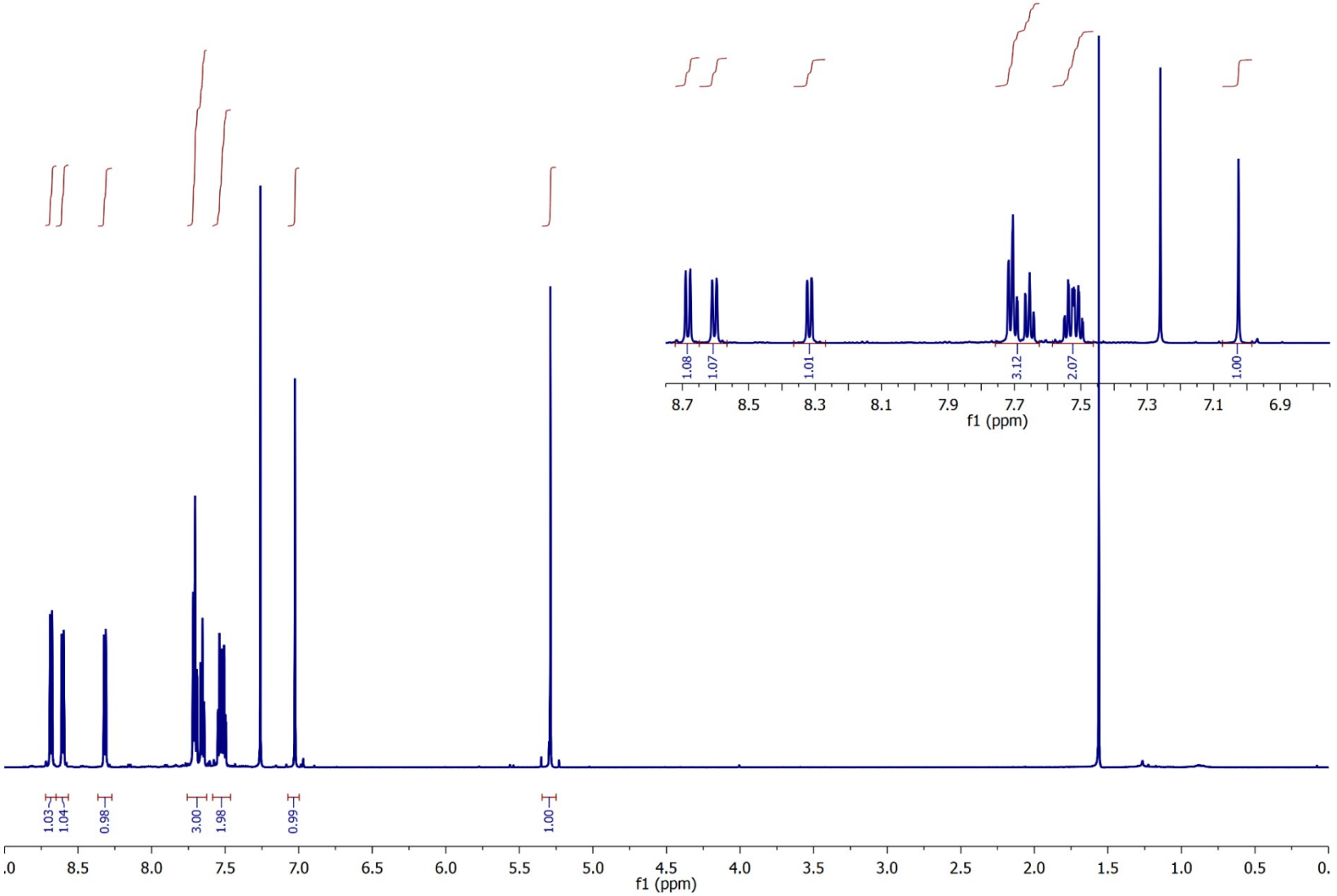

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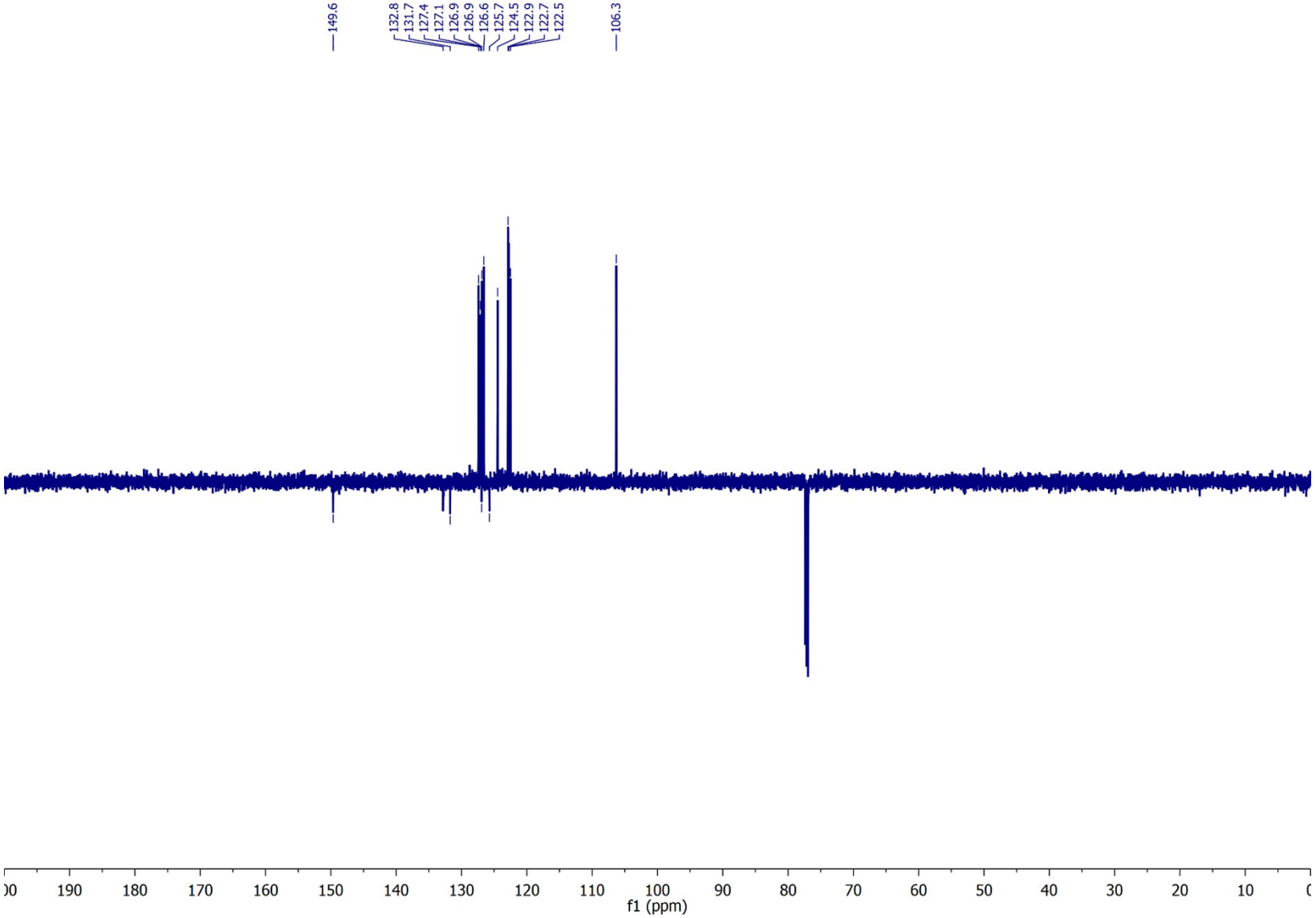
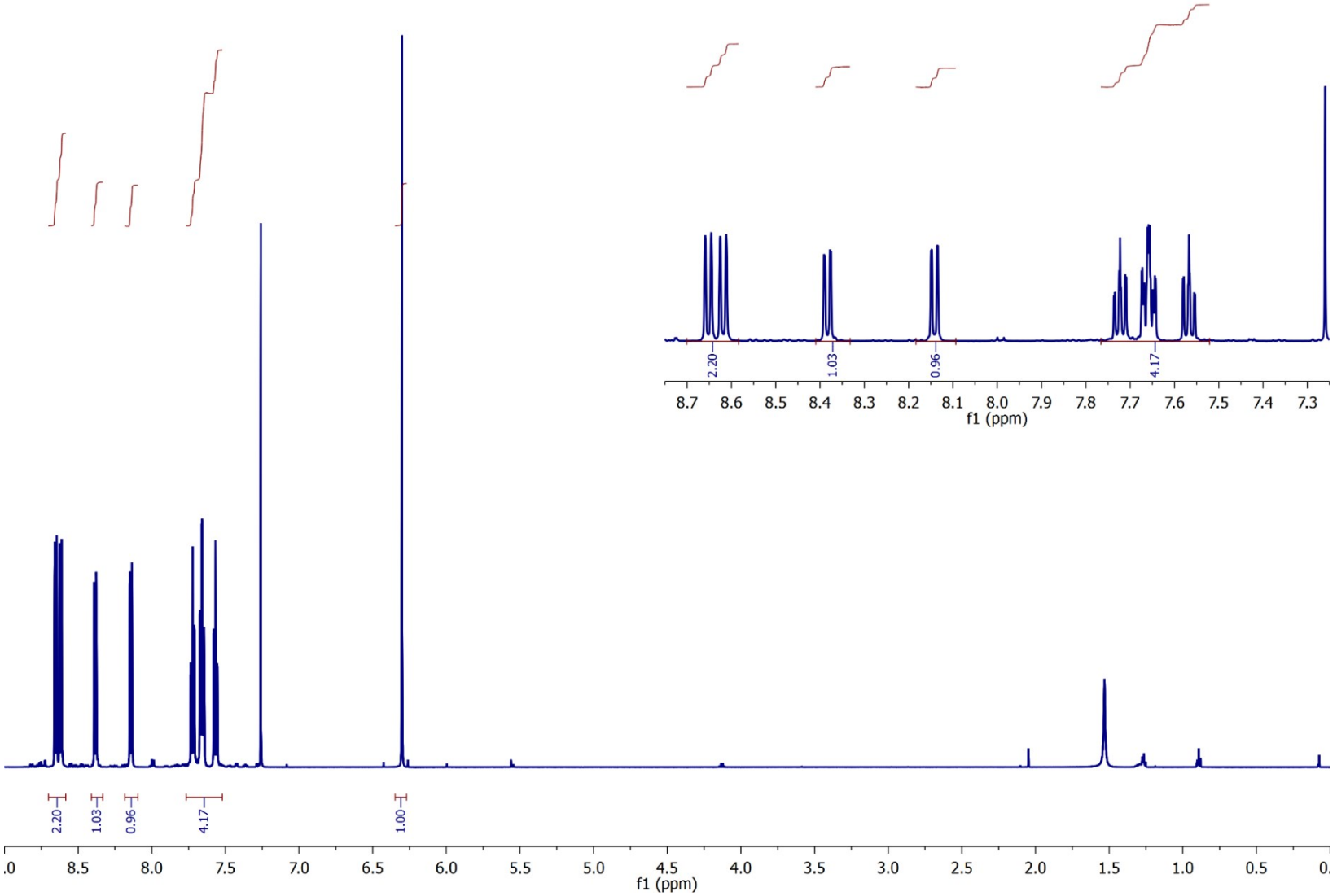
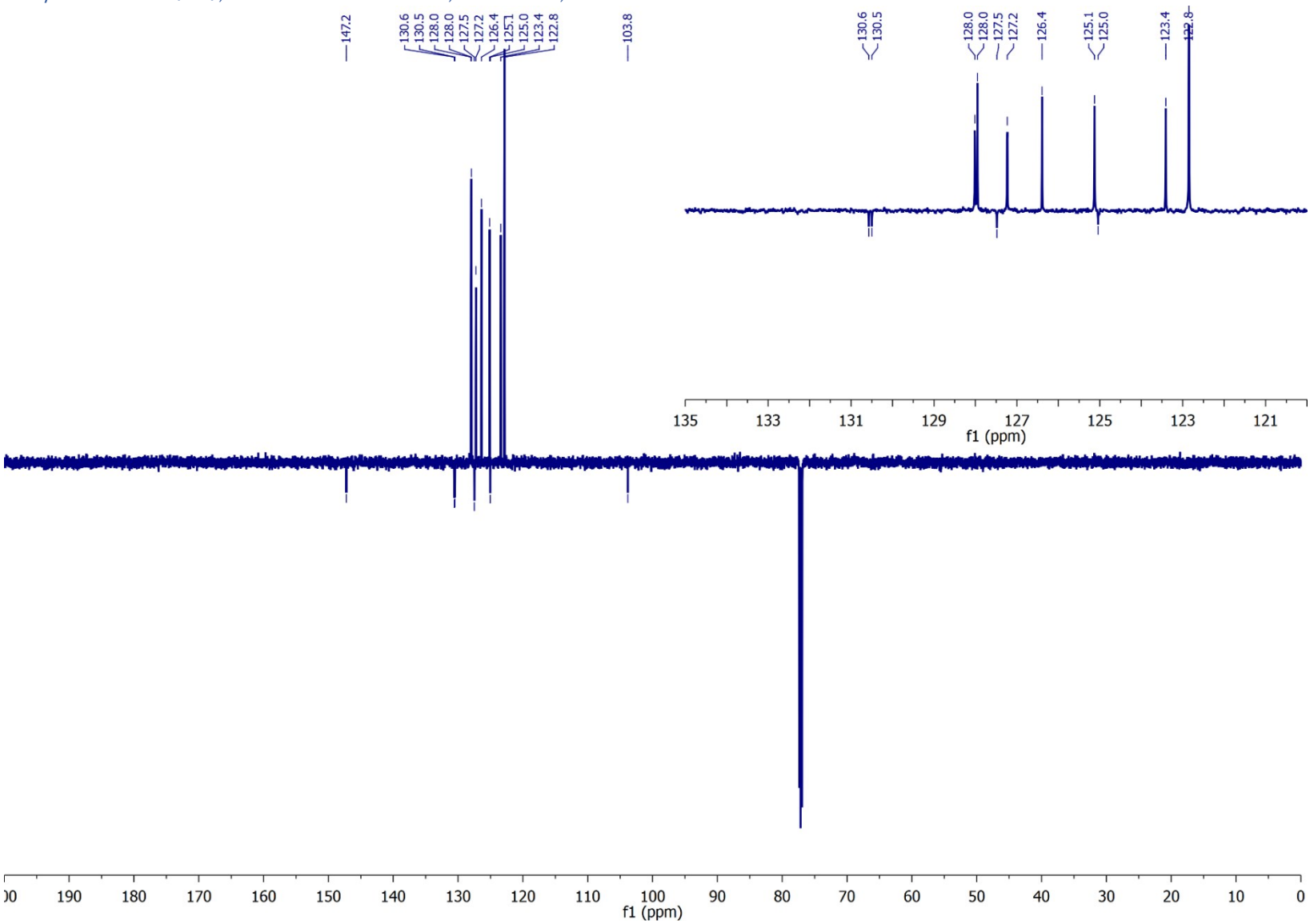


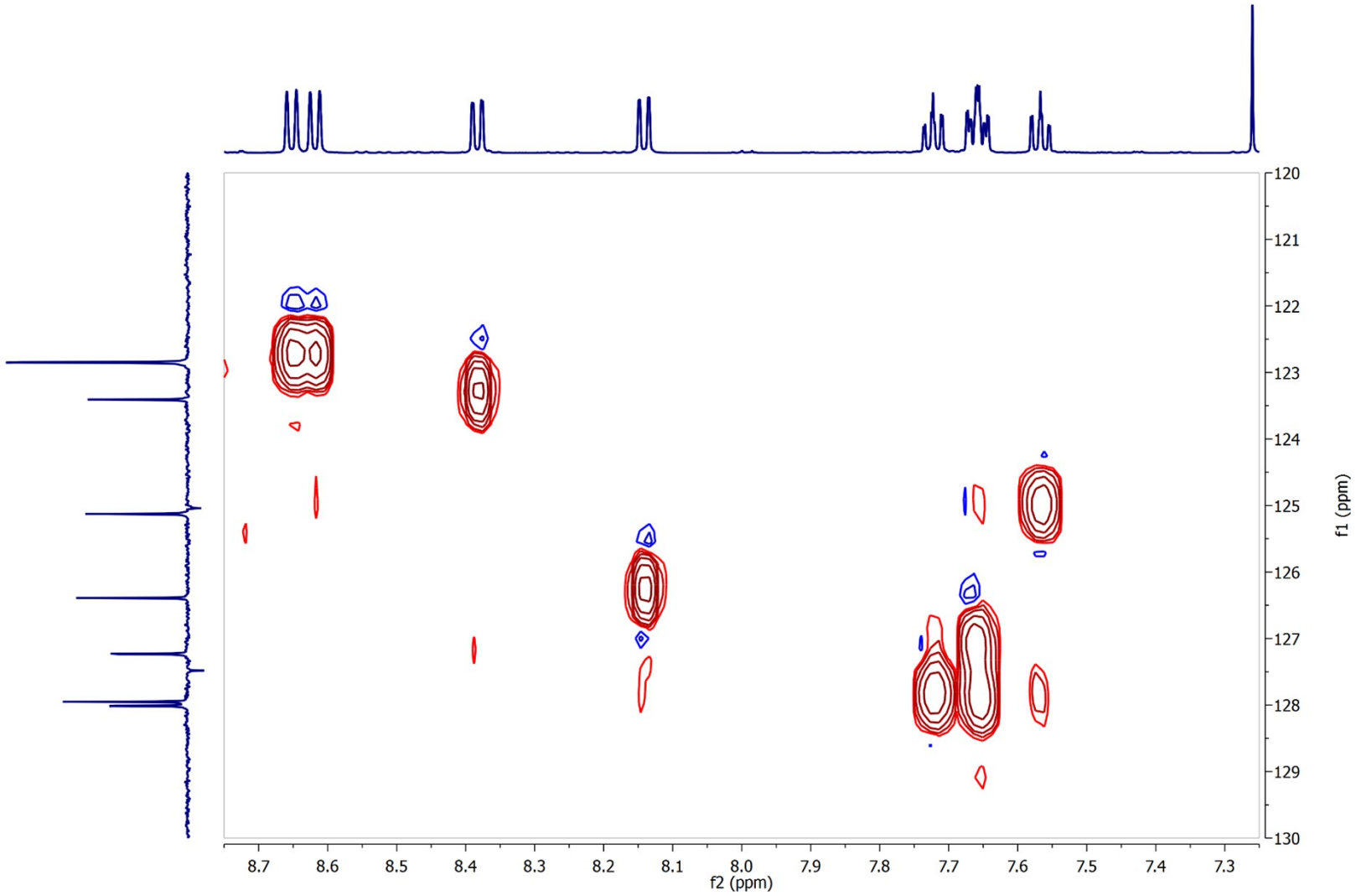
*9-Bromo-10-phenanthrol (**14**), ^{1}H NMR, 600 MHz, 298 K*



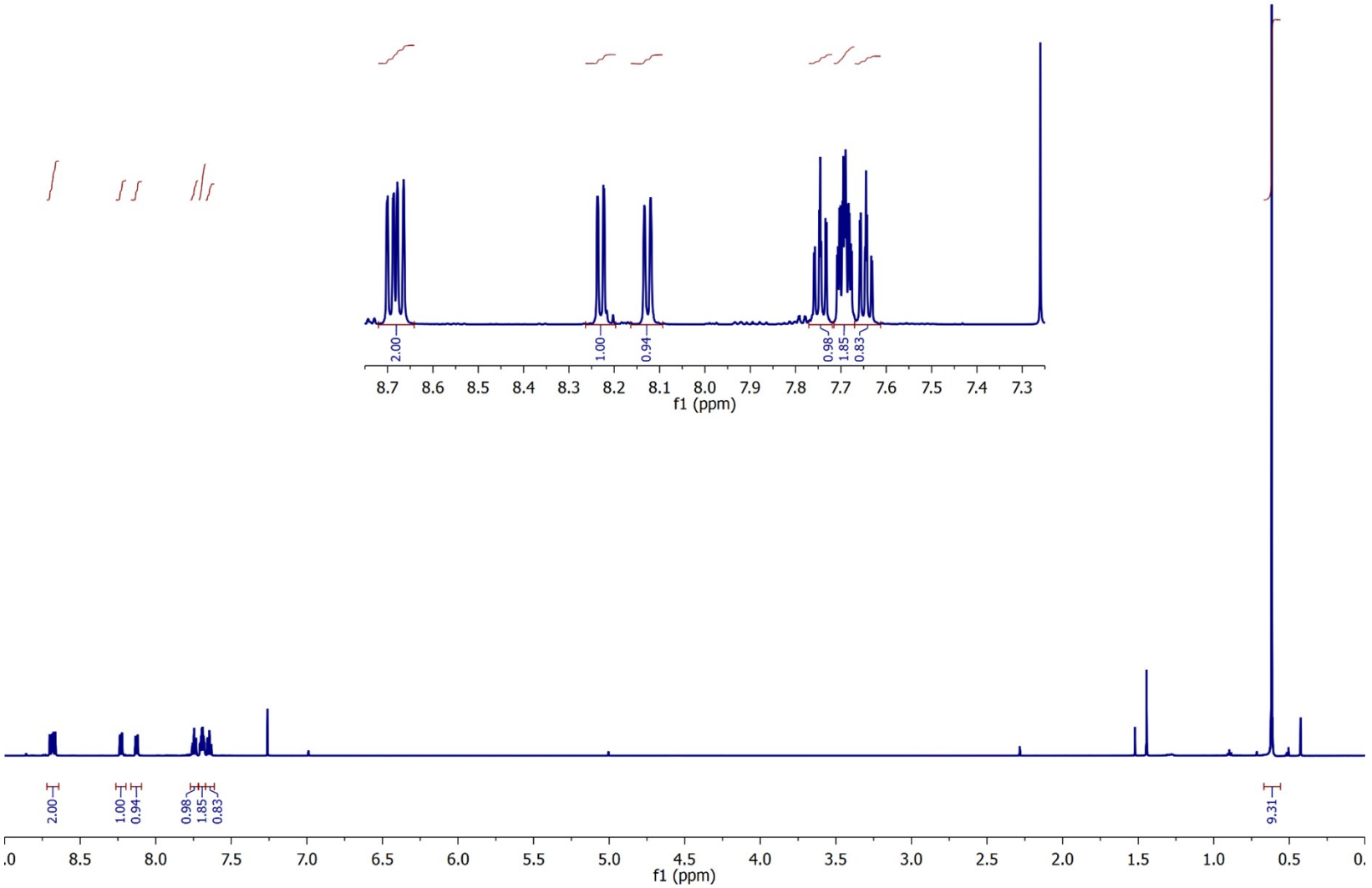
*9-Bromo-10-phenanthrol (**14**), ^{13}C DEPTQ135 NMR, 150 MHz, 298 K*



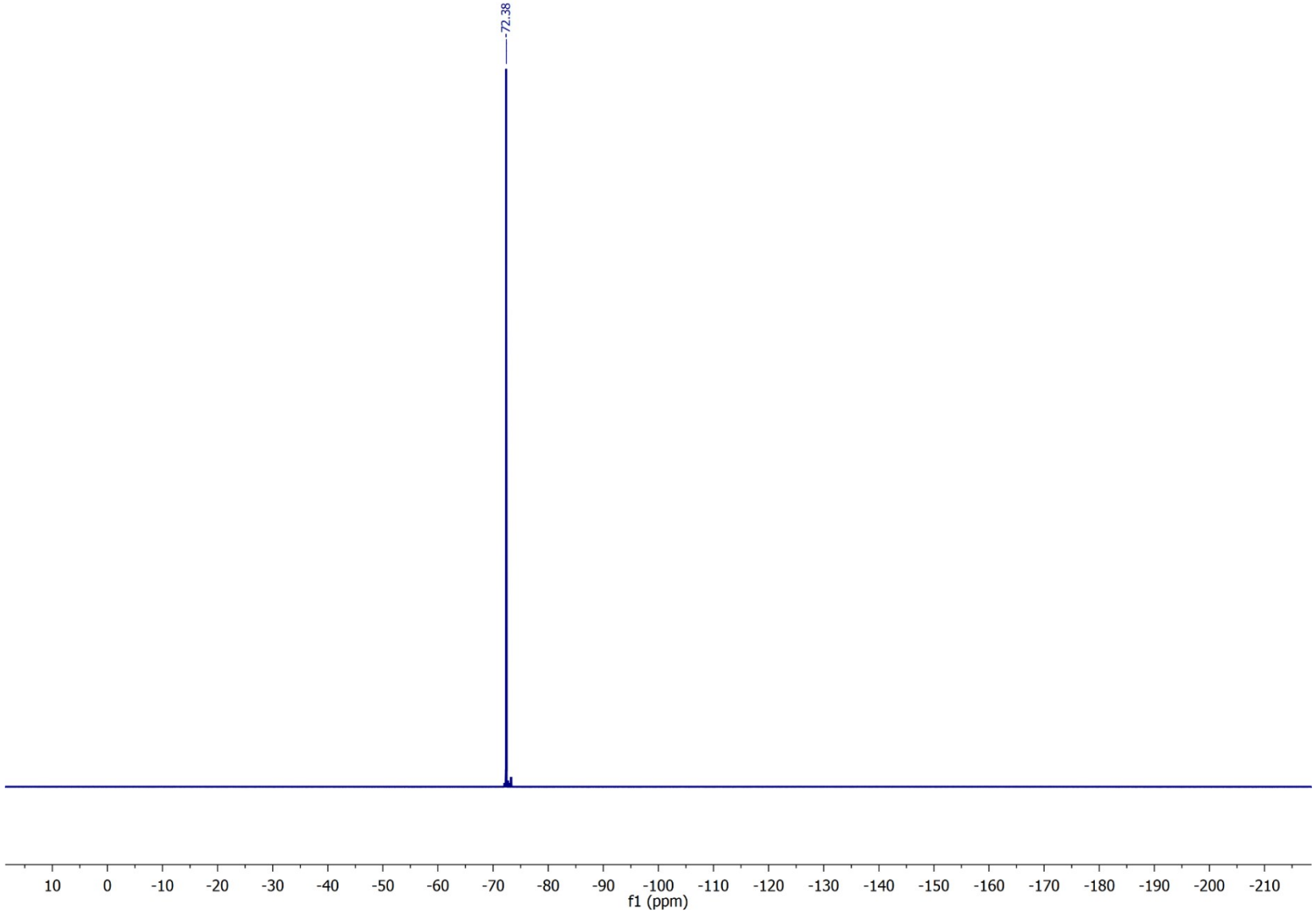
*9-Bromo-10-phenanthrol (**14**), HSQC NMR, 600 MHz, 298 K*



