Supporting Information

Synthesis, Characterization, and Copper (II) Chelates of 1,11-dithia-4,8-diazacyclotetradecane

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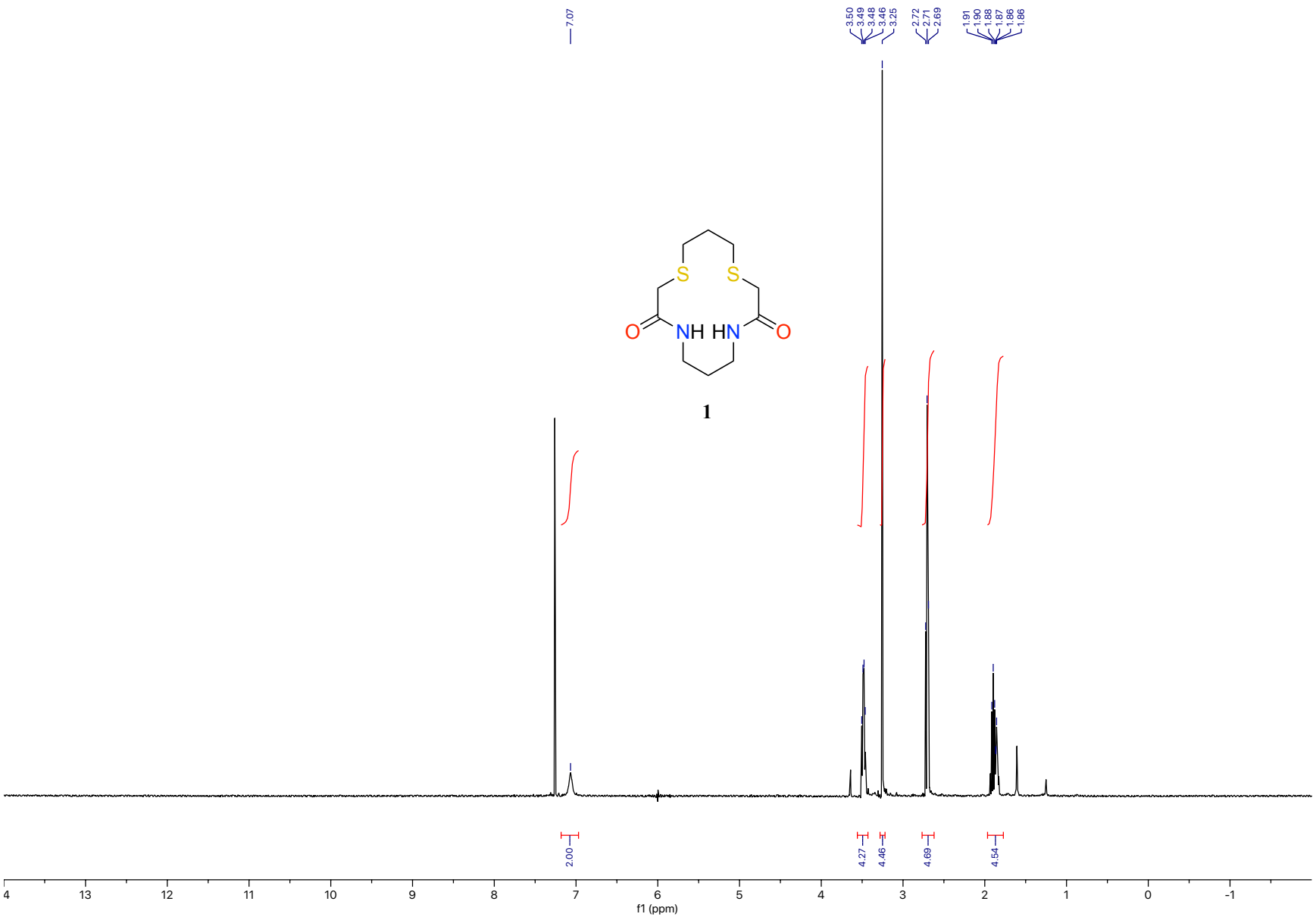
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1.86
1.86
S
S
O
NH HN
O
1
2.00
4.27
4.46
4.69
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10
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3
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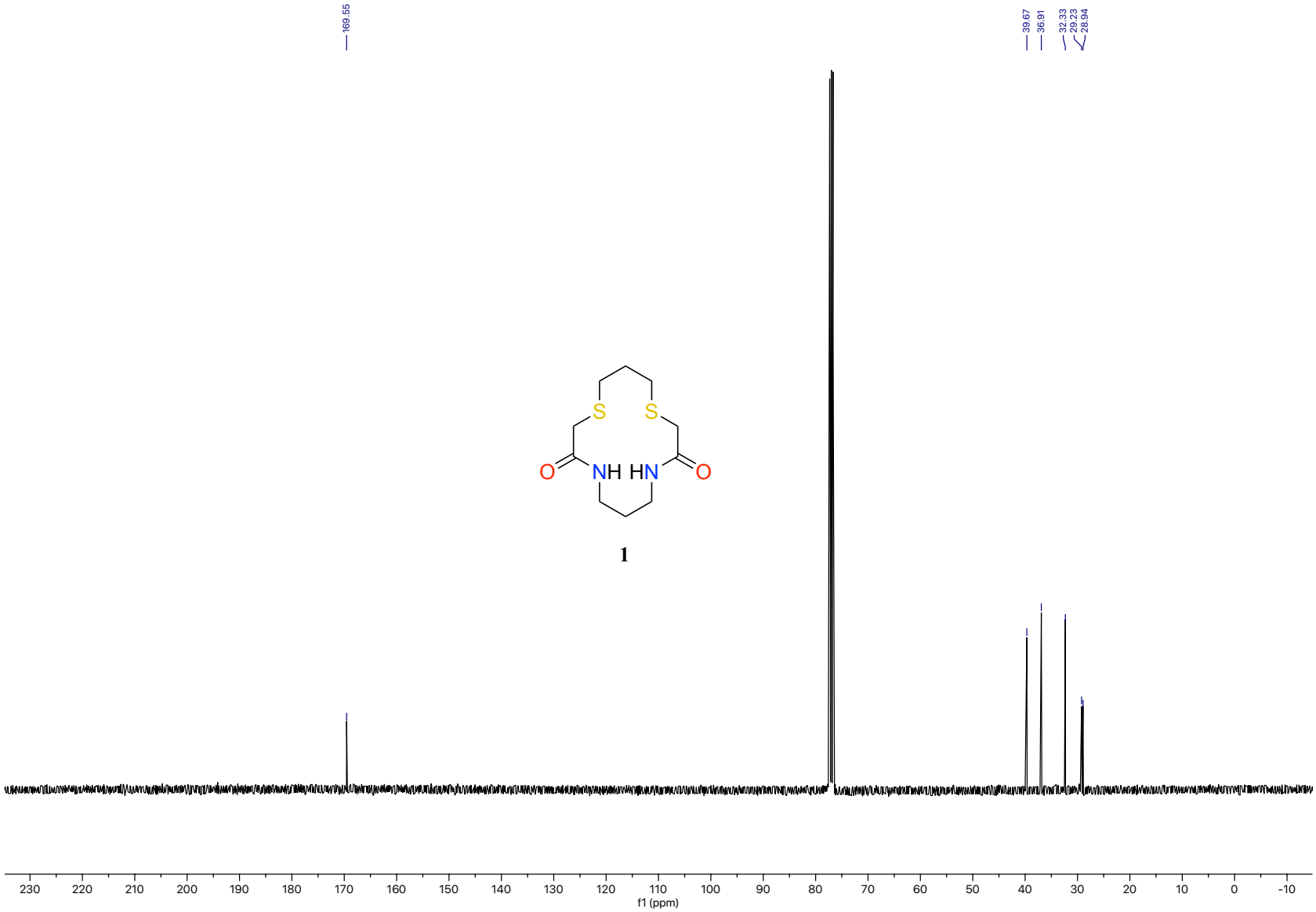
f1 (ppm)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O
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180
170
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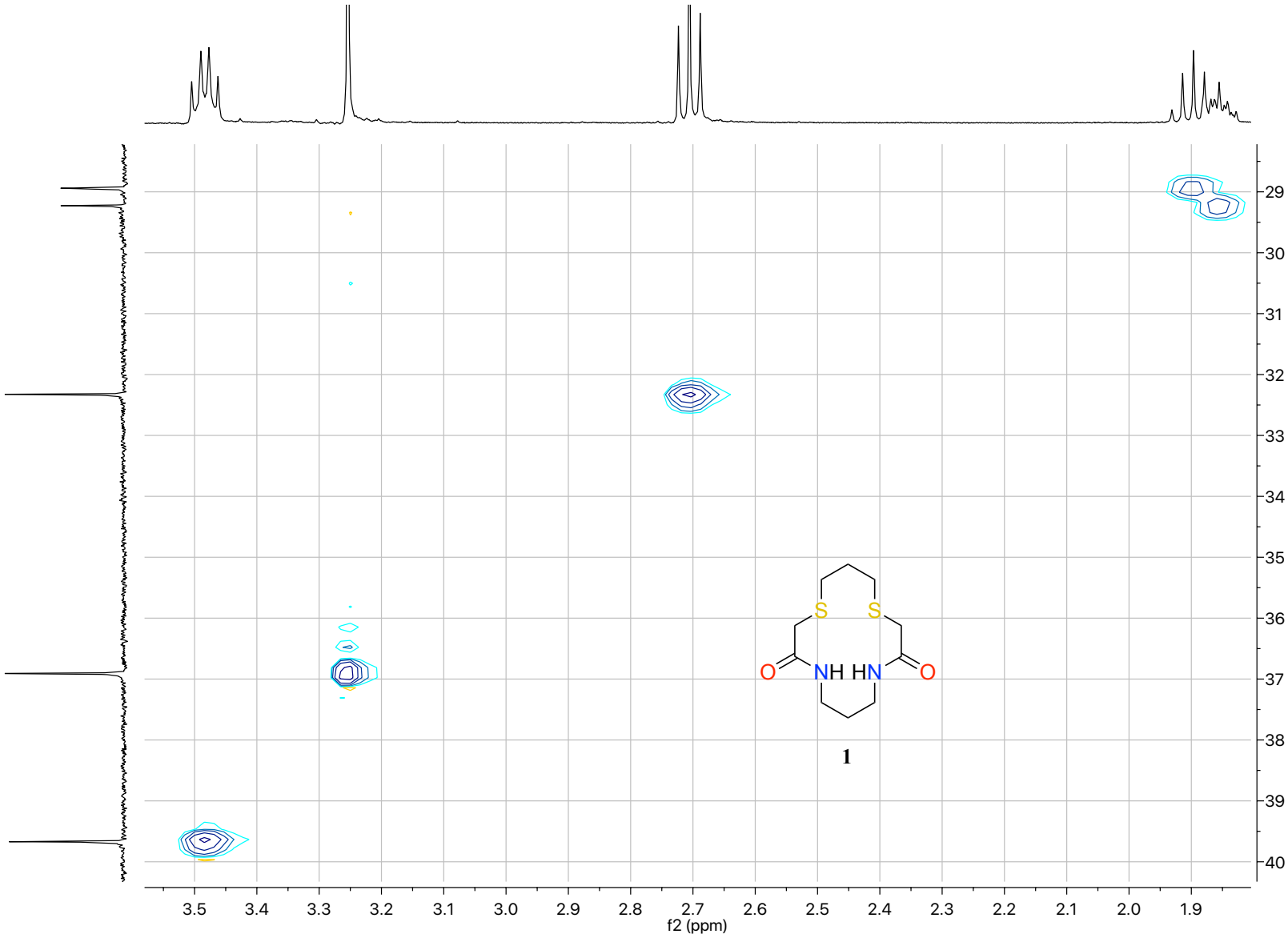
f1 (ppm)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O
NH HN
O
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2.7
2.6
2.5
2.4
2.3
2.2
2.1
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1.9
f2 (ppm)
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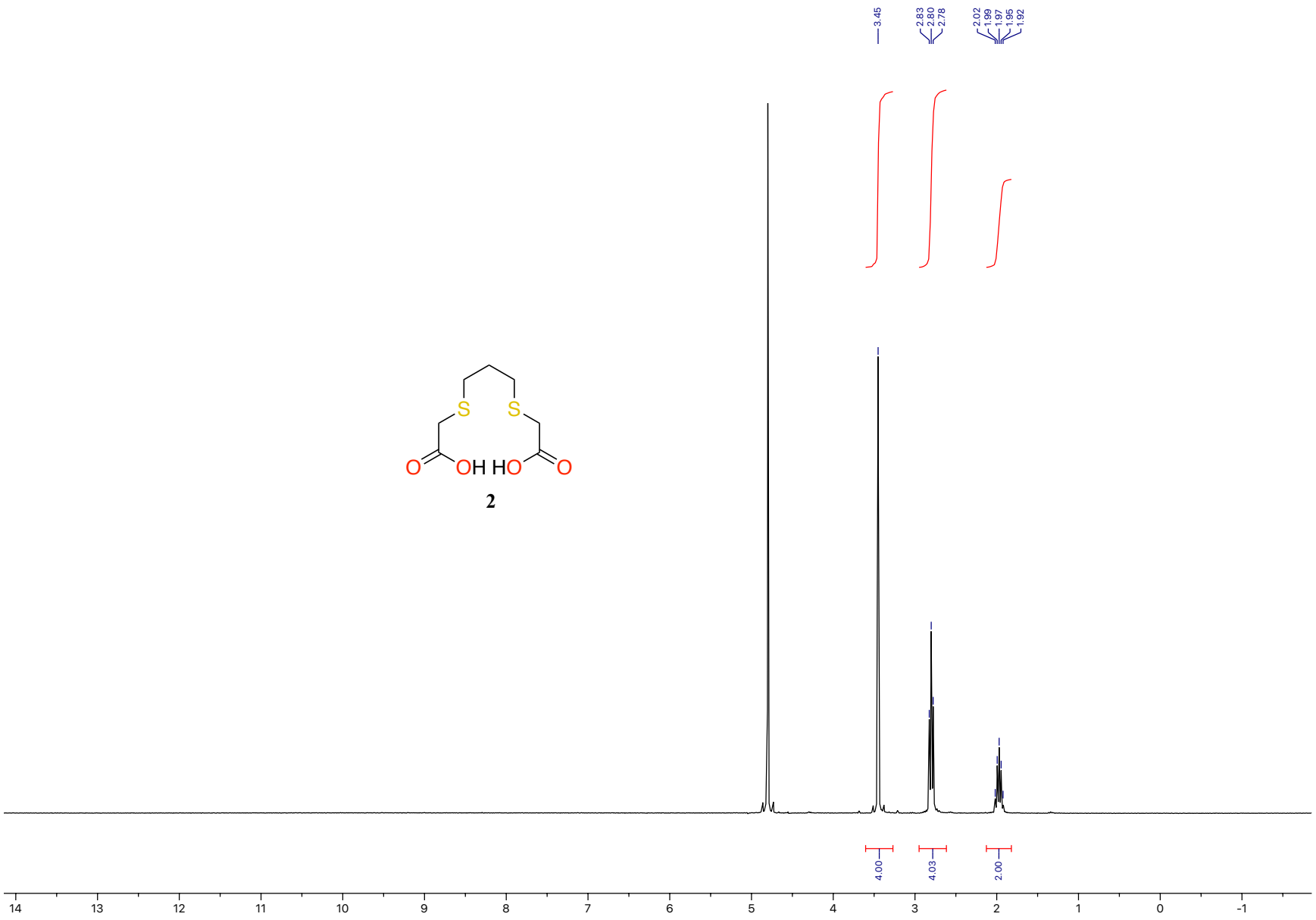
30
31
32
33
34
35
36
37
38
39
40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OH
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O
2
4.00
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10
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5
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3
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1
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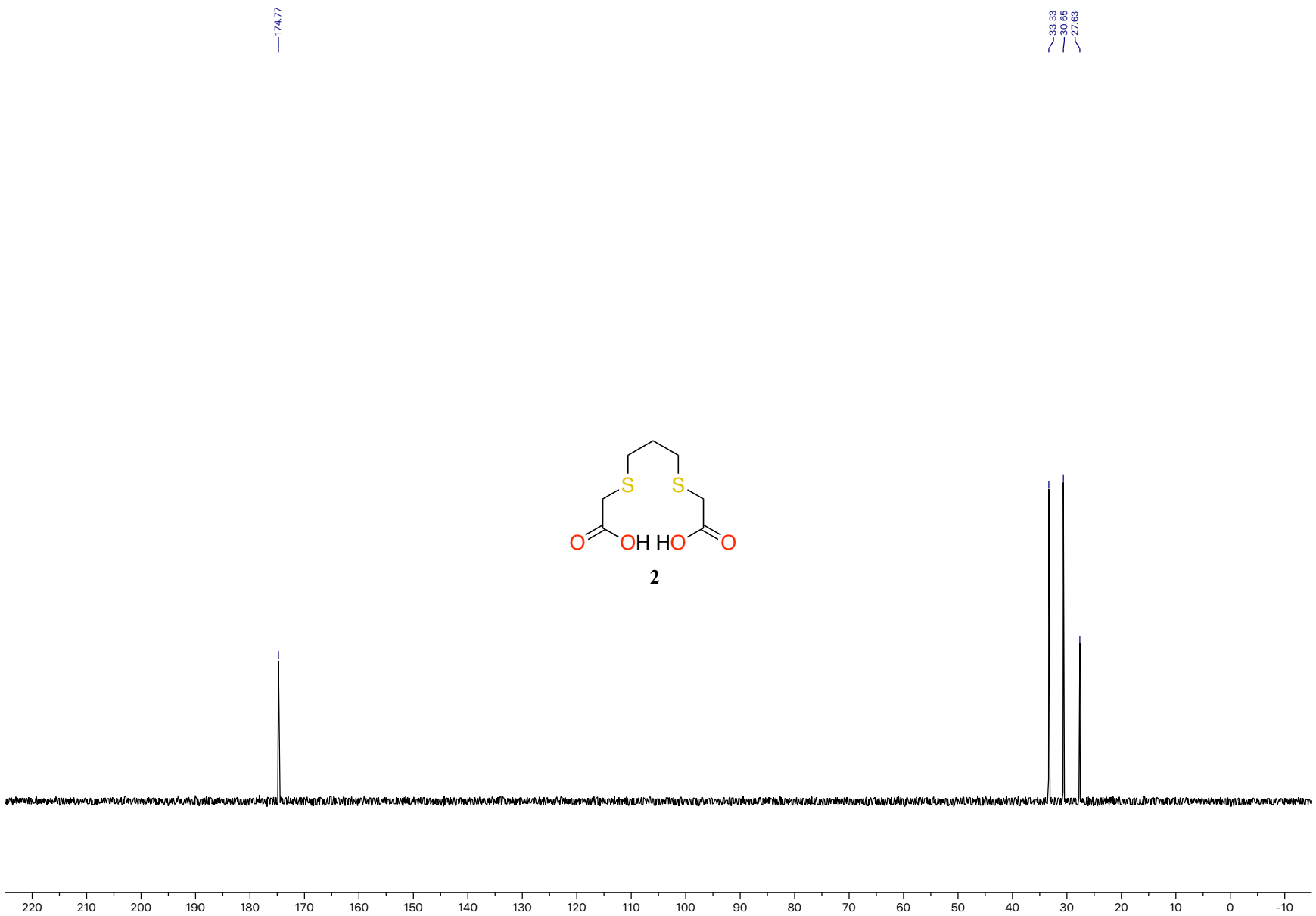
-1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27.63
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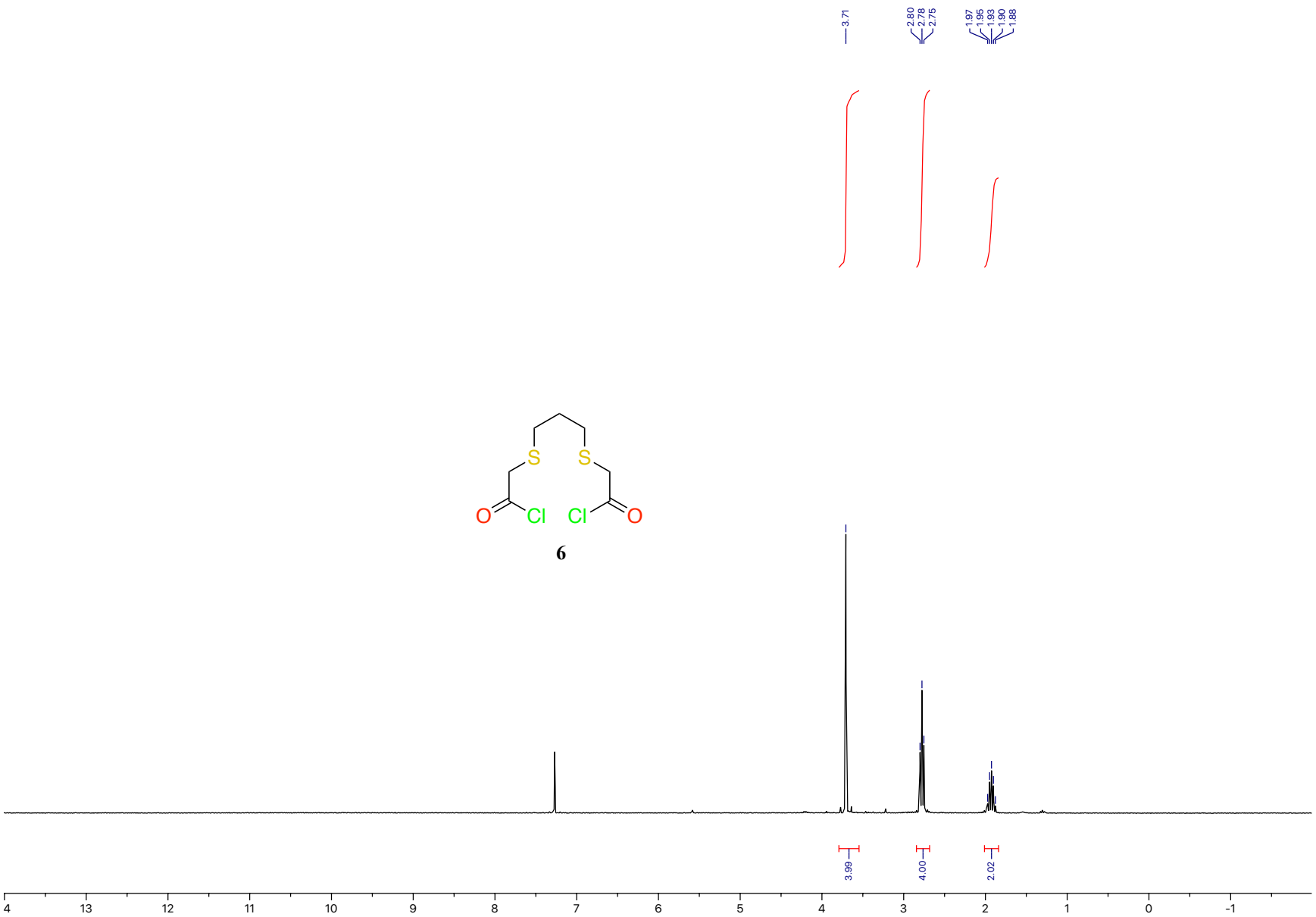
S
O
OH HO
O
2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