*10-(Trimethylsilyl)-9-phenanthryl Trifluoromethanesulfonate (**15**), ^{1}H NMR, 600 MHz, 298 K*



*10-(Trimethylsilyl)-9-phenanthryl Trifluoromethanesulfonate (**15**), ^{19}F NMR, 376 MHz, 298 K*



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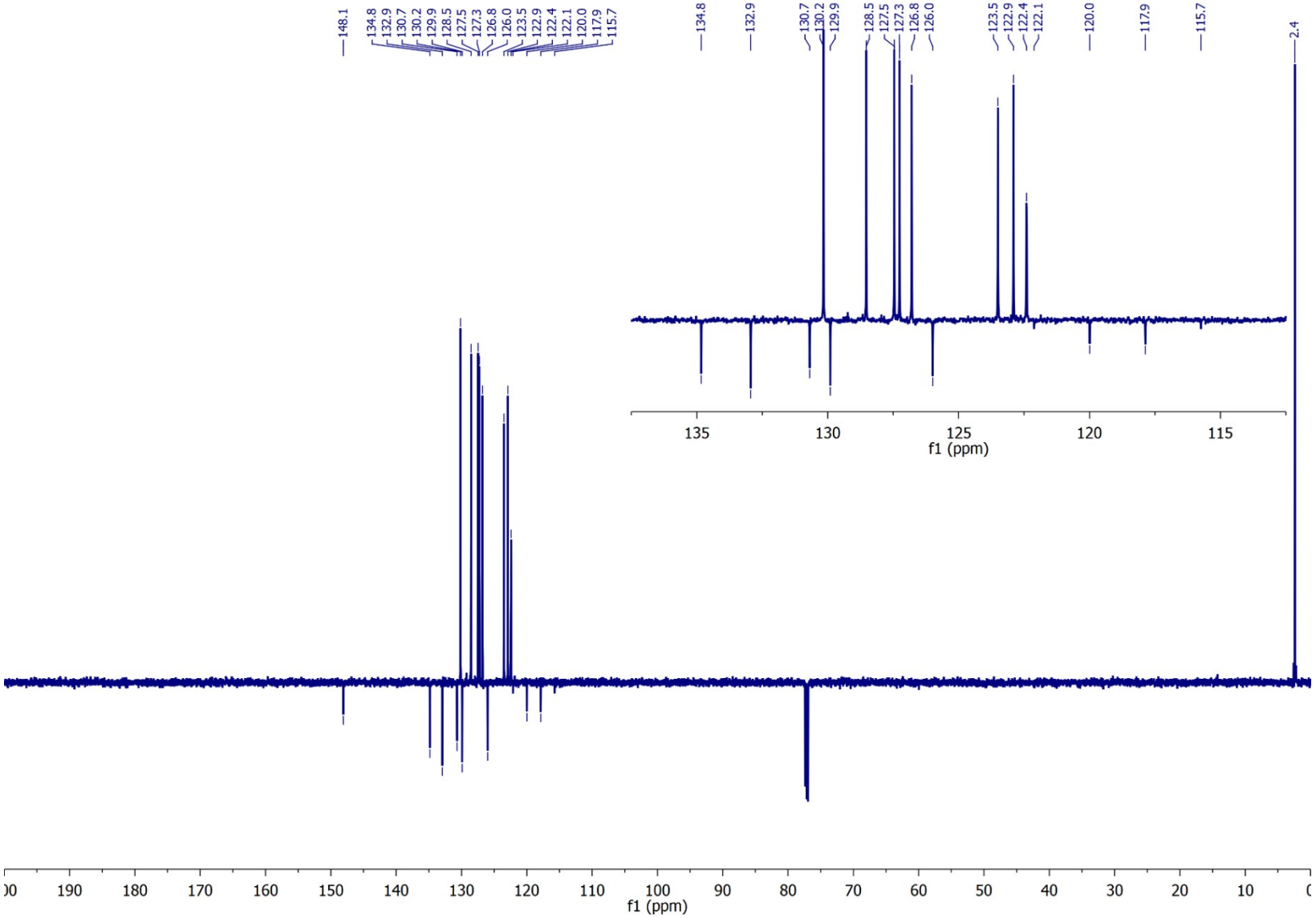
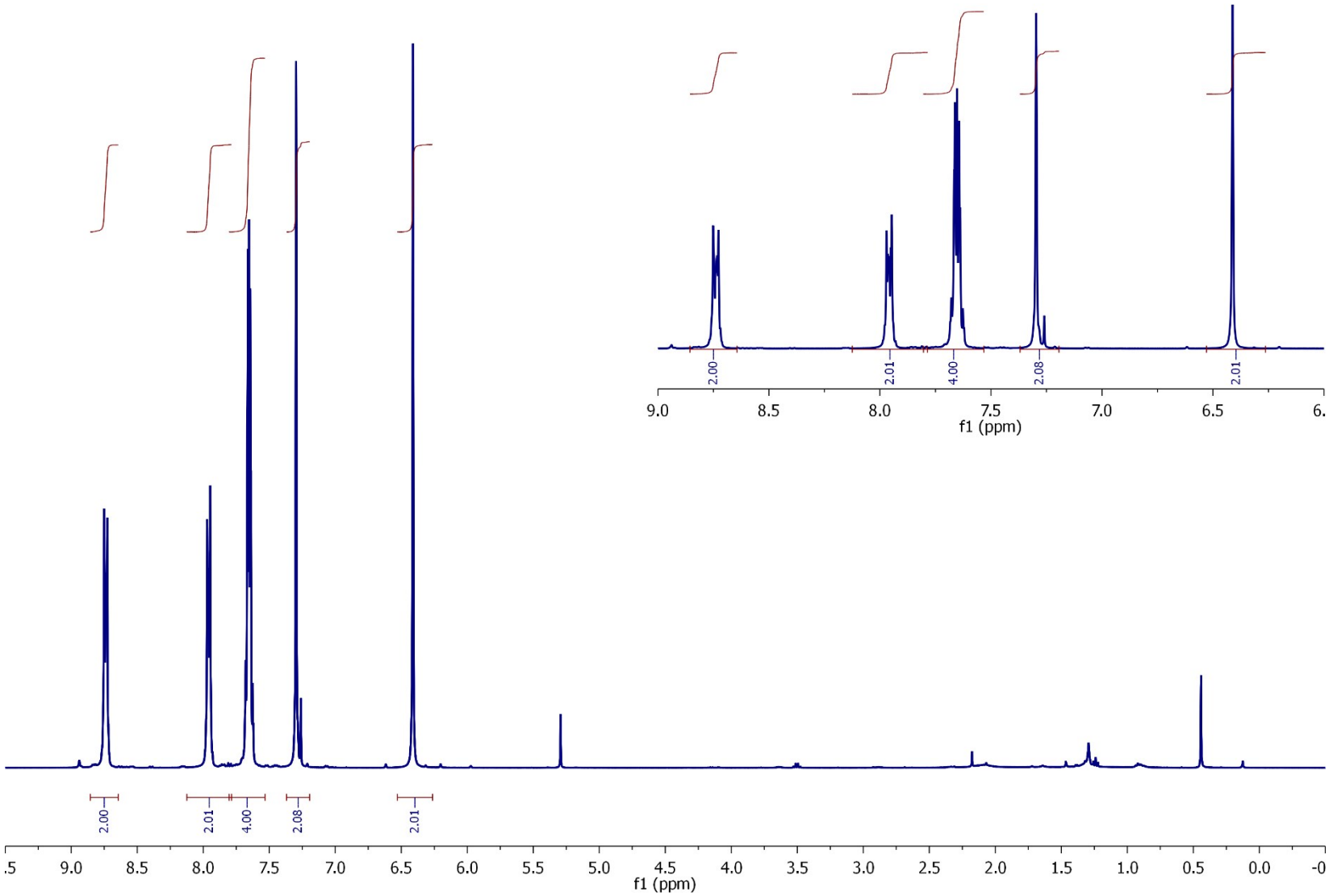
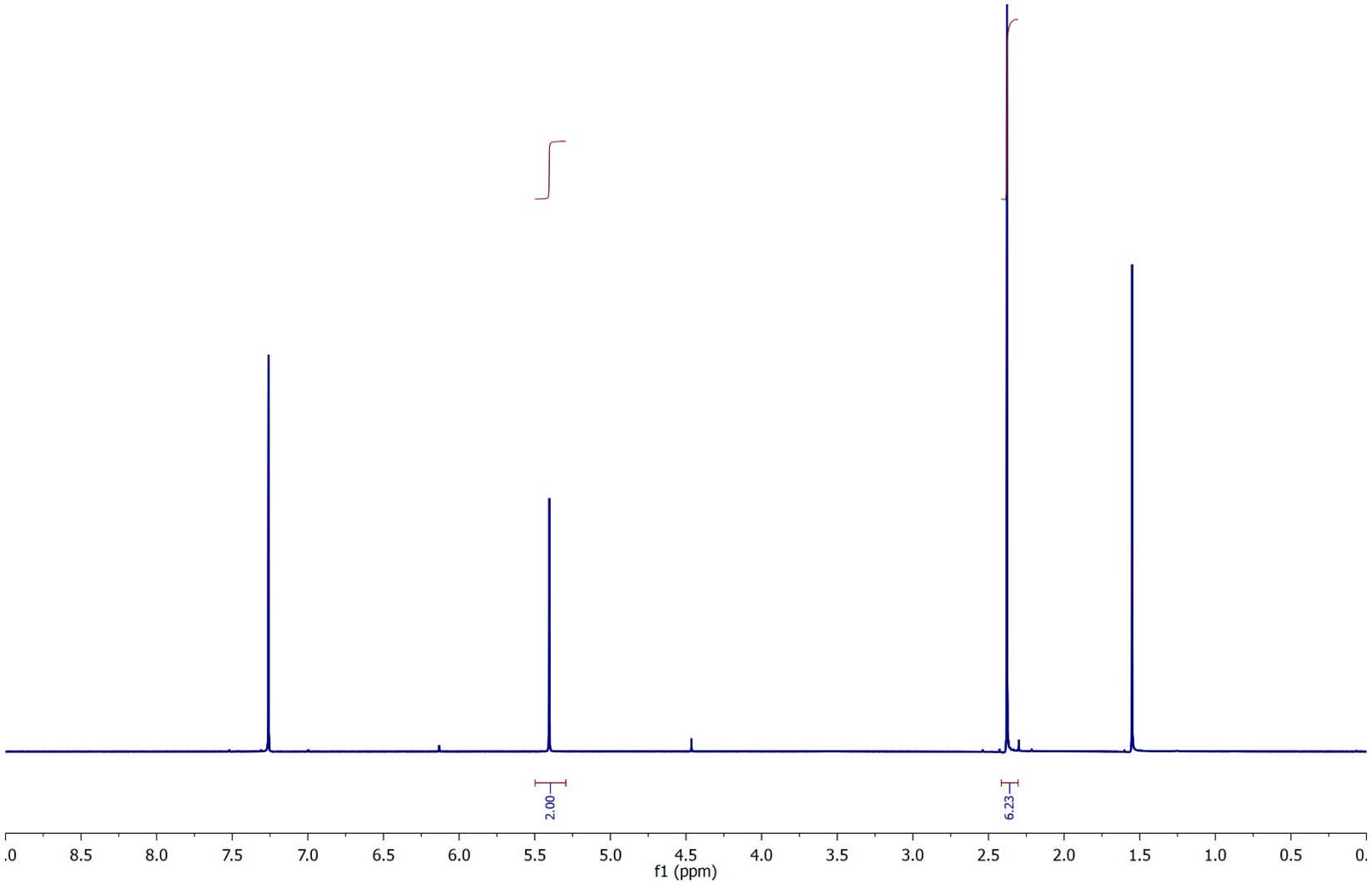


*1,4-Dihydro-1,4-epoxytriphenylene (**20**), ^{1}H NMR, 400 MHz, 298 K*



*2,5-Dibromo-3,6-dimethylhydroquinone (**9**), ^{1}H NMR, 400 MHz, 298 K*



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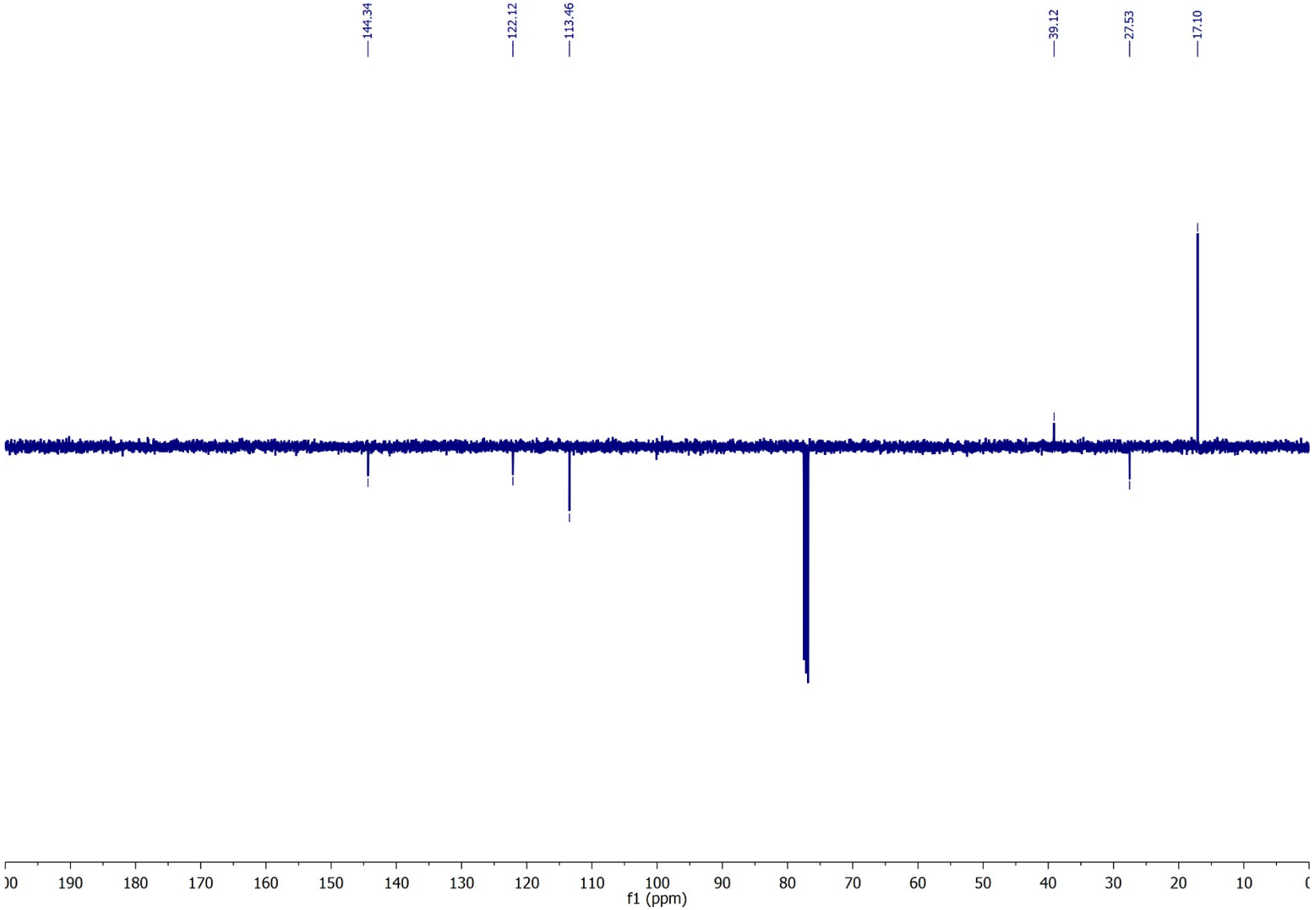
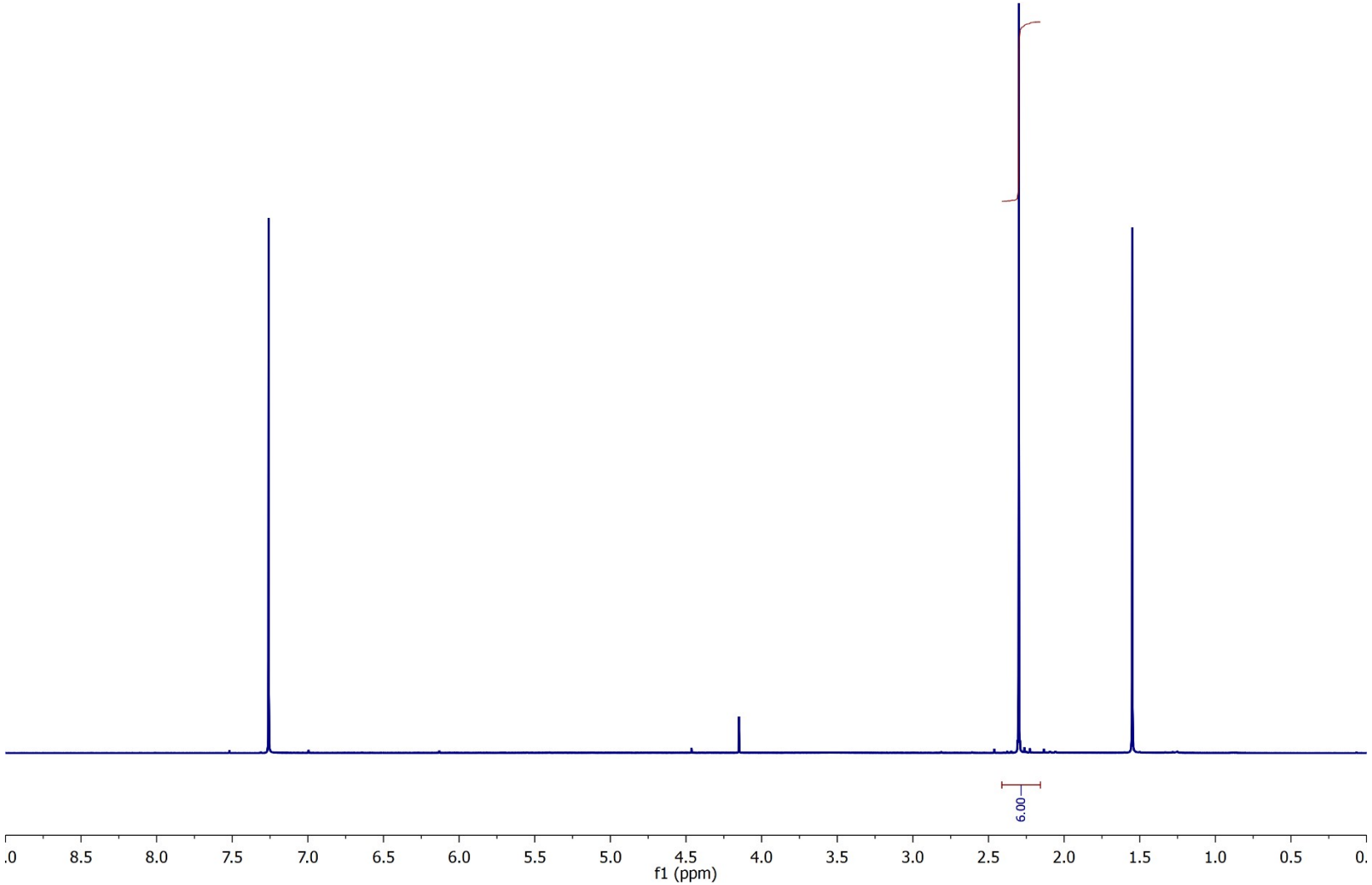
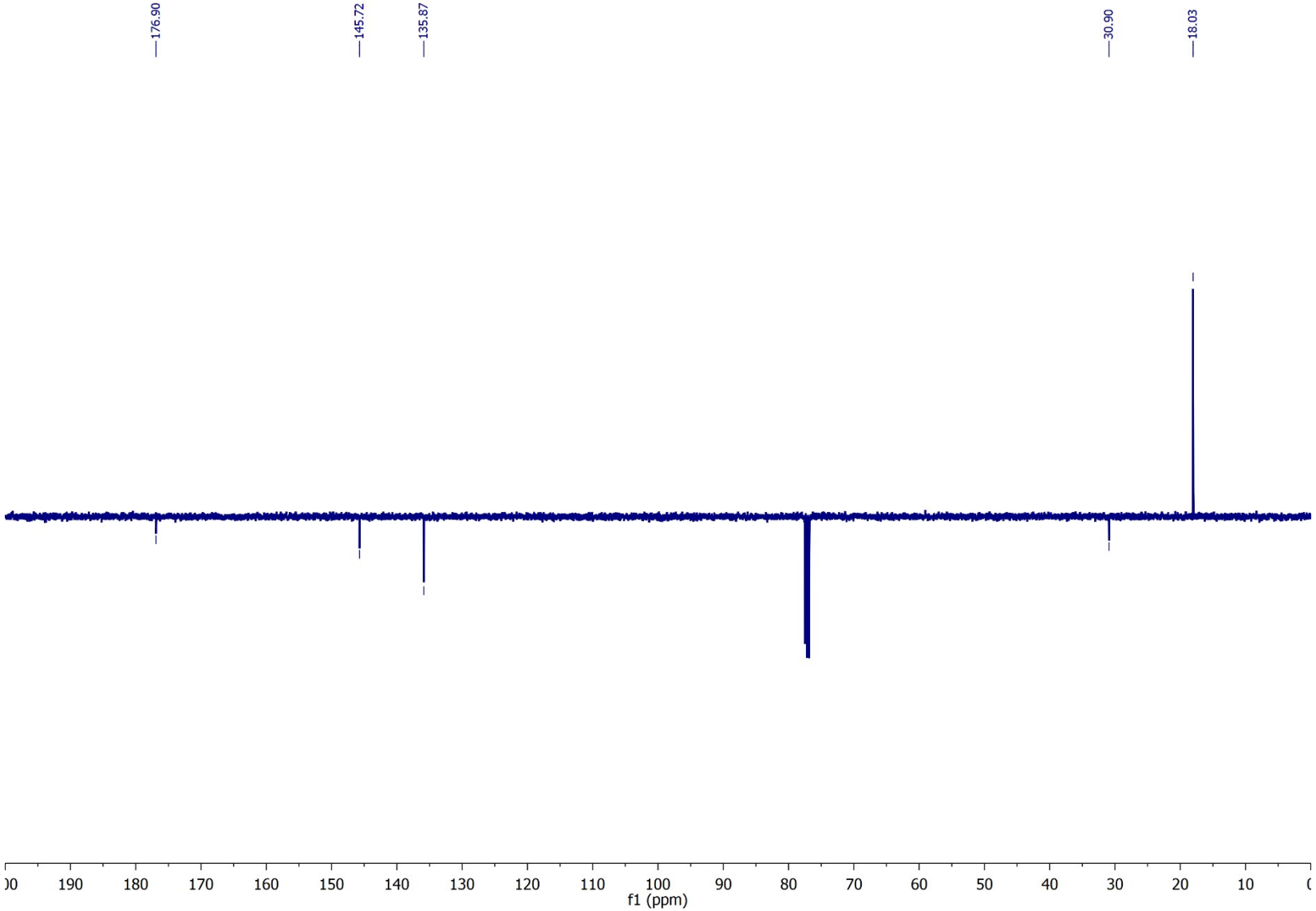


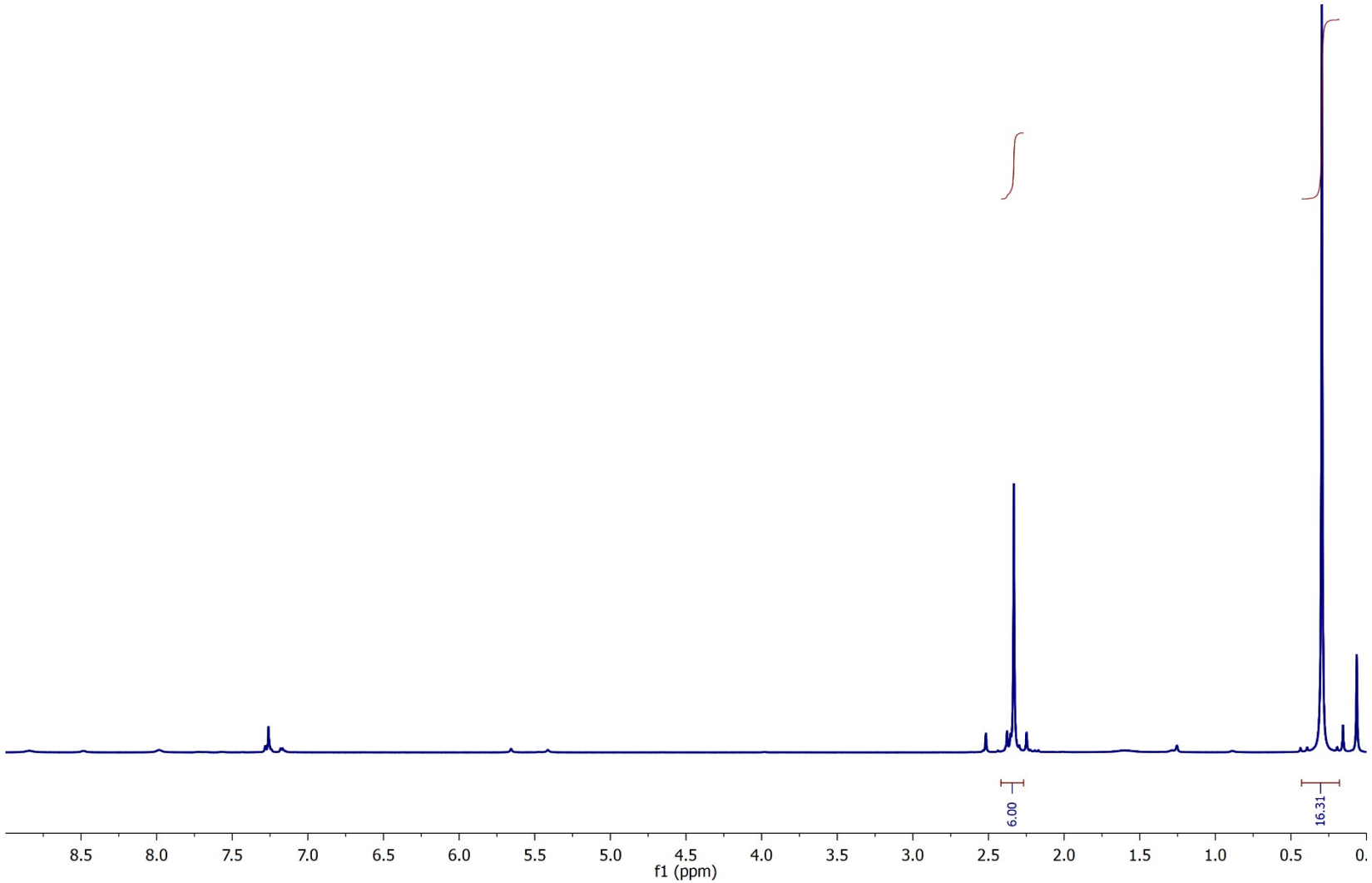
*2,5-Dibromo-3,6-dimethylbenzoquinone (**22**), ^{1}H NMR, 400 MHz, 298 K*