S
S
O
Cl
Cl
O

6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2
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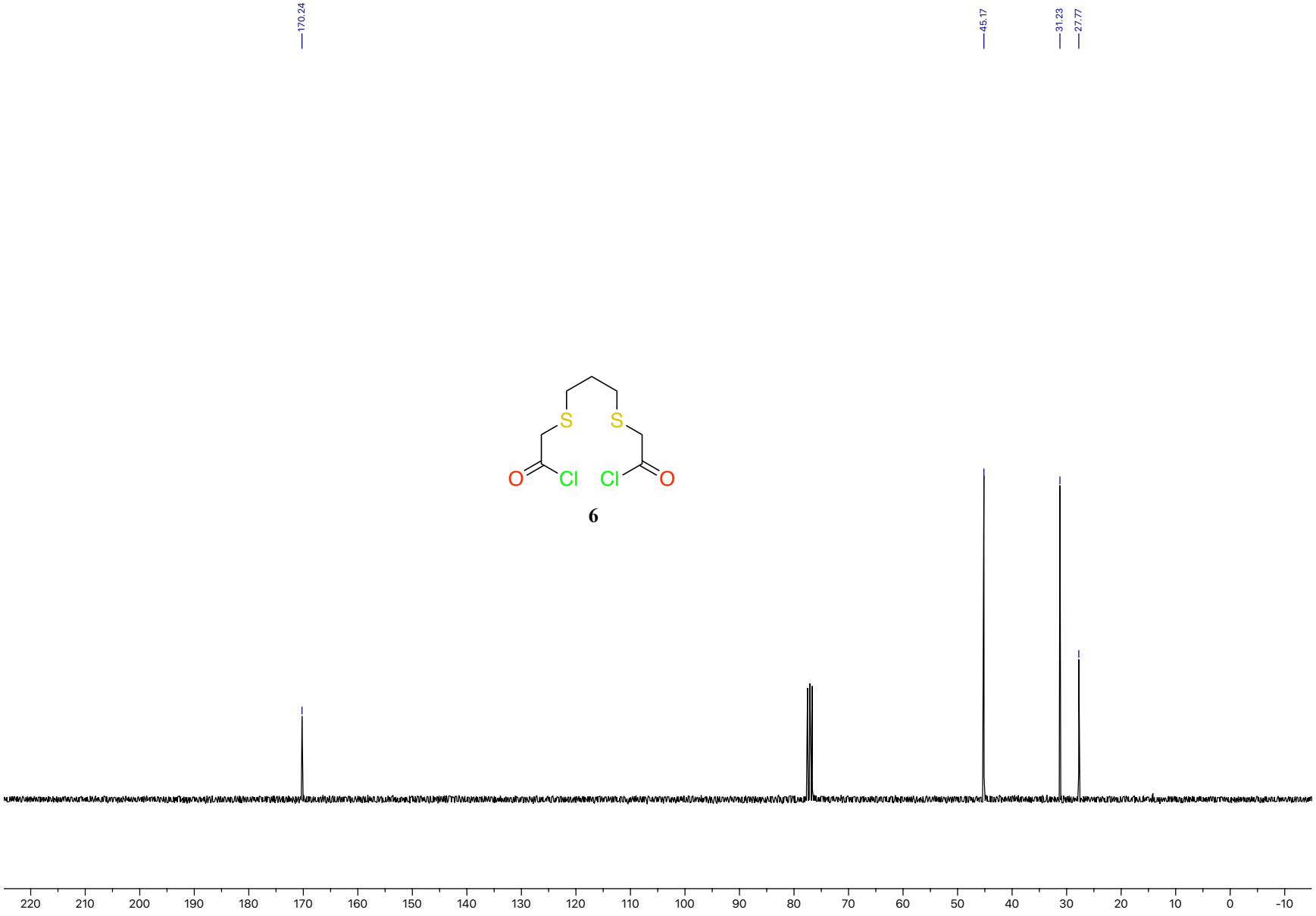
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O
Cl
Cl
O
6
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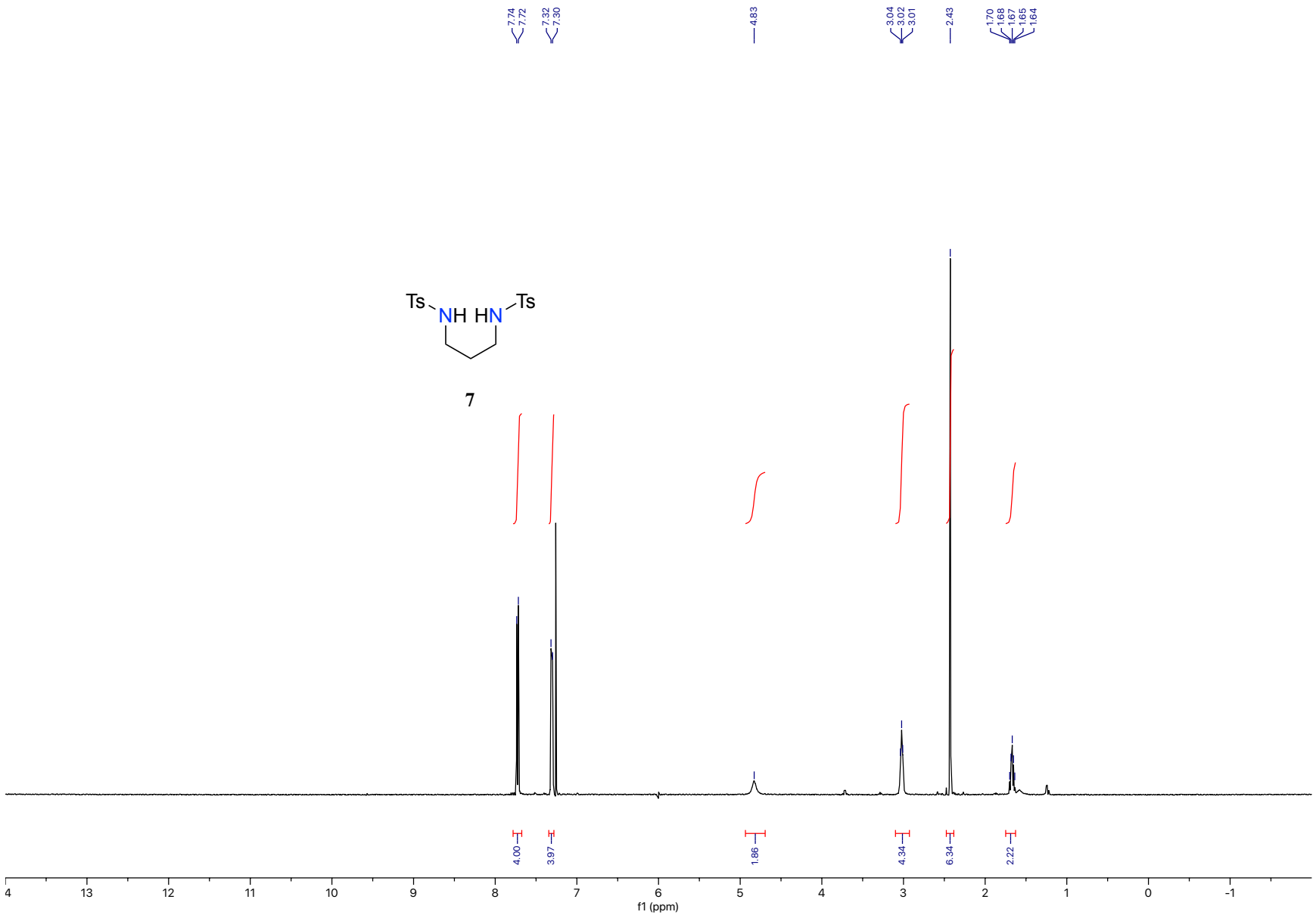
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4.83
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3.02
3.01
2.43
1.70
1.68
1.67
1.65
1.64
Ts
NH HN
Ts
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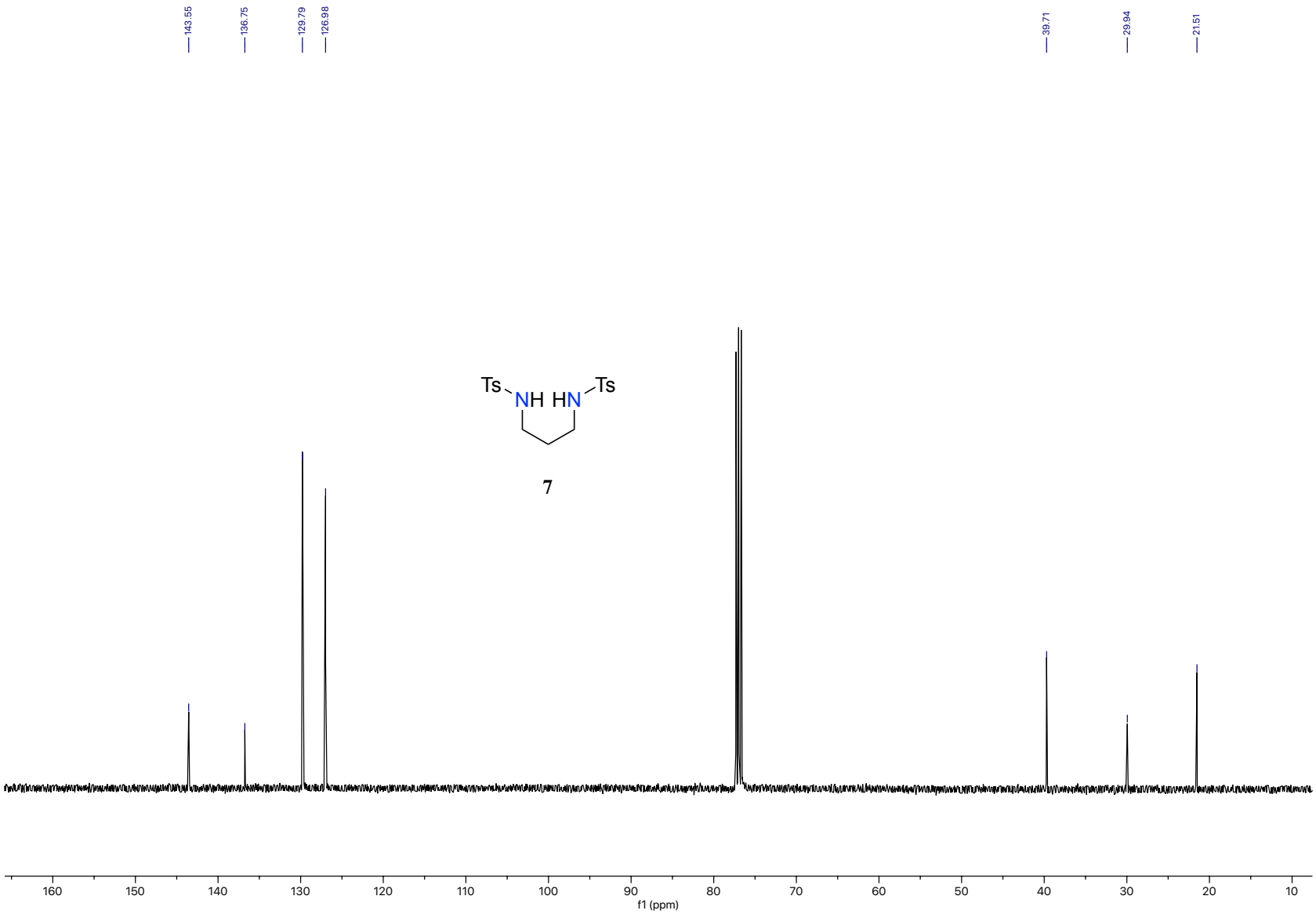
4.00
3.97
1.86
4.34
6.34
2.22
f1 (ppm)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129.79
126.98
39.71
29.94
21.51
Ts
NH HN
Ts
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140
130
120
110
100
90
80
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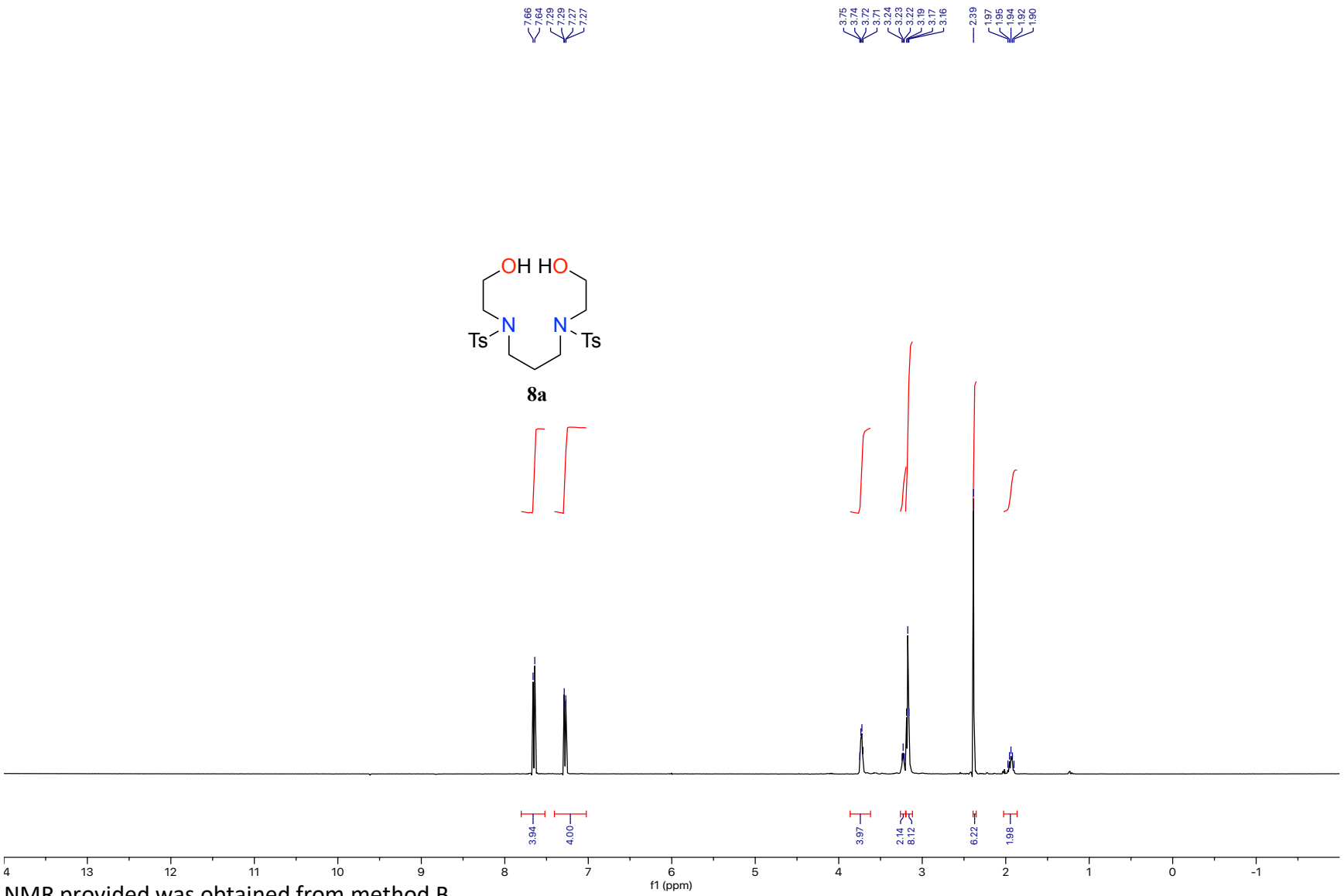
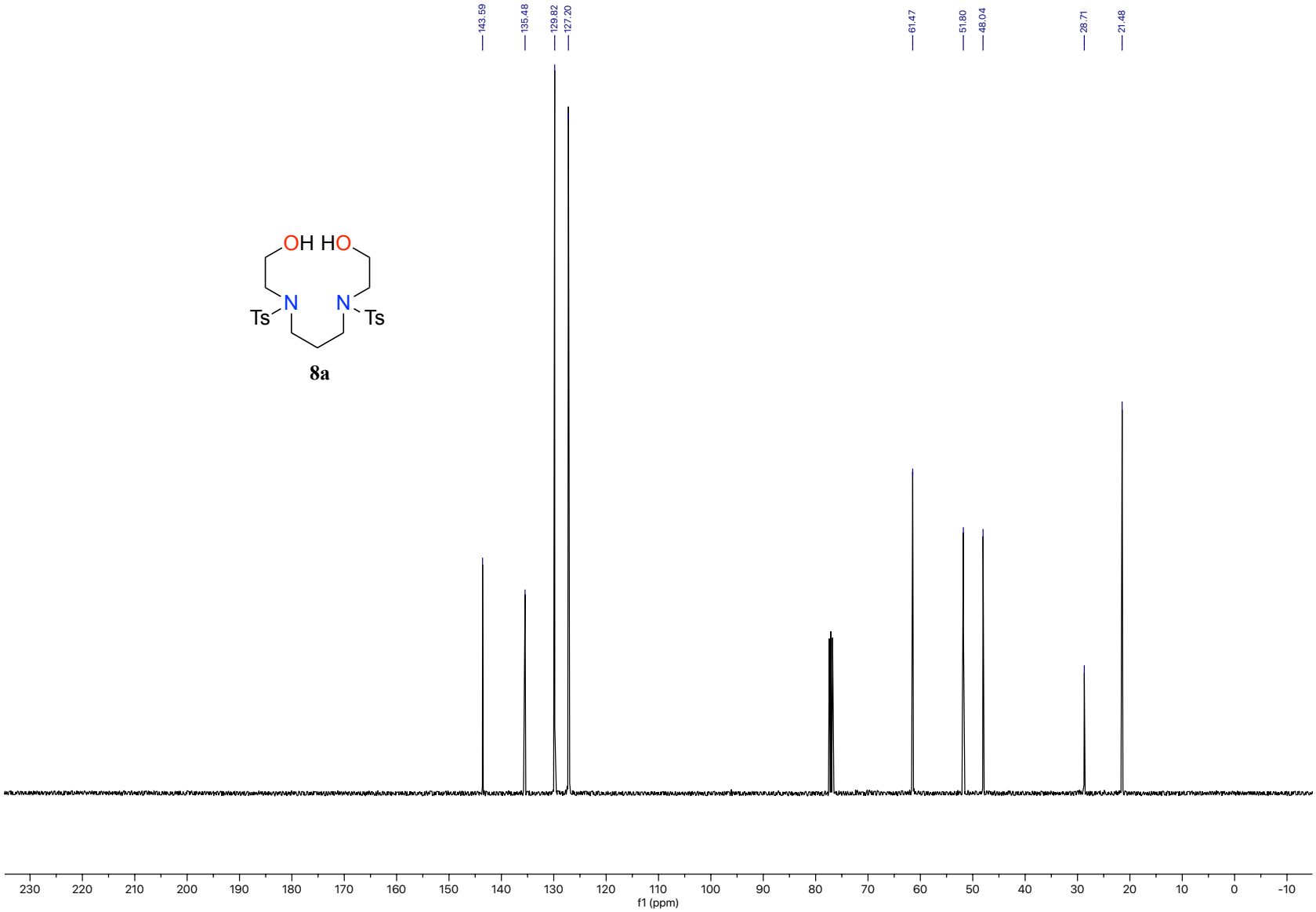
60
50
40
30
20
10
f1 (ppm)



NMR provided was obtained from method B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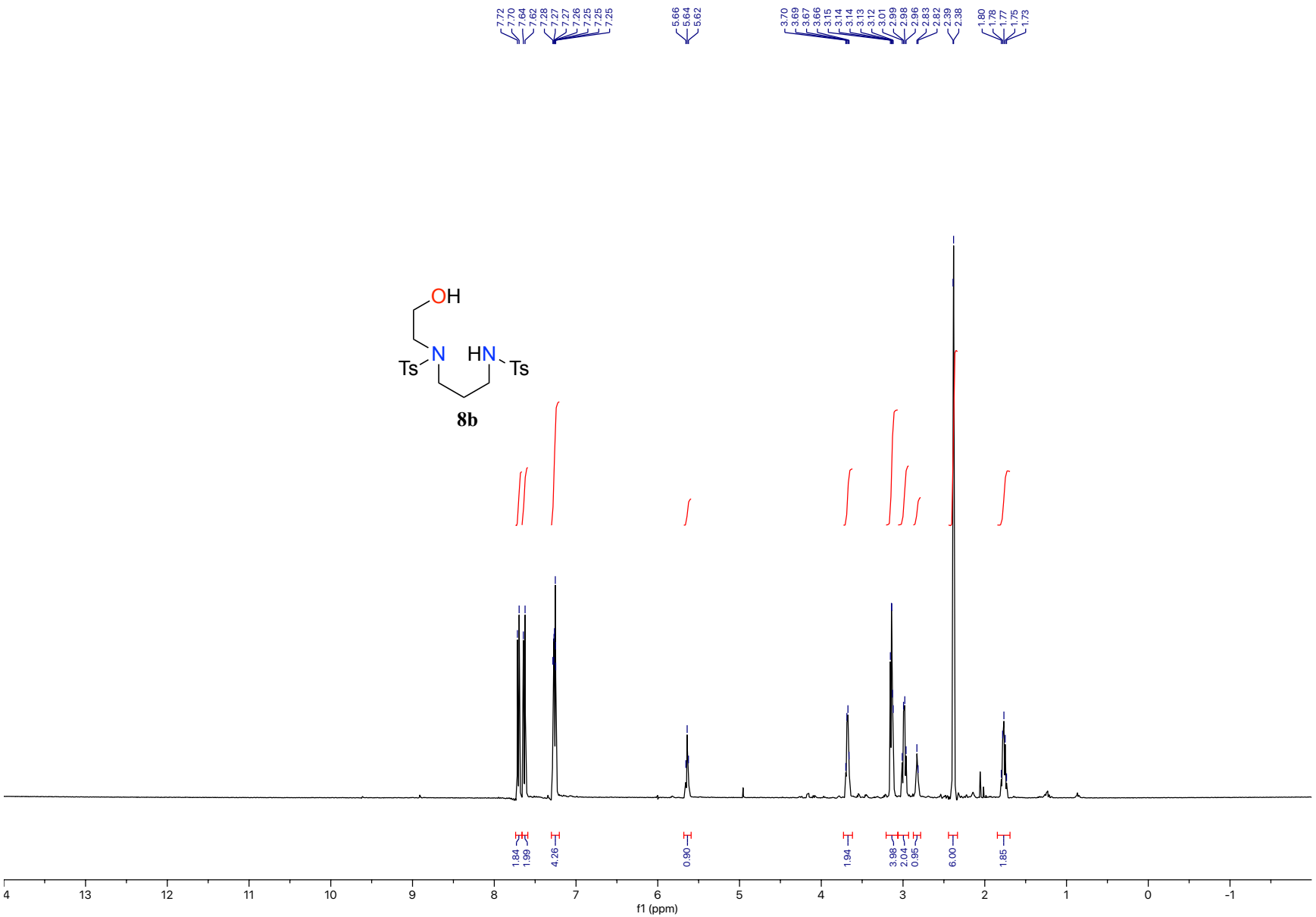
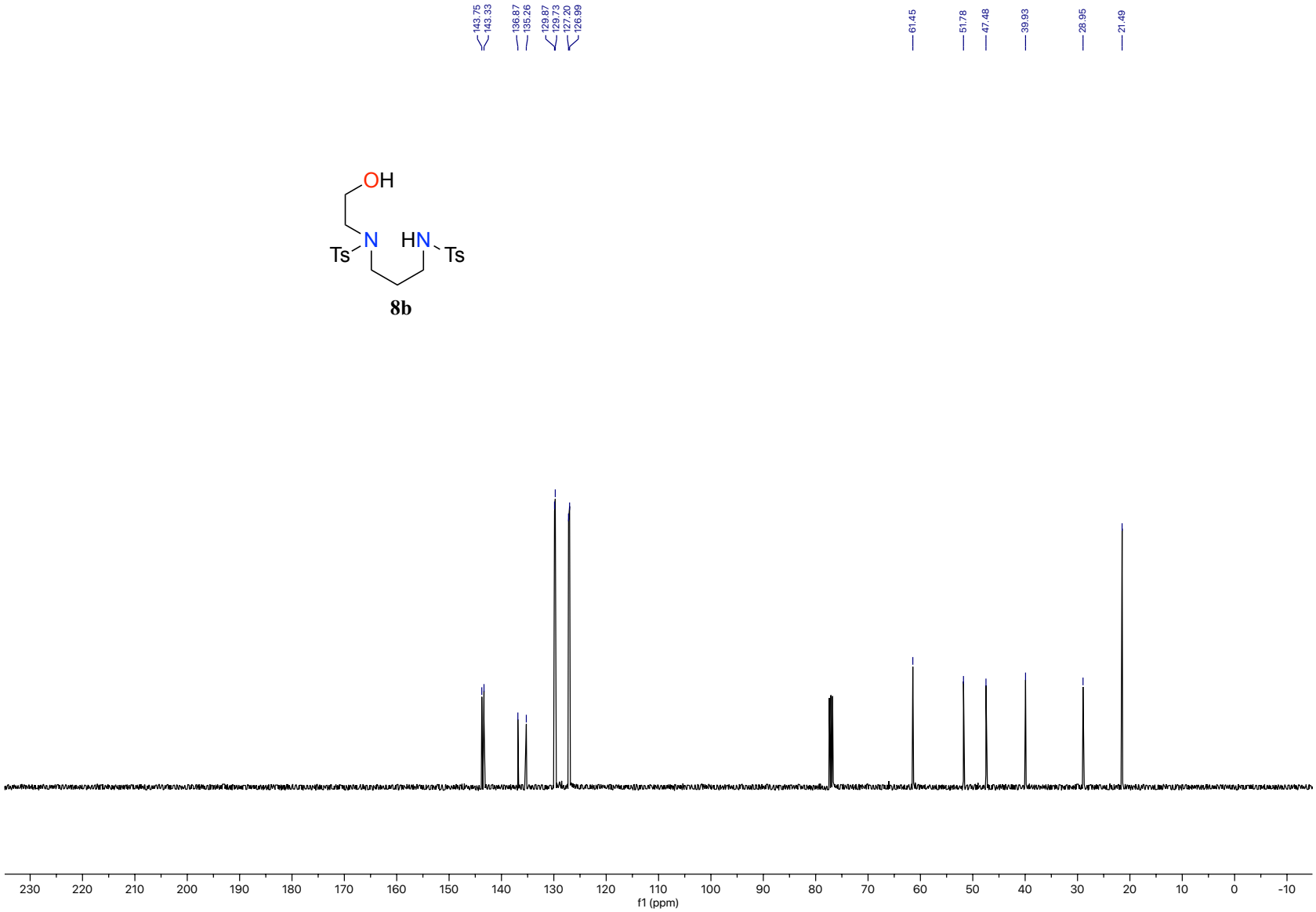
51.80
48.04
28.71
21.48
OH HO
N
N
Ts
Ts
8a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
N
HN
Ts
Ts
8b
f1 (ppm)

OH
N
HN
Ts
Ts

8b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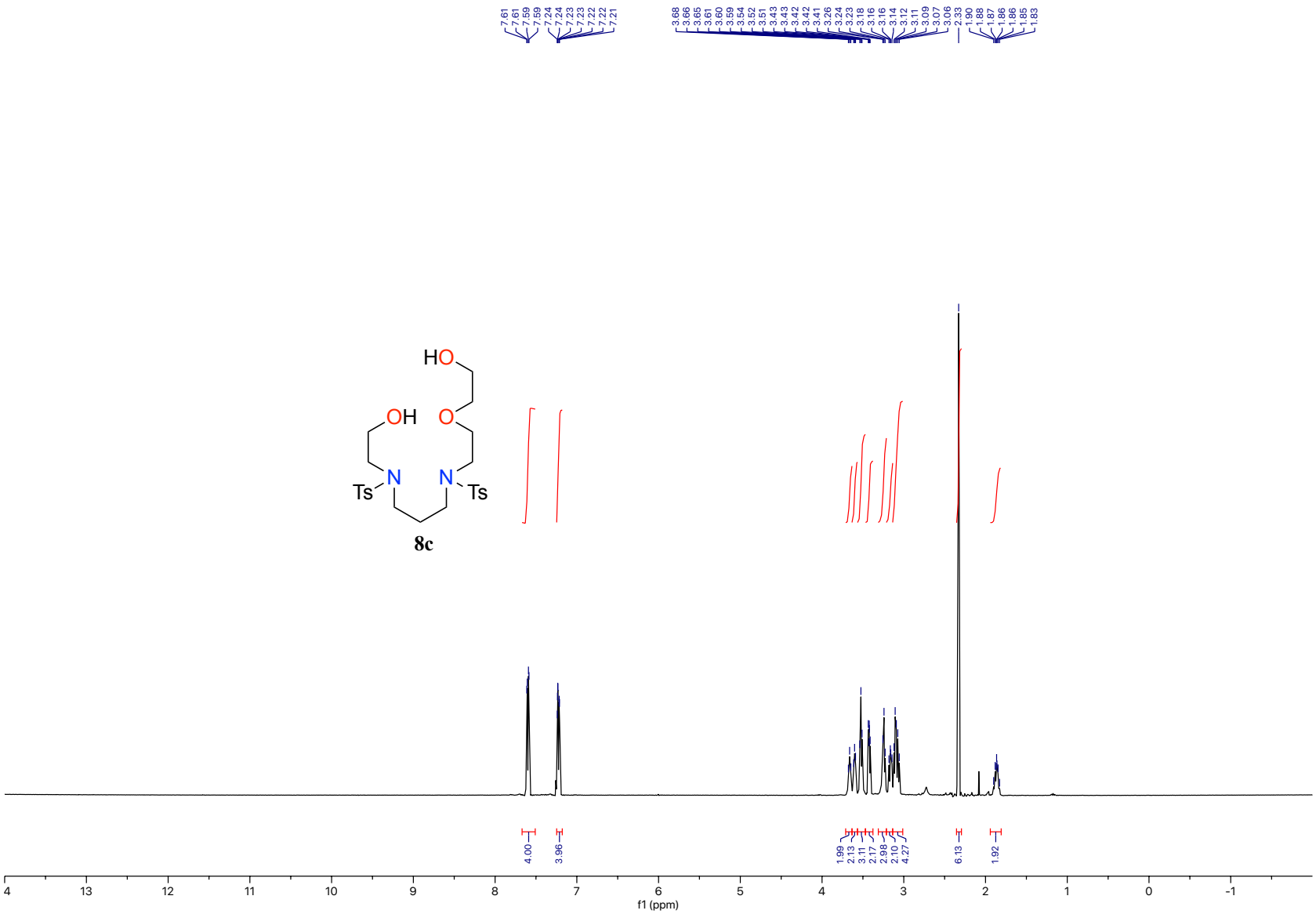
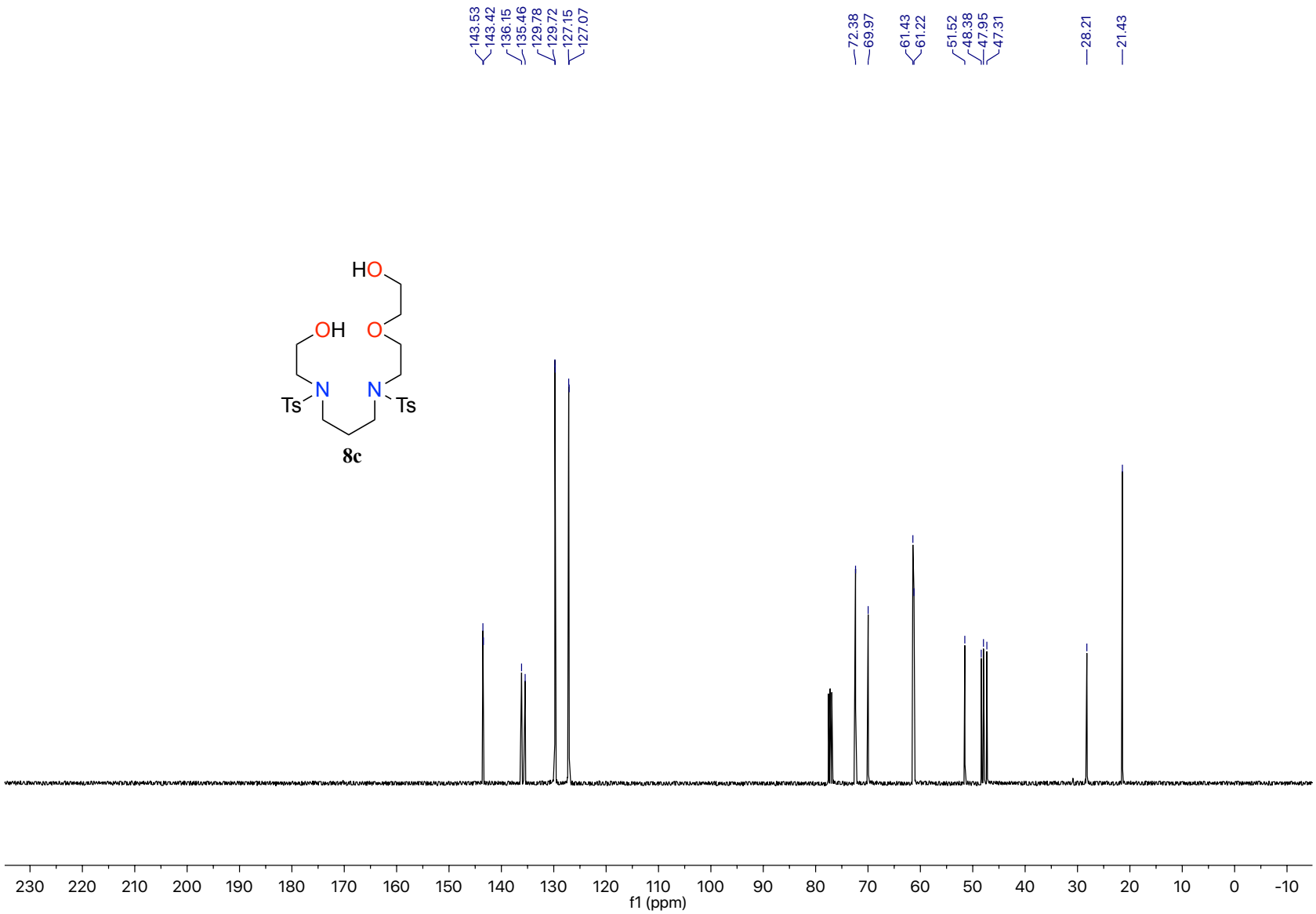
136.87
135.26
129.87
129.73
127.20
126.99
61.45
51.78
47.48
39.93
28.95
21.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
OH
O
N
N
Ts
Ts
8c
f1 (ppm)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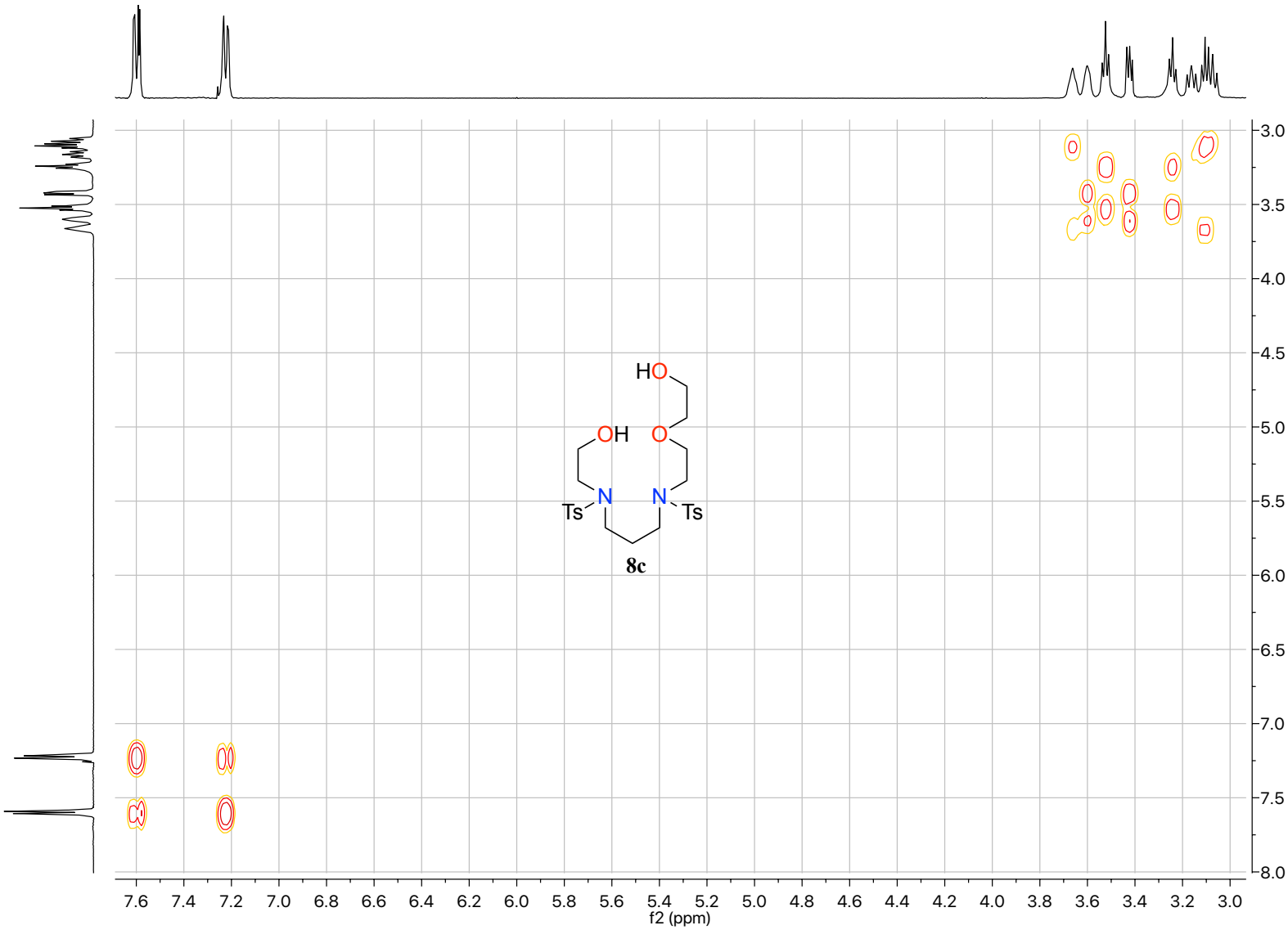
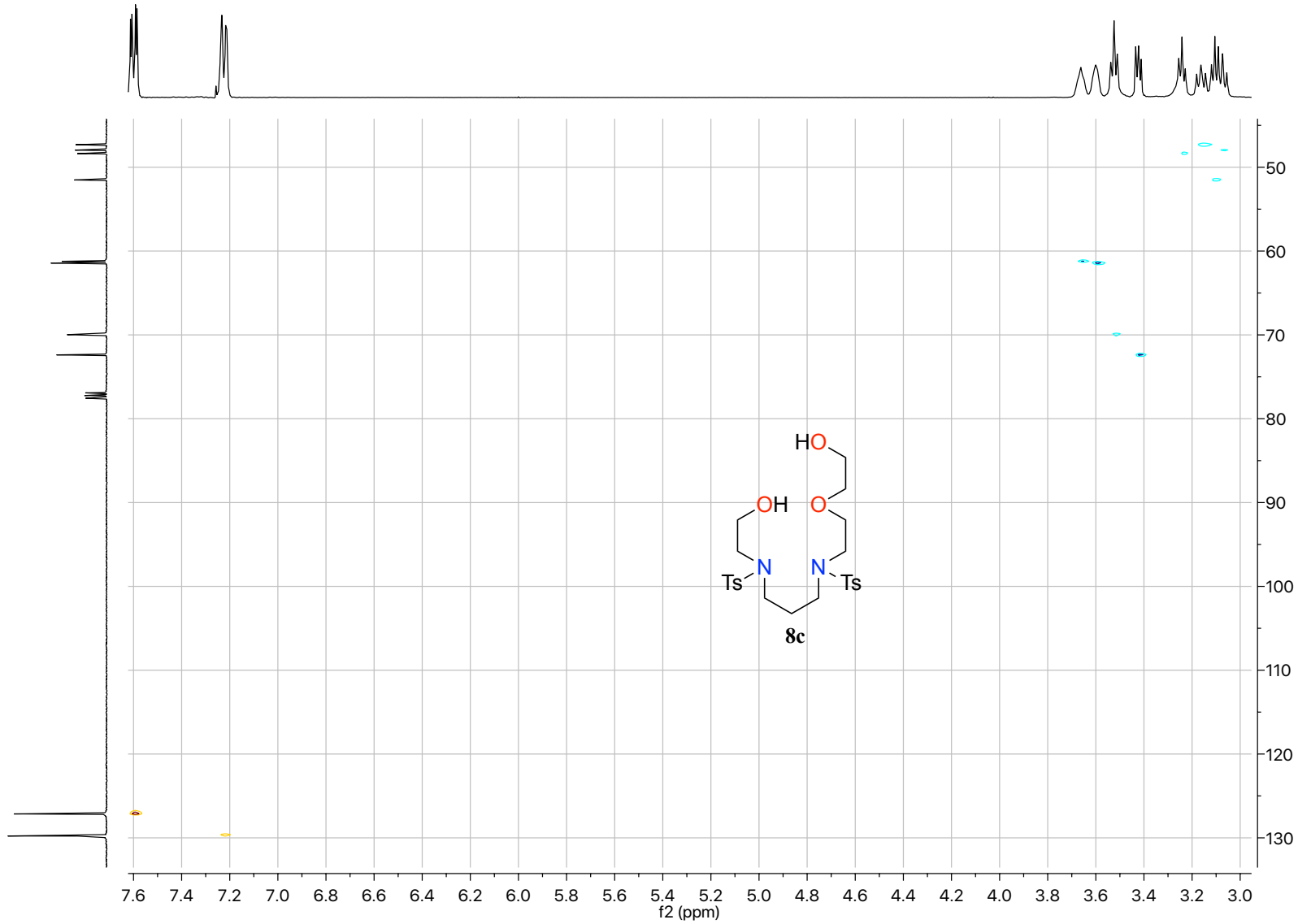
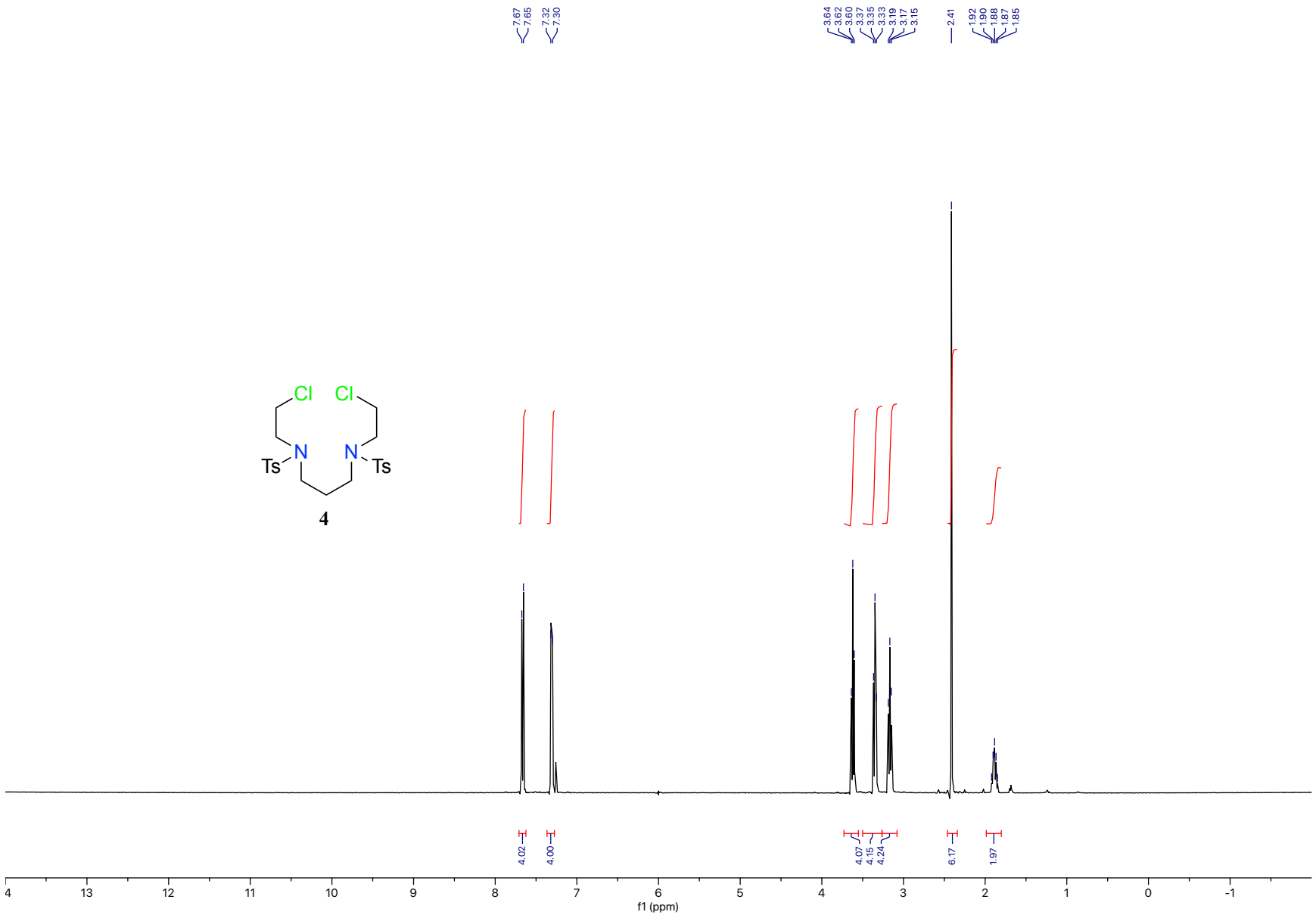
129.72
127.15
127.07
72.38
69.97
61.43
61.22
51.52
48.38
47.95
47.31
28.21
21.43
HO
OH
O
N
N
Ts
Ts
8c
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
OH
O
N
N
Ts
Ts
8c
f2 (ppm)


HO
OH
O
N
N
Ts
Ts
8c
f2 (ppm)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7.32
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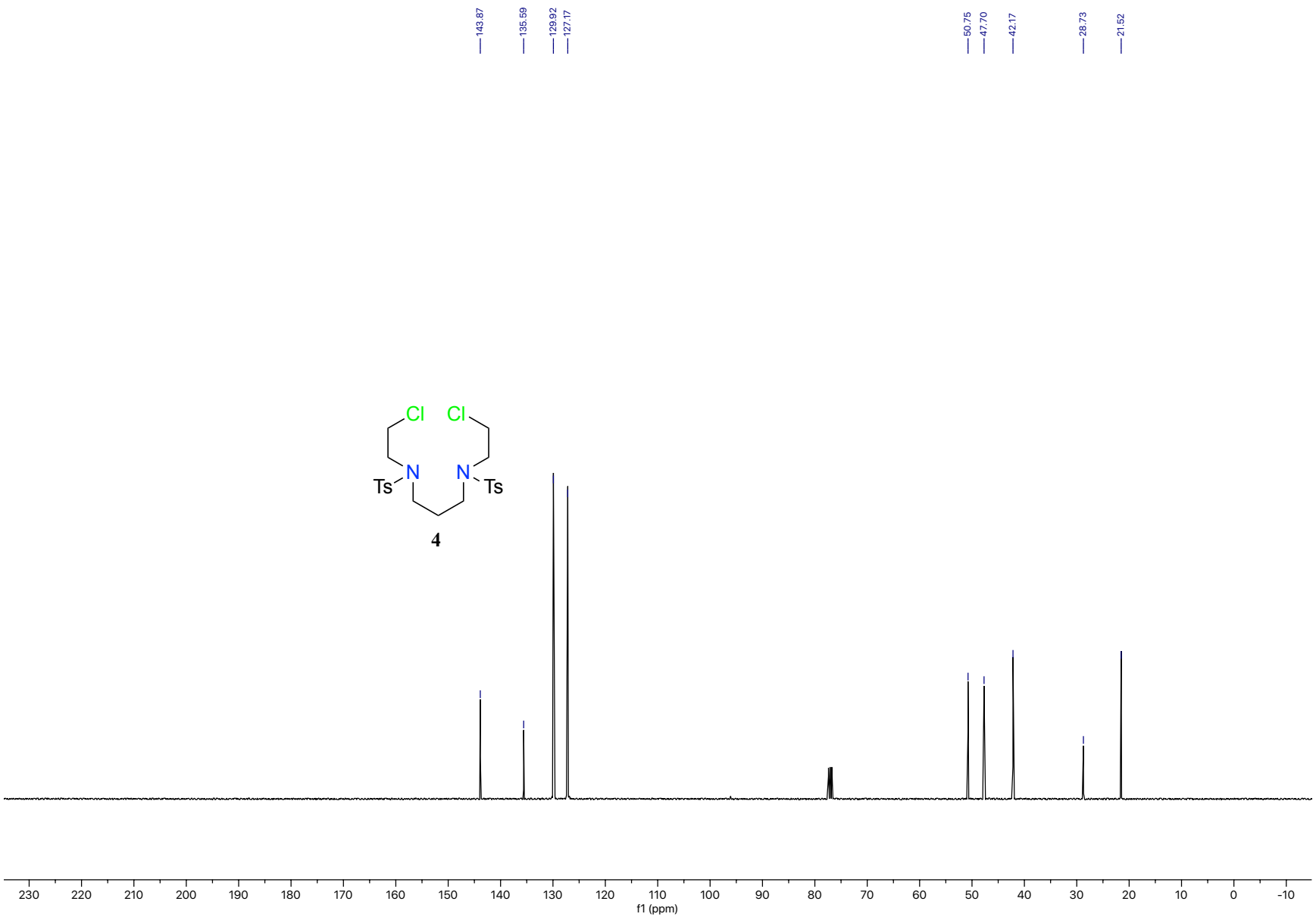
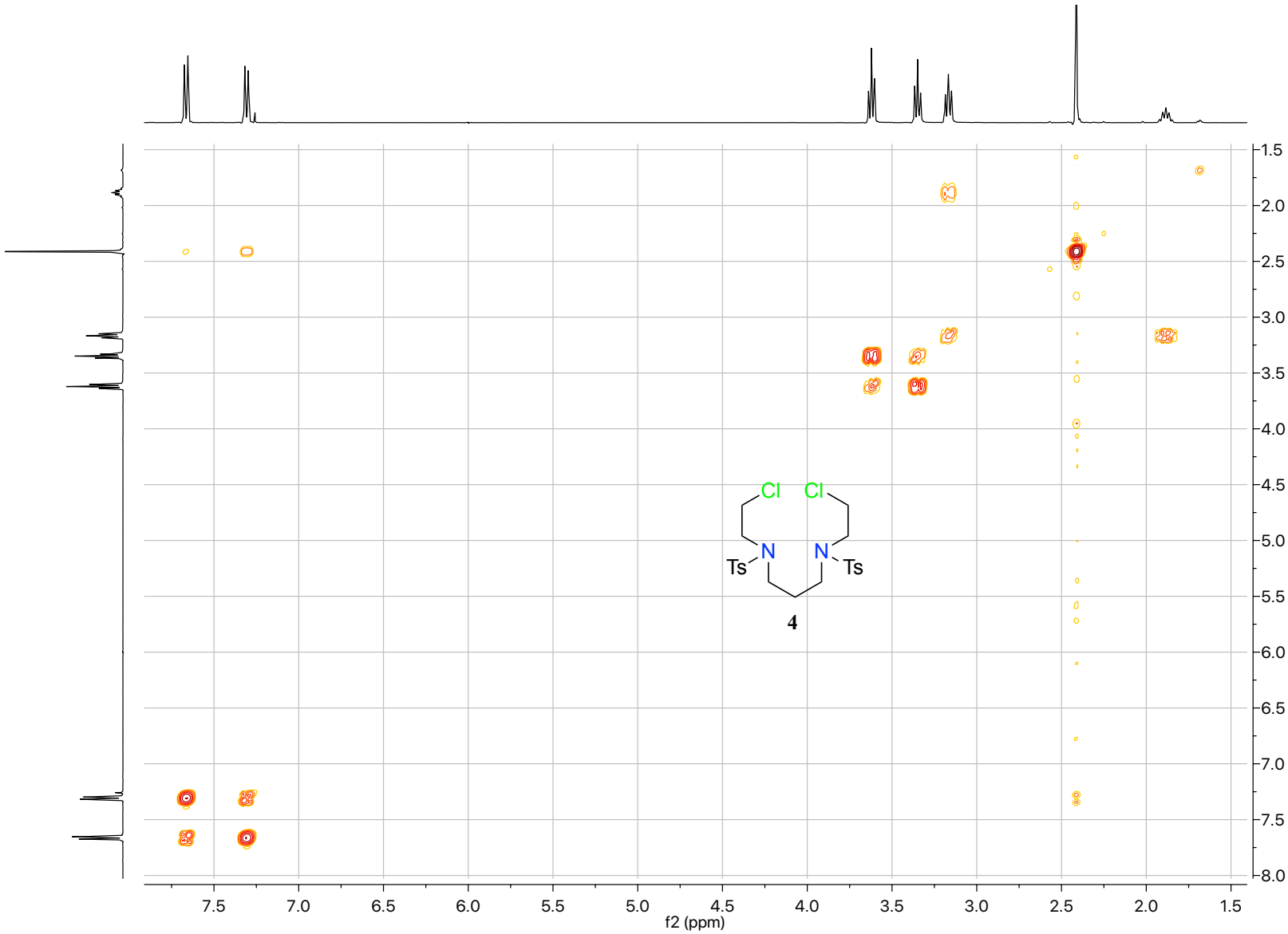
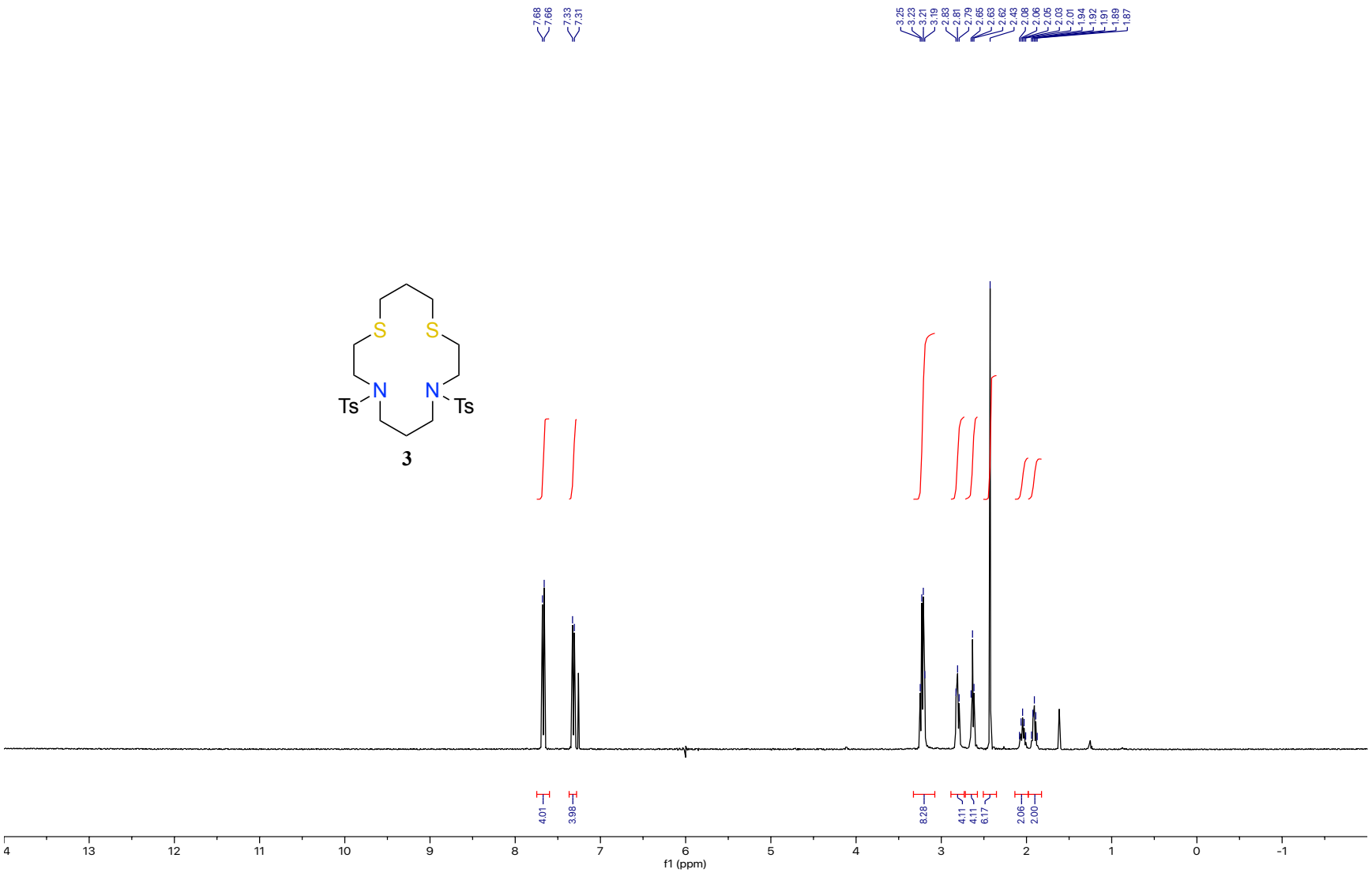
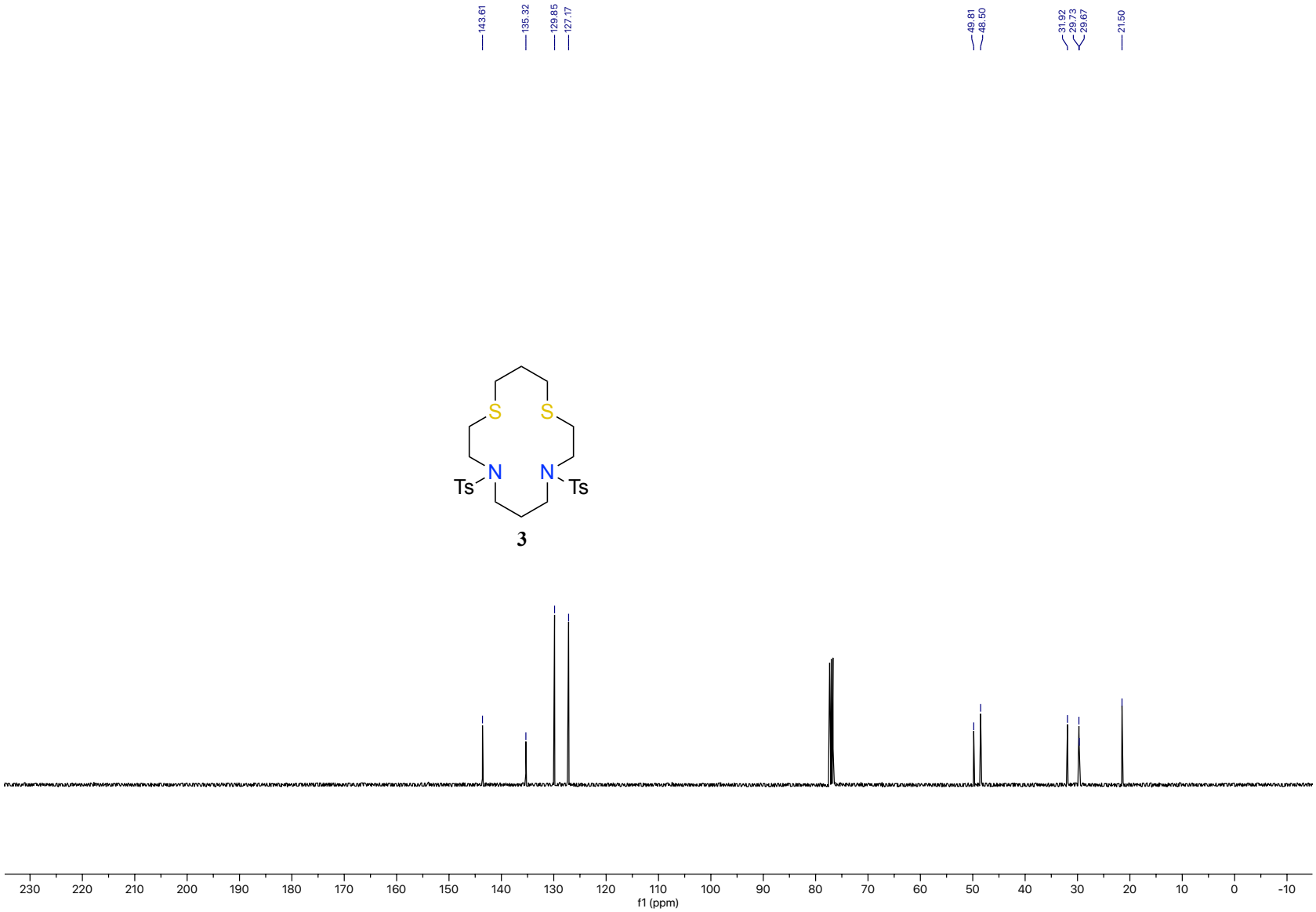
3.64
3.62
3.60
3.37
3.35
3.33
3.19
3.17
3.15
2.41
1.92
1.90
1.88
1.87
1.85
Cl
Cl
N
N
Ts
Ts
4
4.02
4.00
4.07
4.15
4.24
6.17
1.97
f1 (ppm)


143.87
135.59
129.92
127.17
50.75
47.70
42.17
28.73
21.52
Cl
Cl
N
N
Ts
Ts
4
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
Cl
N
N
Ts
Ts
4
f2 (ppm)