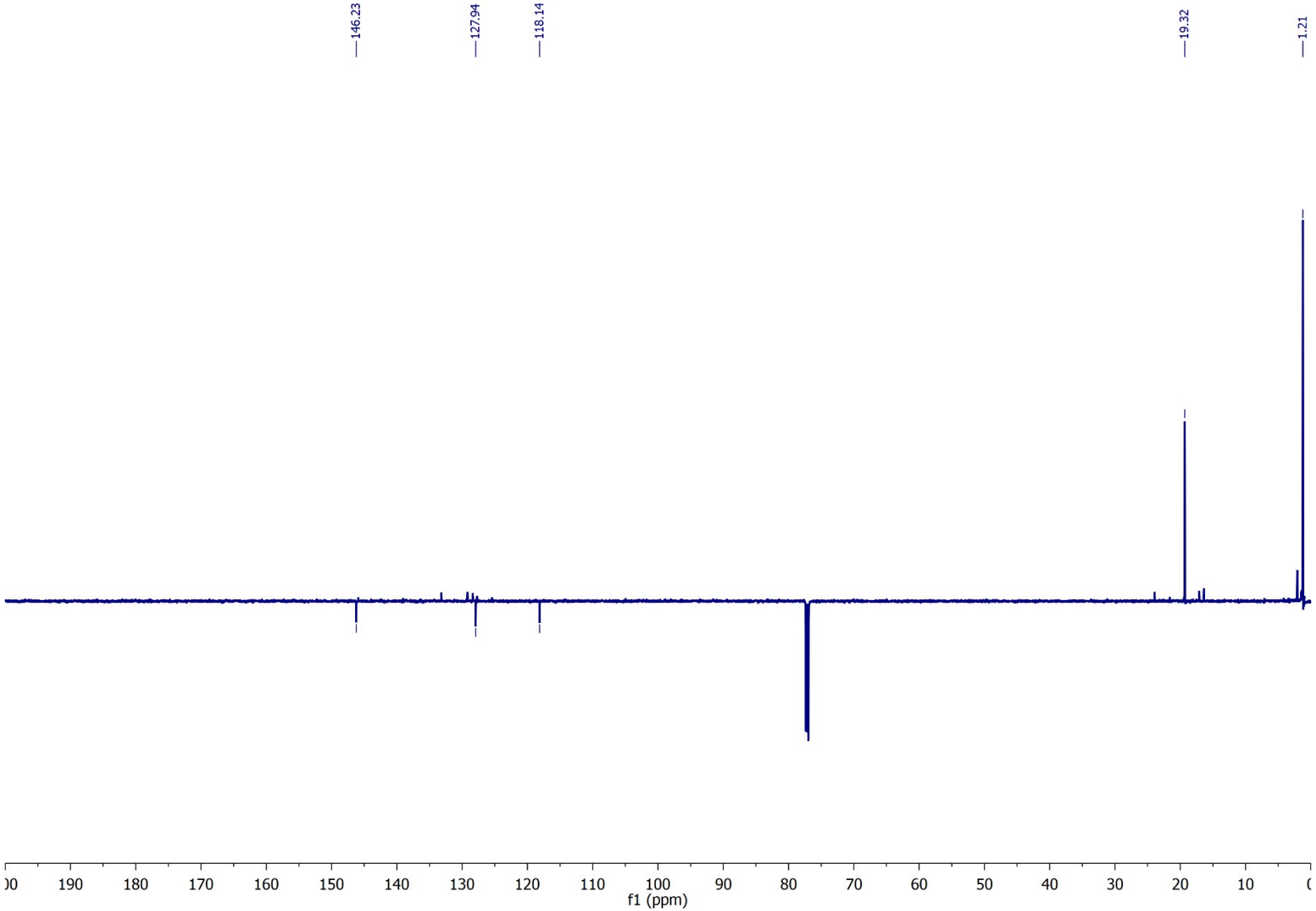
*2,5-Dibromo-3,6-dimethylbenzoquinone (**22**), ^{13}C DEPTQ135 NMR, 100 MHz, 298 K*



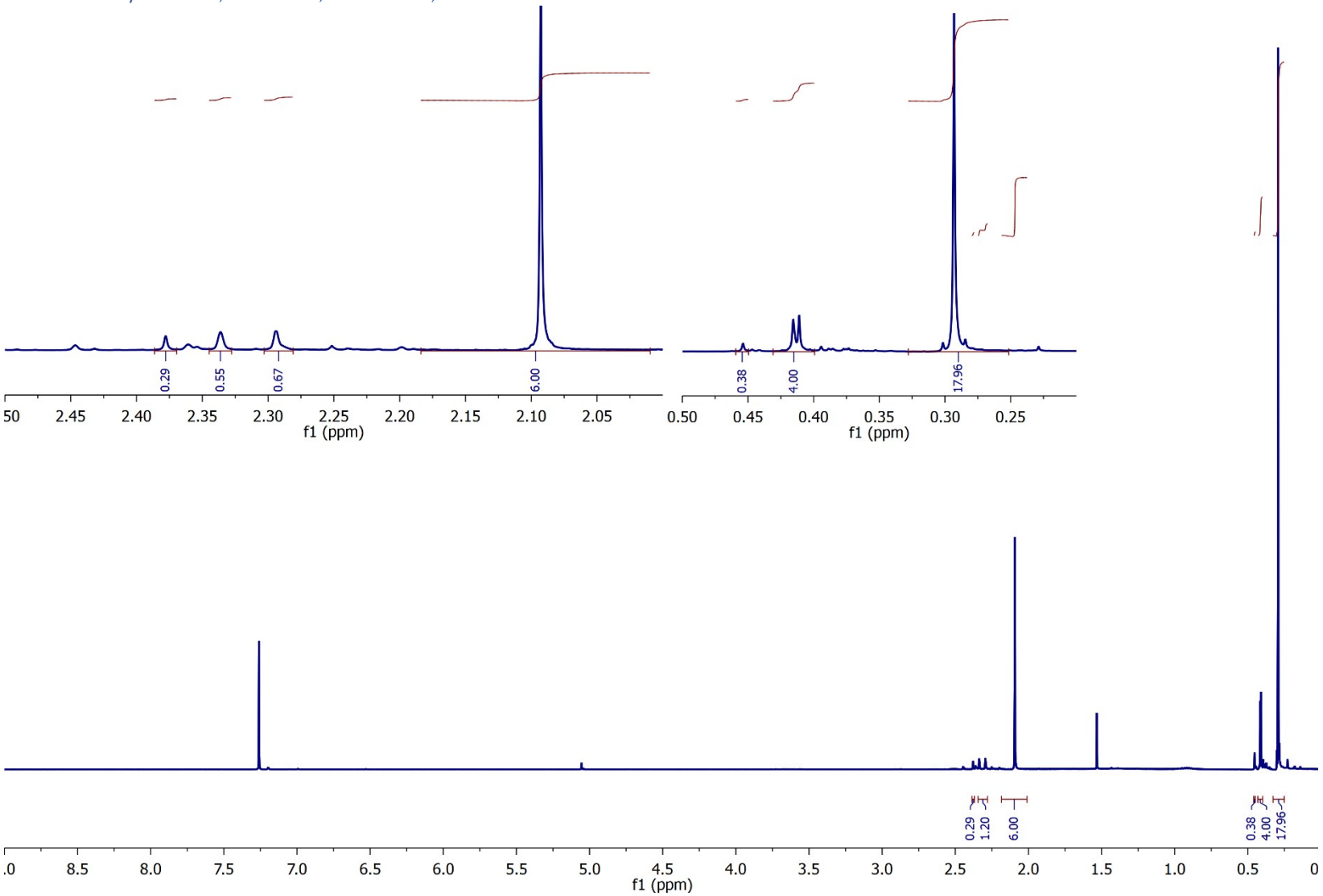
*2,5-Dibromo-3,6-di(trimethylsilyloxy)xylene (**13v**), ^{1}H NMR, 600 MHz, 298 K*



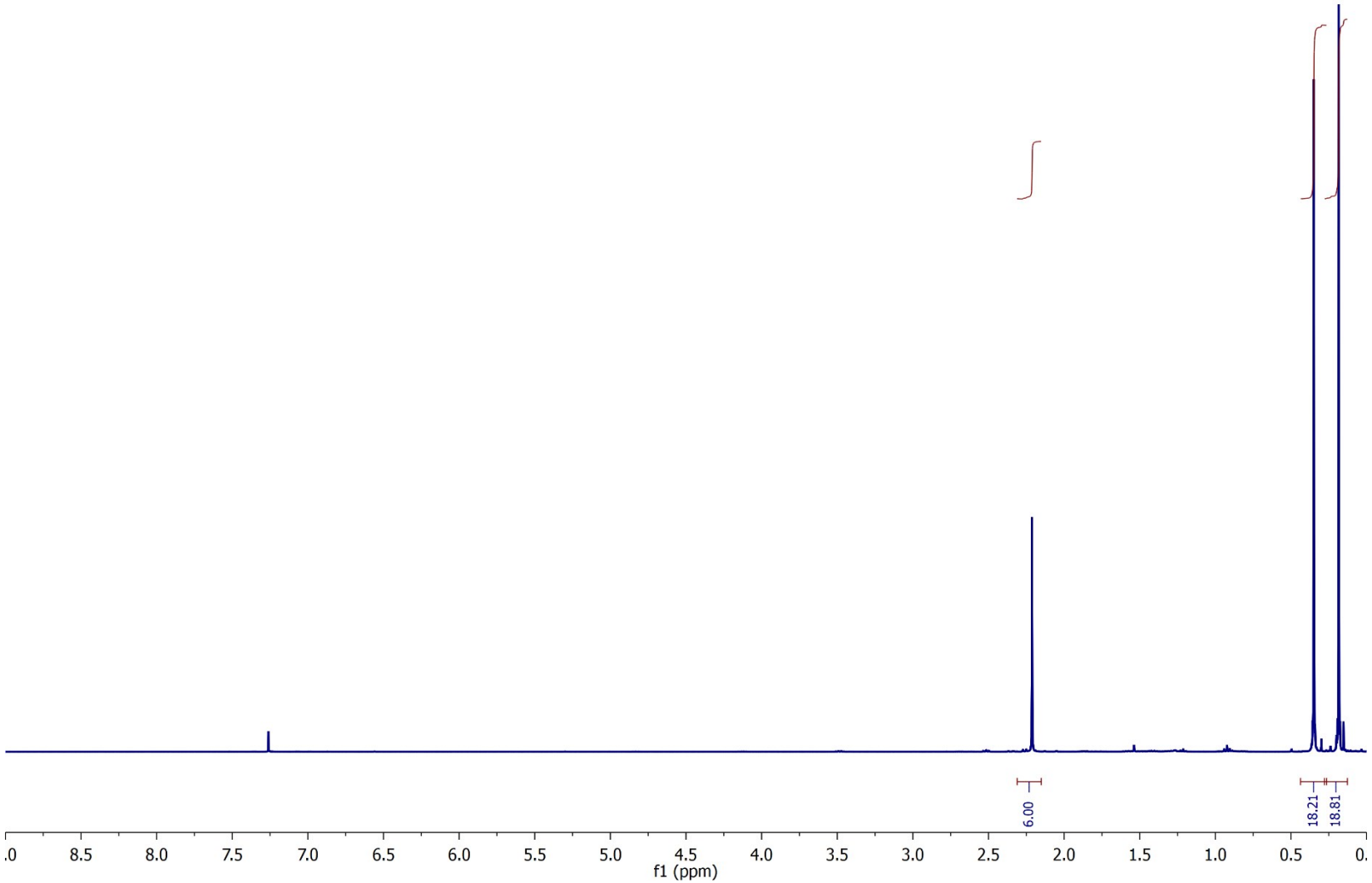
*2,5-Dibromo-3,6-di(trimethylsilyloxy)xylene (**13v**), ^{13}C DEPTQ135 NMR, 150 MHz, 298 K*



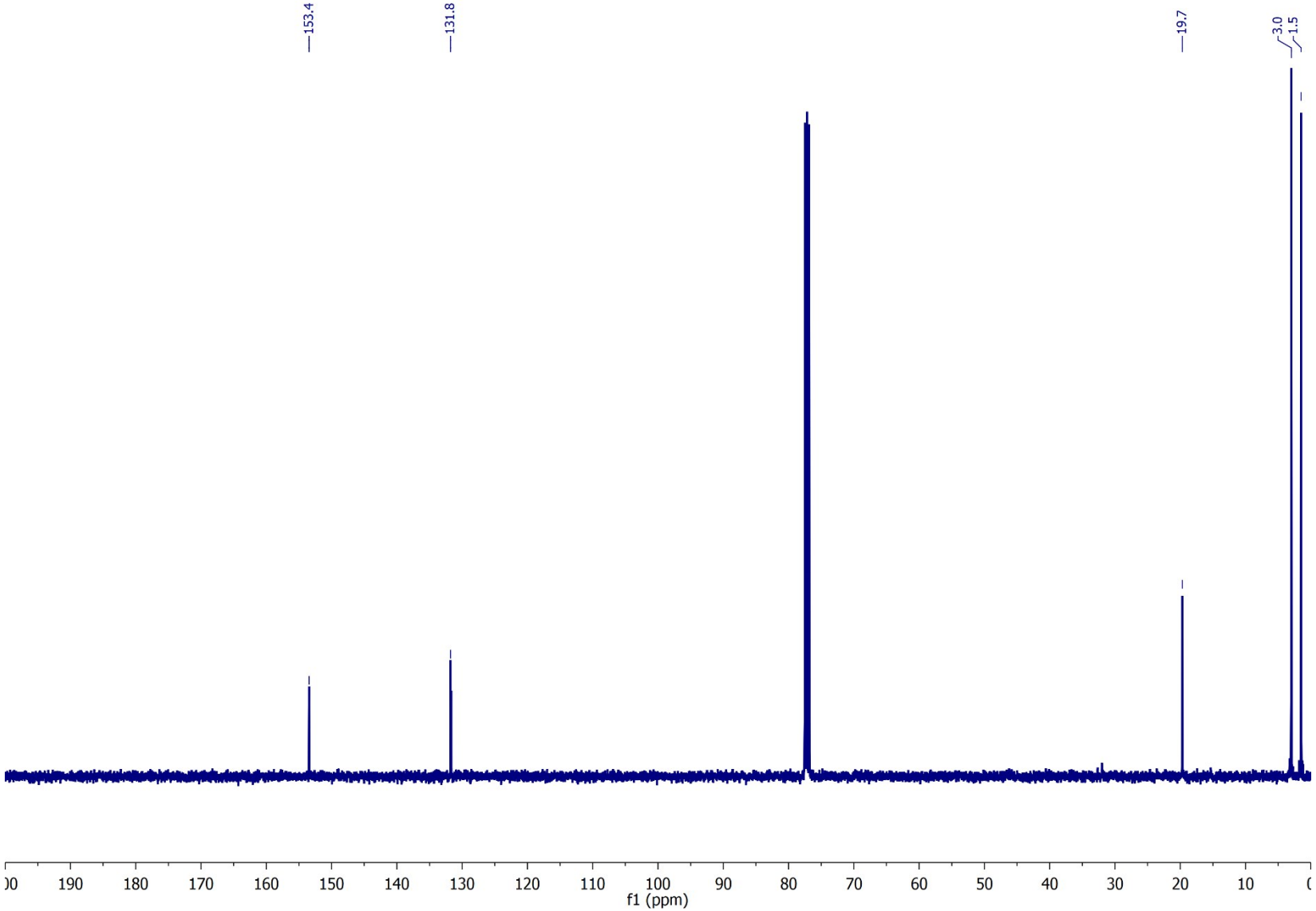
*80% 2,5-dimethyl-3,6-di(trimethylsilyl)benzoquinone (**23**) with 1,4-(2,5-dimethyl-3,6-di(trimethylsilyl)phenylene) ditrifluoromethylsulfonate (**12a**) and other side-products, ^{1}H NMR, 600 MHz, 298 K*



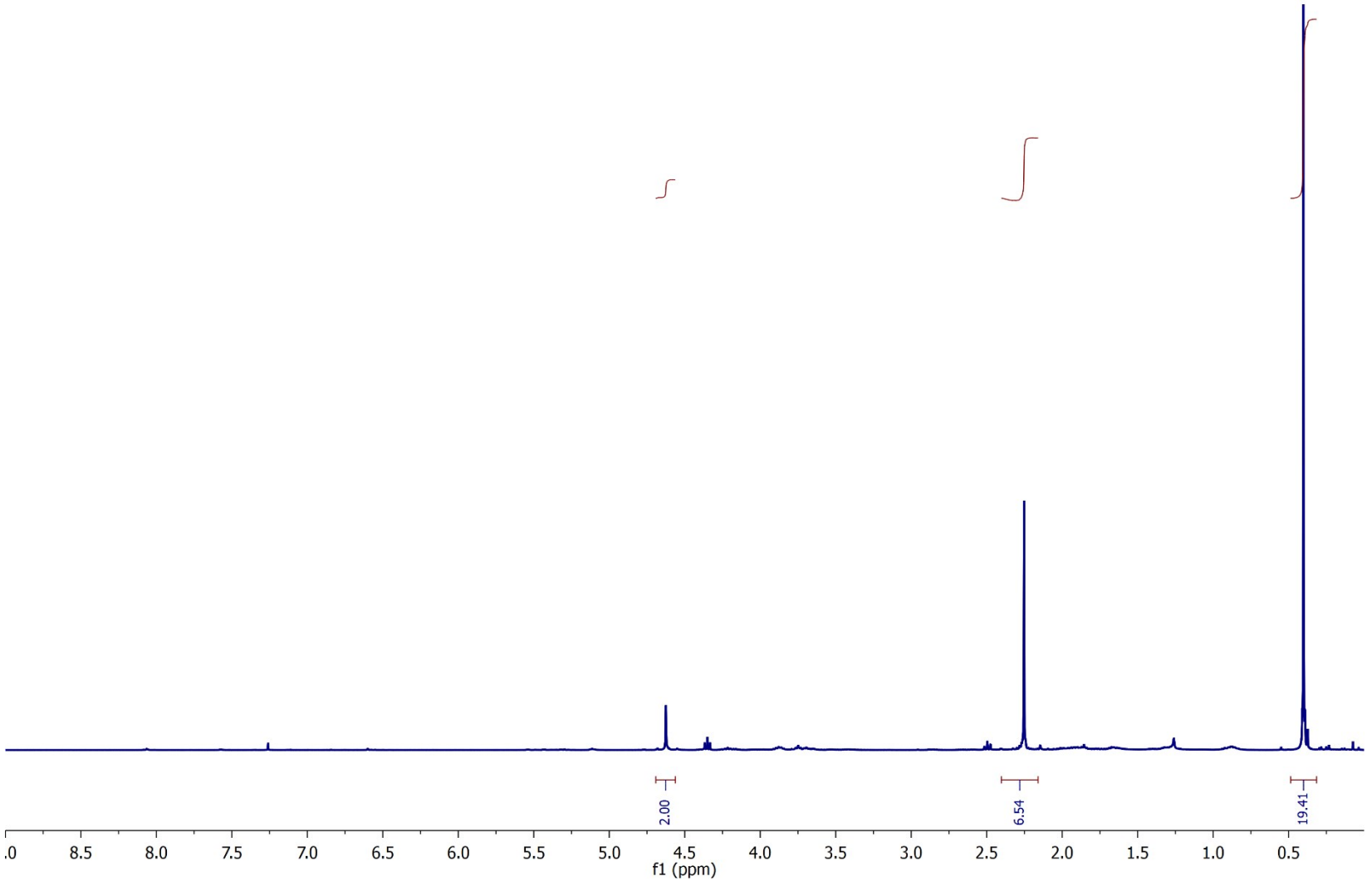
*2,5-Di(trimethylsilyl)-3,6-di(trimethylsilyloxy)xylene (**H**), ^{1}H NMR, 400 MHz, 298 K*



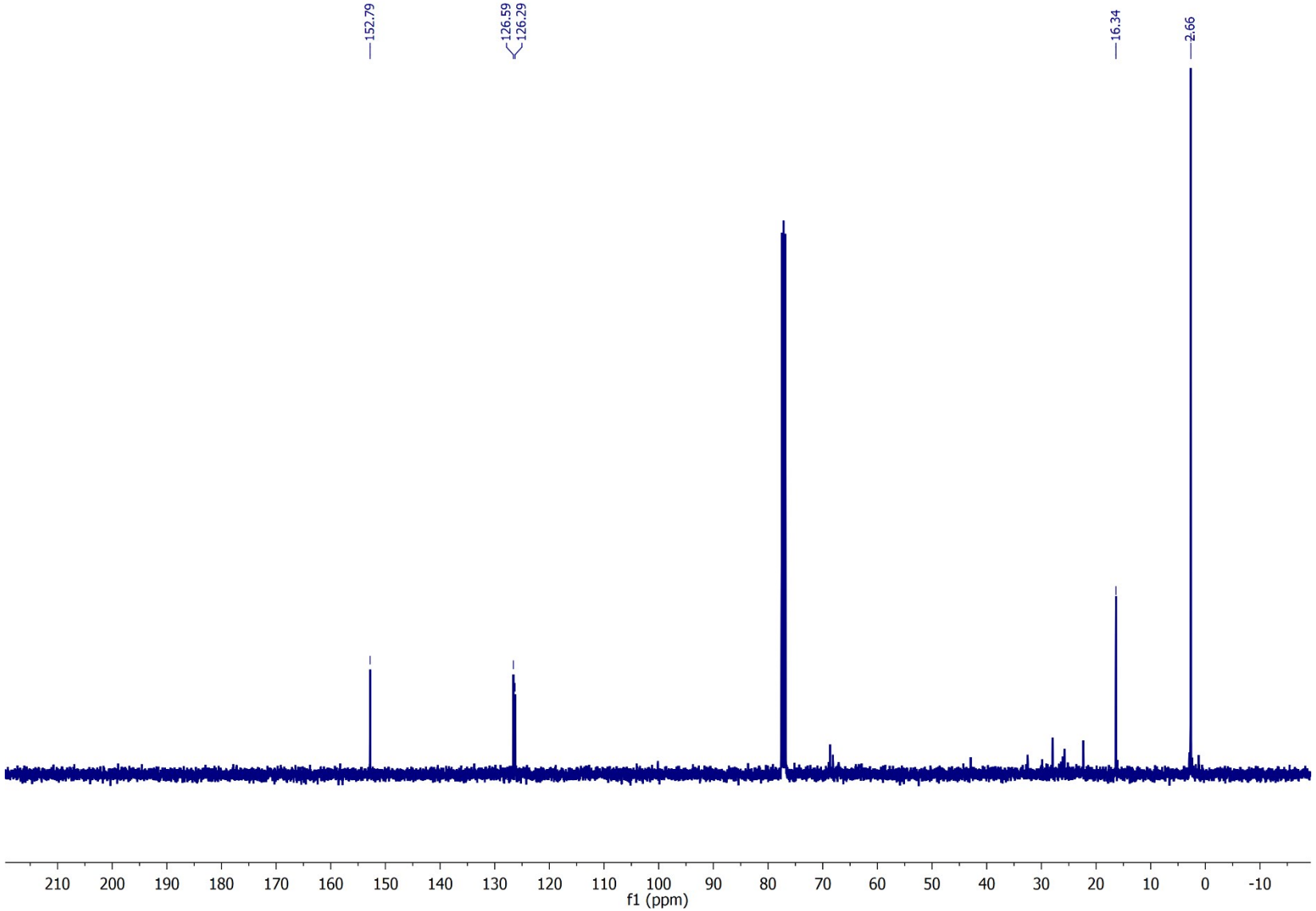
*2,5-Di(trimethylsilyl)-3,6-di(trimethylsilyloxy)xylene (**H**), ^{13}C NMR, 100 MHz, 298 K*