NMR provided was obtained from method B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127.17
49.81
48.50
31.92
29.73
29.67
21.50
S
S
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Ts
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200
190
180
170
160
150
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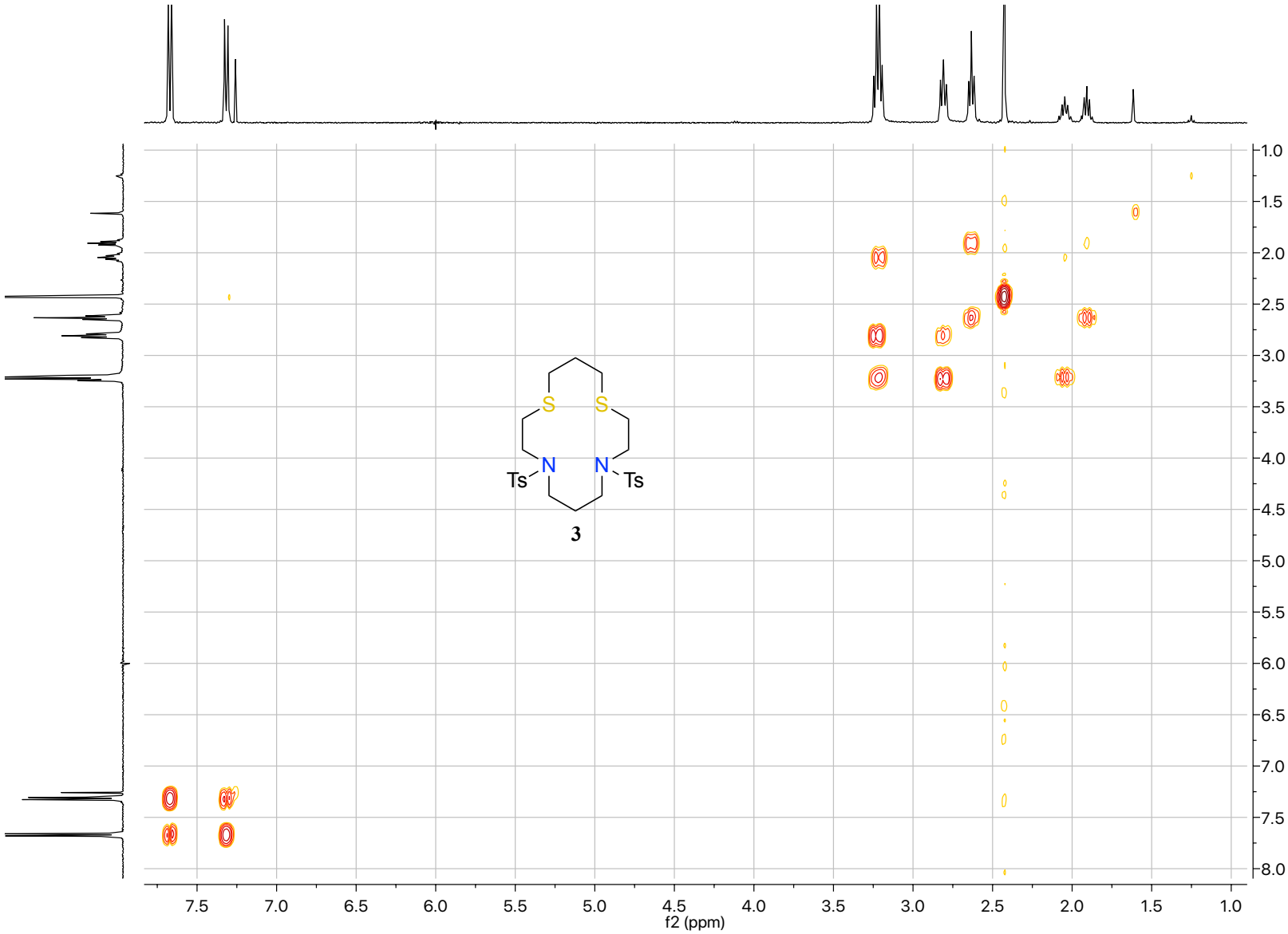
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
N
N
Ts
Ts
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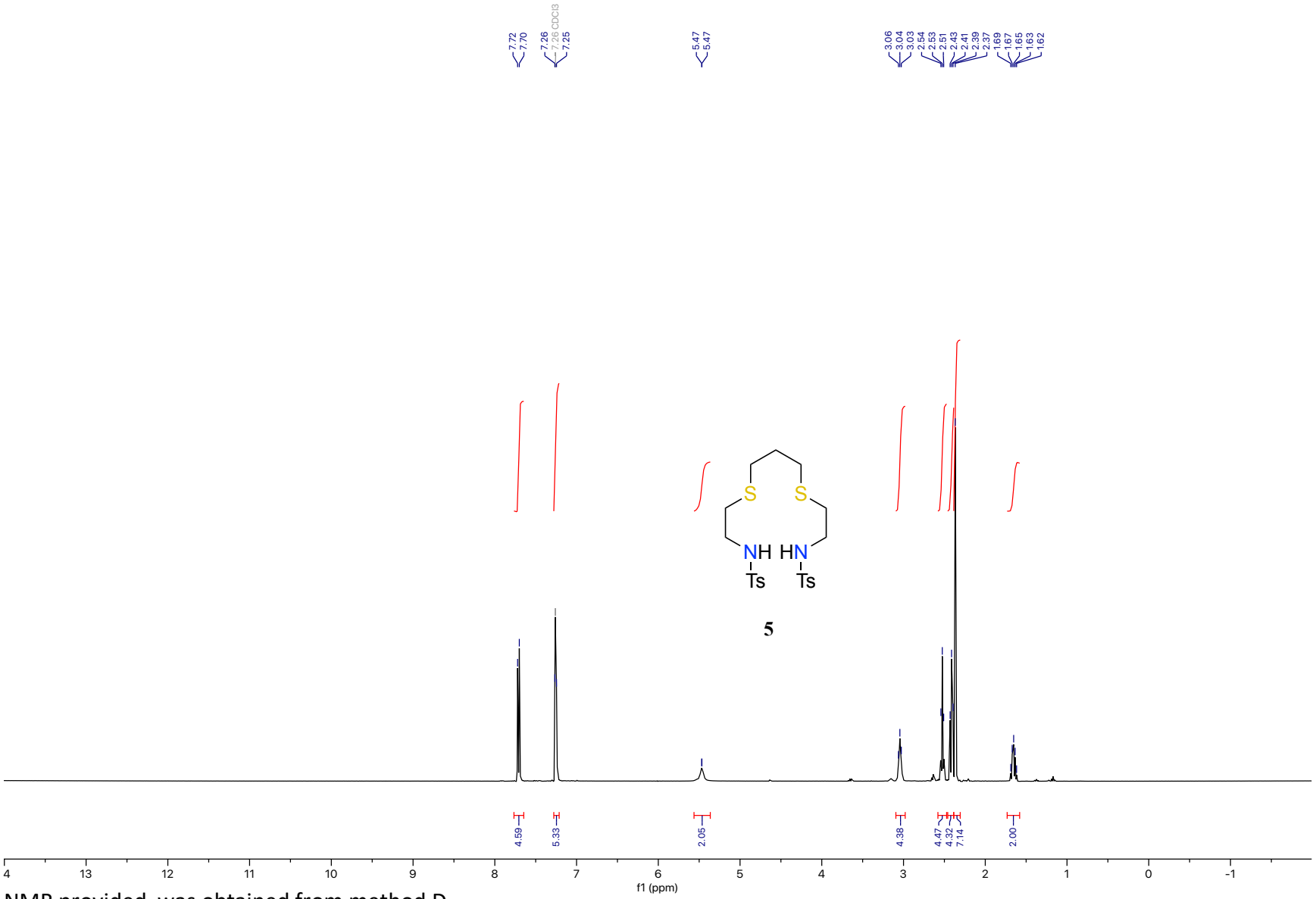
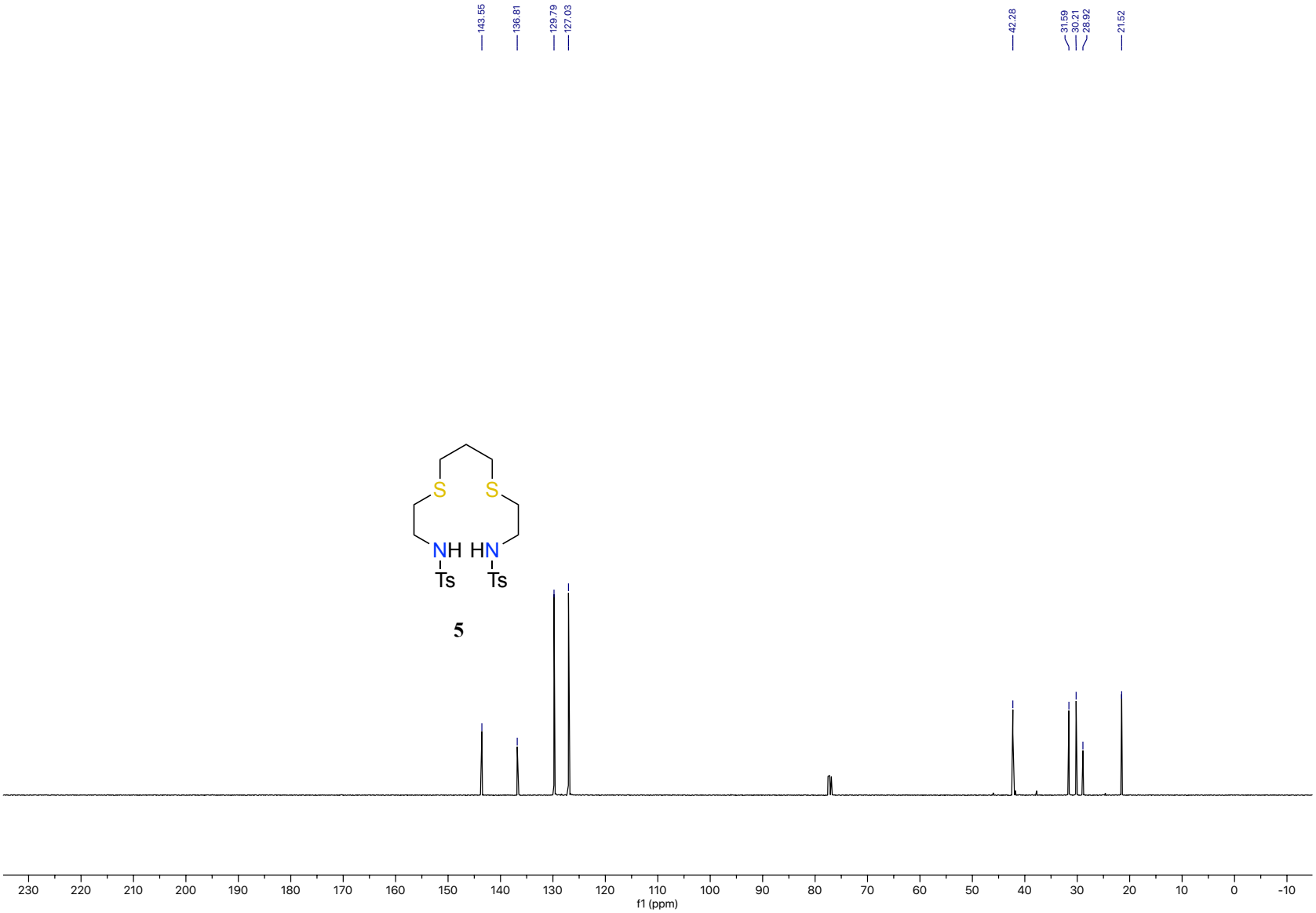
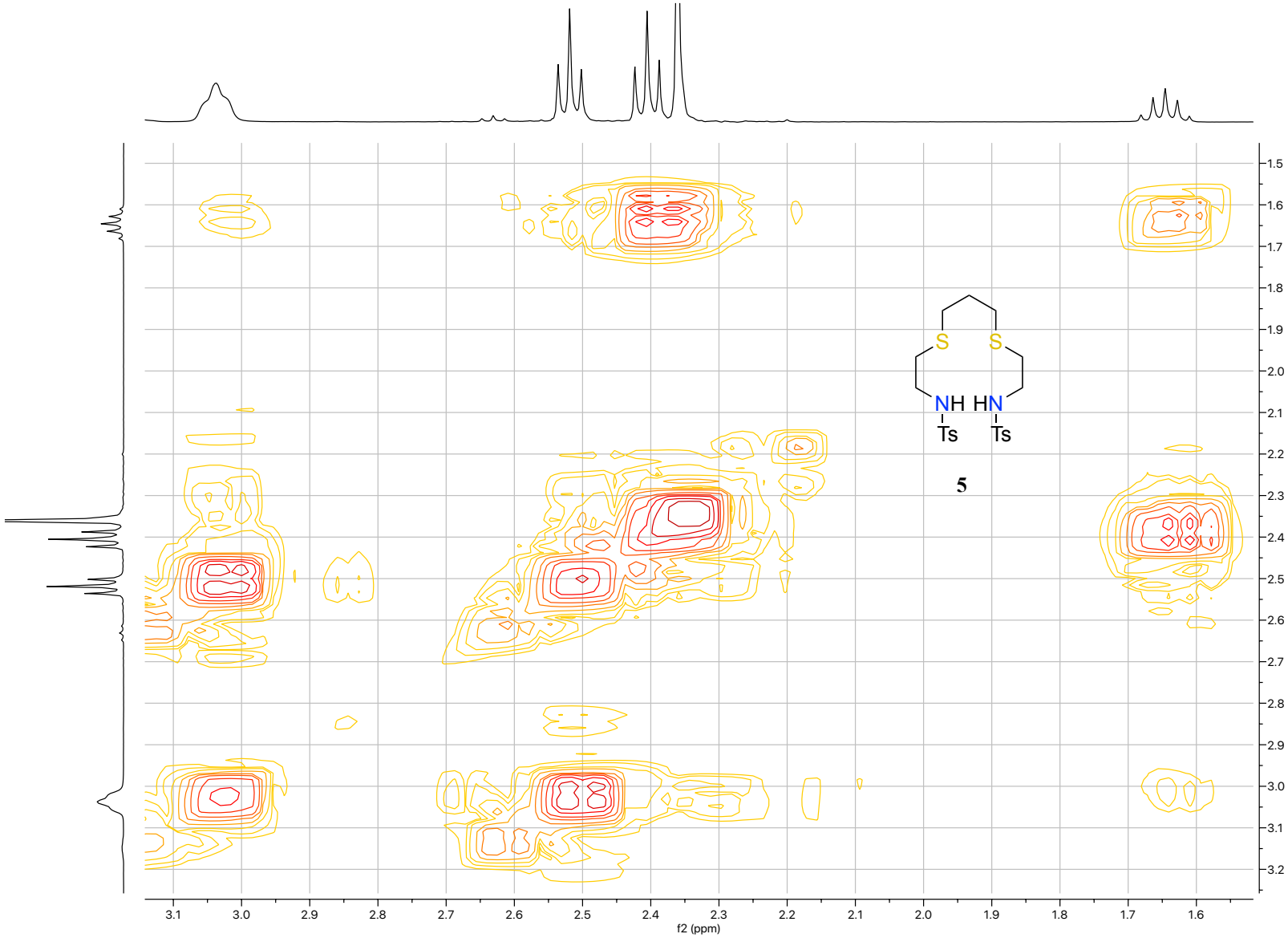
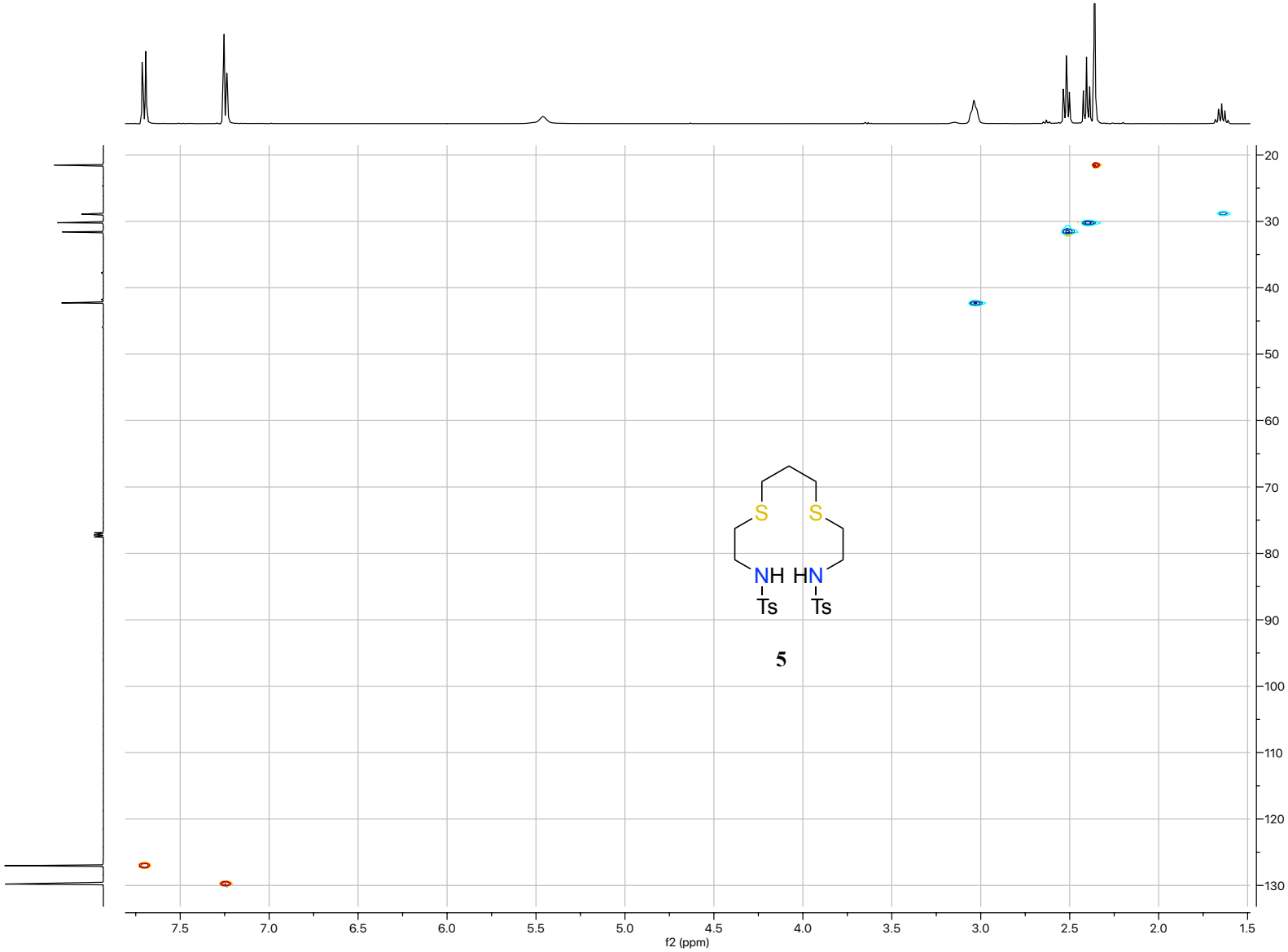
f2 (ppm)



NMR provided was obtained from method D


143.55
136.81
129.79
127.03
42.28
31.59
30.21
28.92
21.52
S
S
NH
HN
Ts
Ts
5
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
NH
HN
Ts
Ts
5
f2 (ppm)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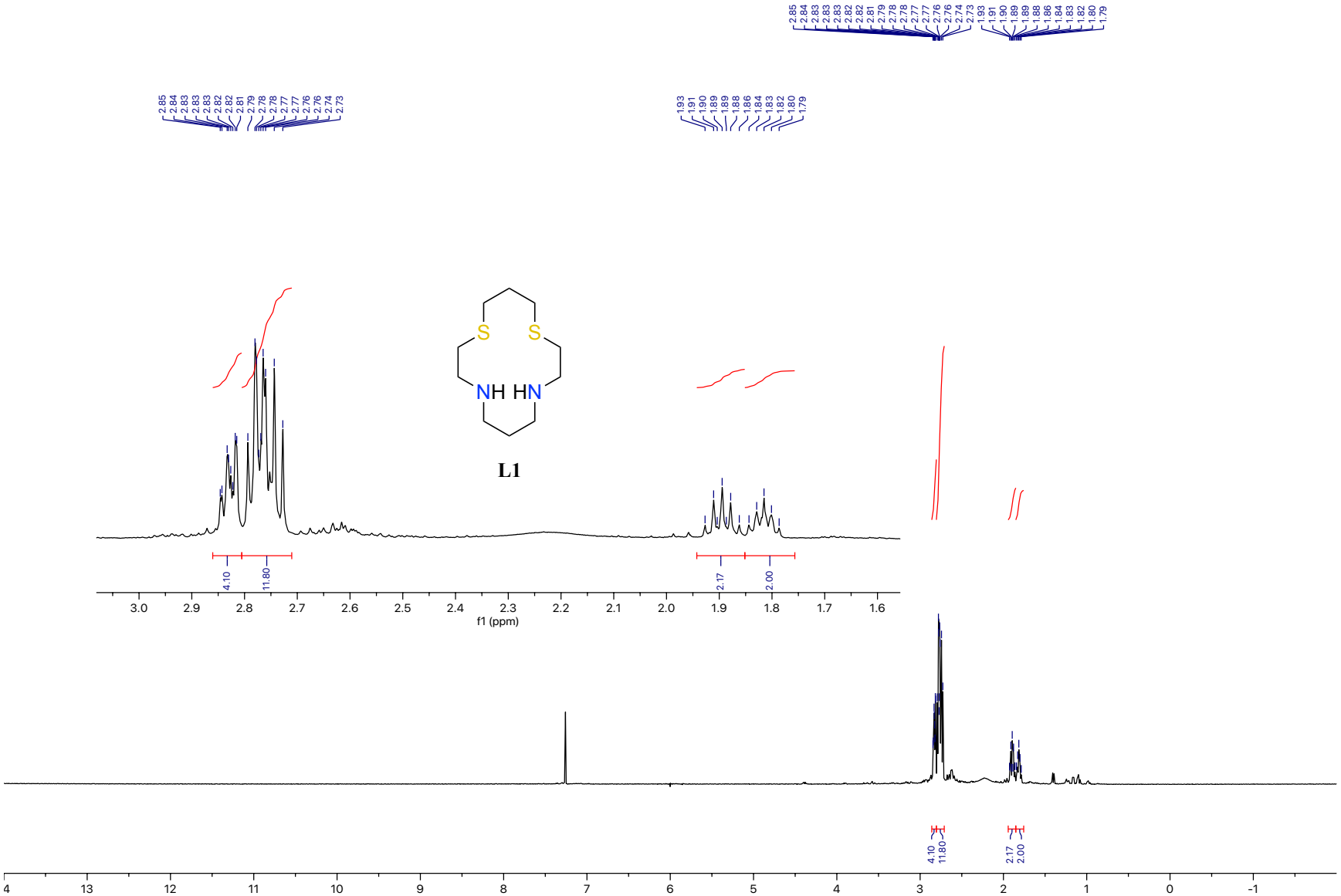
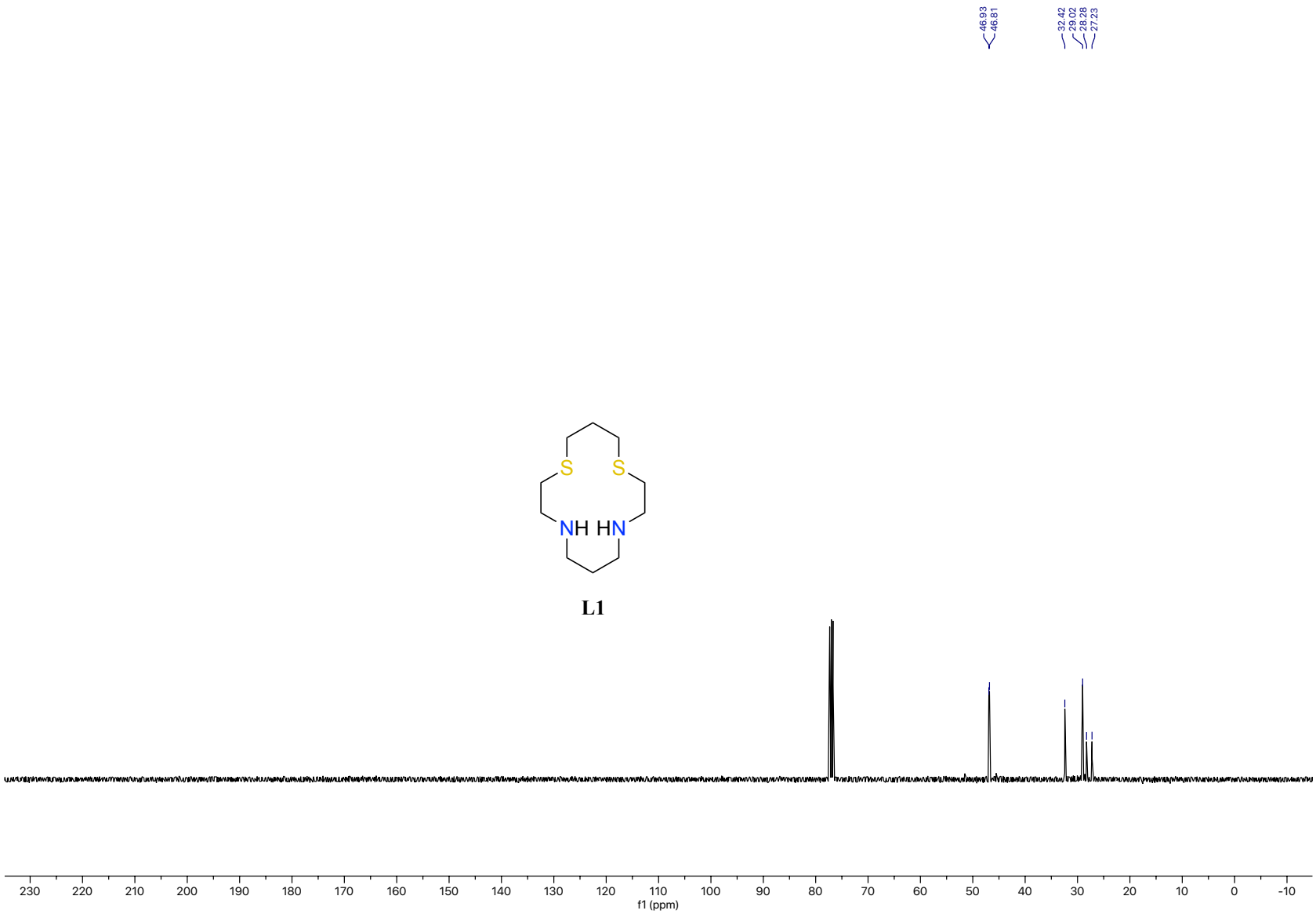
S
NH
HN
Ts
Ts
5
f2 (ppm)

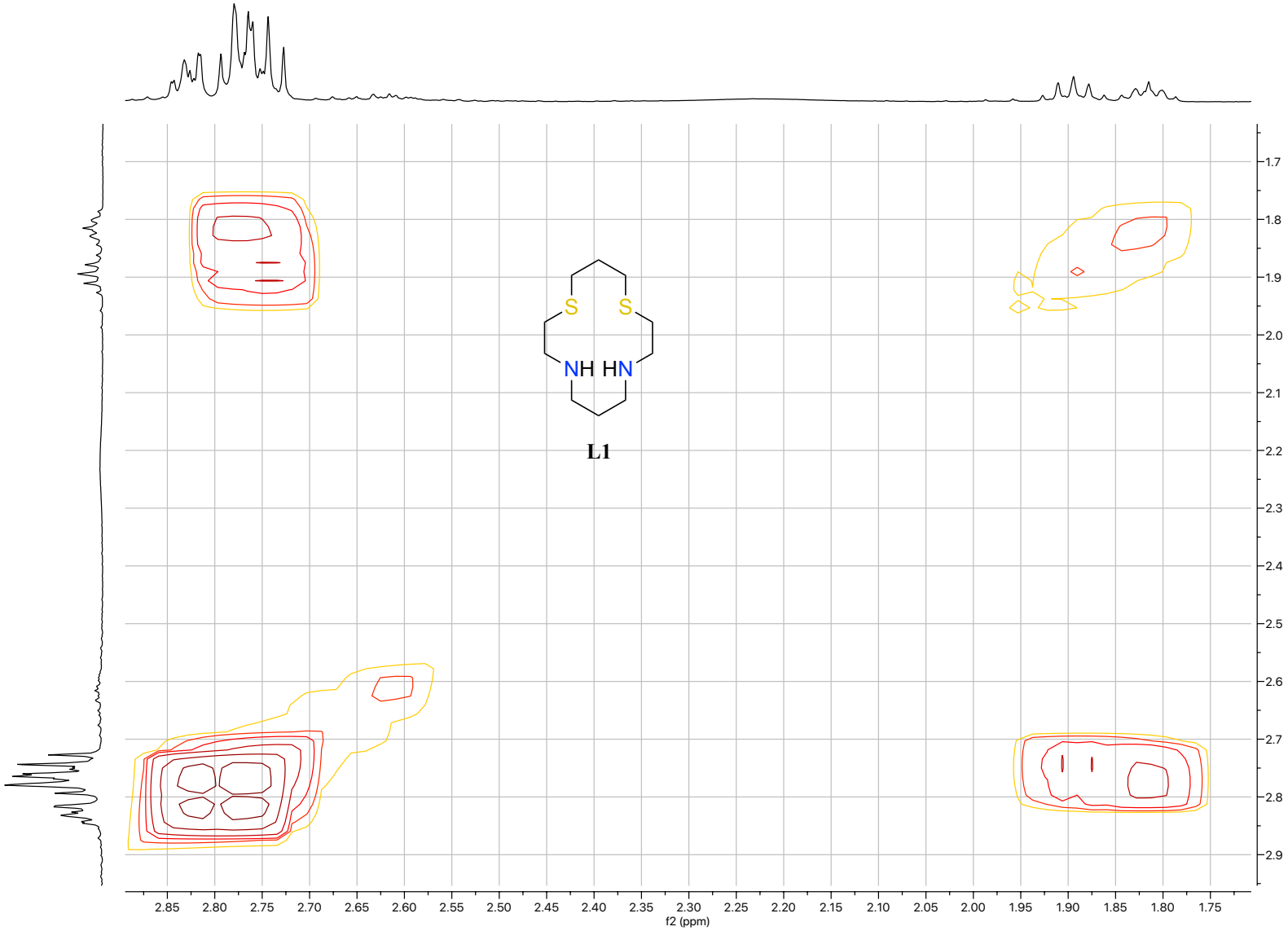


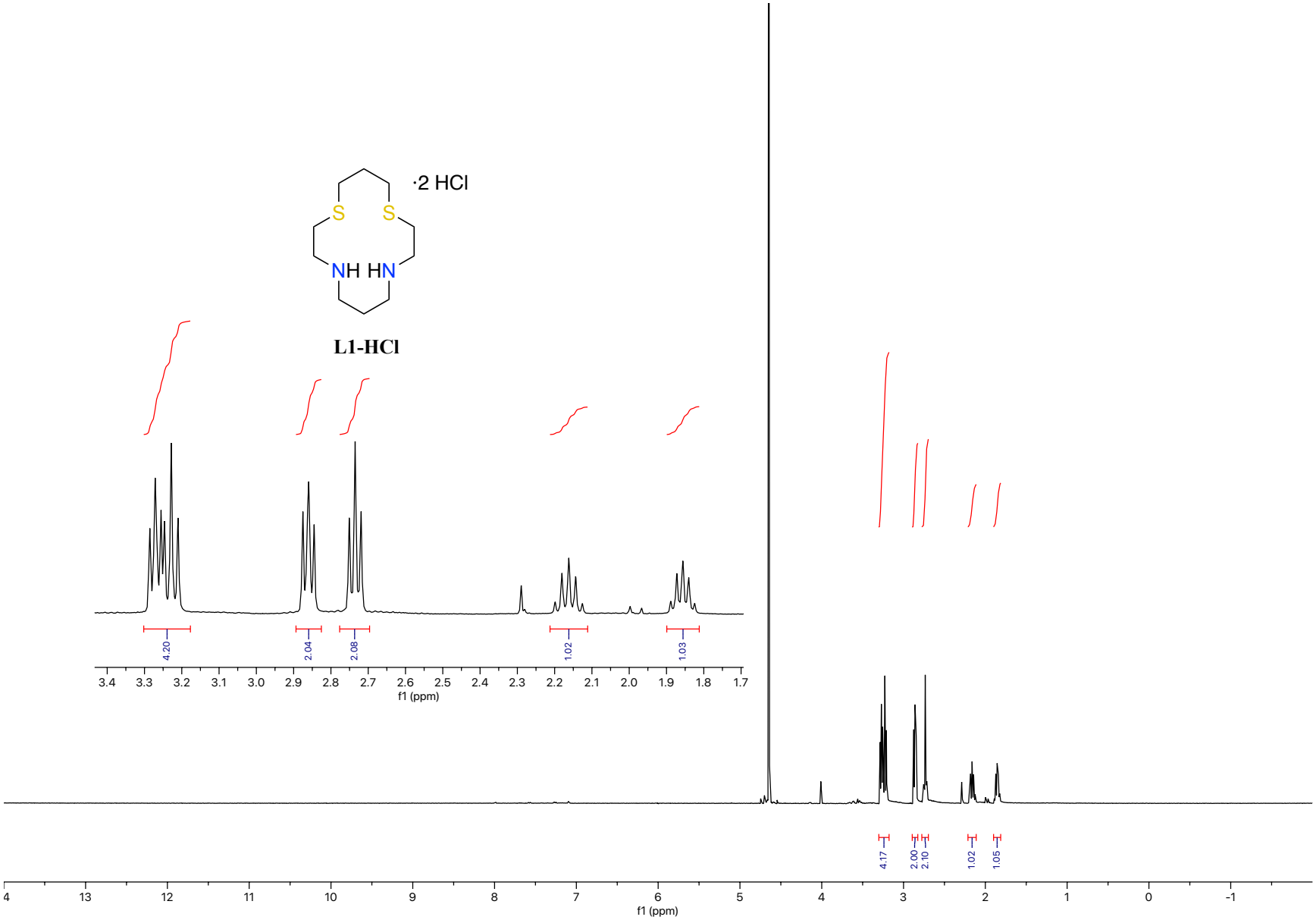
NMR spectroscopy clarified the presence of impurities from the resin on DOWEX 50WX12 column after preconditioning the column with MeOH and 1M HCl.

S
S
NH HN

L1

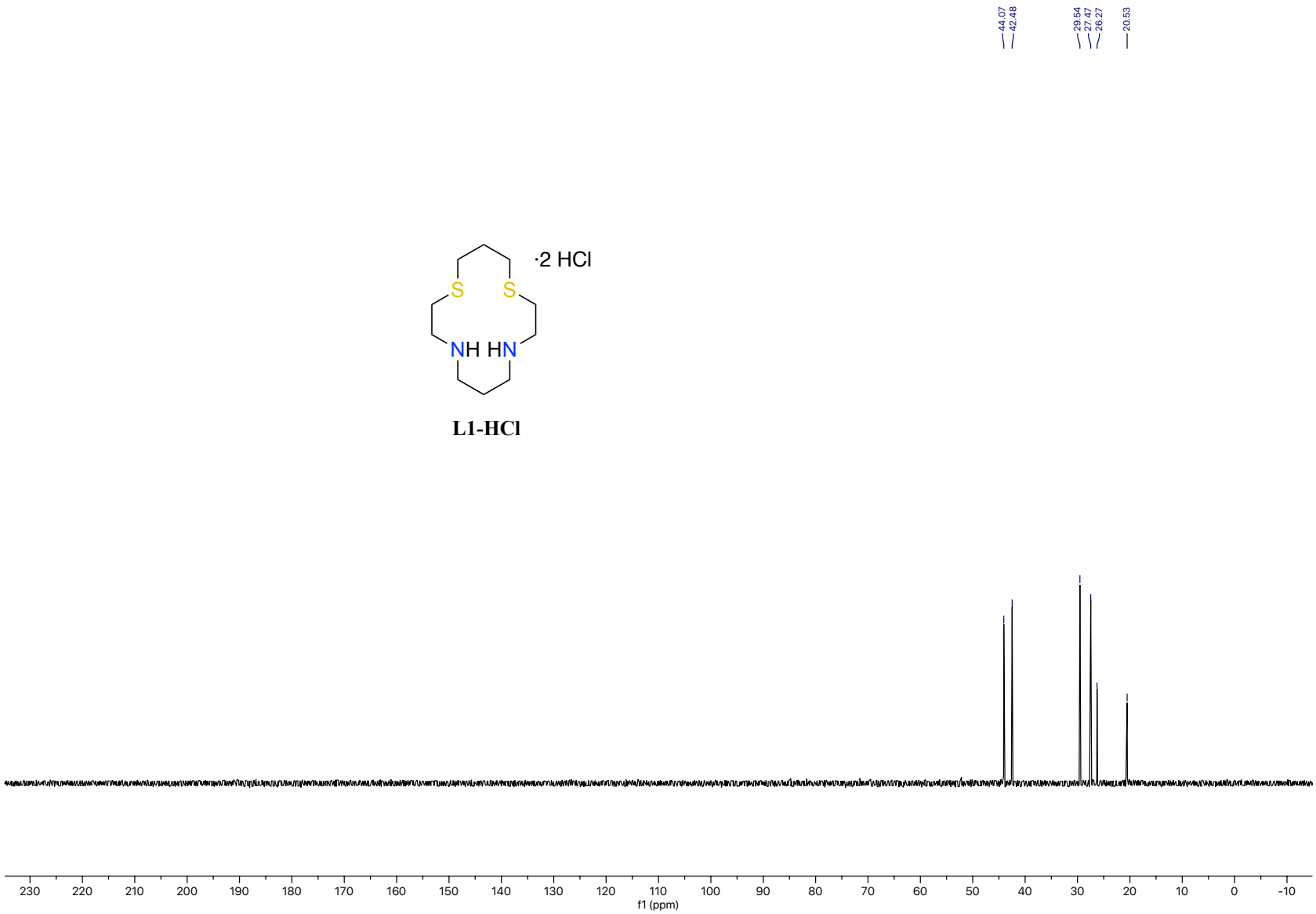

46.93
46.81
32.42
29.02
28.28
27.23
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

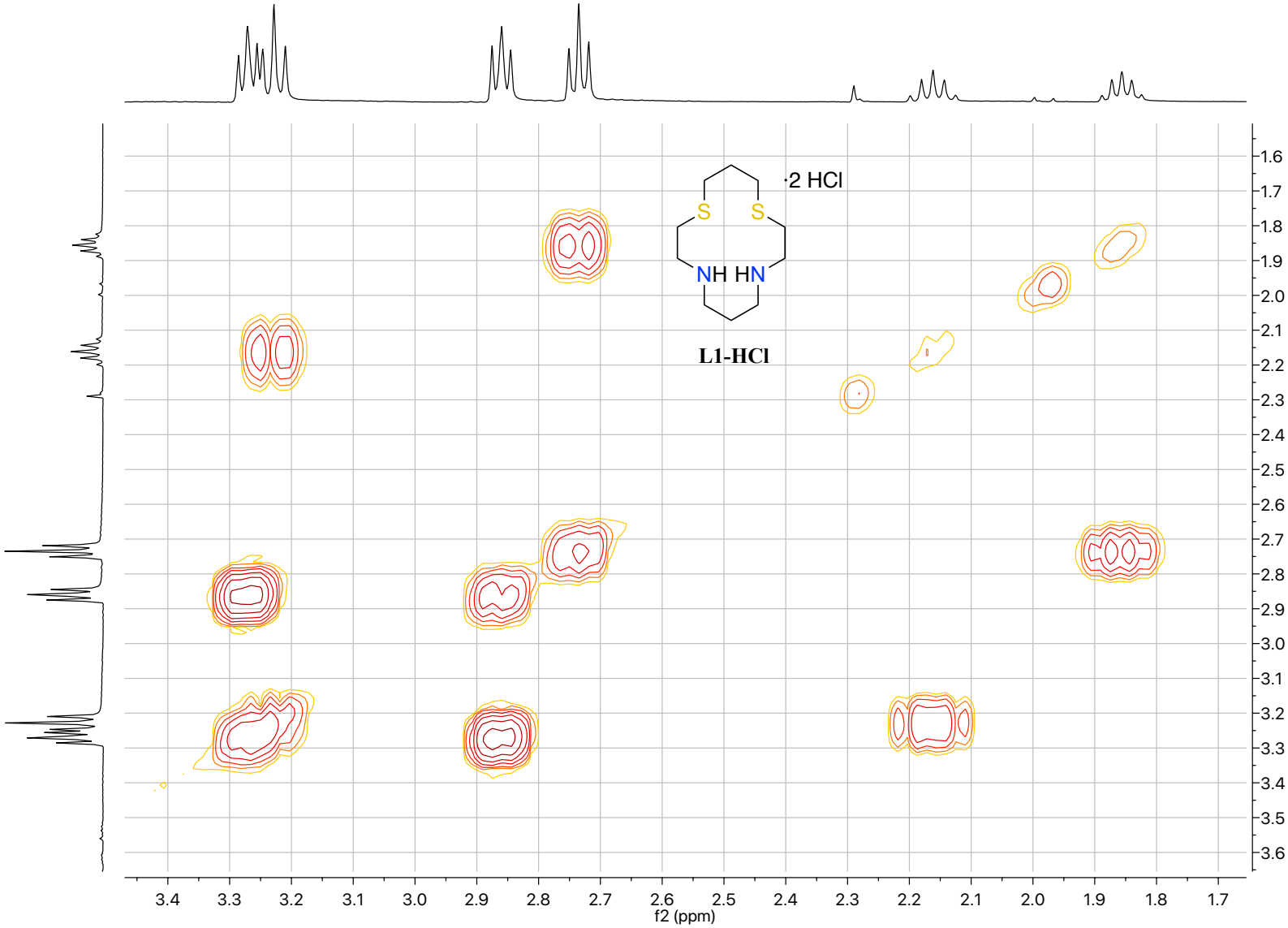

S
S
NH HN
L1
f2 (ppm)

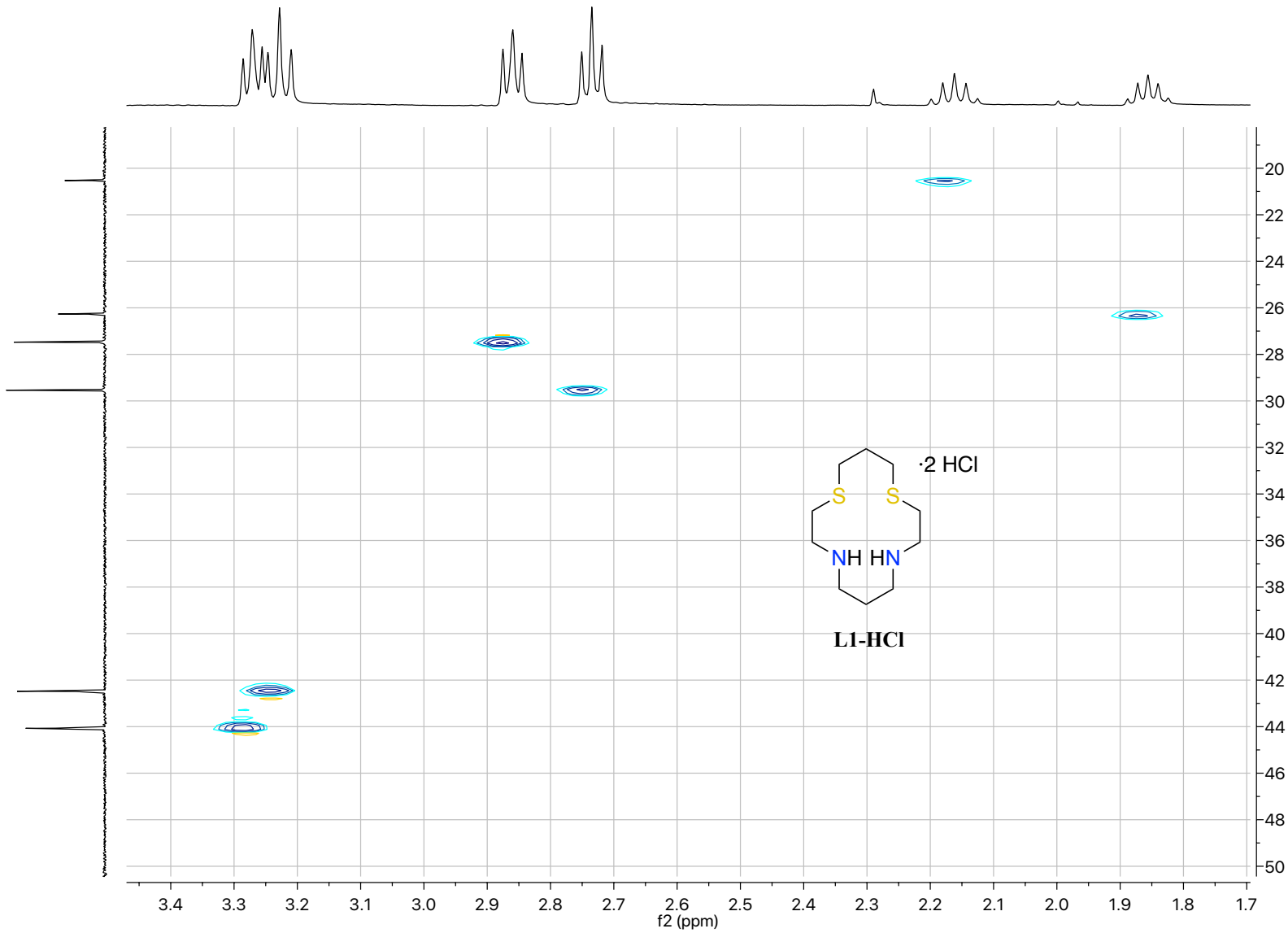

·2 HCl
S
S
NH HN
L1-HCl
4.20
2.04
2.08
1.02
1.03
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)
4.17
2.00
2.10
1.02
1.05
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

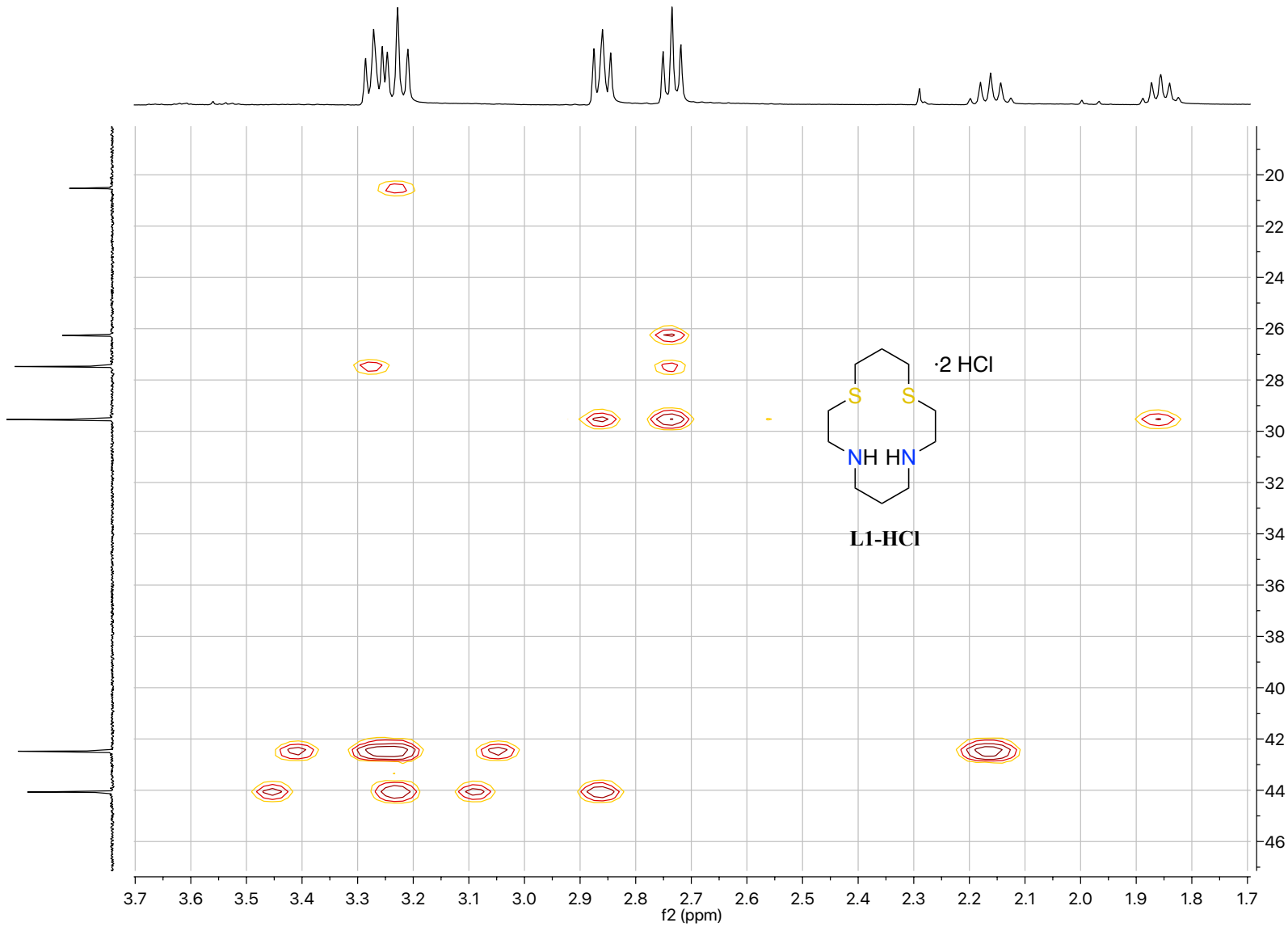
·2 HCl
S
S
NH HN

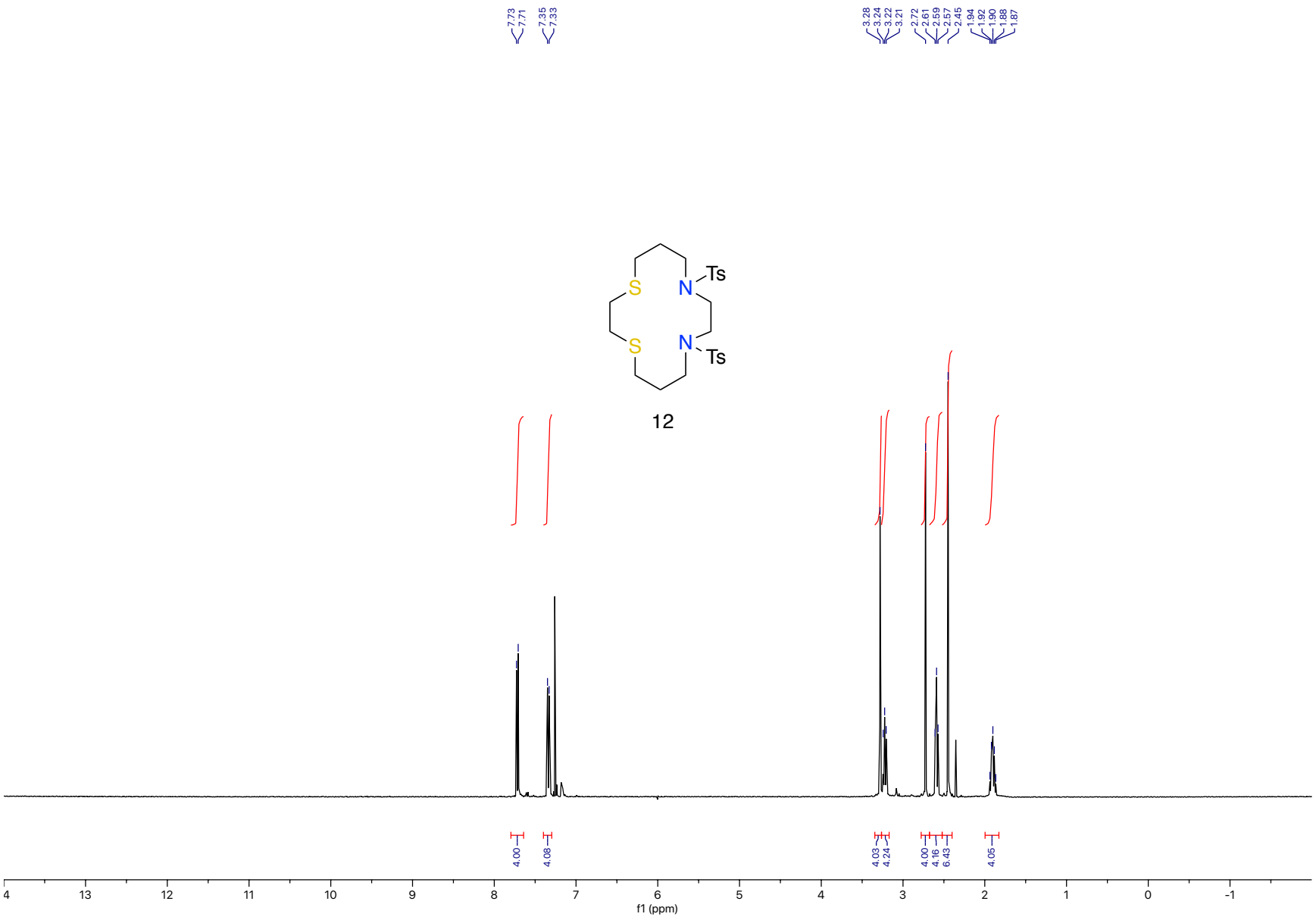
L1-HCl

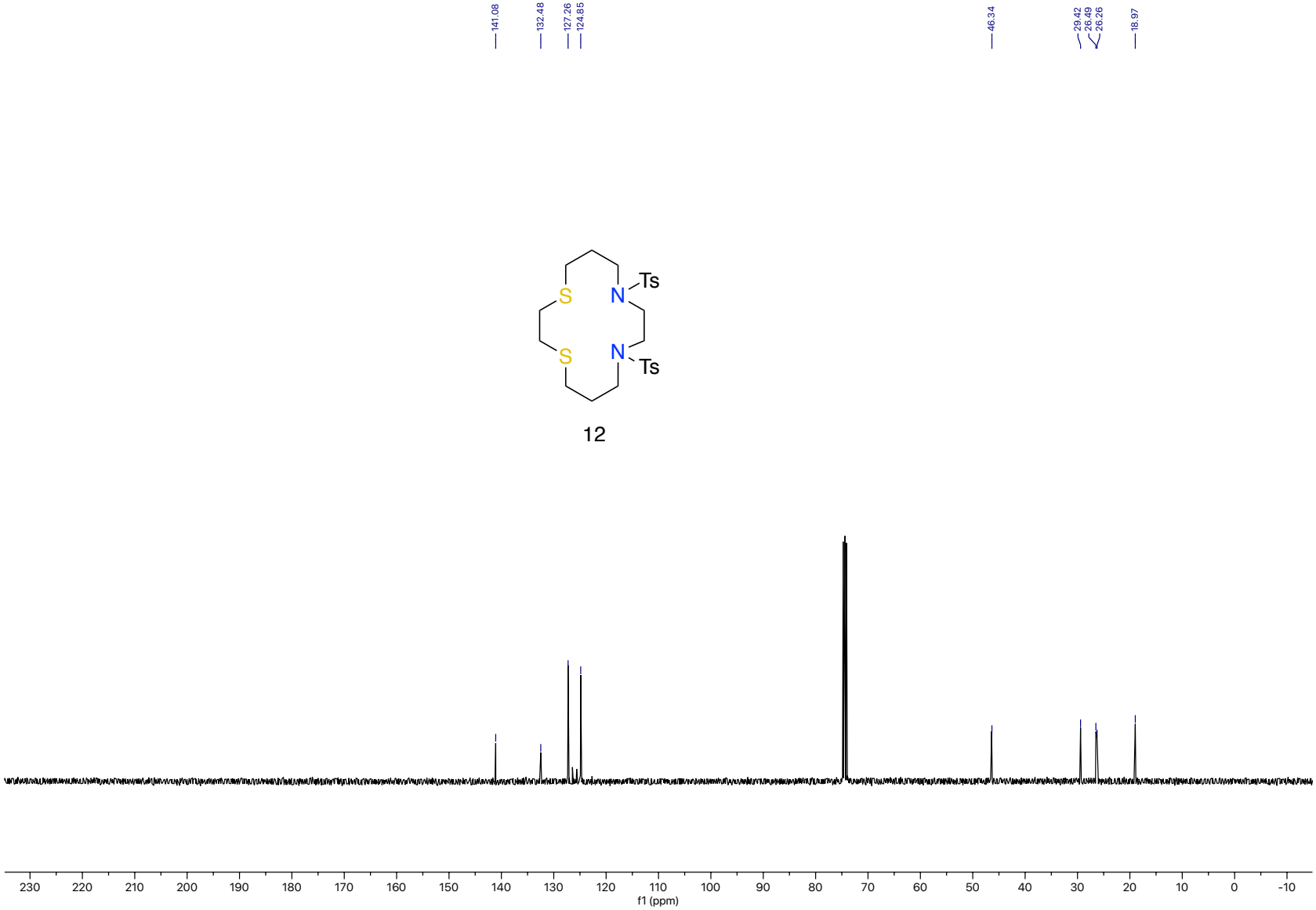

44.07
42.48
29.54
27.47
26.27
20.53
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

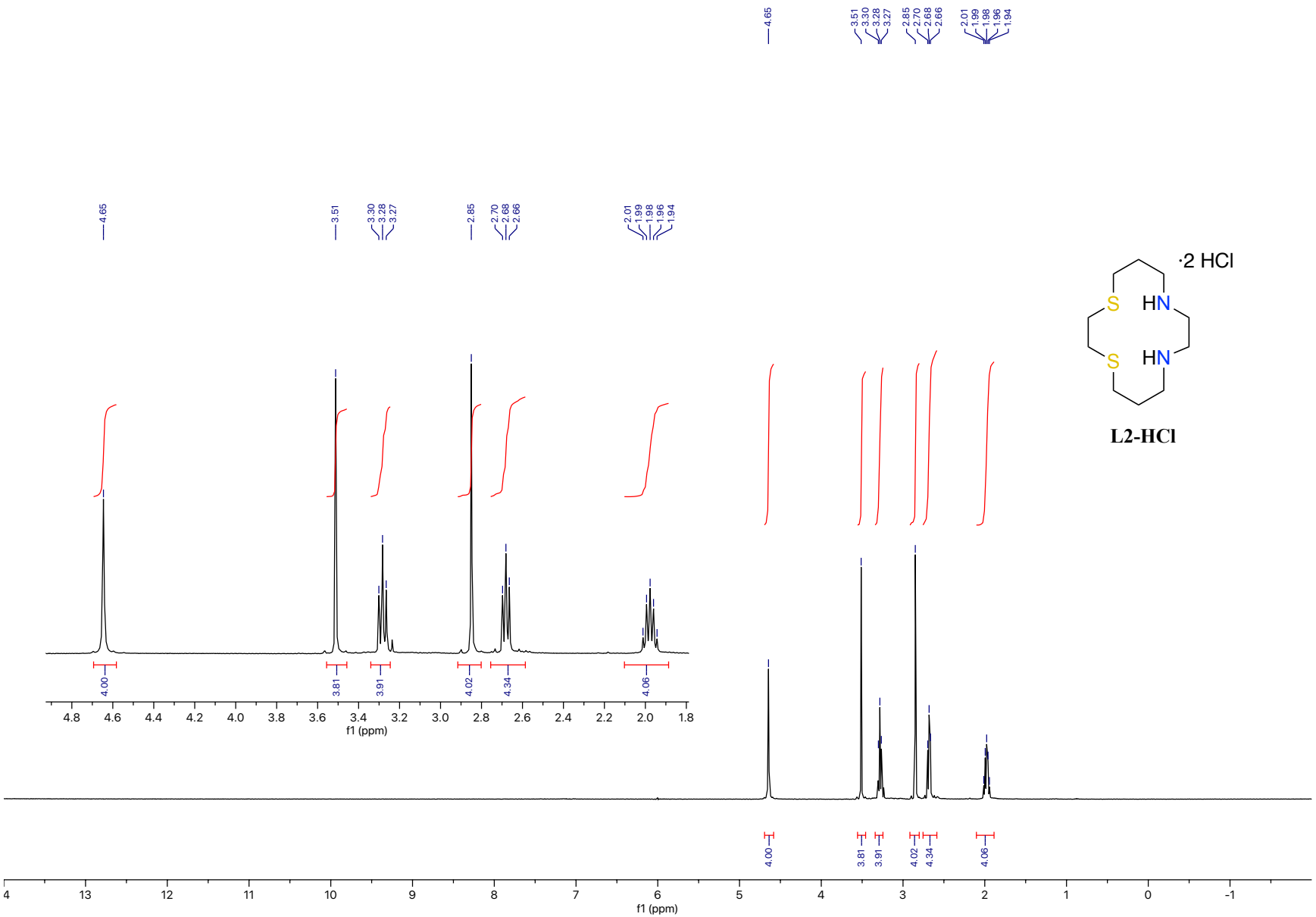

·2 HCl
S
S
NH HN
L1-HCl
f2 (ppm)


·2 HCl
S
S
NH HN
L1-HCl
f2 (ppm)


·2 HCl
S
S
NH HN
L1-HCl
f2 (ppm)

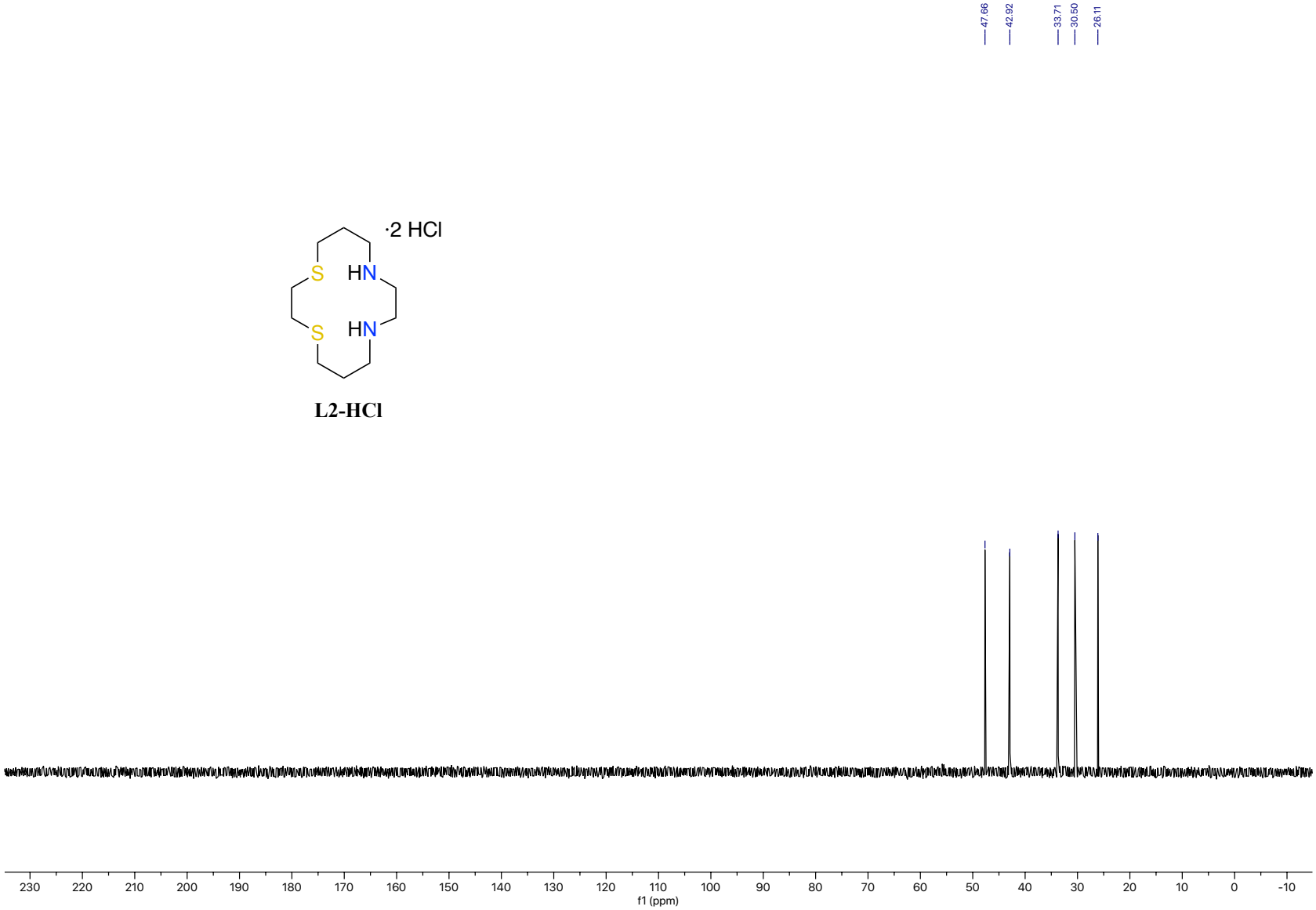

7.73
7.71
7.35
7.33
3.28
3.24
3.22
3.21
2.72
2.61
2.59
2.57
2.45
1.94
1.92
1.90
1.88
1.87
S
N
Ts
S
N
Ts
12
4.00
4.08
4.03
4.24
4.00
4.16
6.43
4.05
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