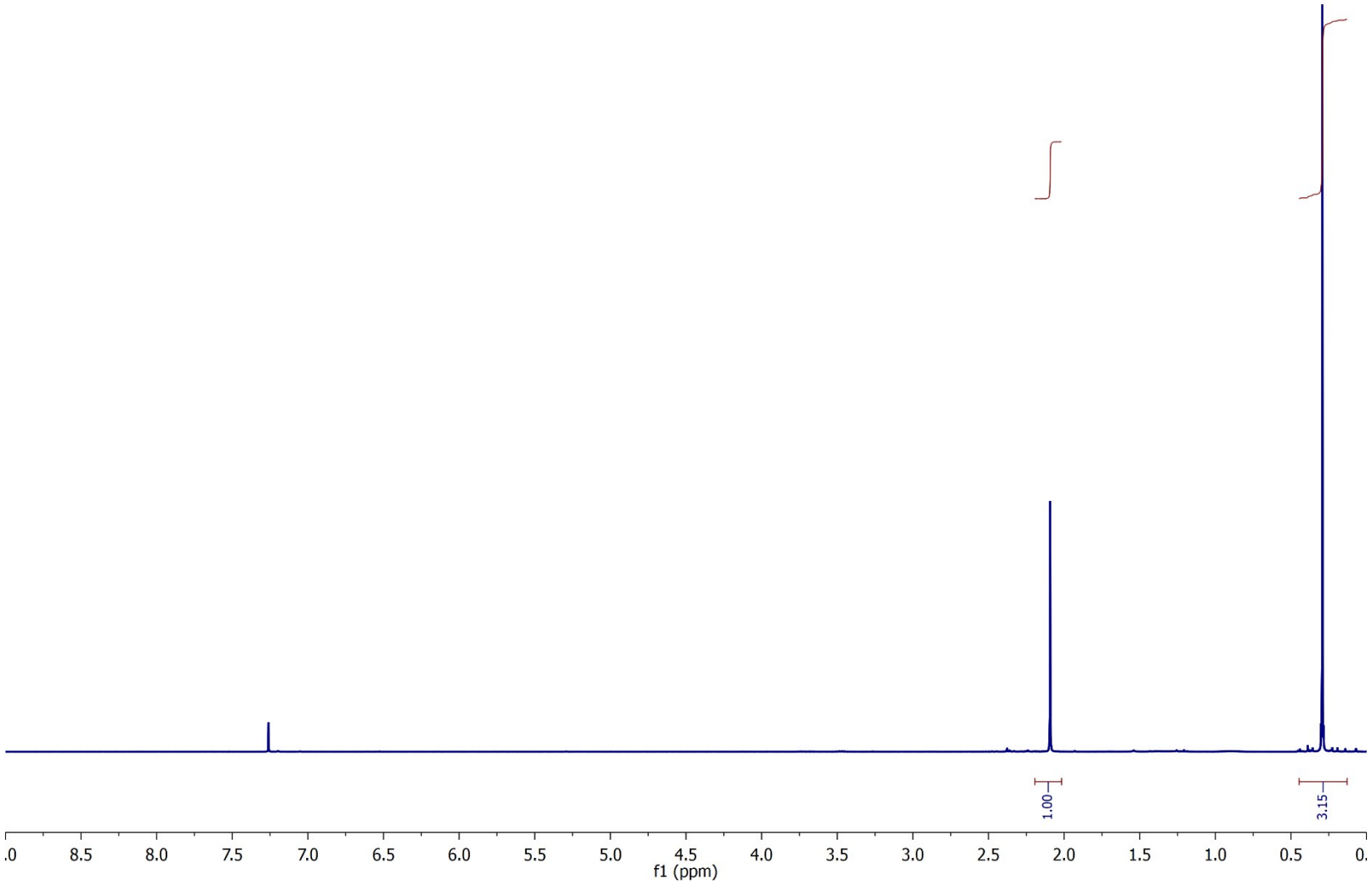
*2,5-Di(trimethylsilyl)-3,6-dimethylhydroquinone (**I**), ^{1}H NMR, 400 MHz, 298 K*



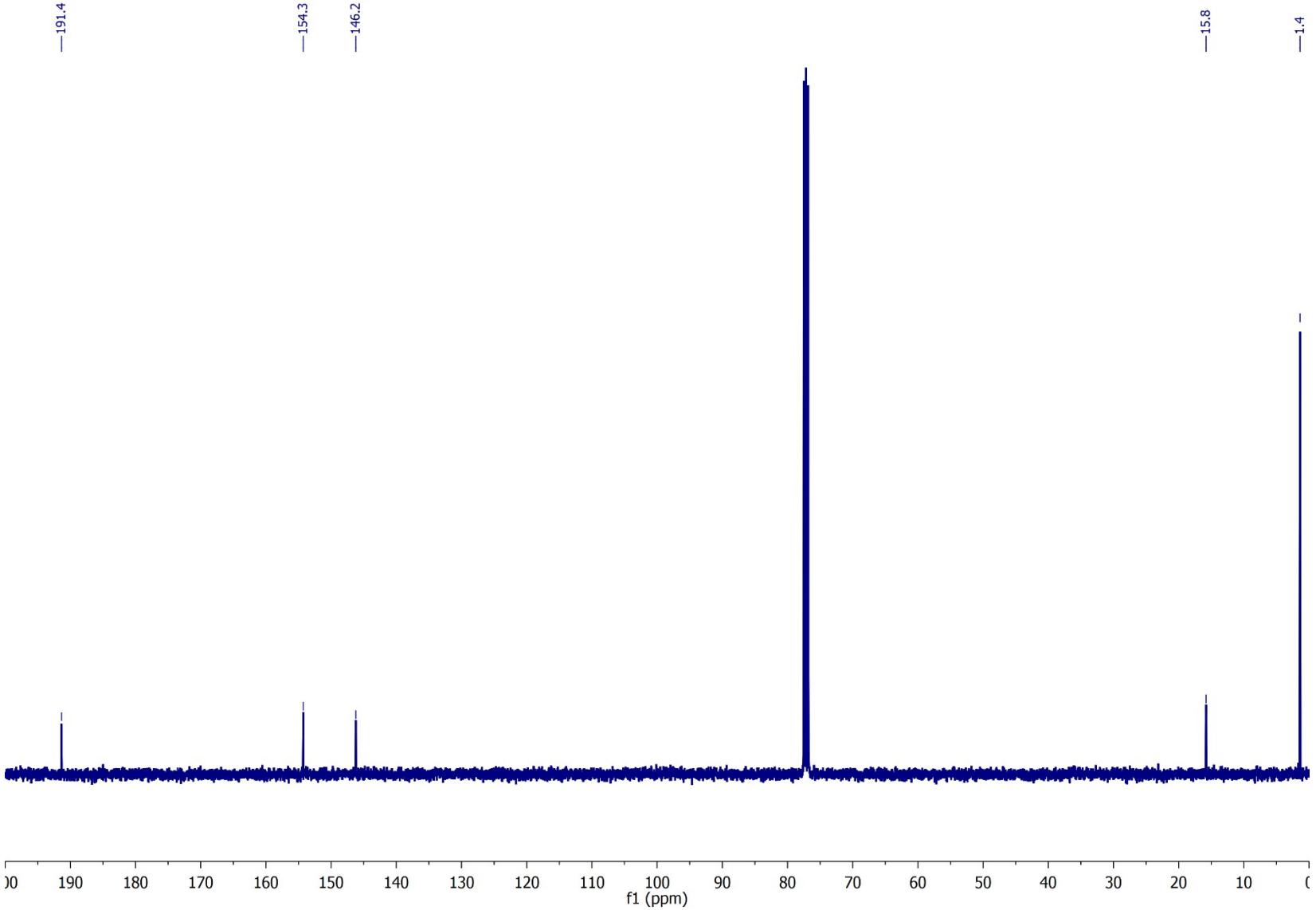
*2,5-Di(trimethylsilyl)-3,6-dimethylhydroquinone (**I**), ^{13}C NMR, 100 MHz, 298 K*



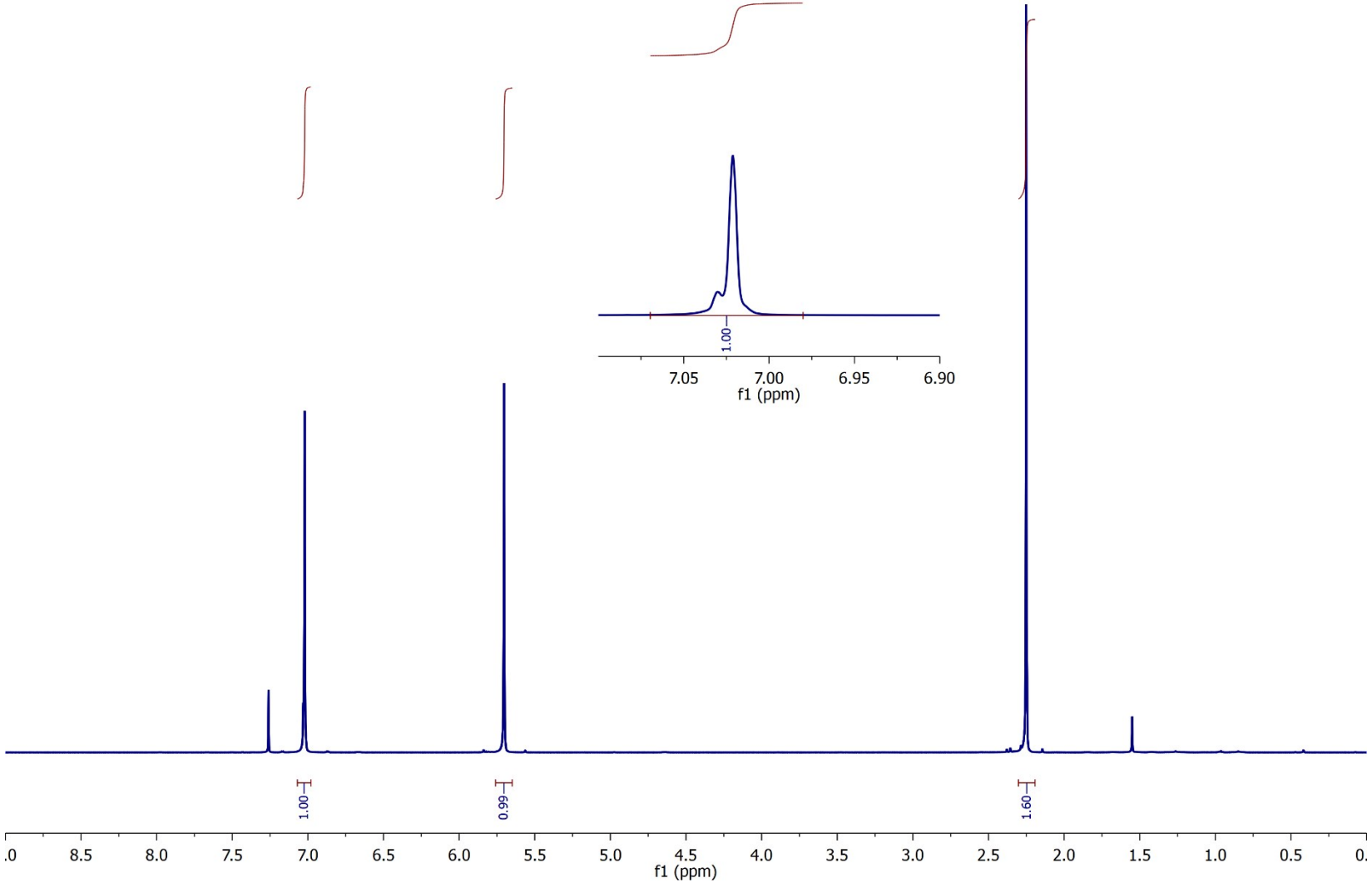
*2,5-Di(trimethylsilyl)-3,6-dimethylbenzoquinone (**23**), ^{1}H NMR, 400 MHz, 298 K*



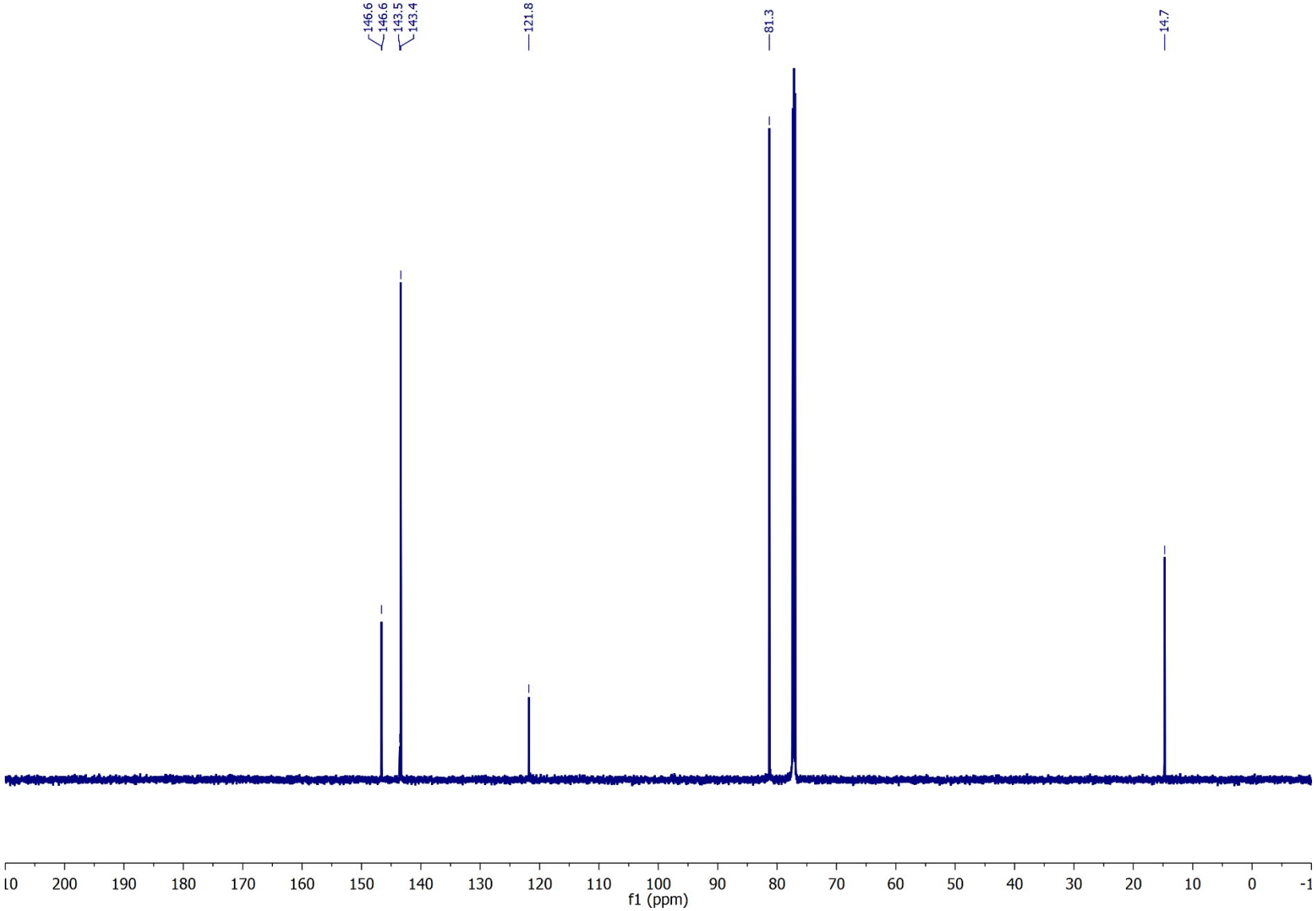
*2,5-Di(trimethylsilyl)-3,6-dimethylbenzoquinone (**23**), ^{13}C NMR, 100 MHz, 298 K*



*Anti-9,10-Dimethyl-1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene (anti-**24**), ^{1}H NMR, 600 MHz, 298 K*

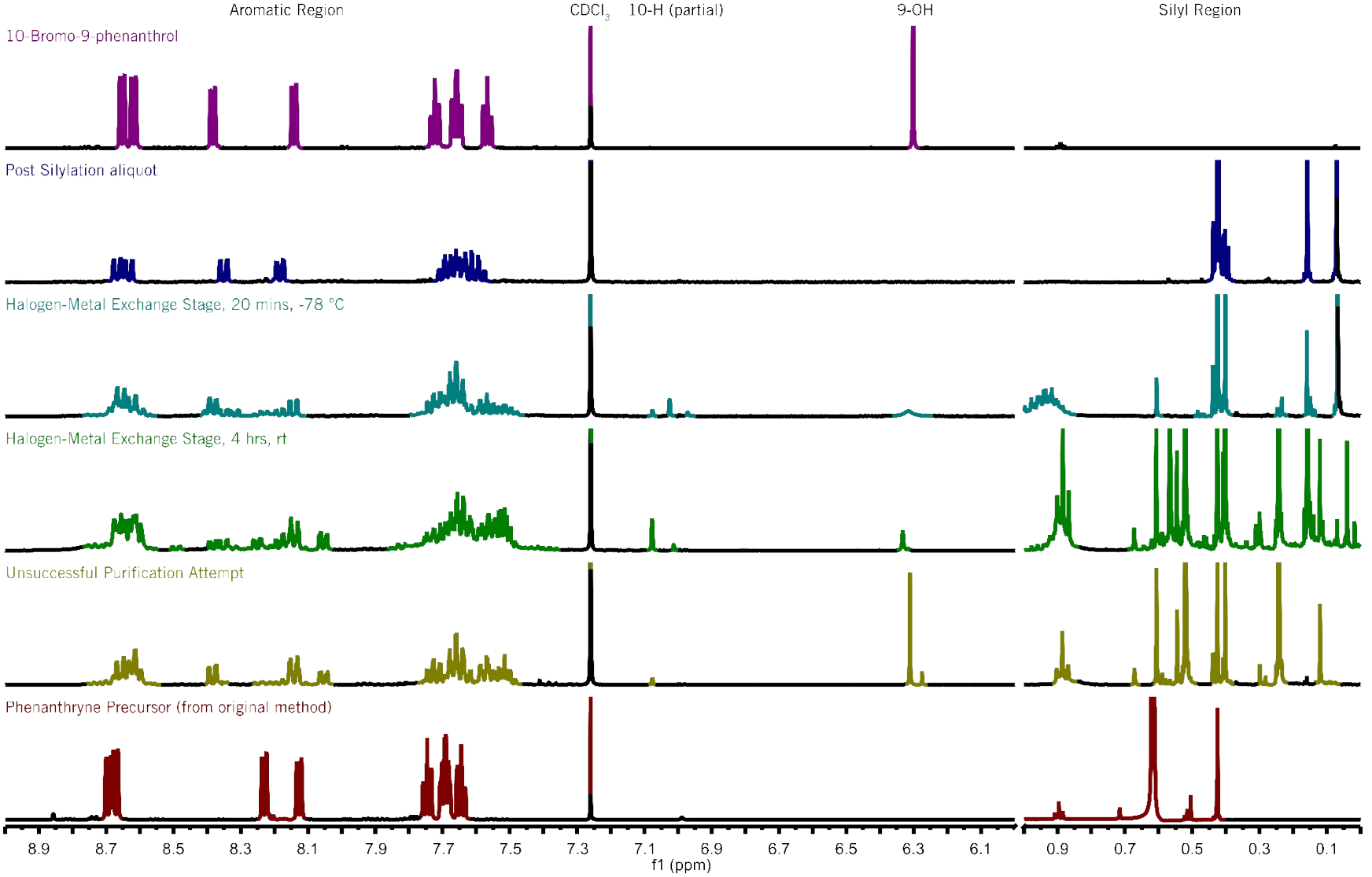


*Anti-9,10-Dimethyl-1,4,5,8-tetrahydro-1,4:5,8-diepoxyanthracene (anti-**24**), ^{13}C NMR, 150 MHz, 298 K*

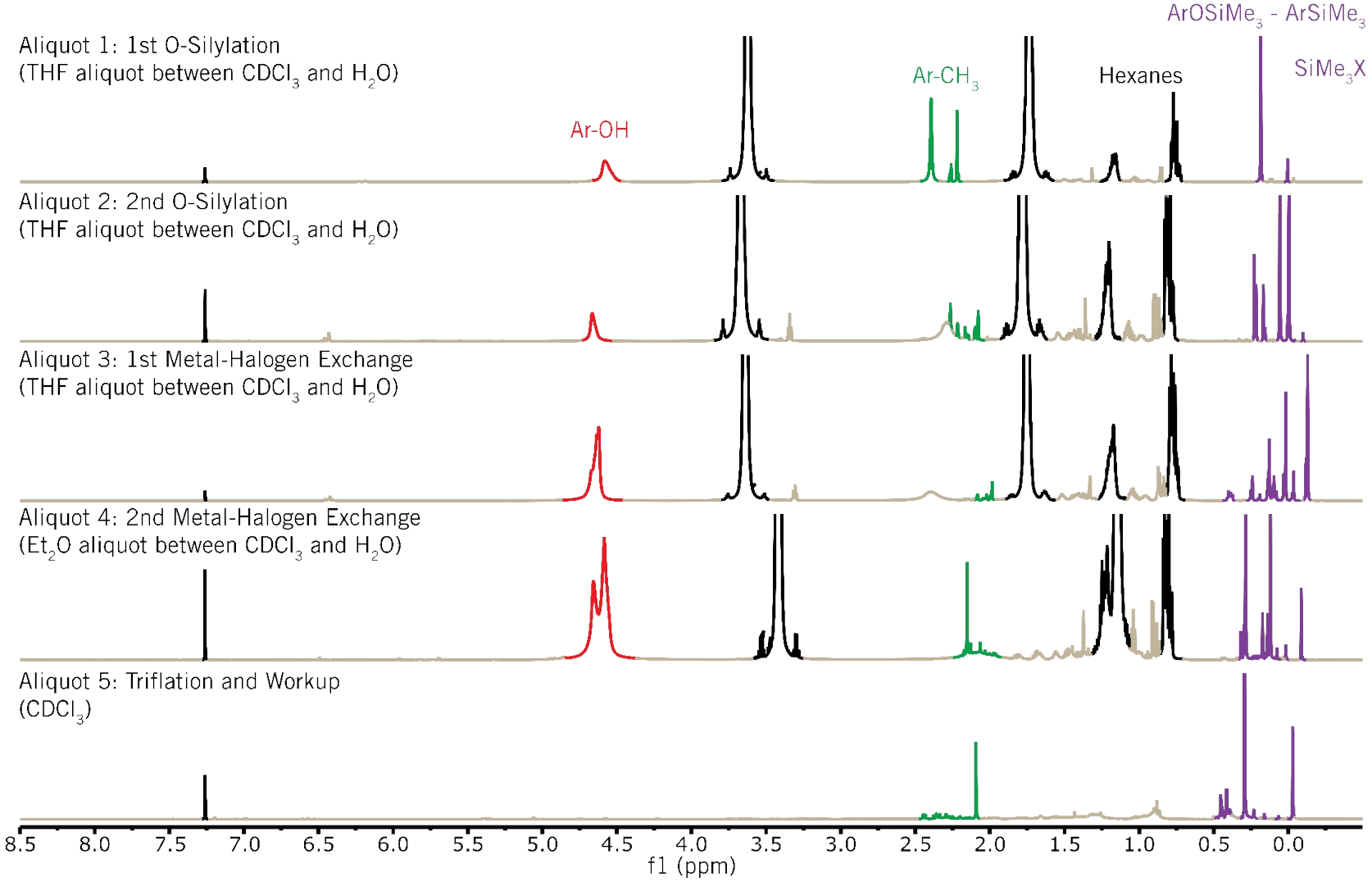


S14. NMR Spectra: Mechanistic Tests

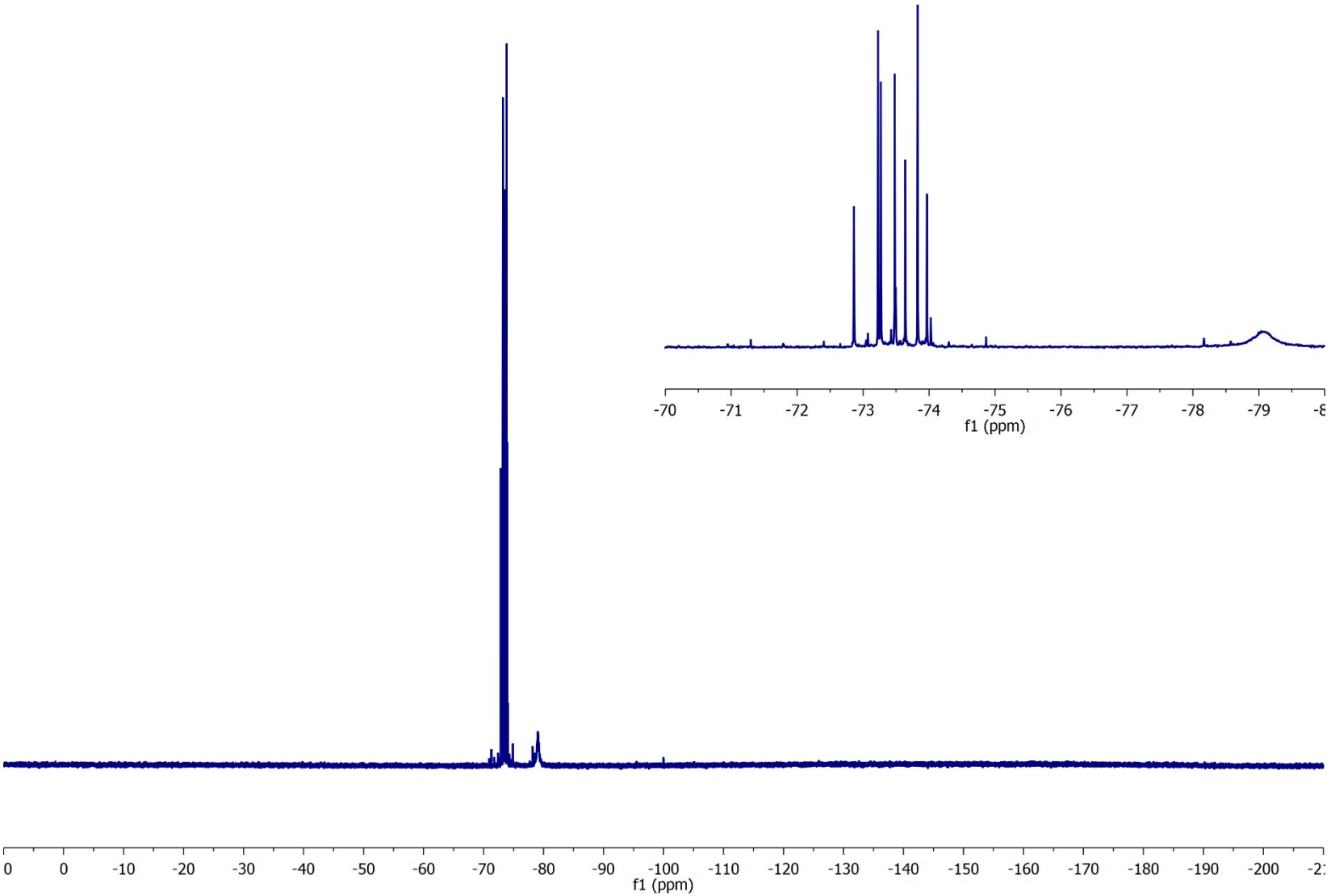
9,10-Phenanthryne Precursor Synthesis HMDS Tests, ^{1}H NMR, 400 MHz (Except top and bottom, 600 MHz), 298 K