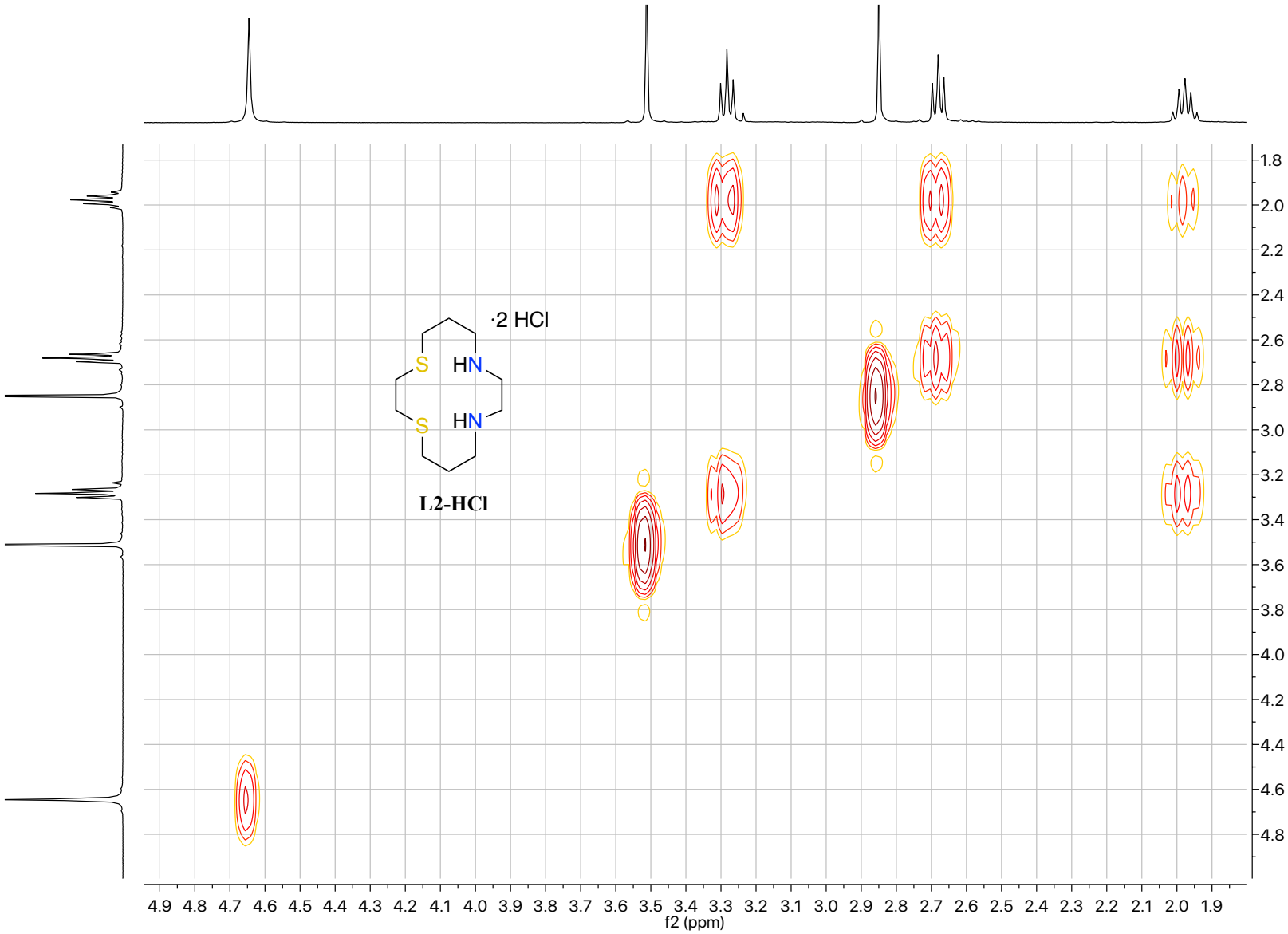

141.08
132.48
127.26
124.85
46.34
29.42
26.49
26.26
18.97
S
N
Ts
S
N
Ts
12
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

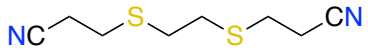

4.65
3.51
3.30
3.28
3.27
2.85
2.70
2.68
2.66
2.01
1.99
1.98
1.96
1.94
4.00
3.81
3.91
4.02
4.34
4.06
f1 (ppm)
·2 HCl
S
HN
S
HN
L2-HCl

·2 HCl
S
HN
S
HN

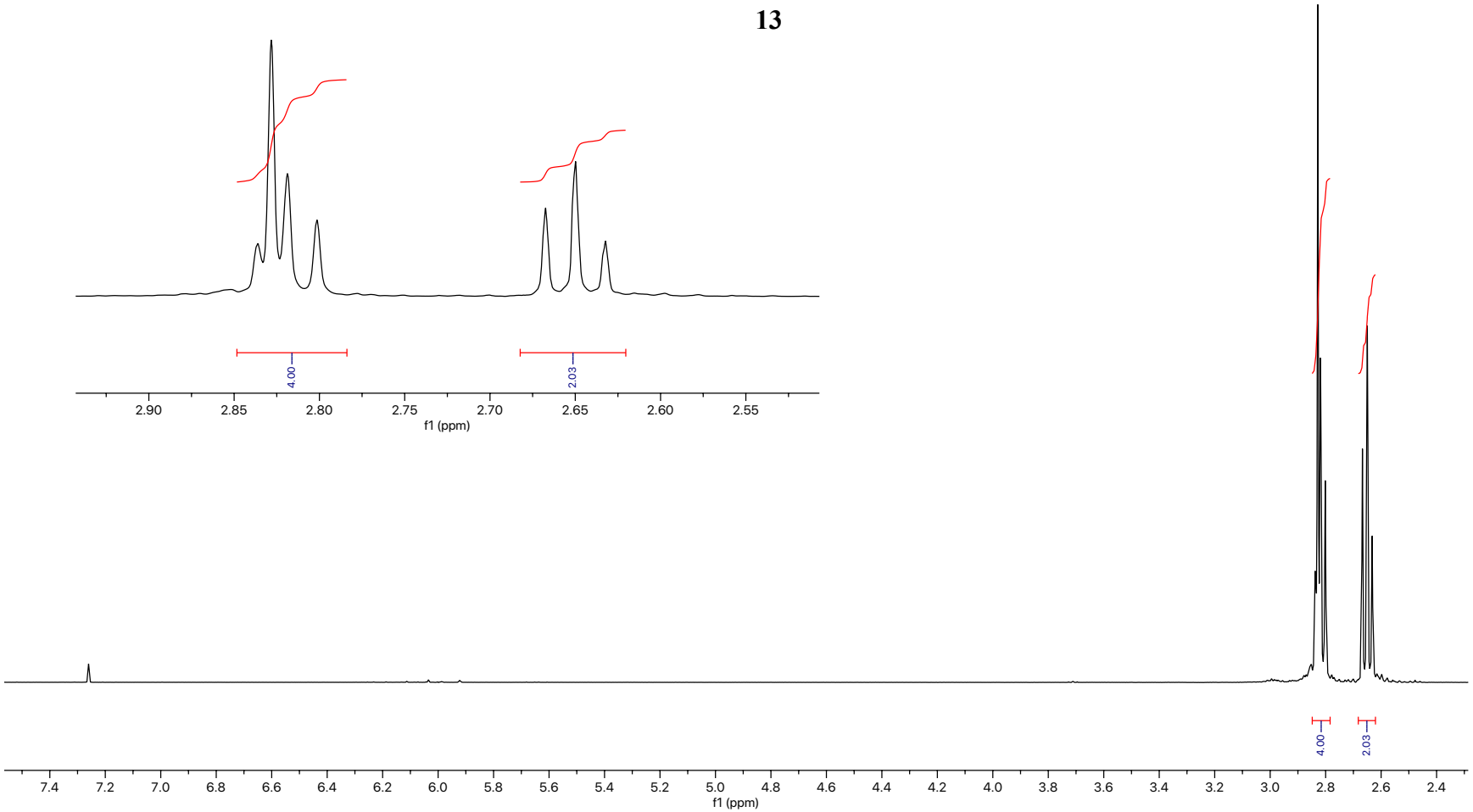
L2-HCl

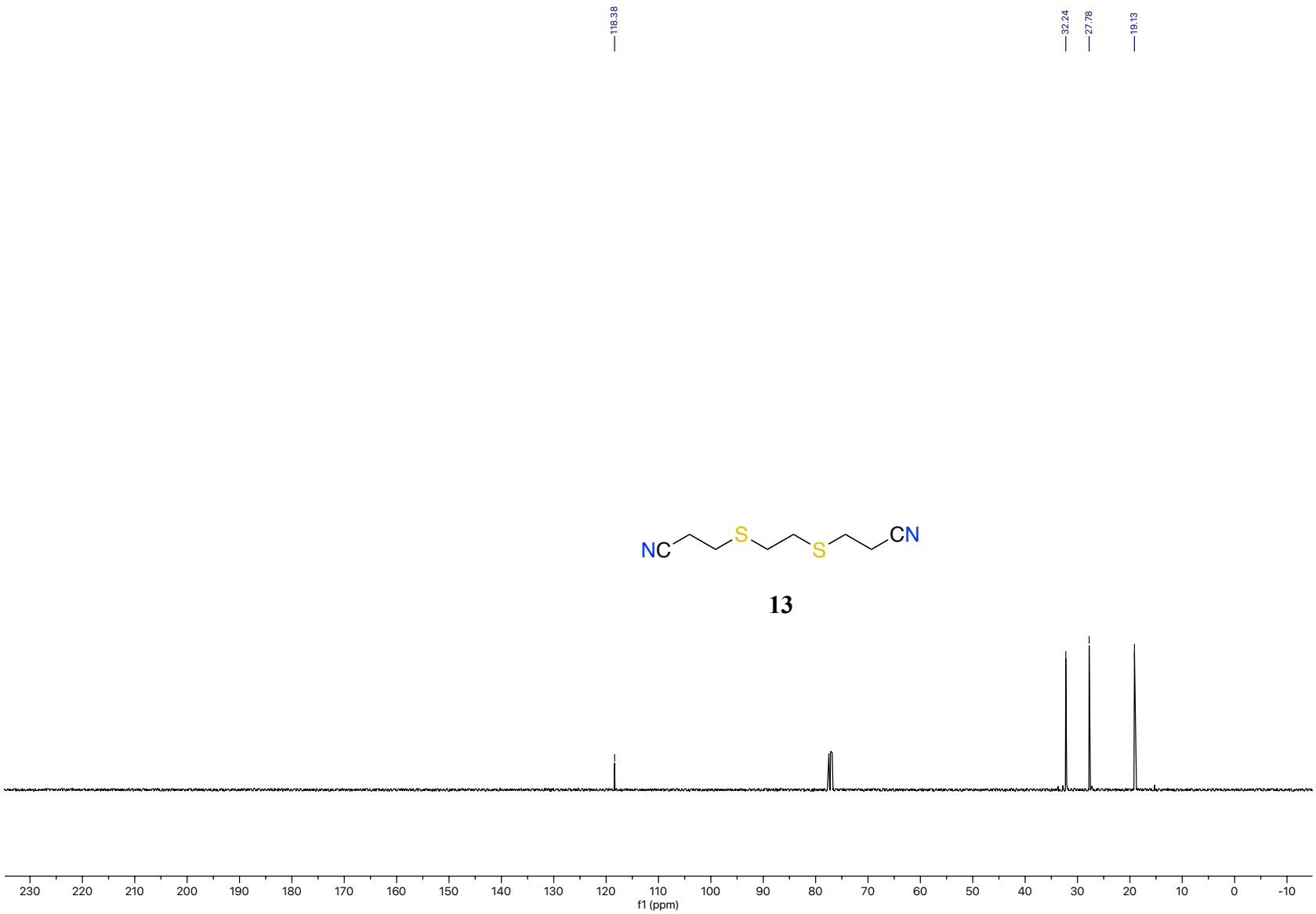

47.66
42.92
33.71
30.50
26.11
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

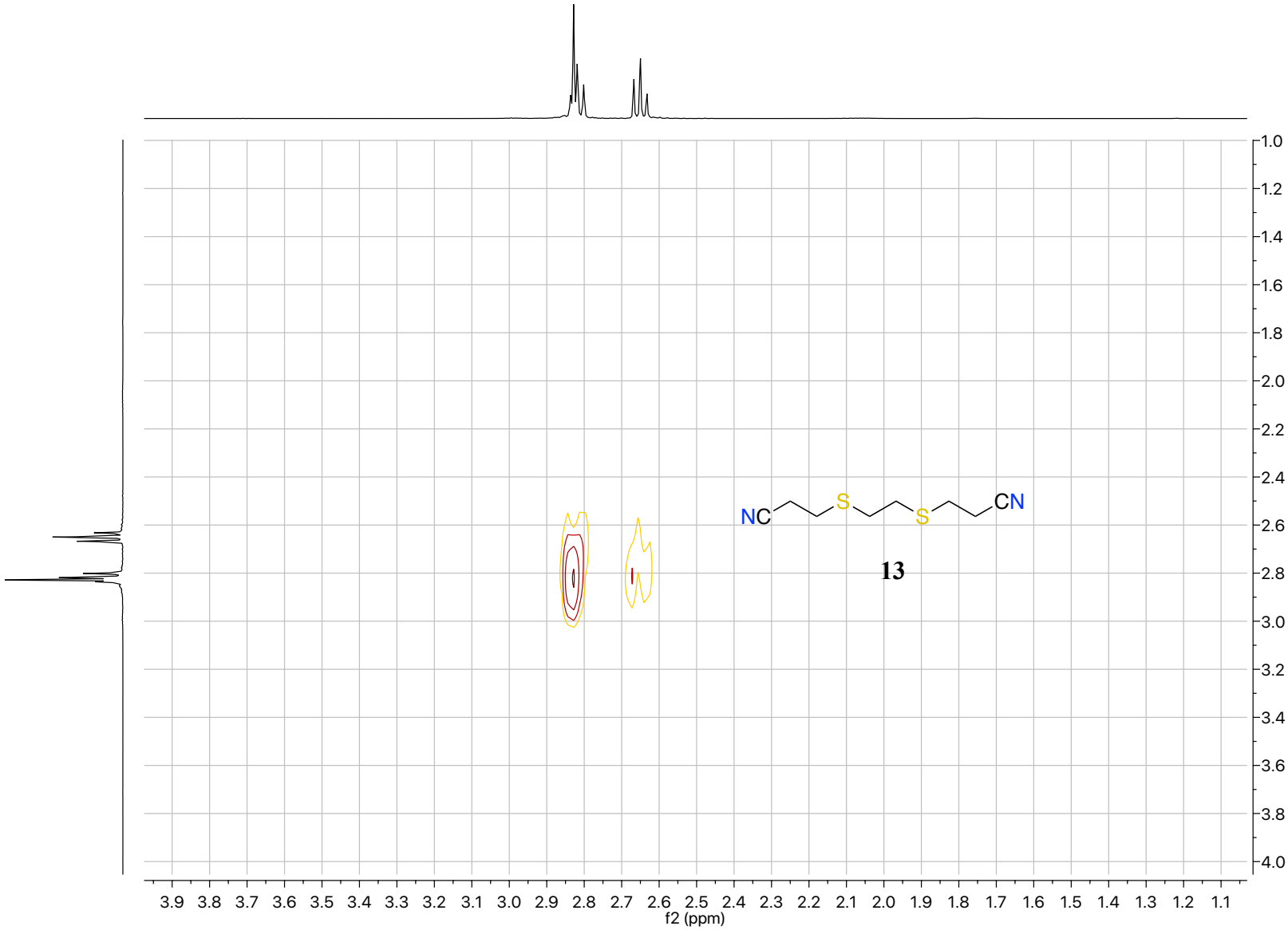

·2 HCl
S
HN
S
HN
L2-HCl
f2 (ppm)

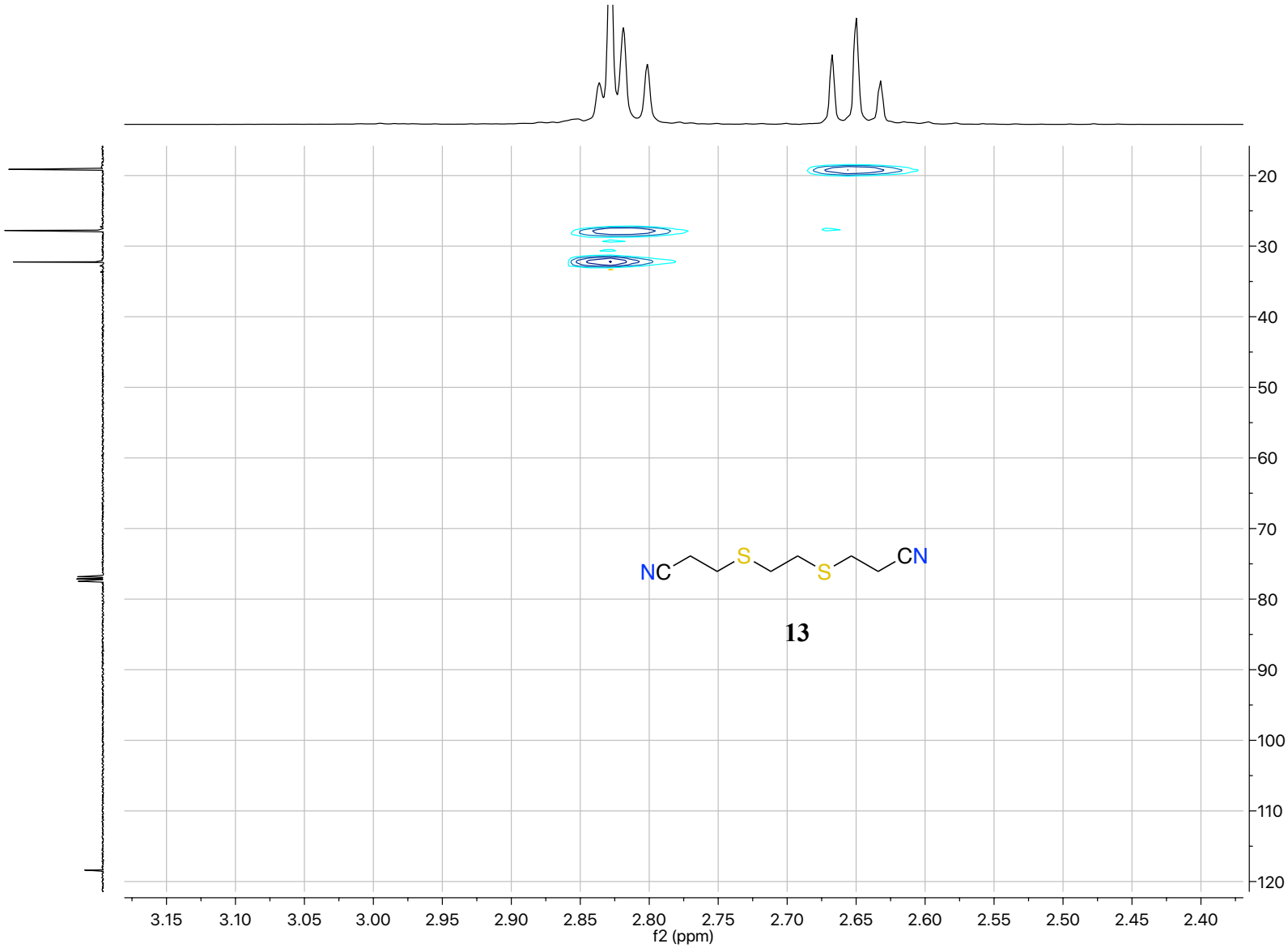

NC
S
S
CN

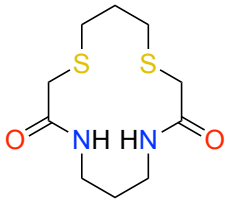
13


4.00
2.03
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
f1 (ppm)
4.00
2.03
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f1 (ppm)


118.38
32.24
27.78
19.13
NC
S
S
CN
13
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

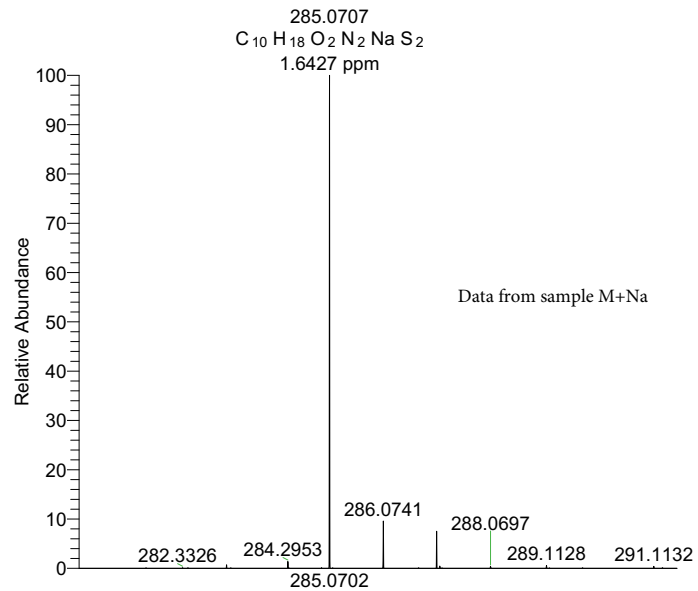

NC
S
S
CN
13
f2 (ppm)


NC
S
S
CN
13
f2 (ppm)

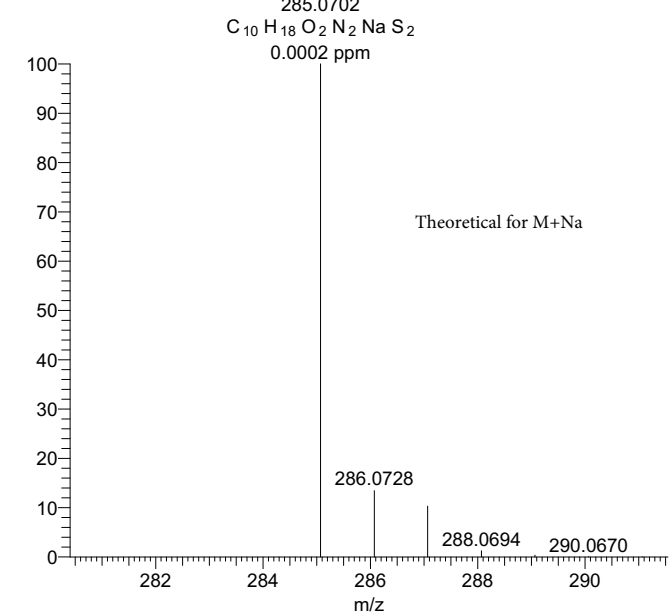


1

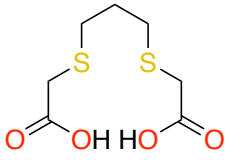
C:\Xcalibur\data\2018\October\it-01-207 10/25/2018 2:09:48 PM



NL:
1.65E6
it-01-207#25-30 RT:
0.26-0.31 AV: 6 T: FTMS + p
ESI Full ms [100.00-2000.00]



NL:
7.98E5
C 10 H 18 N 2 O 2 S 2 Na:
C 10 H 18 N 2 O 2 S 2 Na 1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM



2

Mass Spectrometry & Proteomics Facility

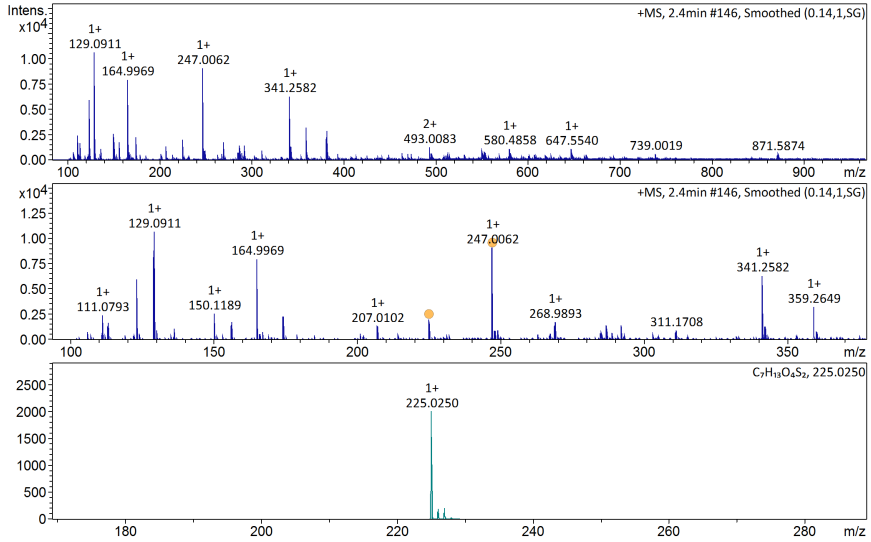
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\0901\TW1-bis-thio acid.d	Acquisition Date	9/1/2016 4:14:45 PM
Method	050916_ns_tune_low_pos.m	Operator	BDAL@DE
Sample Name	bis-thio acid	Instrument / Ser#	micrOTOF II 8213750.1 0314
Comment			

Acquisition Parameter

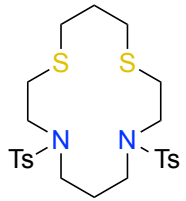
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1650 m/z	n/a	n/a	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
225.022842	1	C7H13O4S2	225.024977	9.5	4752.5	1.5	ok	even	n.a.	205.5	n.a.	n.a.	n.a.	n.a.
247.006167	1	C7H12NaO4S2	247.006922	3.1	2067.6	1.5	ok	even	4.6	9.3	n.a.	n.a.	n.a.	n.a.

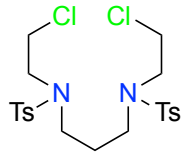
Bruker Compass DataAnalysis 4.2 printed: 9/2/2016 3:07:56 PM Page 1 of 1

This material is based upon work supported by the National Science Foundation under CHE-0741793



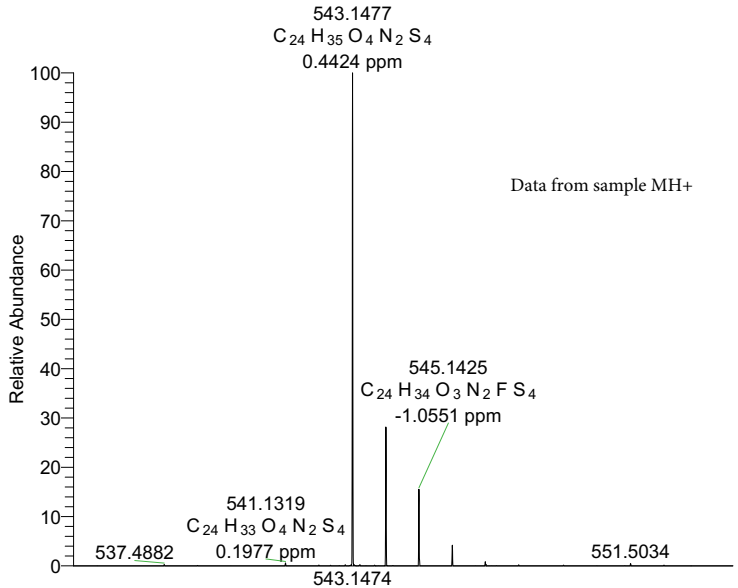
3

O:\Xcalibur\...\2018\September\it-01-228

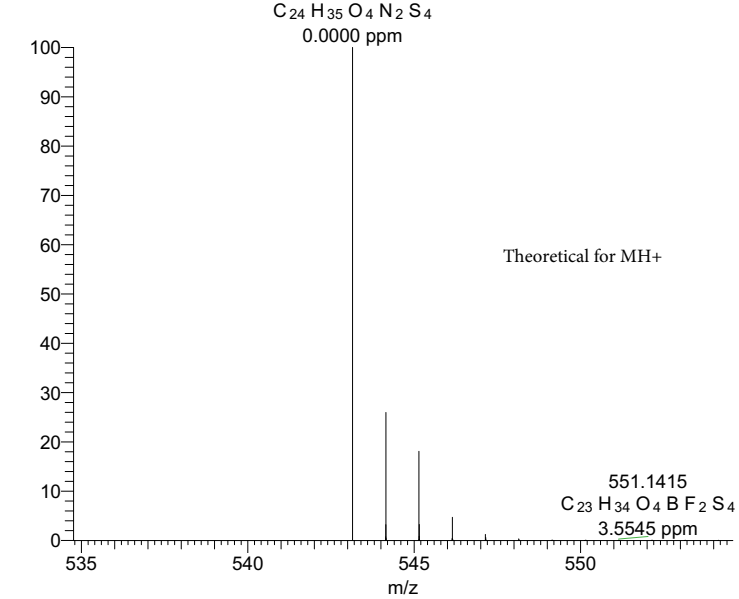


4

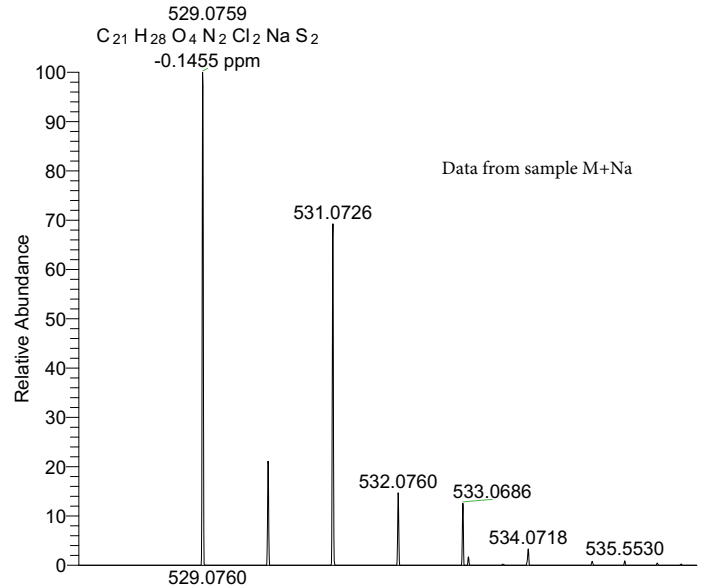
C:\Xcalibur\data\2018\June\it-01-217 6/14/2018 3:39:14 PM



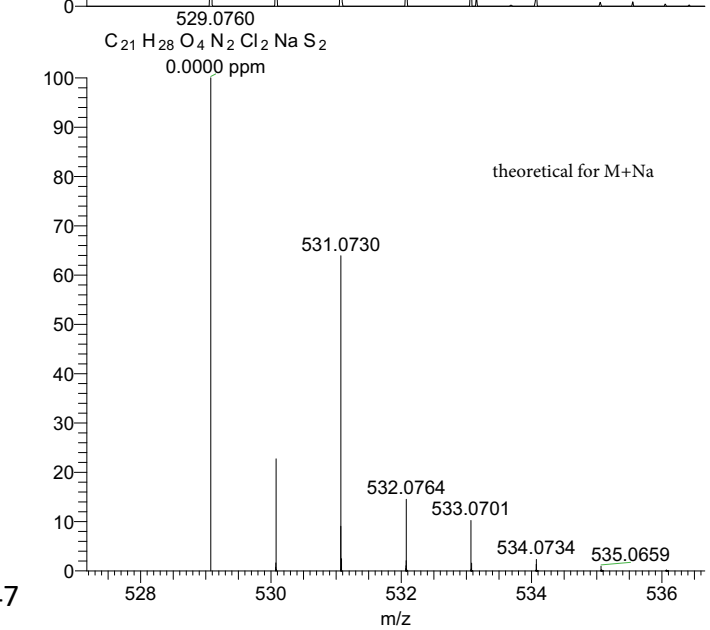
NL:
1.79E7
it-01-228#30-36 RT: 0.28-0.33 AV: 7 T: FTMS + p APCI corona Full ms [100.00-1800.00]



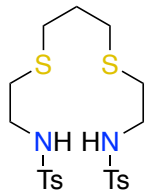
NL:
6.14E5
$C_{24}H_{35}N_2O_4S_4$: $C_{24}H_{35}N_2O_4S_4$ pa Chrg 1



NL:
6.10E6
it-01-217#34-35 RT: 0.30-0.31 AV: 2 T: FTMS + p ESI Full ms [100.00-2000.00]

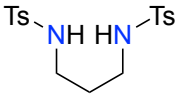


NL:
4.05E5
$C_{21}H_{28}N_2O_4S_2Cl_2Na$: $C_{21}H_{28}N_2O_4S_2Cl_2Na_1$ pa Chrg 1



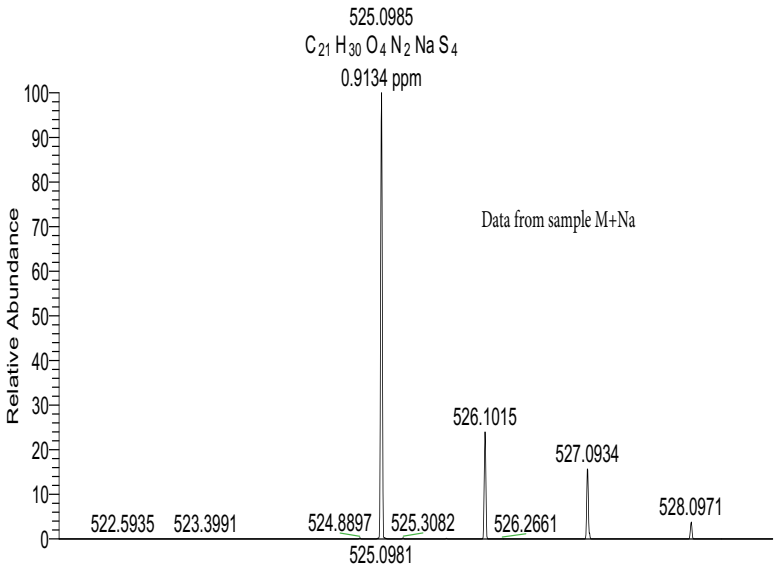
5

C:\Xcalibur\data\2019\January\it-01-256 1/3/2019 12:11:52 PM

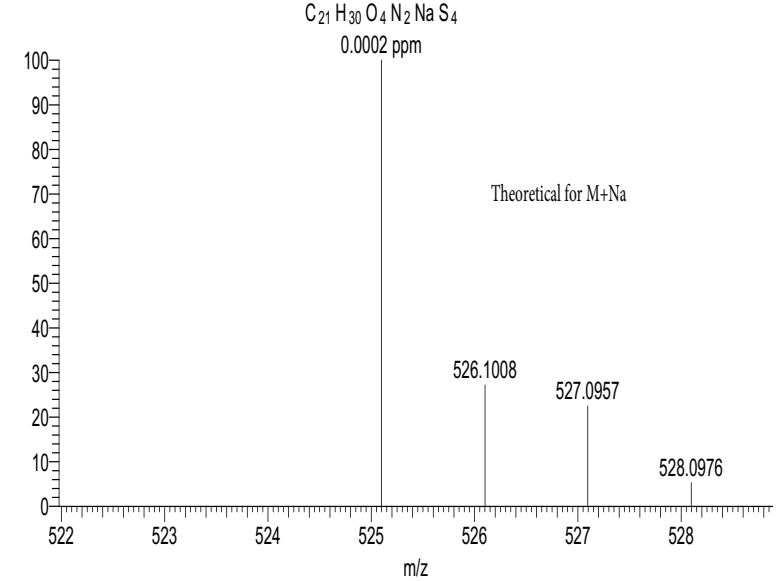


7

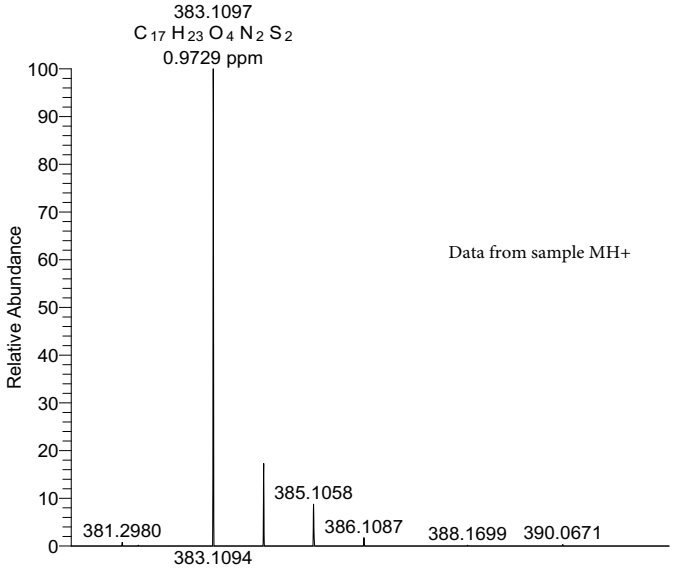
C:\Xcalibur\...\it-01-prop-bistosyl 10/25/2018 2:07:05 PM



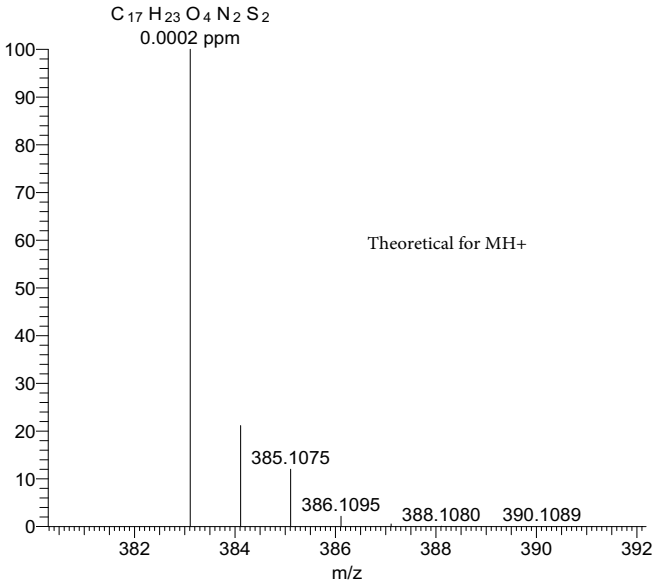
NL:
8.41E7
it-01-256#61-99 RT: 0.54-0.91 AV: 39 T: FTMS + p ESI Full ms [100.00-2000.00]



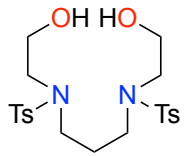
NL:
6.35E5
C 21 H 30 N 2 S 4 O 4 Na:
C 21 H 30 N 2 S 4 O 4 Na 1
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM



NL:
9.40E5
it-01-prop-bistosyl#42-44 RT: 0.43-0.45 AV: 3 T: FTMS + p ESI Full ms [100.00-2000.00]



NL:
7.36E5
C 17 H 23 N 2 O 4 S 2:
C 17 H 23 N 2 O 4 S 2
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM



8a

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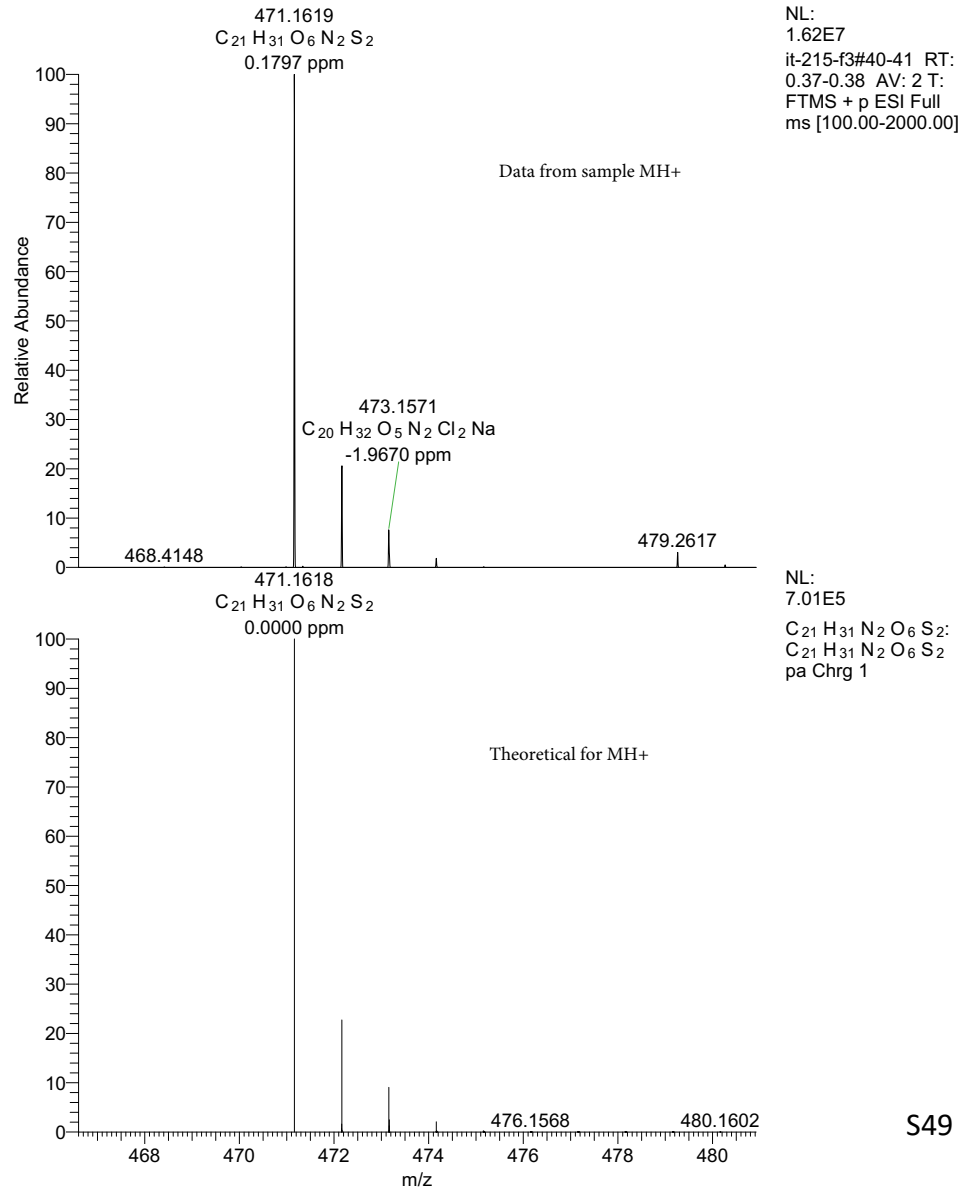
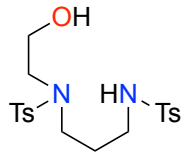
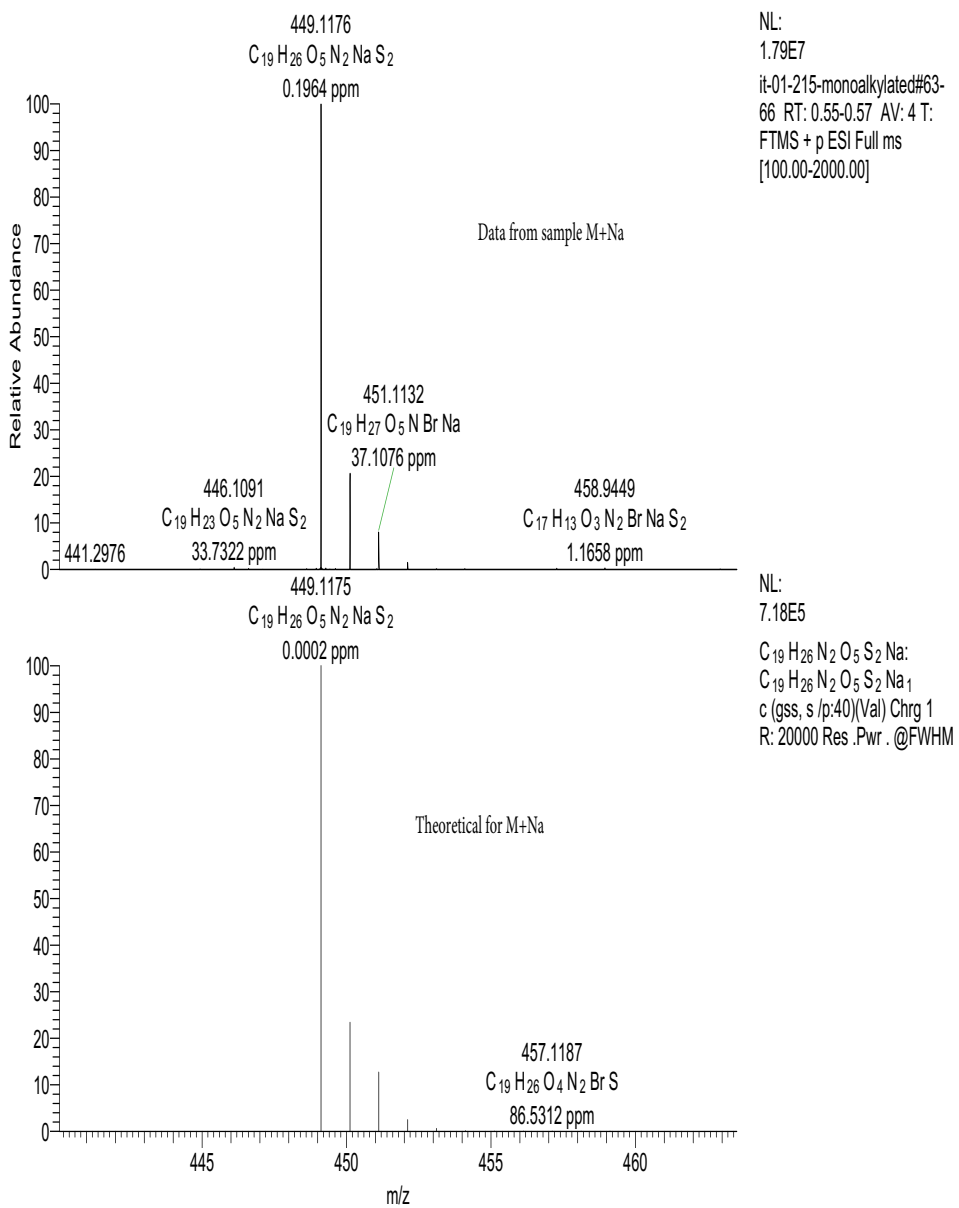
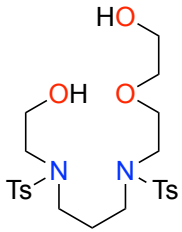




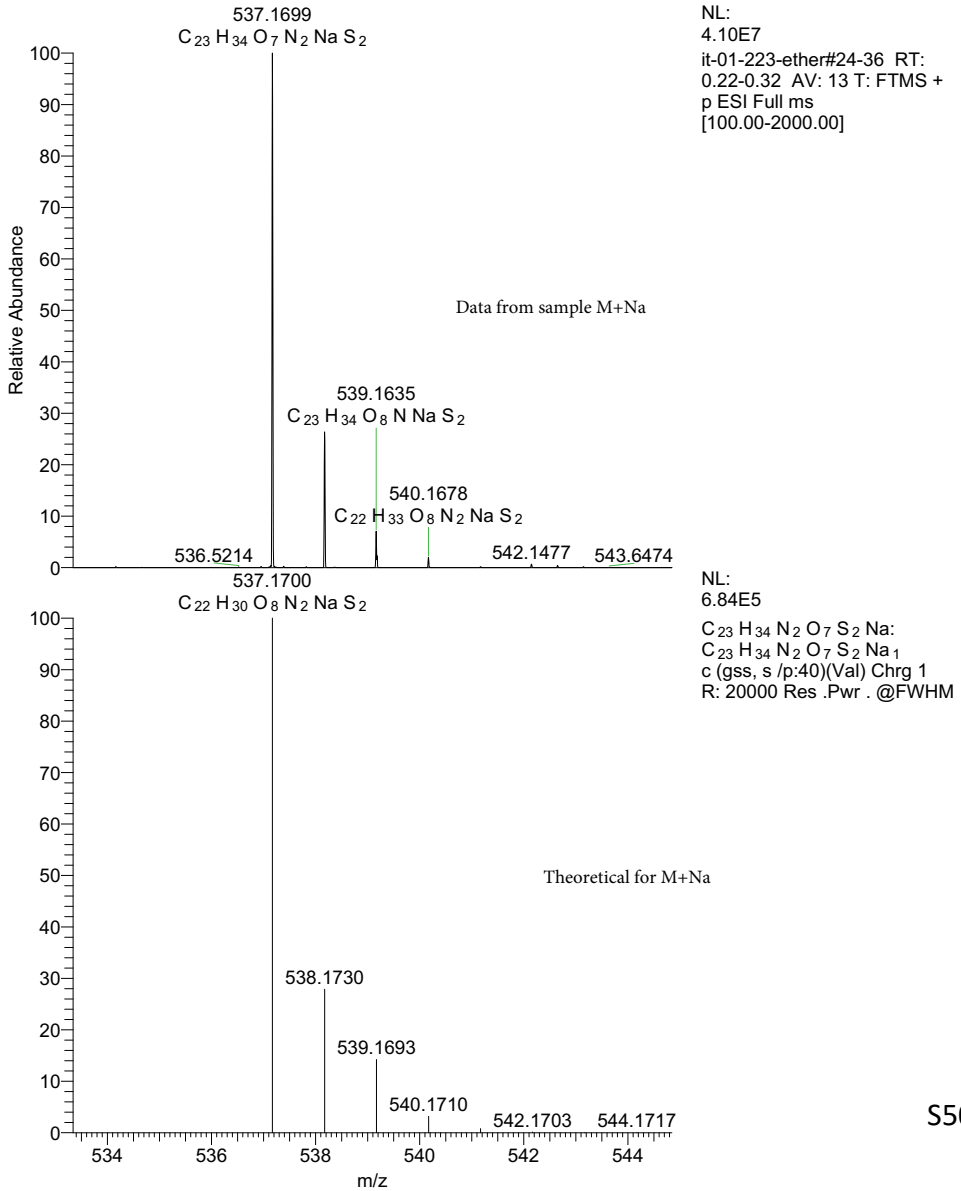
C:\Xcalibur\...\it-01-215-monoalkylated **8b** 2/19/2019 10:24:55 AM

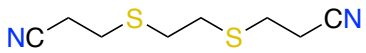




8c

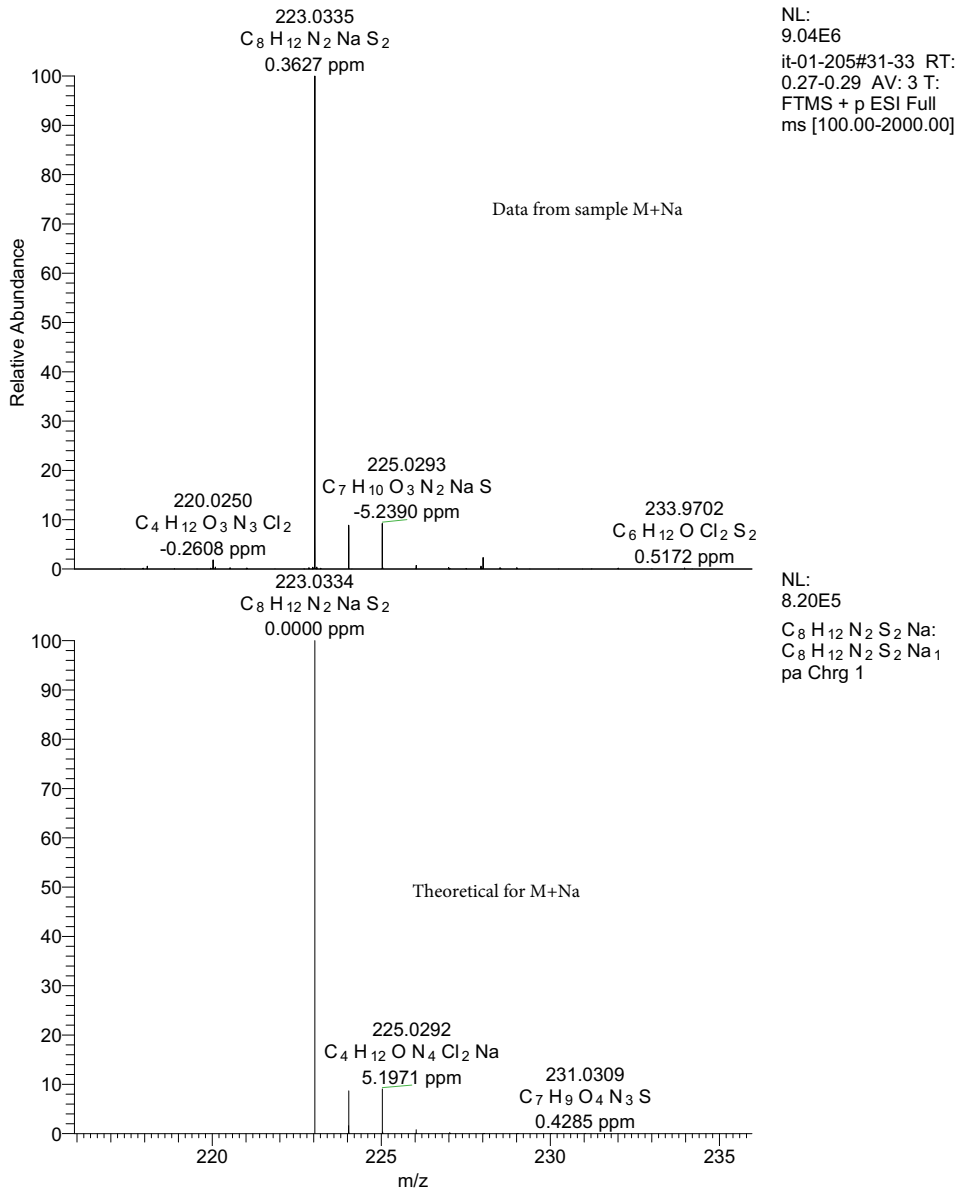
O:\Xcalibur\...\November\it-01-223-ether 11/1/2018 11:36:09 AM

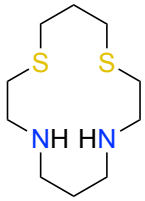




13

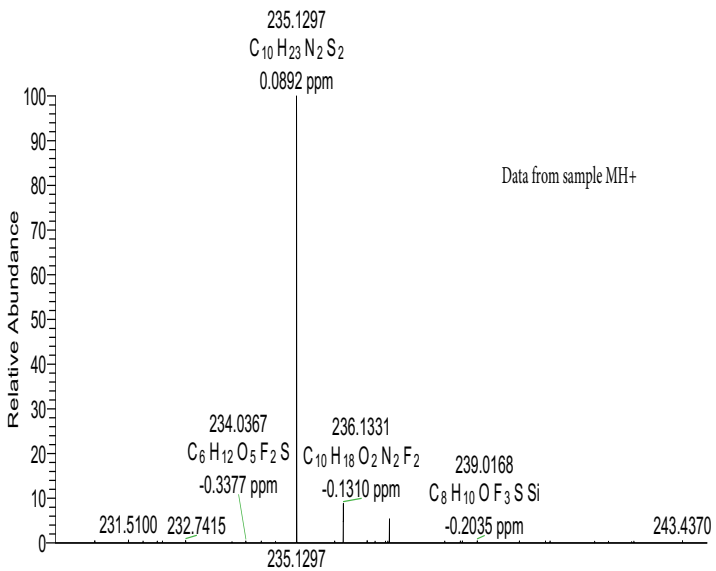
C:\Xcalibur\data\2018\June\it-01-205 6/14/2018 3:51:19 PM



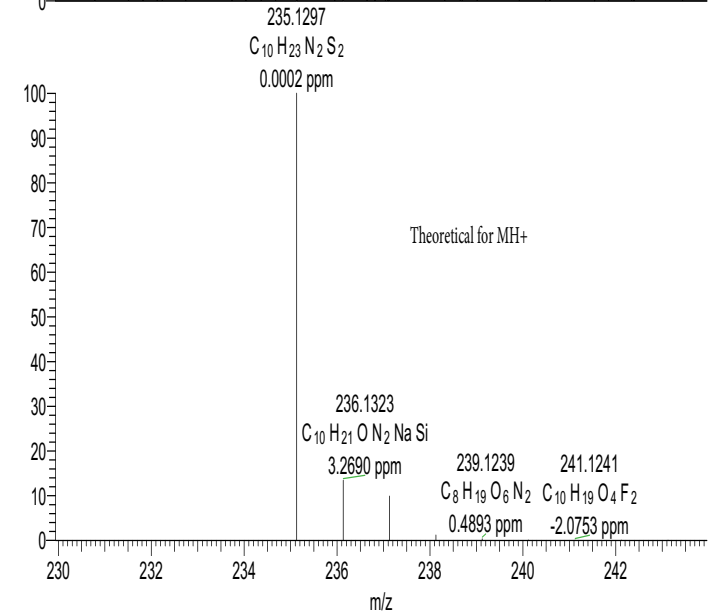


L1

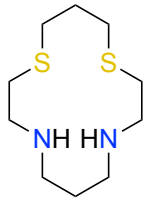
C:\Xcalibur\data\2019\February\it-01-272 2/11/2019 11:47:35 AM



NL:
1.03E6
it-01-272#28-40 RT:
0.23-0.33 AV: 13 SB: 68
0.03-0.12 , 1.33-1.79 T:
FTMS + p ESI Full ms
[100.00-2000.00]



NL:
8.01E5
C10 H23 N2 S2:
C10 H23 N2 S2
c (gss, s /p:40)(Val) Chrg 1
R: 20000 Res .Pwr . @FWHM