Bisbenzyne Mechanistic Study Aliquot Stack Plot, ^{1}H NMR, 600 MHz (Except Work-Up, 400 MHz), 298 K

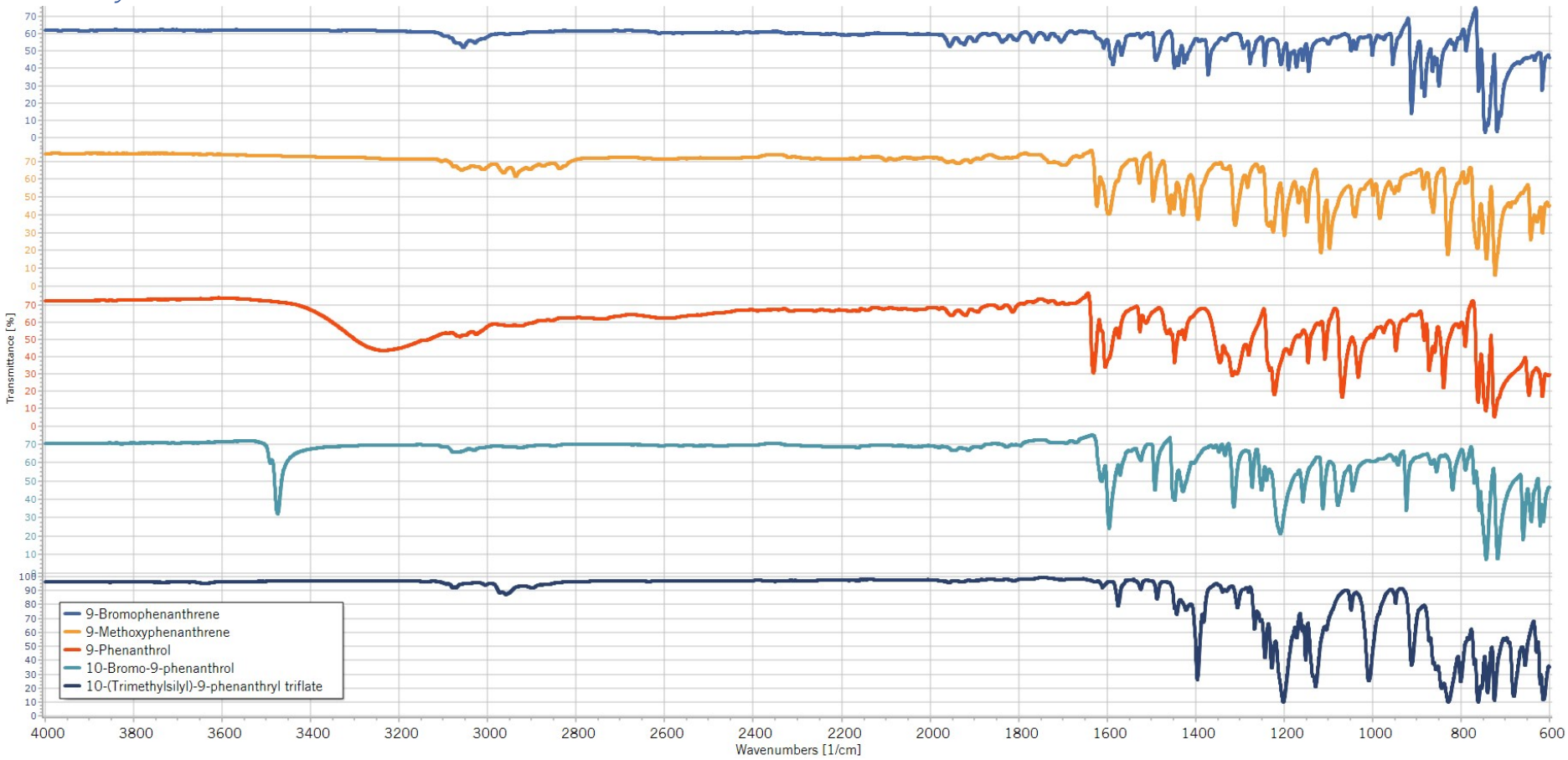


Work-up Mixture, ^{19}F NMR, 376 MHz, 298 K

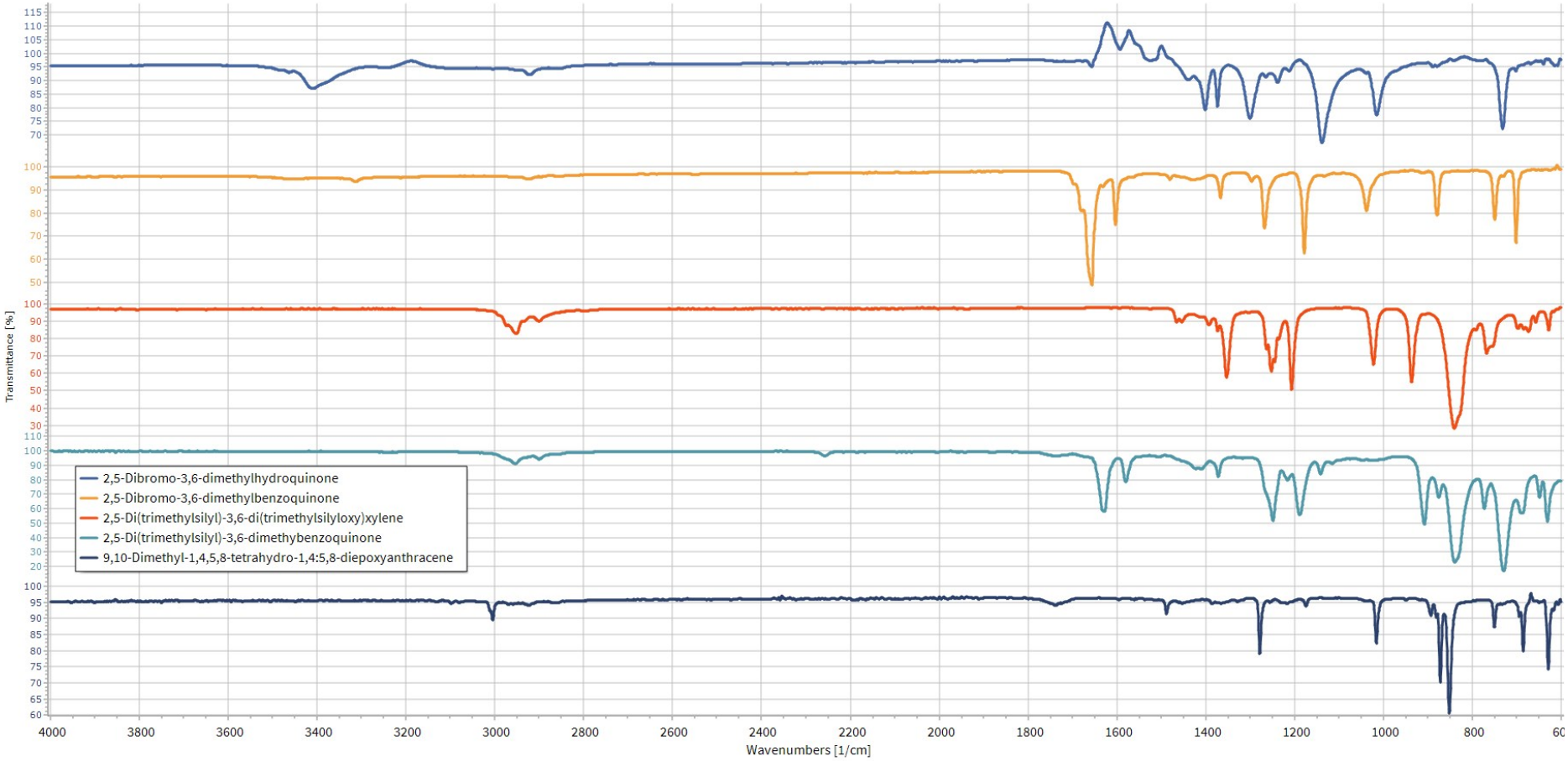


S15. IR Spectra

Phenanthryne Precursor Series



Bisbenzyne Precursor Series



S16. GC/MS Analyses: 9,10-Phenanthryne Series

9-Bromophenanthrene (17)

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Misc Info  : EAN-149-Char
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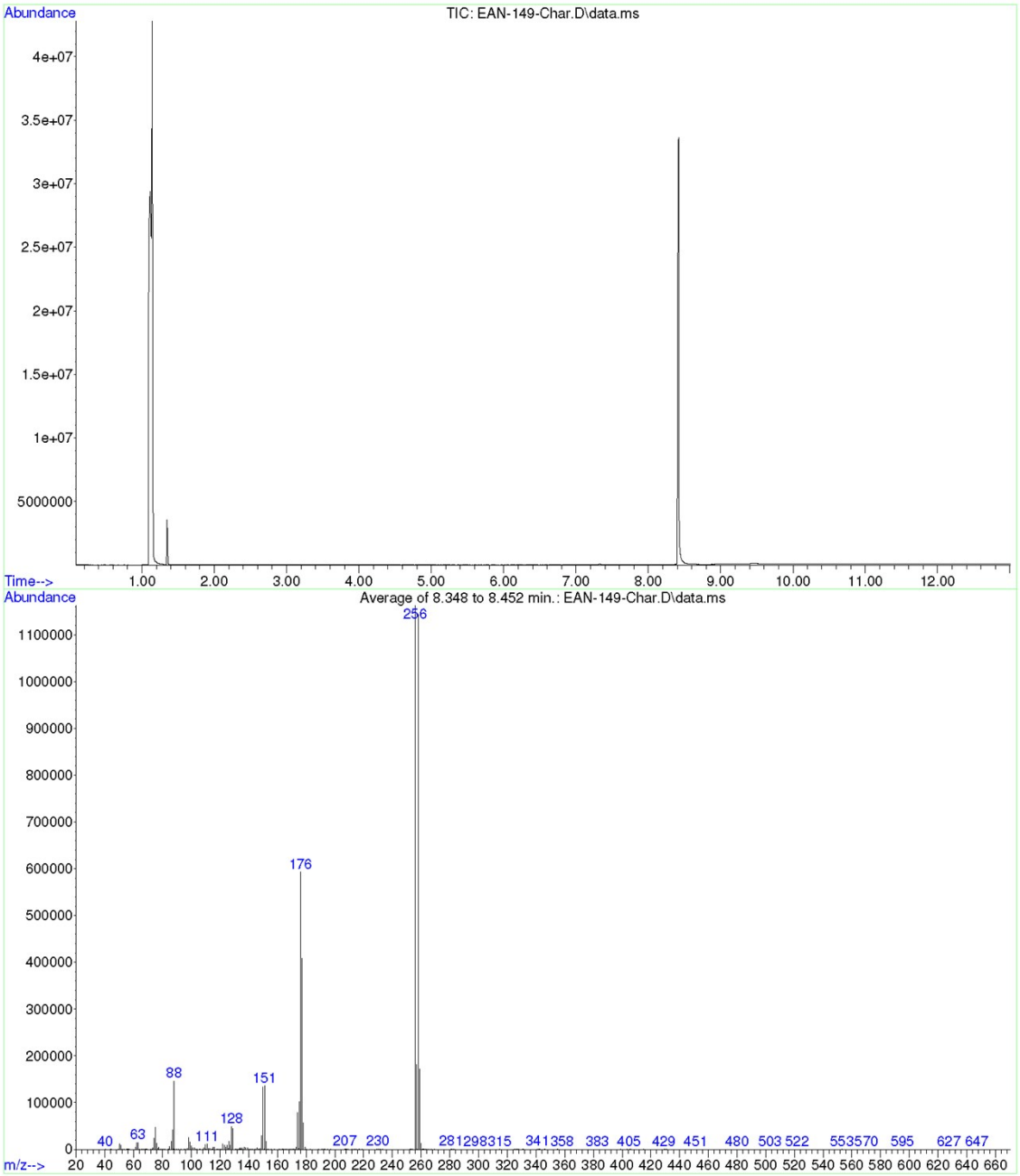

*9-Methoxyphenanthrene (**18**)*

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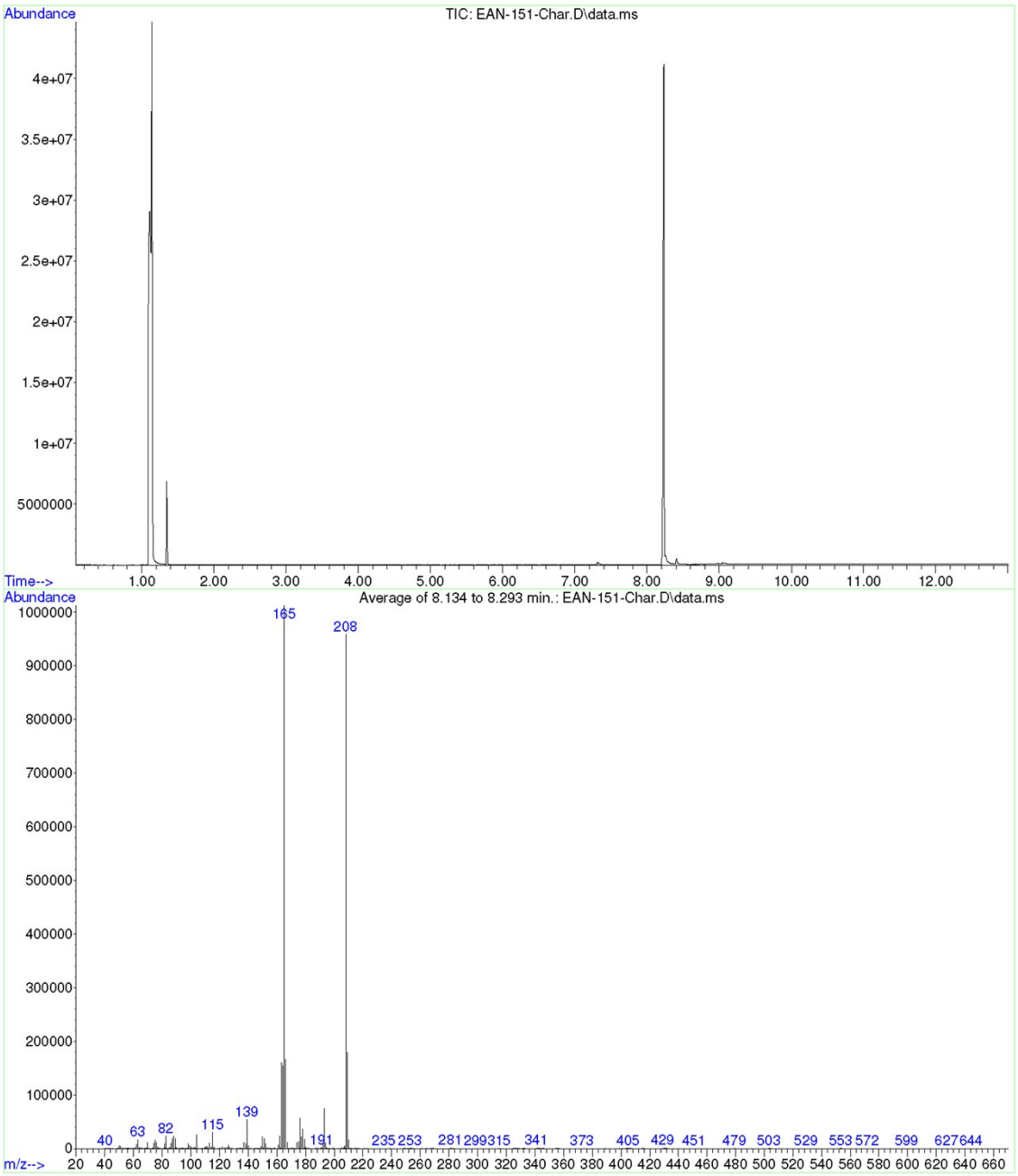

*9-Phenanthrol (**19**)*

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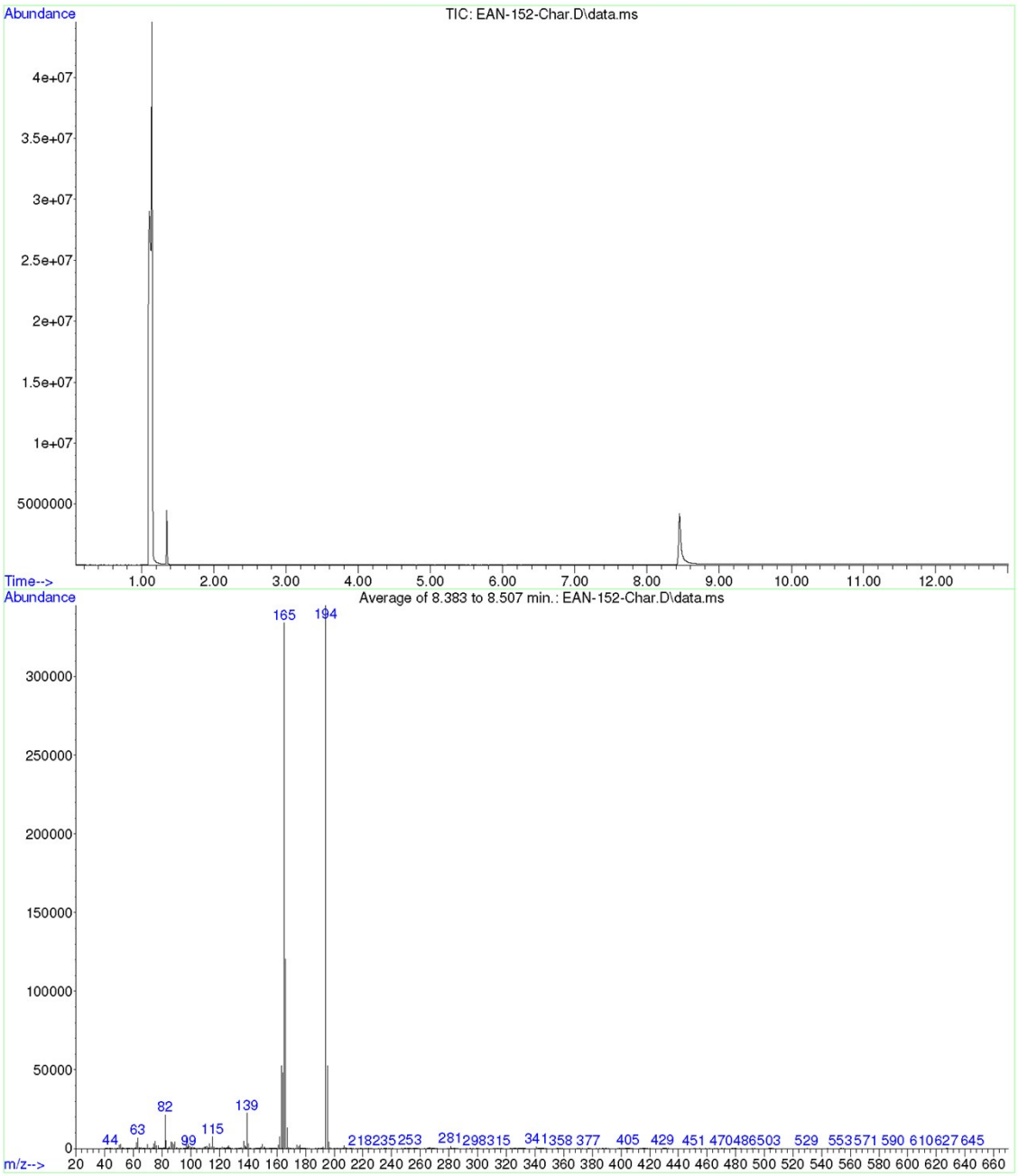

*10-Bromo-9-phenanthrol (**14**)*

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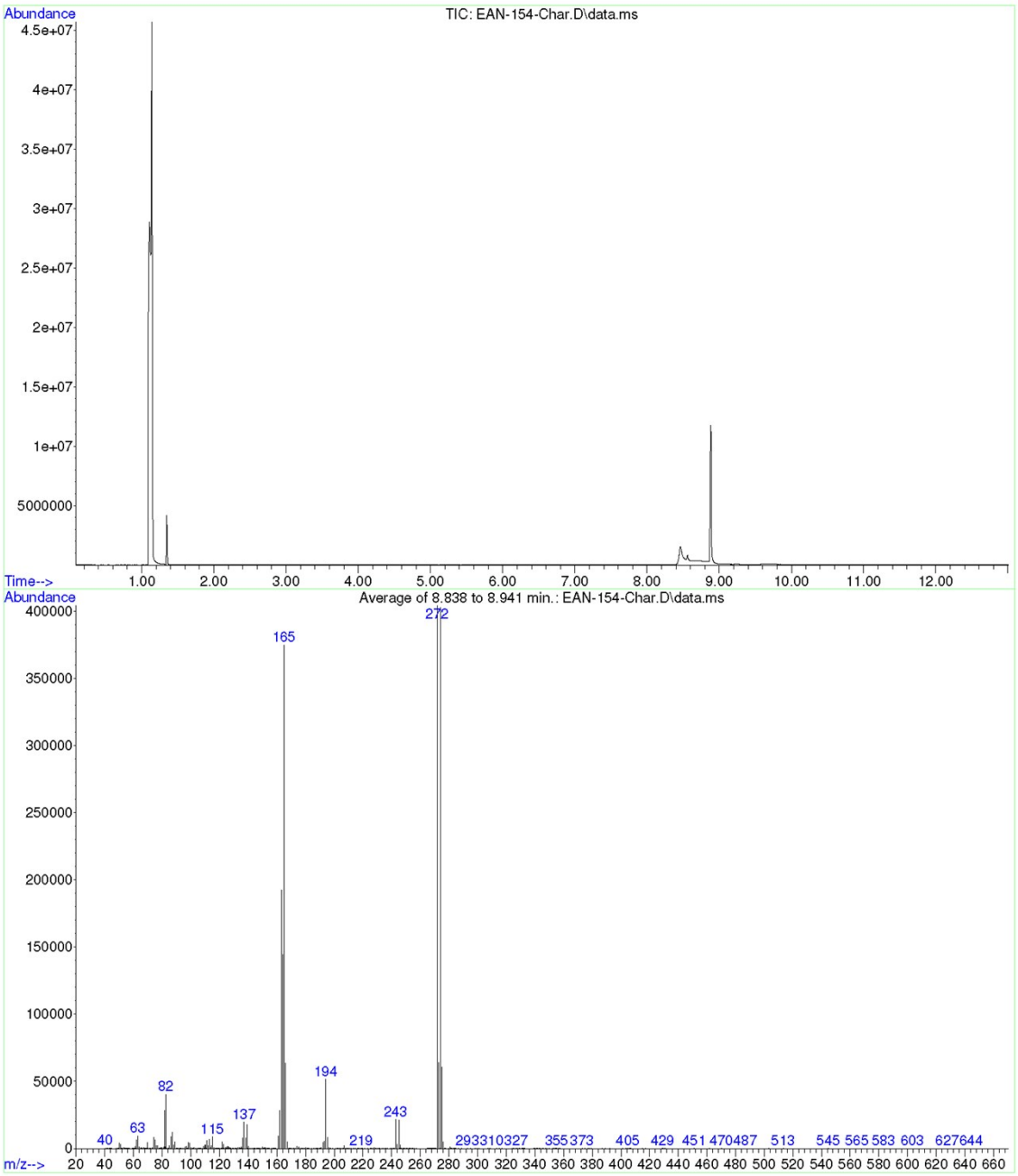

*10-(Trimethylsilyl)-9-phenanthryl trifluoromethanesulfonate (**15**)*

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Misc Info  : EAN-155-Char
Vial Number: 20
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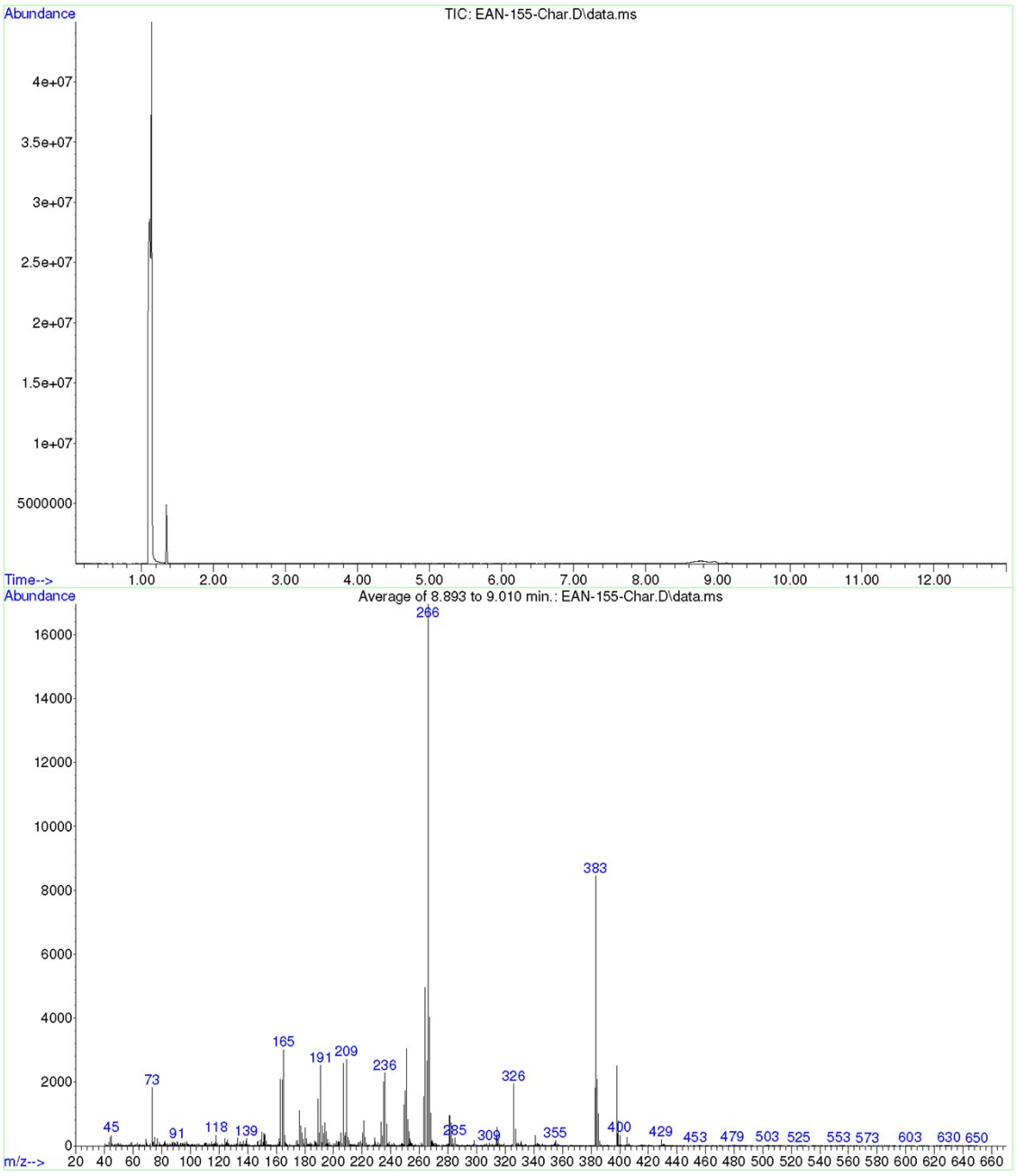

S17. GC/MS Analyses: Bisbenzyne Series

*2,5-Dibromo-3,6-dimethylhydroquinone (**9**)*

Analysis shown of a partially oxidised mixture to demonstrate the separation

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Vial Number: 1
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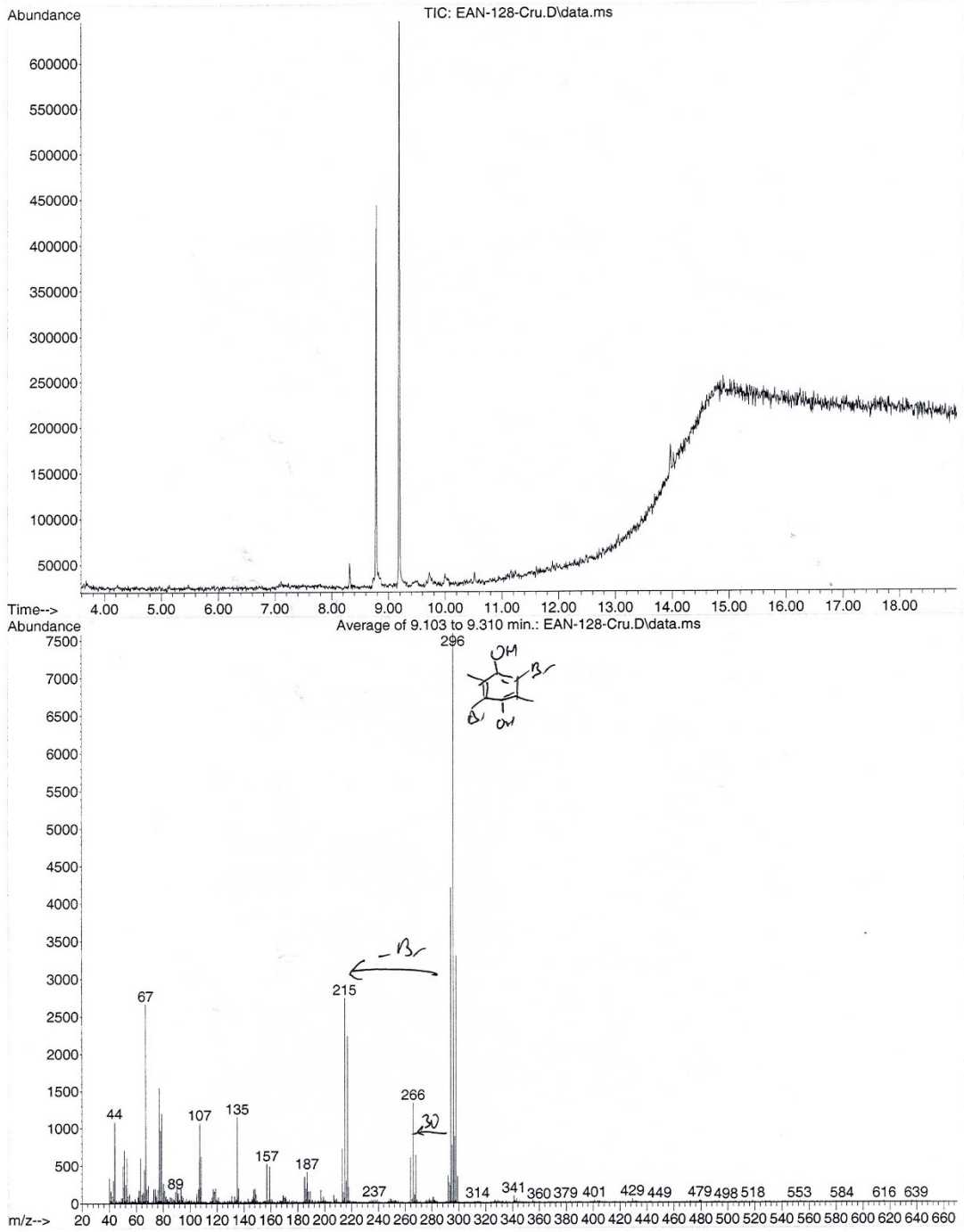
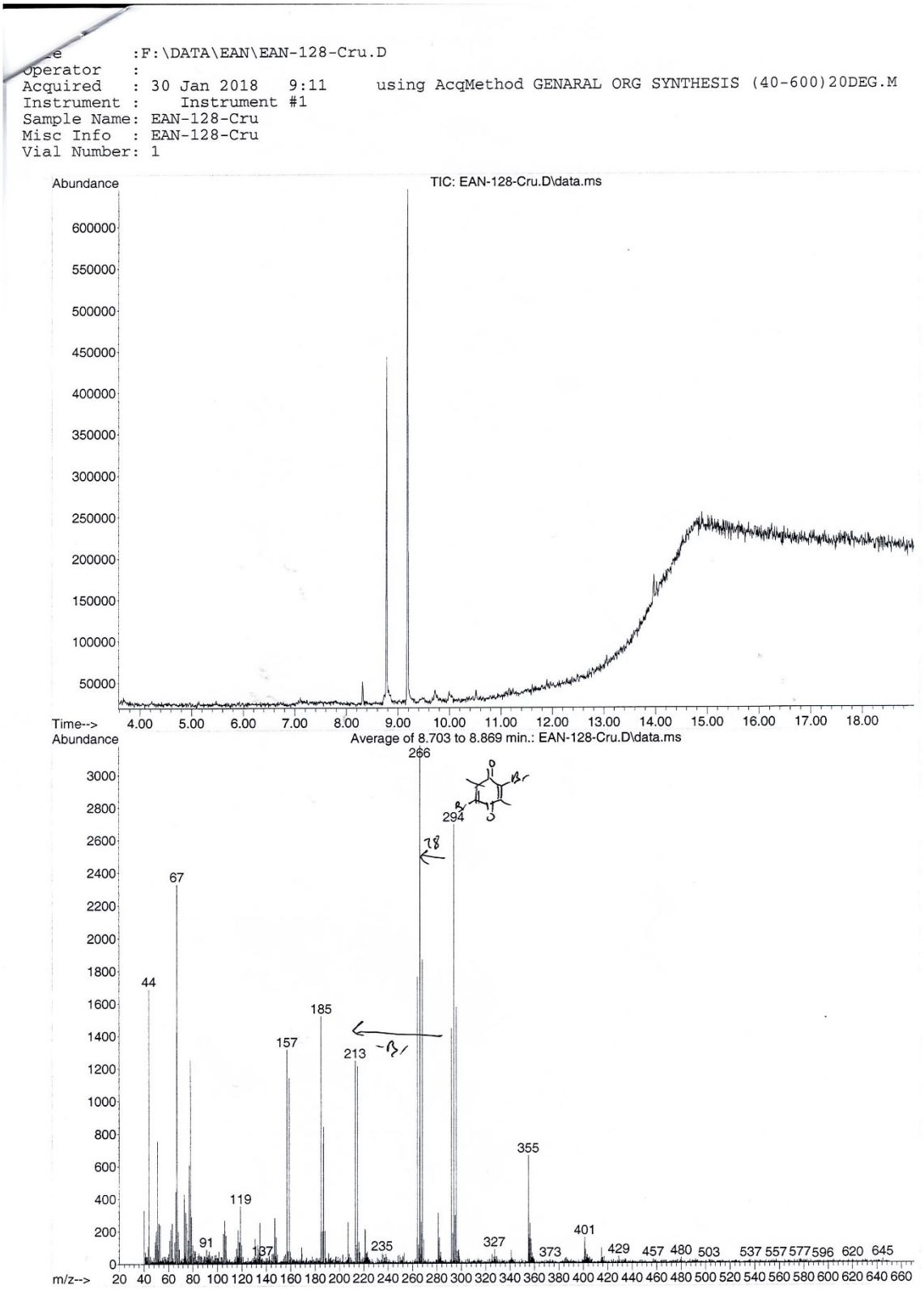
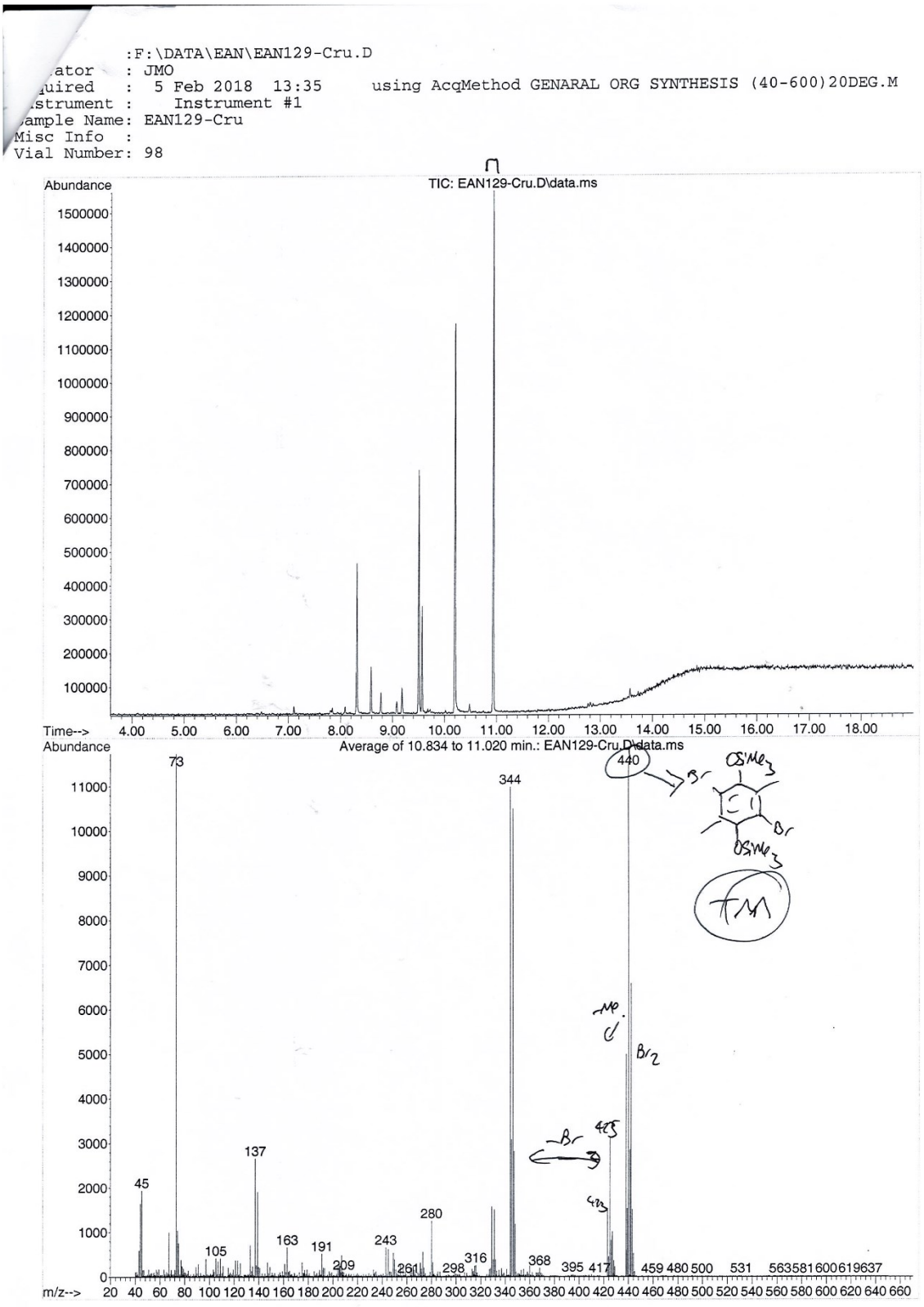


*2,5-Dibromo-3,6-dimethylbenzoquinone (**23**)*



*2,5-Dibromo-3,6-di(trimethylsilyloxy)xylene (**13v**)*



S18. GC/MS Analyses: Bisbenzyne Mechanistic Tests

Aliquot 1: First Silylation

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Instrument :    Instrument #1
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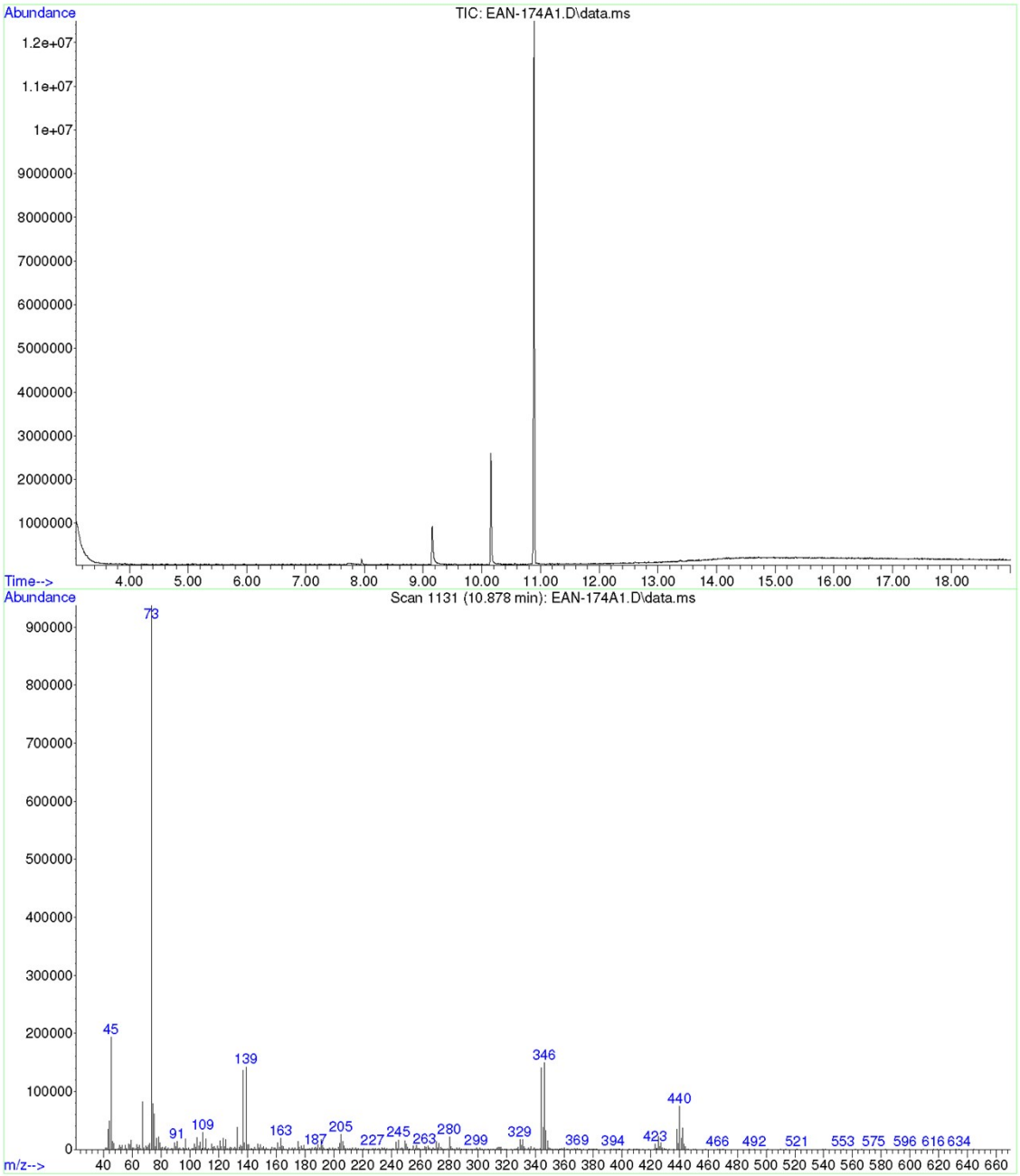
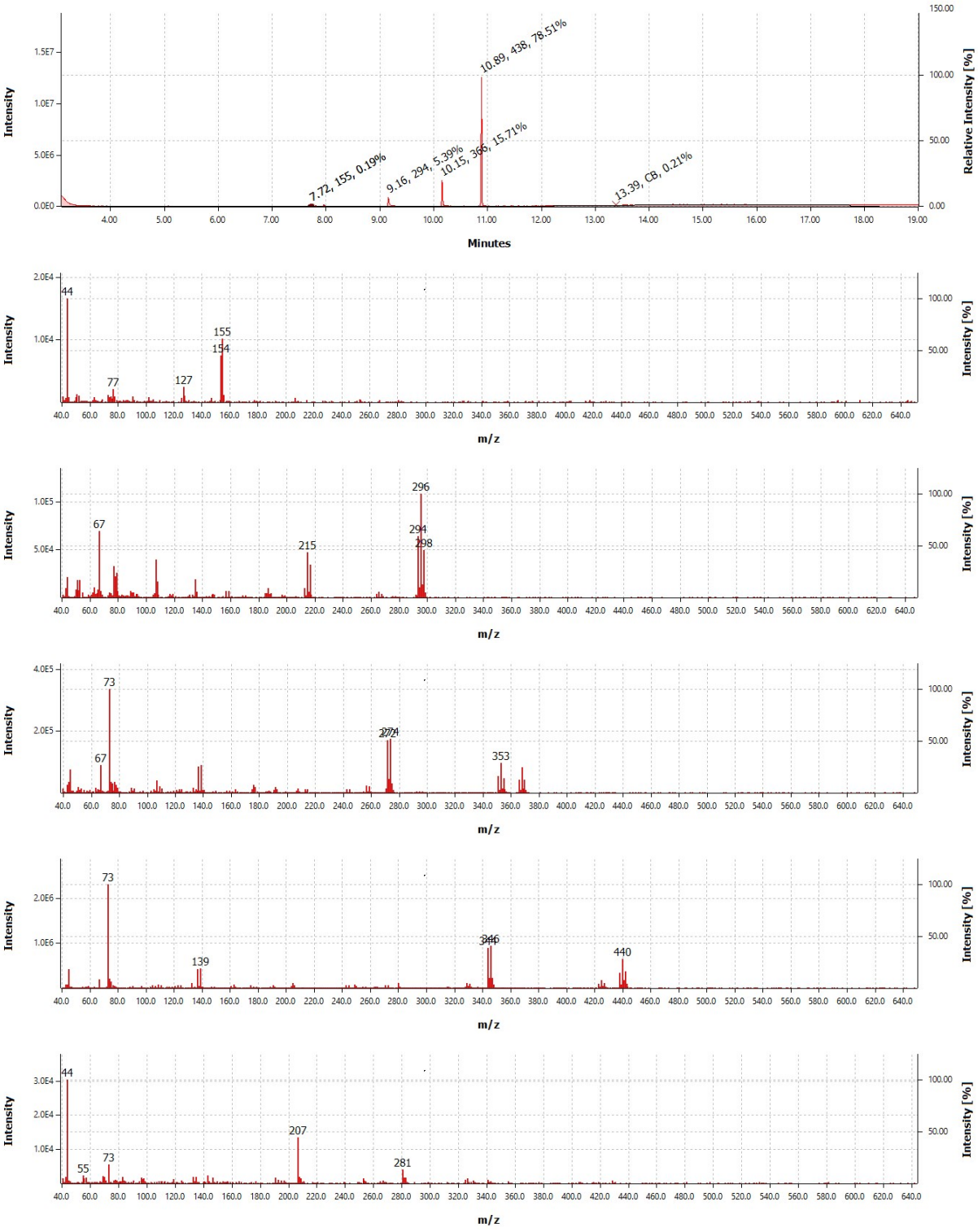
Misc Info  :
Vial Number: 21
```

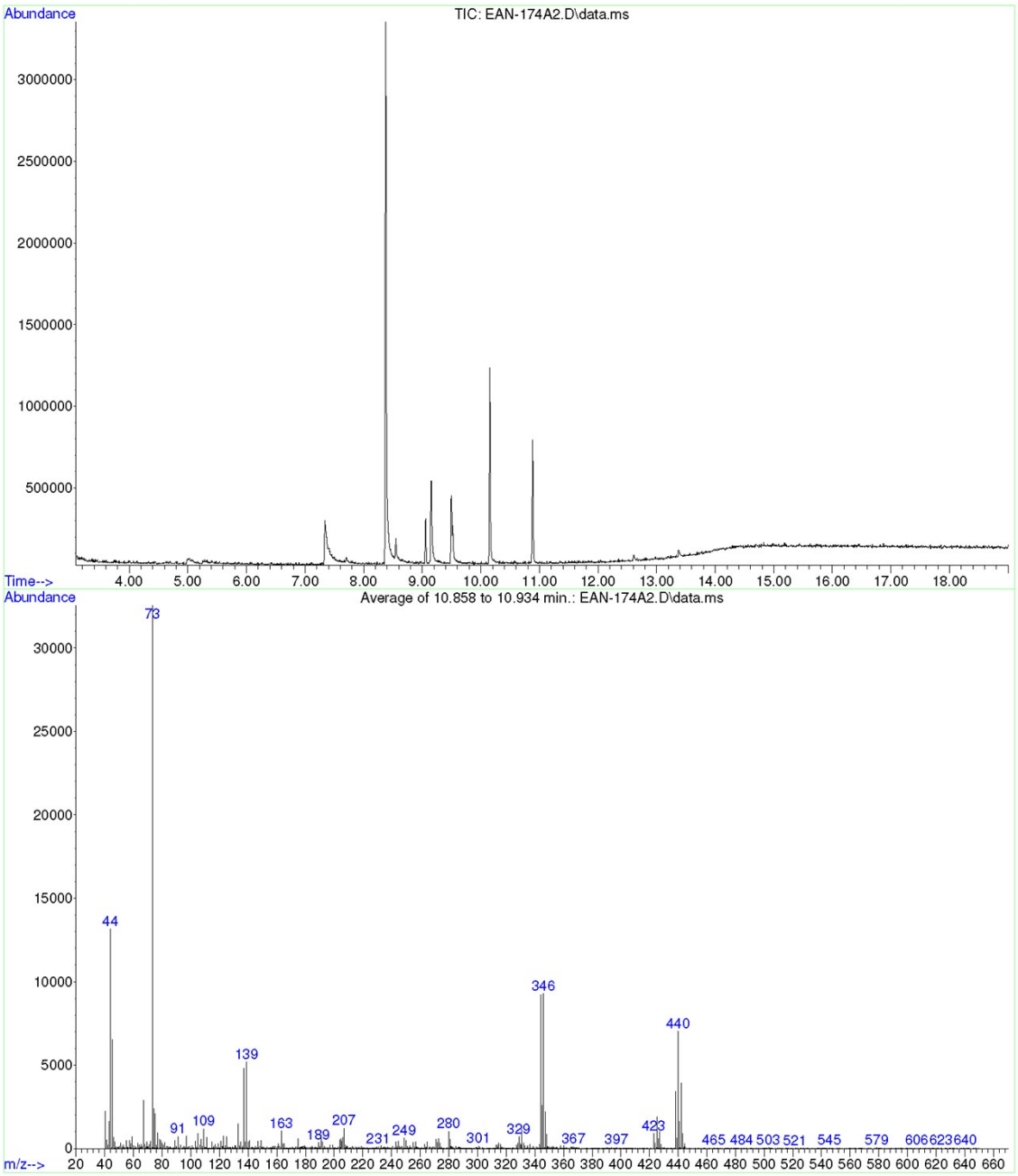


R_f/min	7.72	9.16	10.15	10.89	13.39
Int./ %	0.19	5.39	15.71	78.51	0.21
m/z	*155*	*294*	*366*	*438*	*281*
Species	-	A	B	C	Bleed
Ion		M^+	M^+	M^+	

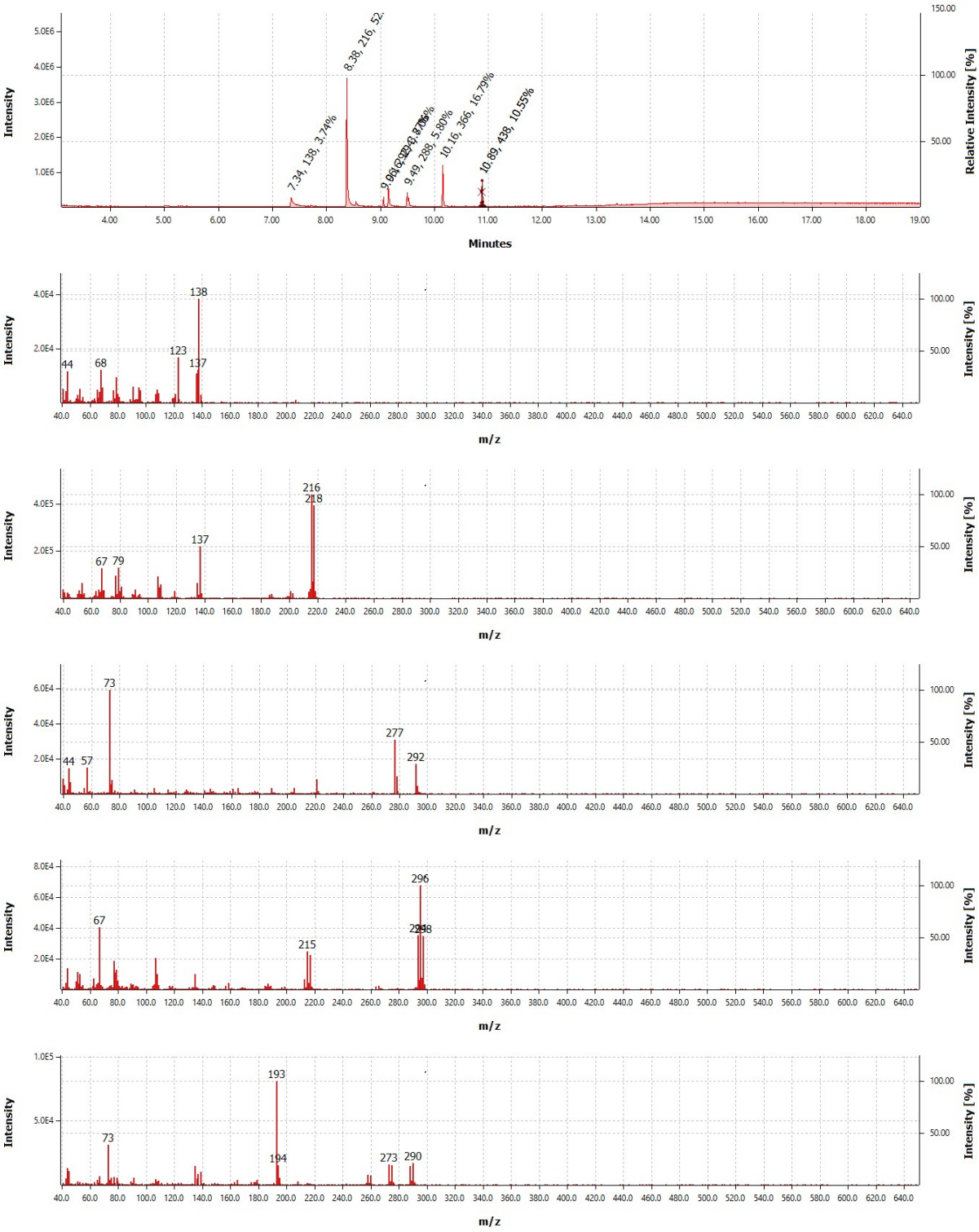

Intensity
Relative Intensity [%]
Minutes
7.72, 155, 0.19%
9.16, 294, 5.39%
10.15, 366, 15.71%
10.89, 438, 78.51%
13.39, CB, 0.21%
Intensity [%]
m/z
44
155
154
77
127
296
294
298
67
215
73
272
353
139
346
440
207
281
55

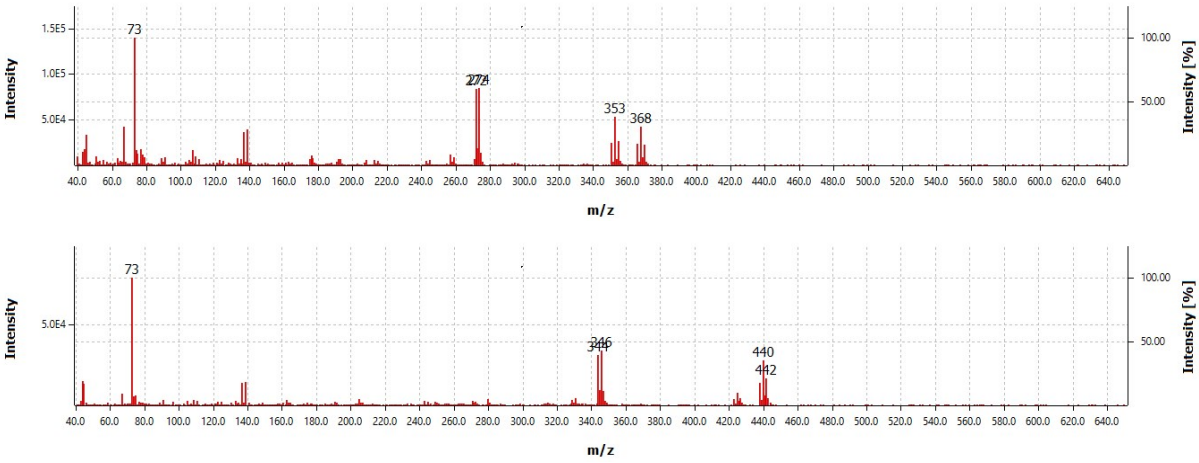
Aliquot 2: Second Silylation

```
File       :C:\DATA\EAN\EAN-174A2.D
Operator   :
Acquired   : 14 Jan 2019  17:25     using AcqMethod METH1_40_300_19MINS.M
Instrument :    Instrument #1
Sample Name: EAN-174A2
Misc Info  :
Vial Number: 22
```

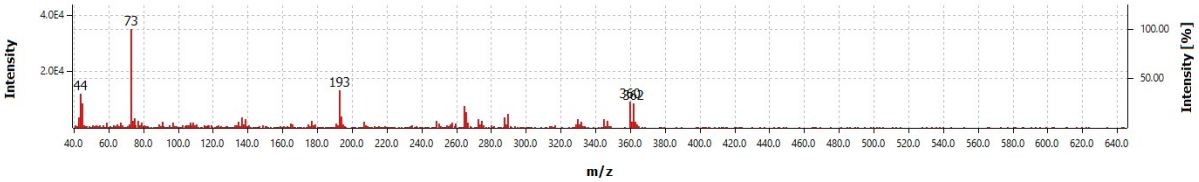


R_f/min	7.34	8.38	9.06	9.16	9.49	10.16	10.89
Int./ %	3.74	52.2	3.87	7.06	5.80	16.79	10.55
m/z	*138*	*216*	*292*	*294*	*288*	*366*	*438*
Species	V	T	AQ	A	S, D	B	C
Ion	M^+	M^+	M^+	M^+	M^+	M^+	M^+


Intensity
Relative Intensity [%]
Minutes
7.34, 138, 3.74%
8.38, 216, 52.
10.16, 366, 16.79%
10.89, 438, 10.55%
m/z
Intensity [%]
138
123
137
44
68
216
218
67
79
73
277
292
57
296
215
193
194
273
290

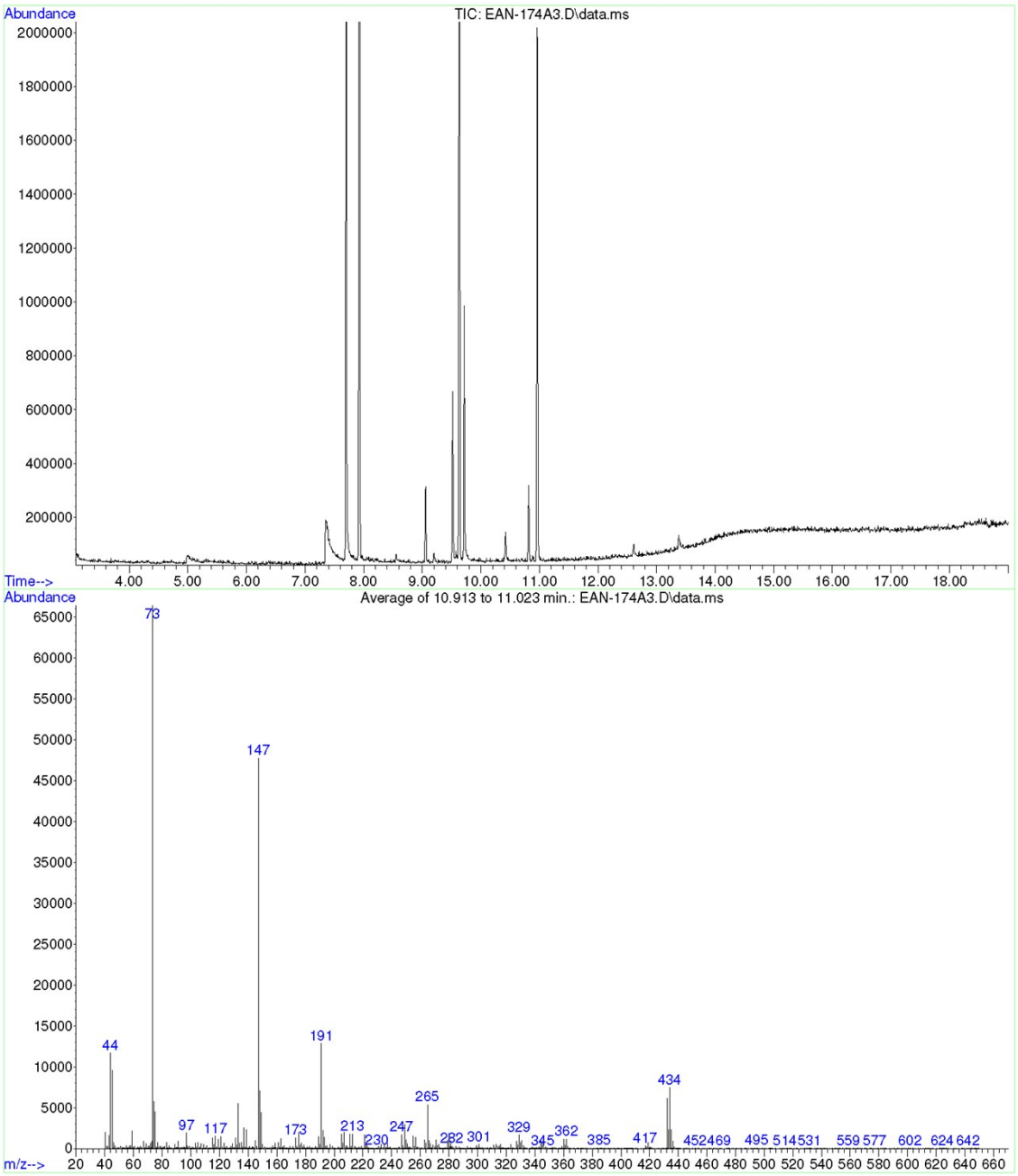


The right-hand side of the peak at 9.49 min (*m/z* 288) contains a second product at *m/z* 360. This matches the peak in the next aliquot at 9.52 min and therefore two species are overlapping above:

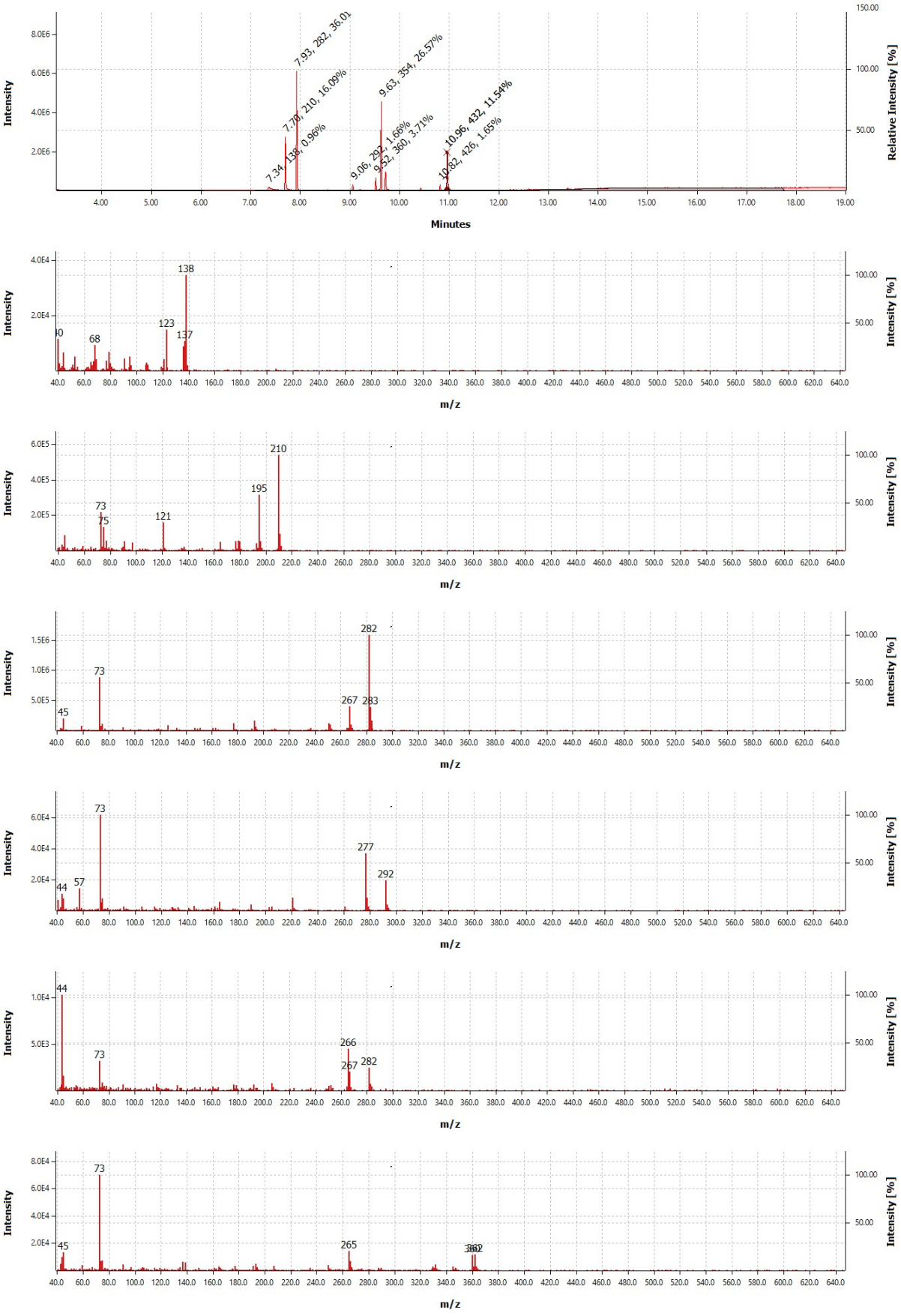


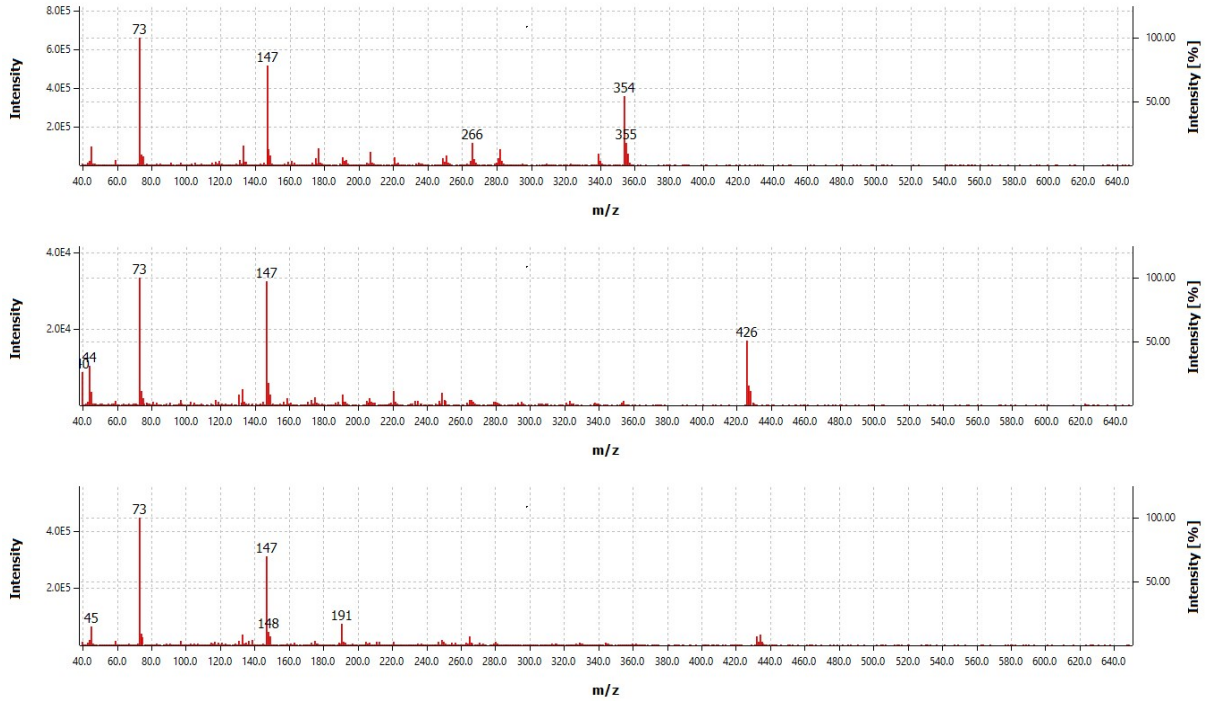
Aliquot 3: First Halogen-Metal Exchange

```
File       :C:\DATA\EAN\EAN-174A3.D
Operator   :
Acquired   : 14 Jan 2019  17:55     using AcqMethod METH1_40_300_19MINS.M
Instrument :    Instrument #1
Sample Name: EAN-174A3
Misc Info  :
Vial Number: 23
```

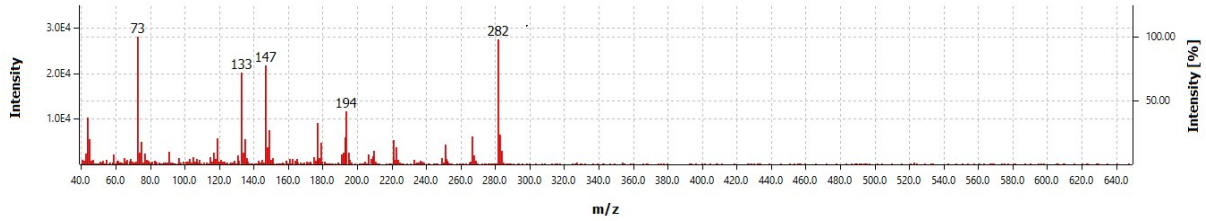


R_f/min	7.34	7.70	7.93	9.06	9.20	9.52	9.63	9.72	10.82	10.96
Int./ %	0.96	16.09	36.01	1.66	0.22	3.71	26.87	0.62	1.65	11.54
m/z	*138*	*210*	*282*	*292*	*282*	*360*	*354*	*282*	*426*	*432*
Species	V	U	DD	AQ	I	D	G	W	H	E
Ion	M^+	M^+	M^+	M^+	M^+	M^+	M^+	M^+	M^+	M^+


7.93, 282, 36.01
7.70, 210, 16.09%
9.63, 354, 26.57%
7.34, 138, 0.96%
9.06, 292, 1.66%
9.52, 360, 3.71%
10.96, 432, 11.54%
10.82, 426, 1.65%
Intensity
Relative Intensity [%]
Minutes
m/z
Intensity [%]

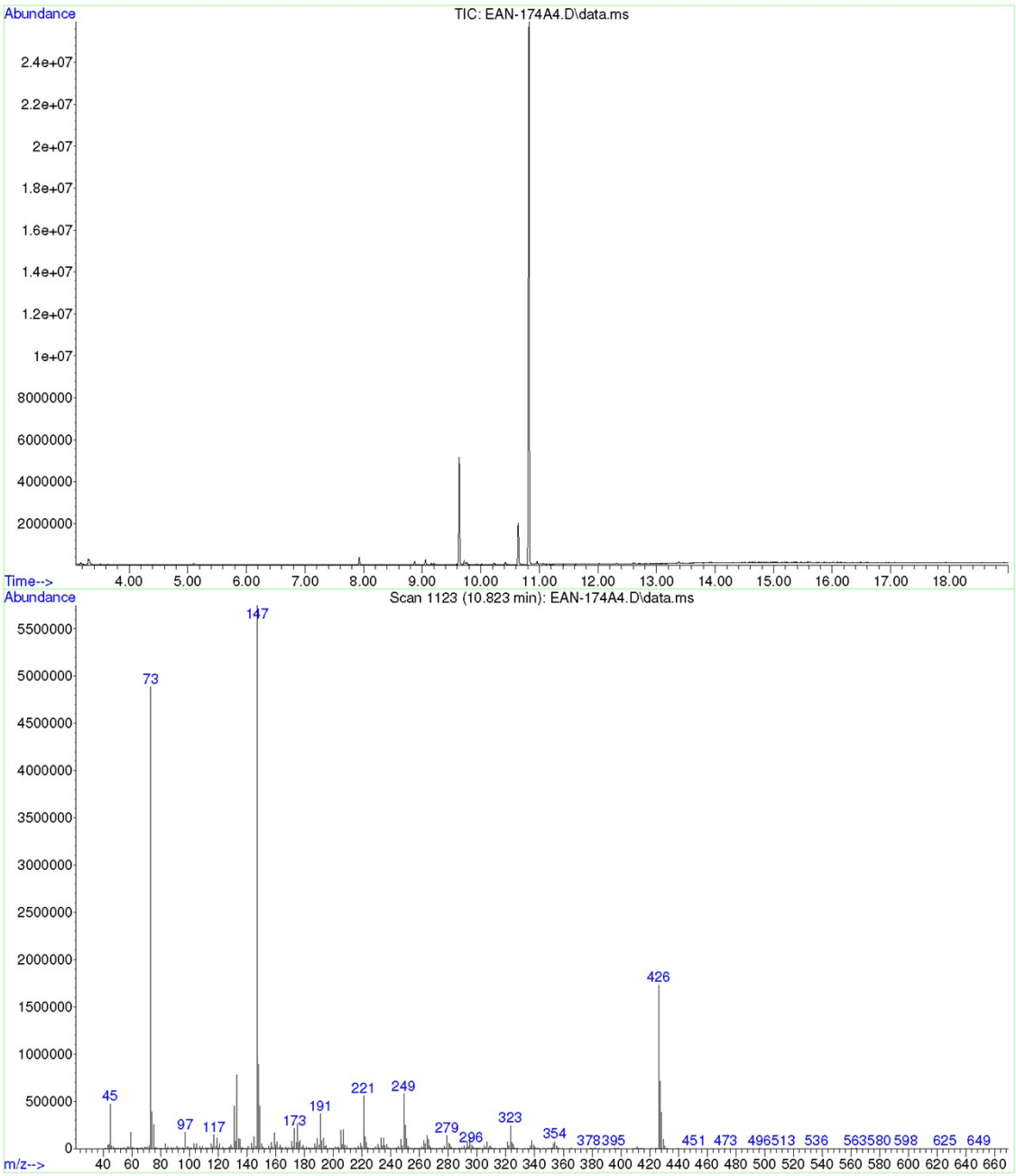


The peak at 9.72 not detected by the algorithm corresponds to 282 *m/z*:

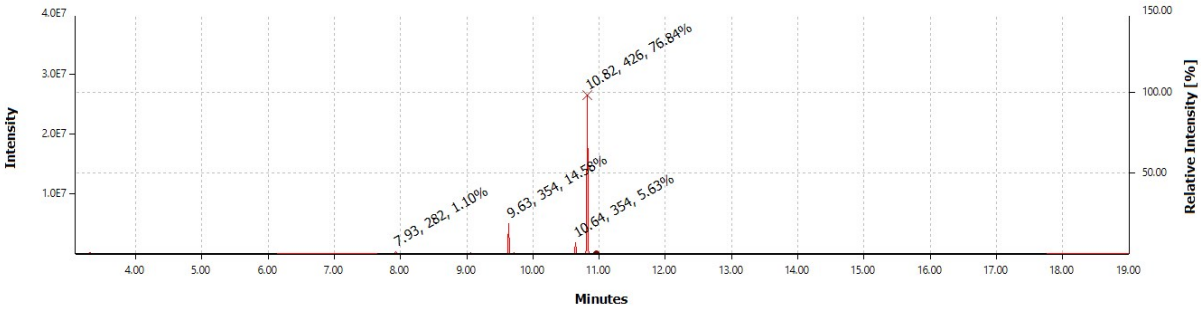


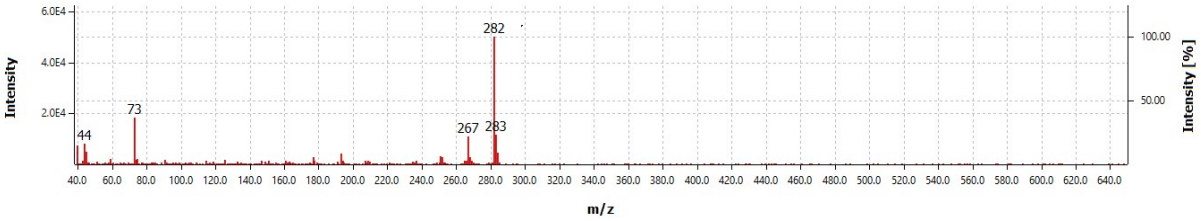
Aliquot 4: Second Halogen-Metal Exchange/Retro-Brook

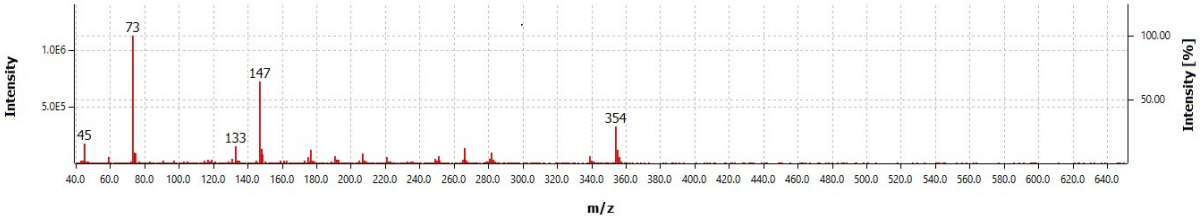
```
File       :C:\DATA\EAN\EAN-174A4.D
Operator   :
Acquired   : 14 Jan 2019  18:25     using AcqMethod METH1_40_300_19MINS.M
Instrument :    Instrument #1
Sample Name: EAN-174A4
Misc Info  :
Vial Number: 24
```

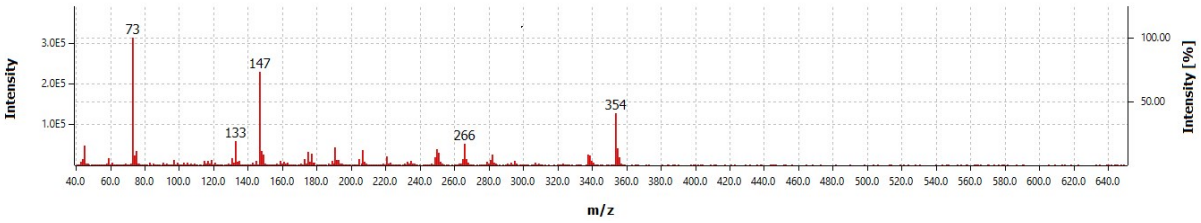


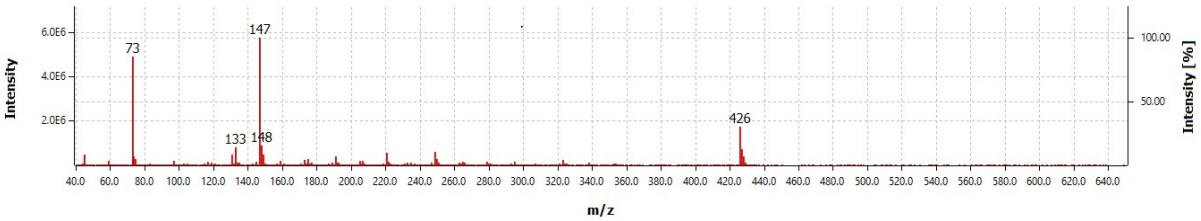
R_f/min	7.93	9.63	10.64	10.82
Int./ %	1.10	14.58	5.63	76.84
m/z	*282*	*354*	*354*	*426*
Species	DD	G	F	H
Ion	M^+	M^+	M^+	M^+


Intensity
Relative Intensity [%]
10.82, 426, 76.84%
9.63, 354, 14.58%
10.64, 354, 5.63%
7.93, 282, 1.10%
Minutes


Intensity
Intensity [%]
282
73
44
267
283
m/z

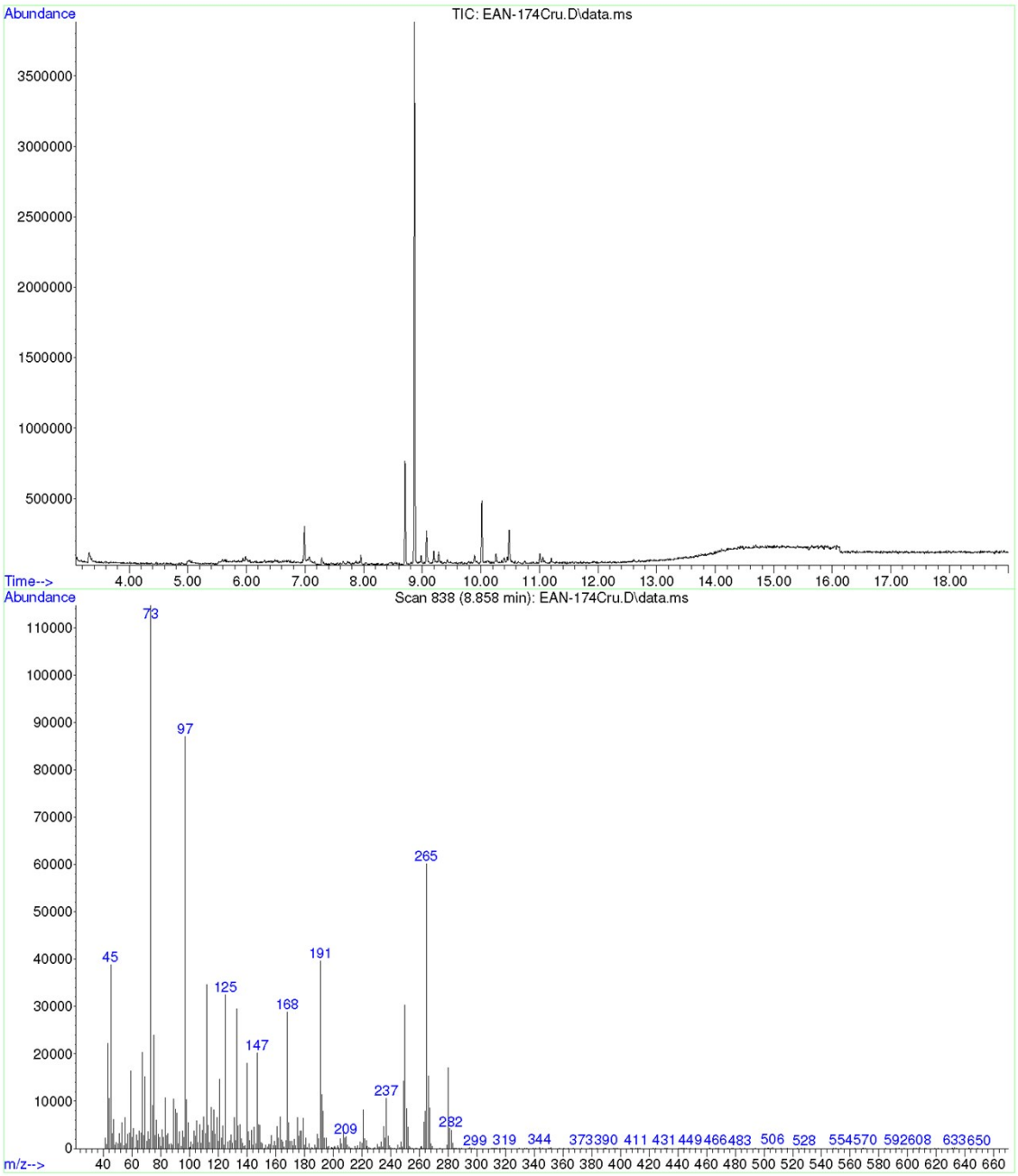

Intensity
Intensity [%]
73
147
45
133
354
m/z


Intensity
Intensity [%]
73
147
133
266
354
m/z

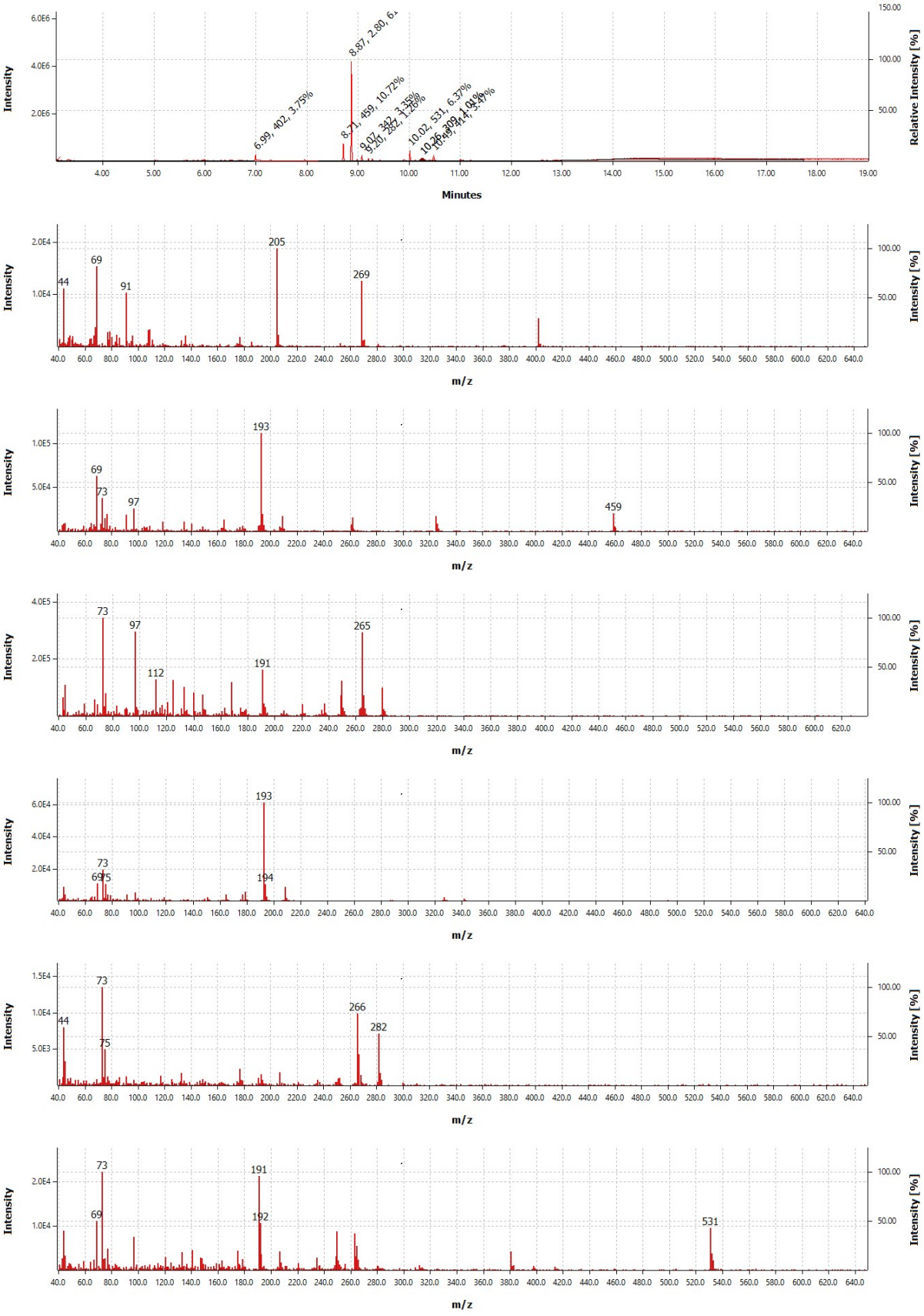

Intensity
Intensity [%]
147
73
133
148
426
m/z

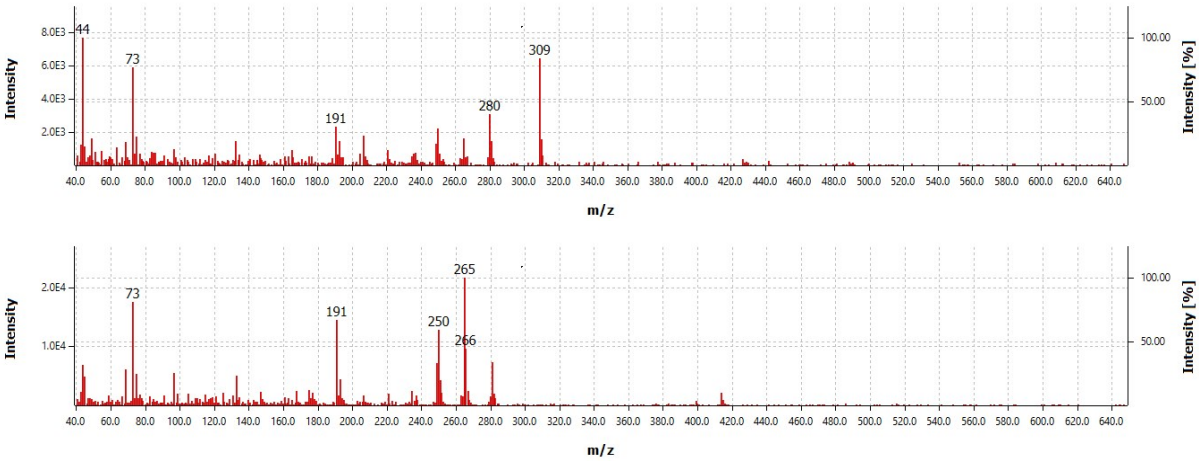
*Aliquot 5: Crude Workup, 3,6-Dimethyl-2,5-di(trimethylsilyl)benzoquinone (**23**)*

```
File       :C:\DATA\EAN\EAN-174Cru.D
Operator   :
Acquired   : 14 Jan 2019  18:54     using AcqMethod METH1_40_300_19MINS.M
Instrument :    Instrument #1
Sample Name: EAN-174Cru
Misc Info  :
Vial Number: 25
```



R_f/min	6.99	8.71	8.87	9.07	9.20	10.02	10.26	10.49
Int./ %	3.75	10.72	61.78	3.35	1.26	6.37	1.01	3.47
m/z	*402*	*459*	*280*	*342*	*282*	*531*	*309*	*414*
Species	X	Z	KQ	Y	I	K	-	J
Ion	M^+	$M\text{-}Me^+$	M^+	M^+	M^+	$M\text{-}Me^+$	M^+	M^+

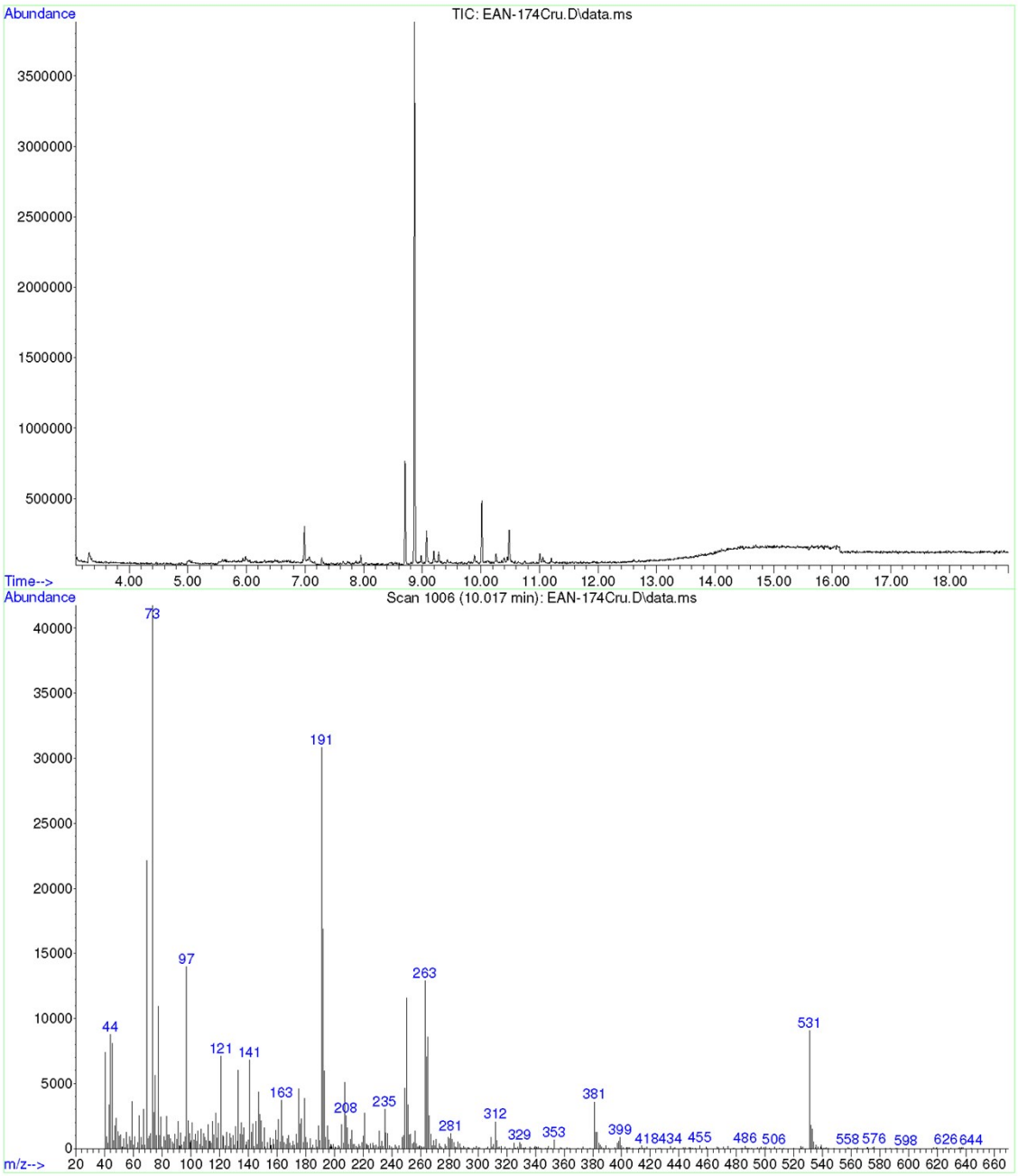

Intensity
Relative Intensity [%]
Minutes
6.99, 402, 3.75%
8.71, 459, 10.72%
10.02, 531, 6.37%
m/z
Intensity [%]
205
69
44
91
269
193
73
97
459
265
112
191
194
75
266
282
531
192


Intensity
8.0E3
6.0E3
4.0E3
2.0E3
44
73
191
280
309
100.00
50.00
Intensity [%]
40.0 60.0 80.0 100.0 120.0 140.0 160.0 180.0 200.0 220.0 240.0 260.0 280.0 300.0 320.0 340.0 360.0 380.0 400.0 420.0 440.0 460.0 480.0 500.0 520.0 540.0 560.0 580.0 600.0 620.0 640.0
m/z

Intensity
2.0E4
1.0E4
73
191
250
265
266
100.00
50.00
Intensity [%]
40.0 60.0 80.0 100.0 120.0 140.0 160.0 180.0 200.0 220.0 240.0 260.0 280.0 300.0 320.0 340.0 360.0 380.0 400.0 420.0 440.0 460.0 480.0 500.0 520.0 540.0 560.0 580.0 600.0 620.0 640.0
m/z

*3,6-dimethyl-2,5-di(trimethylsilyl)phenylene ditrifluoromethanesulfonate (**12a**)*

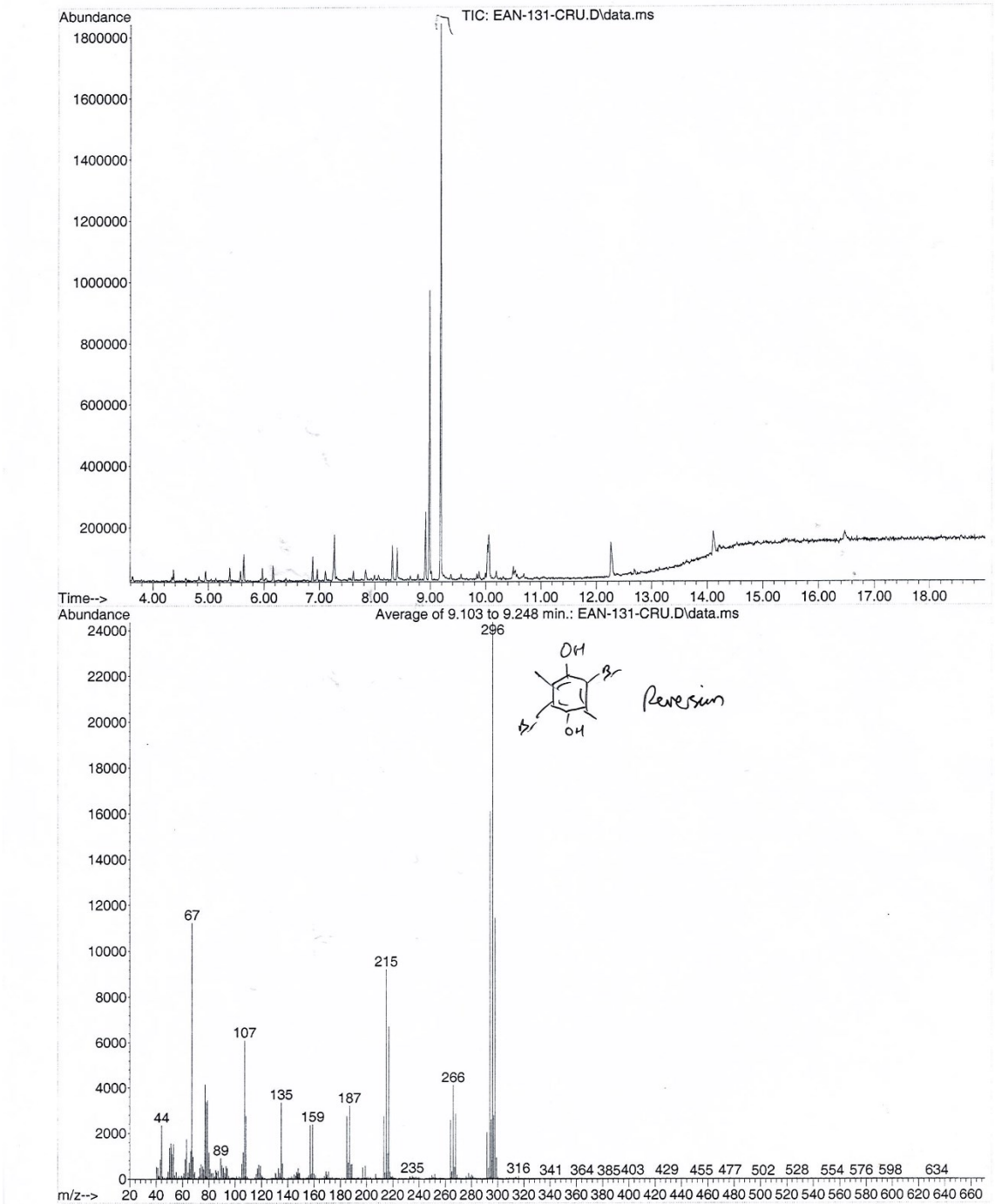
```
File       :C:\DATA\EAN\EAN-174Cru.D
Operator   :
Acquired   : 14 Jan 2019  18:54     using AcqMethod METH1_40_300_19MINS.M
Instrument :    Instrument #1
Sample Name: EAN-174Cru
Misc Info  :
Vial Number: 25
```



*Validation Test: 2,5-Dibromo-3,6-dimethylhydroquinone (**9**)*

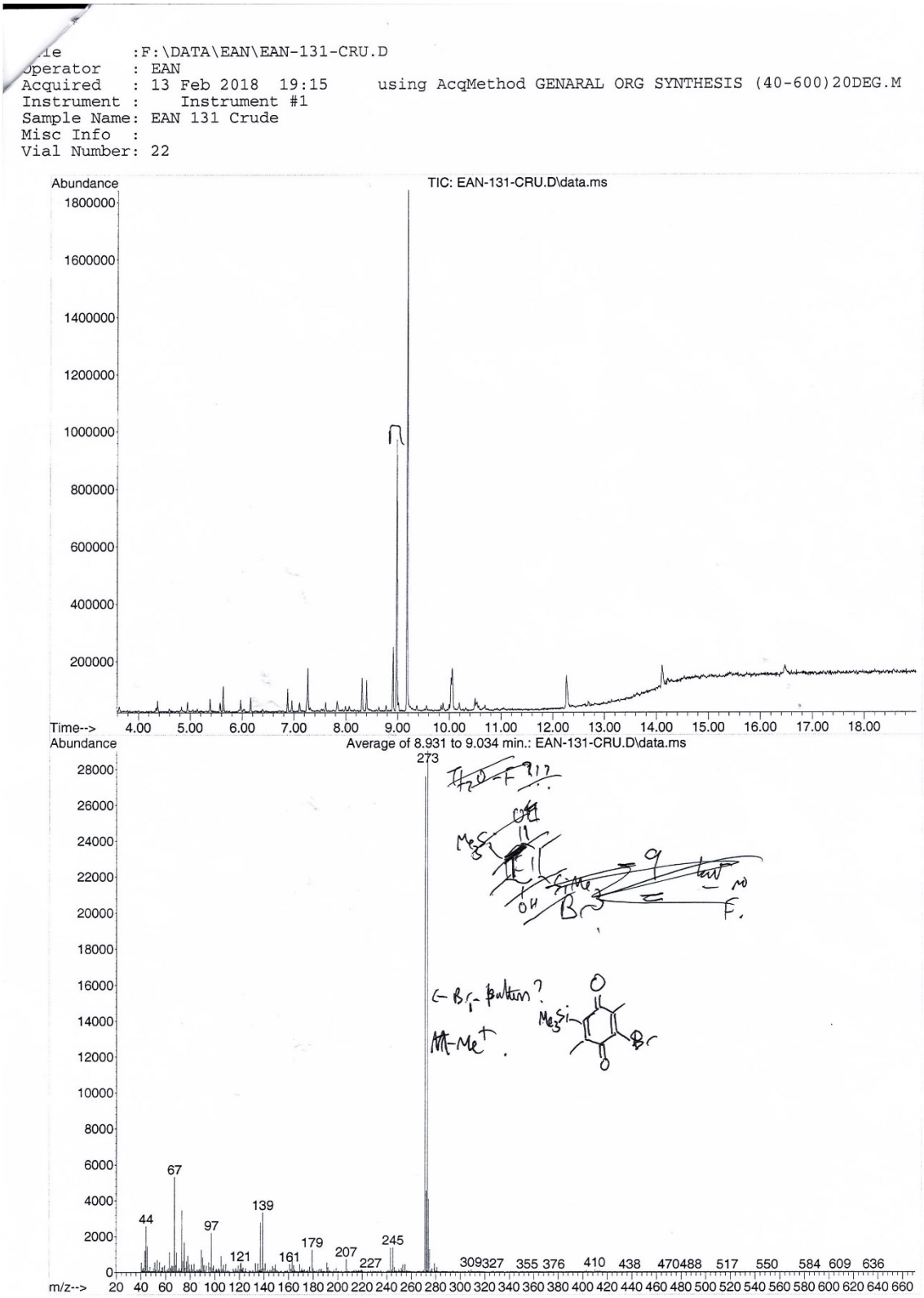
From double desilylation of starting material:

```
File       :F:\DATA\EAN\EAN-131-CRU.D
Operator   : EAN
Acquired   : 13 Feb 2018  19:15     using AcqMethod GENARAL ORG SYNTHESIS (40-600)20DEG.M
Instrument :    Instrument #1
Sample Name: EAN 131 Crude
Misc Info  :
Vial Number: 22
```



Validation Test: 2-Bromo-3,6-dimethyl-5-(trimethylsilyl)benzoquinone

From oxidation of singly *C*-silylated product:



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