·2 HCl

L1-HCl

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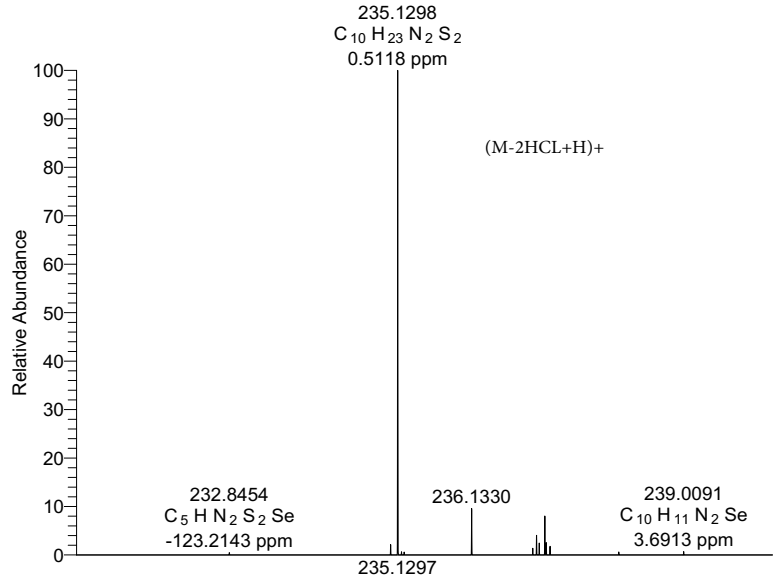

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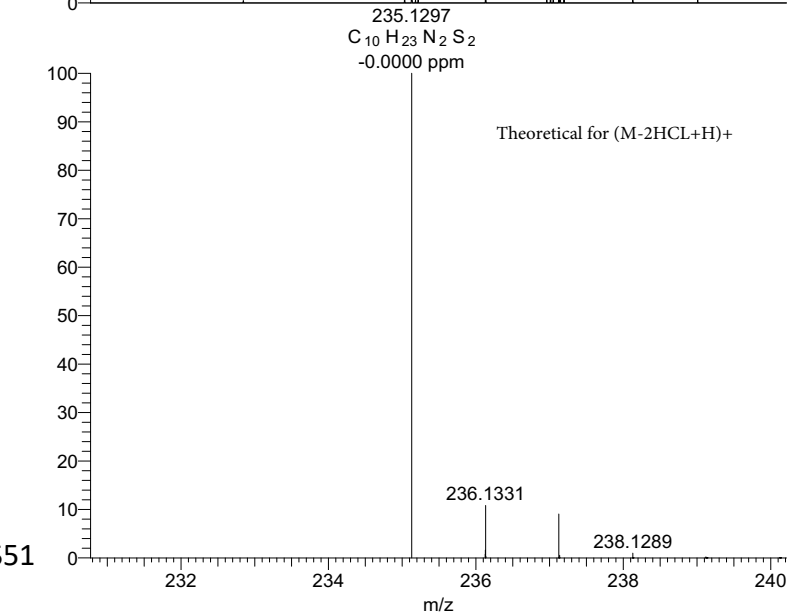
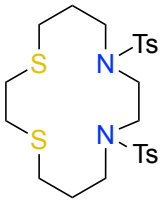
1.73E6
it-01-221#28 RT:
0.24 AV: 1 T:
FTMS + p ESI Full ms
[100.00-2000.00]



NL:
8.01E5
C10 H23 N2 S2:
C10 H23 N2 S2
pa Chrg 1



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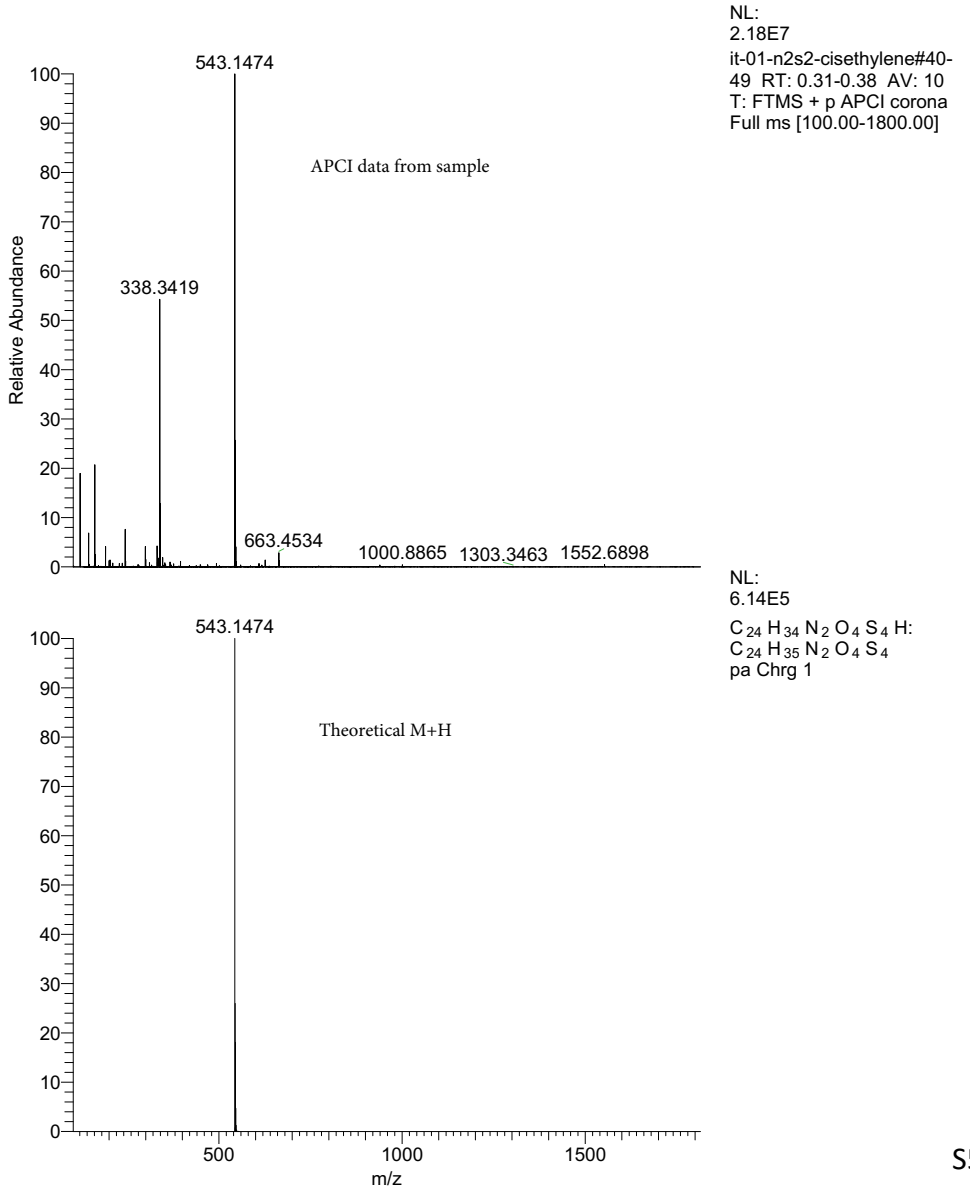
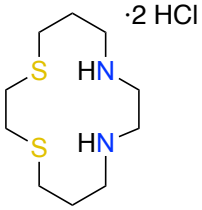




C:\Xcalibur\data\2018\June\it-01-220 6/18/2018 12:36:36 PM **L2-HCl**

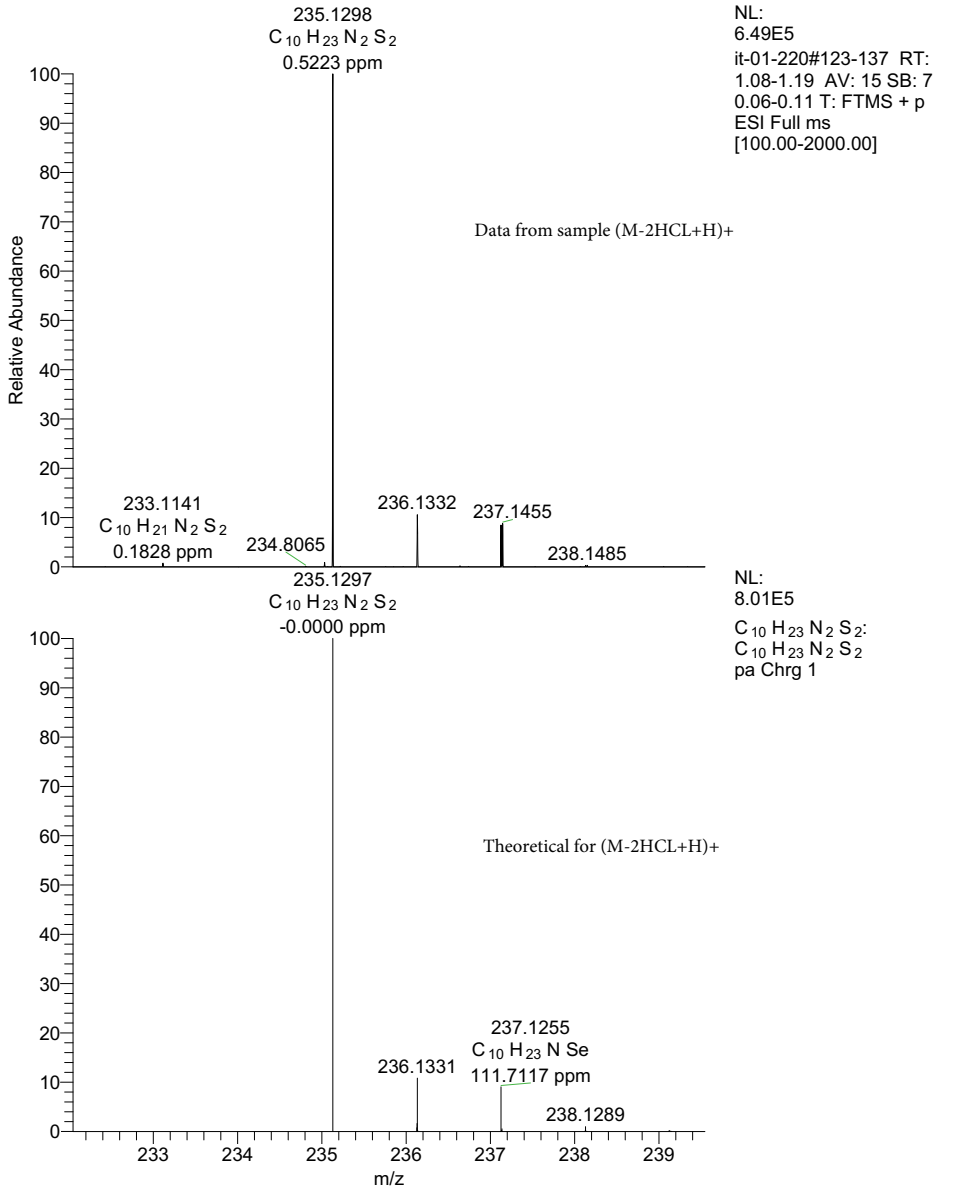


Table S1. Crystal structure and refinement data for ligands shown in Scheme 3, 4

	7	**8b**	**4**	**3**	**10**
CCDC number	1912553	1912554	1912555	1912556	1912557
Emp. formula	$C_{17}H_{22}N_2O_4S_2$	$C_{19}H_{26}N_2O_5S_2$	$C_{21}H_{28}Cl_2N_2O_4S_2$	$C_{24}H_{34}N_2O_4S_2$	$C_{17}H_{29}ClN_2O_2S_3$
Form. weight	382.48	426.54	507.47	542.77	425.05
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	Aba2	$P2_1/c$	$P2_1/c$	Pbca	$P2_1/c$
a (Å)	12.1657(6)	11.3988(6)	5.296(2)	16.7399(7)	18.4619(12)
b (Å)	17.8449(9)	7.7257(5)	22.476(14)	12.0024(5)	7.3383(5)
c (Å)	8.3153(4)	24.0175(14)	19.70(2)	27.0312(12)	15.6731(9)
α (°)	90	90	90	90	90
β (°)	90	101.992(4)	92.09(3)	90	93.296(3)
γ (°)	90	90	90	90	90
Volume ($Å^3$)	1805.22(15)	2068.9(2)	2343(3)	5431.1(4)	2119.9(2)
Z	4	4	4	8	4
Dc (Mg/m^3)	1.407	1.369	1.438	1.328	1.332
μ (mm^{-1})	0.320	0.290	4.419	3.480	0.489
F(000)	808	904	1064	2304	904
Reflections collected	15843	20100	16281	35206	19906
Data/Restraints/Parameters	2248 / 1 / 119	5201 / 0 / 260	4057 / 0 / 282	4841 / 0 / 309	5328 / 0 / 227
GOF on F^2	1.012	1.063	1.008	1.042	1.057
R1 (on F_o^2, $I > 2\sigma(I)$)	0.0217	0.0553	0.0395	0.0431	0.0403
wR2 (on F_o^2, $I > 2\sigma(I)$)	0.0594	0.1402	0.1016	0.1197	0.1064
R1 (all data)	0.0223	0.0769	0.0429	0.0467	0.0559
wR2 (all data)	0.0600	0.1519	0.1043	0.1227	0.1162

Table S2. Crystal structure and refinement data for ligands shown in Figure 5, 6

	L1-HCl	**$[(L1Cu)_2\mu\text{-}Cl](ClO_4)_3$**	**$L1Cu(ClO_4)_2$**
CCDC number	1912558	1912559	1912560
Emp. formula	$C_{10}H_{24}Cl_2N_2S_2$	$C_{20}H_{44}Cl_4Cu_2N_4O_{12}S_4$	$C_{10}H_{22}Cl_2CuN_2O_8S_2$
Form. weight	307.33	929.71	494.85
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	Pbca	$P2_1/n$	Pnma
a (Å)	8.8079(7)	12.7943(12)	14.0671(10)
b (Å)	10.9869(10)	15.5553(13)	9.6321(7)
c (Å)	31.112(3)	17.9512(17)	13.0463(9)
α (°)	90	90	90
β (°)	90	104.141(2)	90
γ (°)	90	90	90
Volume ($Å^3$)	3010.8(4)	3464.4(5)	1767.7(2)
Z	8	4	4
Dc (Mg/m^3)	1.356	1.783	1.867
μ (mm^{-1})	0.688	1.839	1.817
F(000)	1312	1912	1020
Reflections collected	27943	34047	20418
Data/Restraints/Parameters	3766 / 0 / 145	8662 / 0 / 431	1675 / 18 / 136
GOF on F^2	1.058	1.048	1.326
R1 (on F_o^2, $I > 2\sigma(I)$)	0.0305	0.0397	0.1251
wR2 (on F_o^2, $I > 2\sigma(I)$)	0.0730	0.0824	0.3006
R1 (all data)	0.0400	0.0625	0.1263
wR2 (all data)	0.0778	0.0998	0.3010

‡ There was disorder observed in one of the perchlorate anions; for two of the oxygen positions, the atoms were restrained with an effective standard deviation so that their U_{ij} components approximated to isotropic behavior.

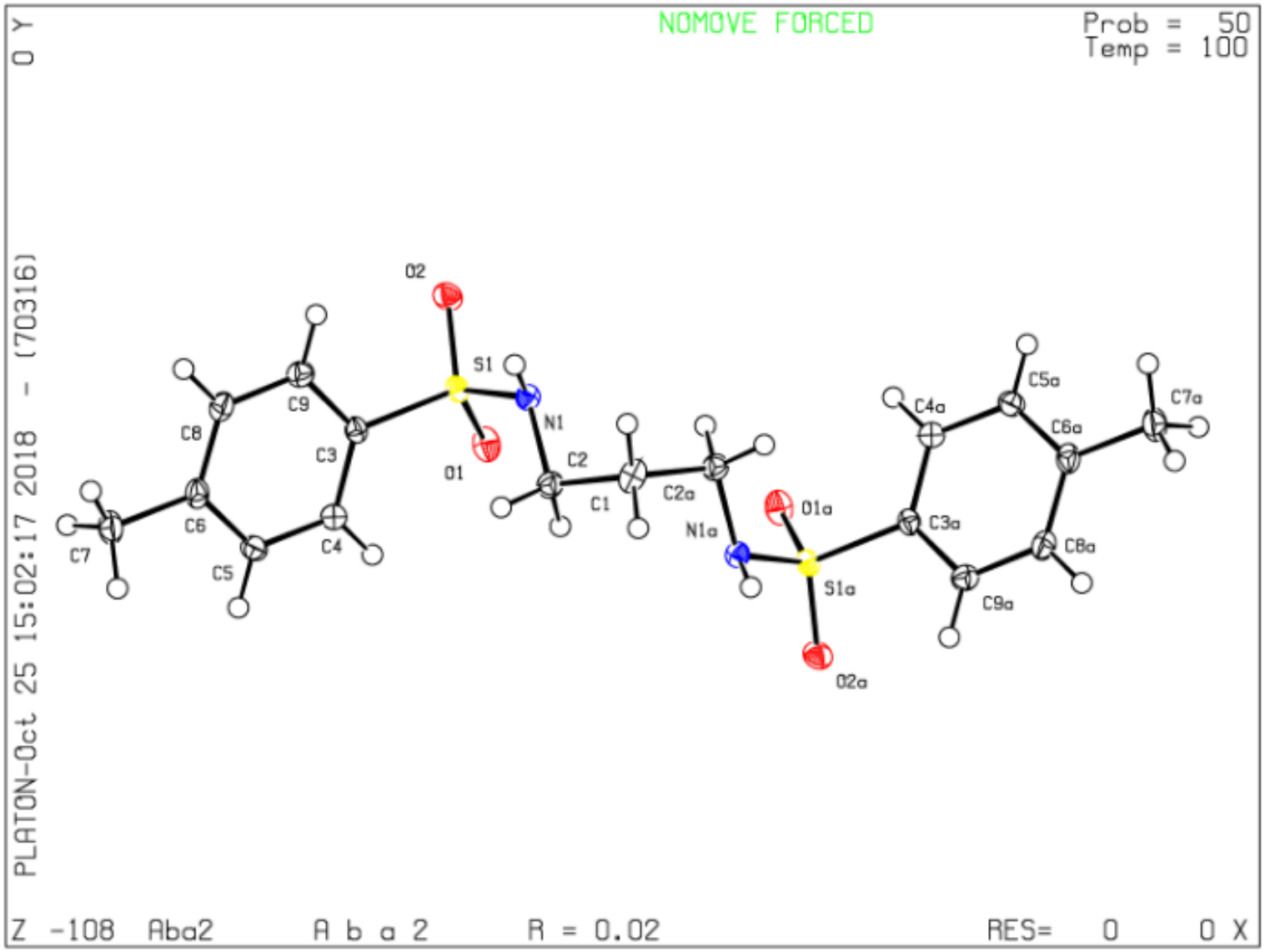


Figure S1. Crystal Structure for *bis*-sulfonamide **7**

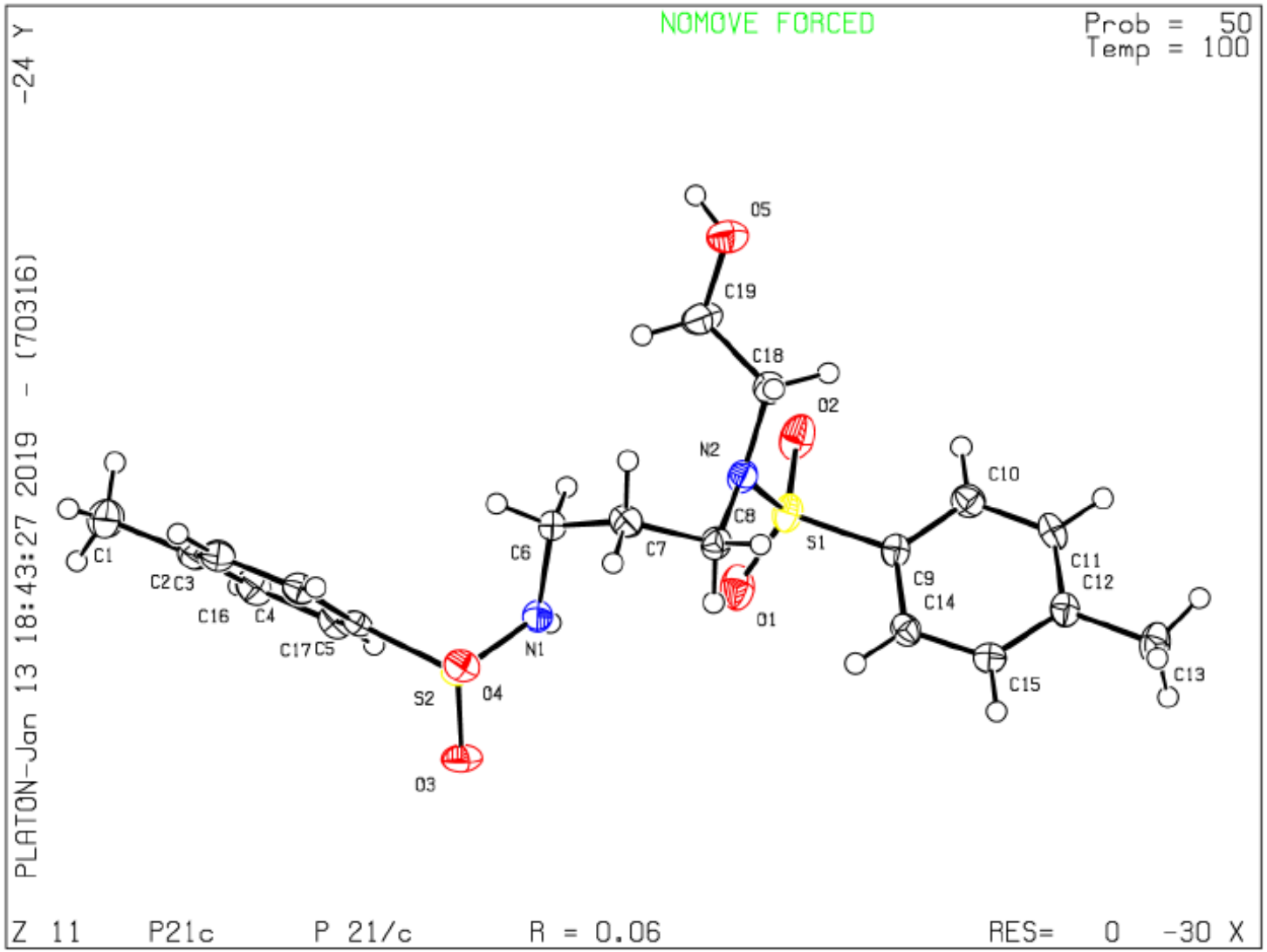


Figure S2. Crystal Structure for mono-alkylated sulfonamide **8b**

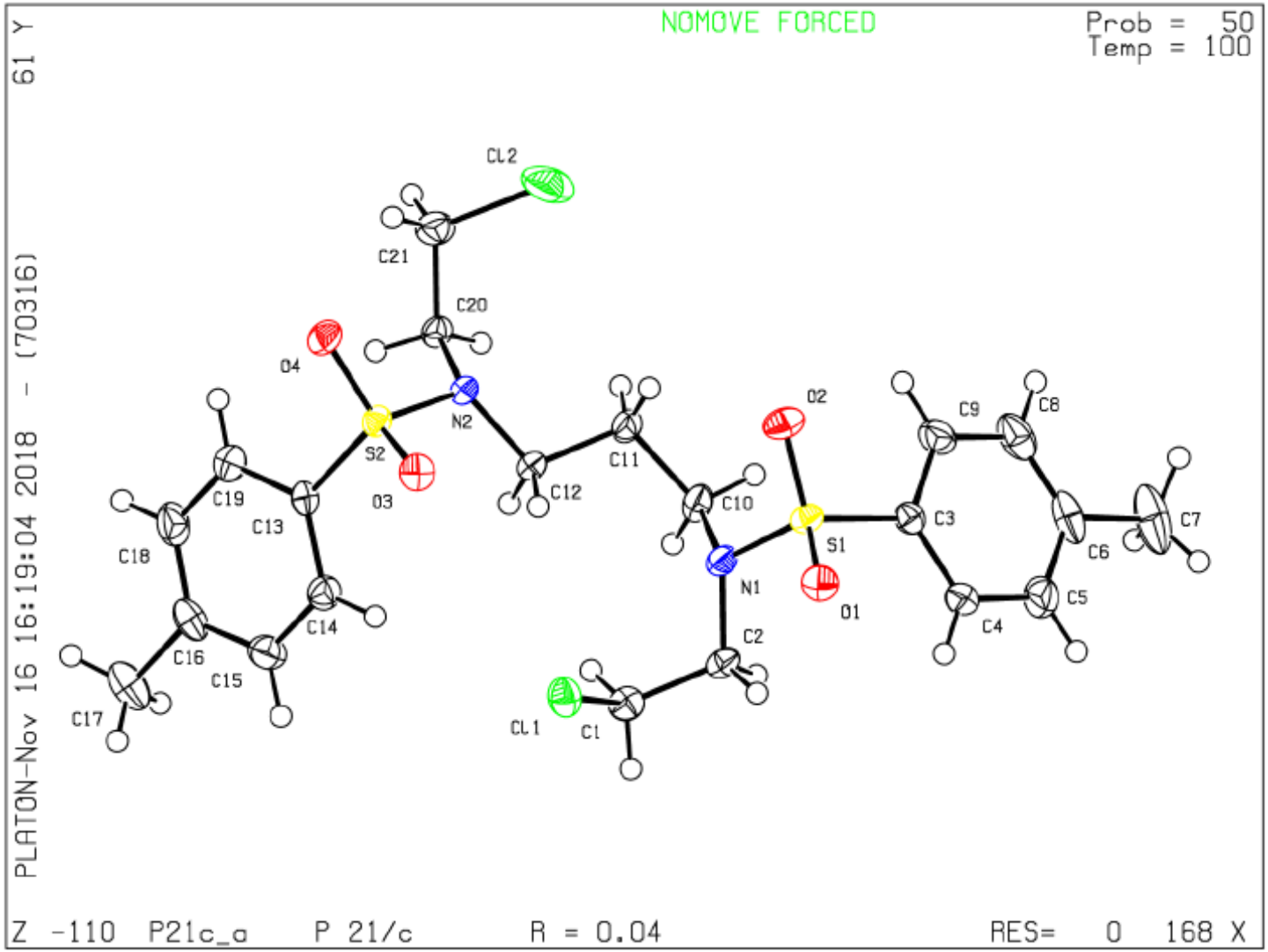


Figure S3. Crystal Structure for *bis*-chloroethyl sulfonamide **4**

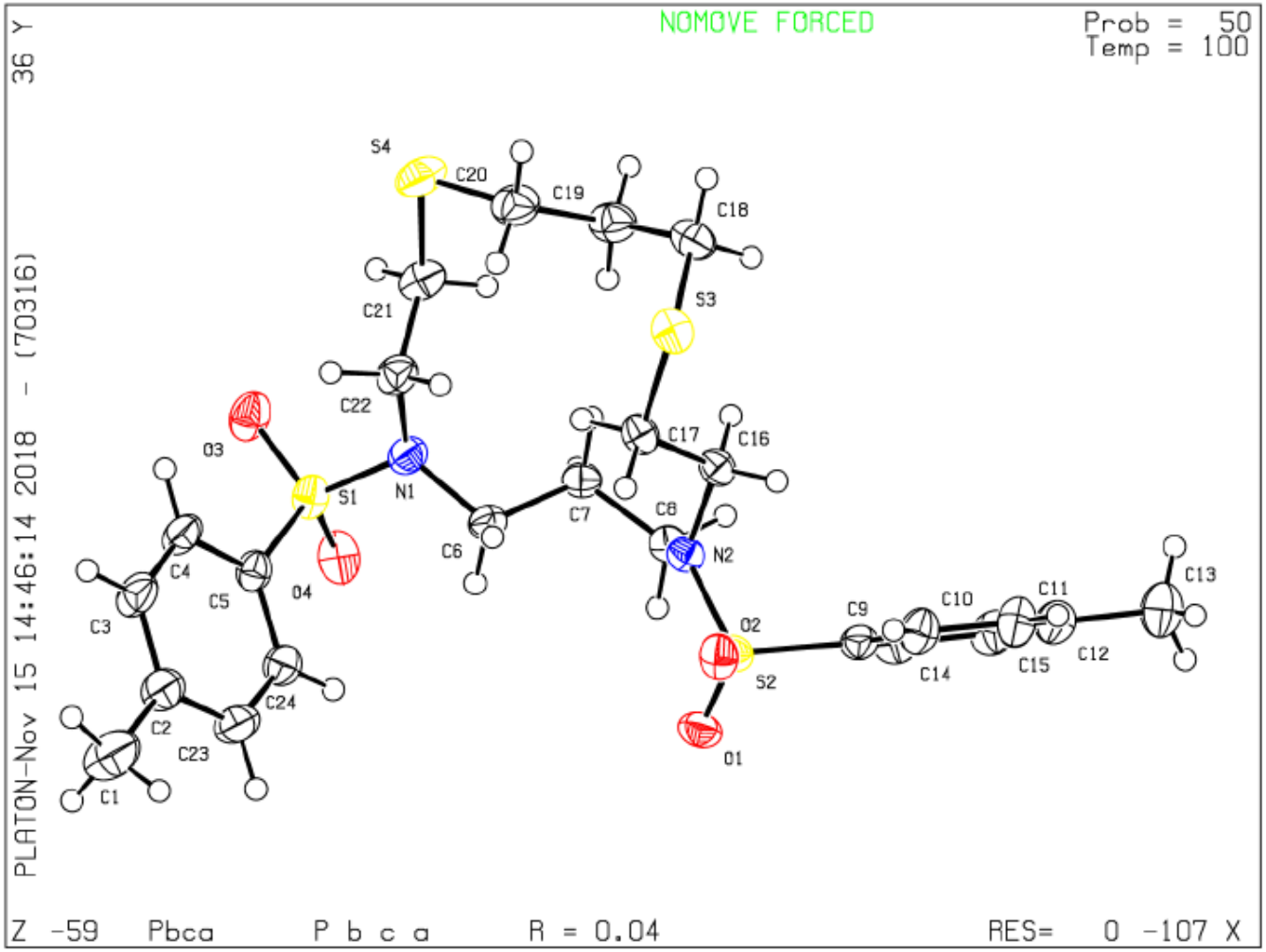


Figure S4. Crystal Structure for cyclized *bis*-sulfonamide **3**

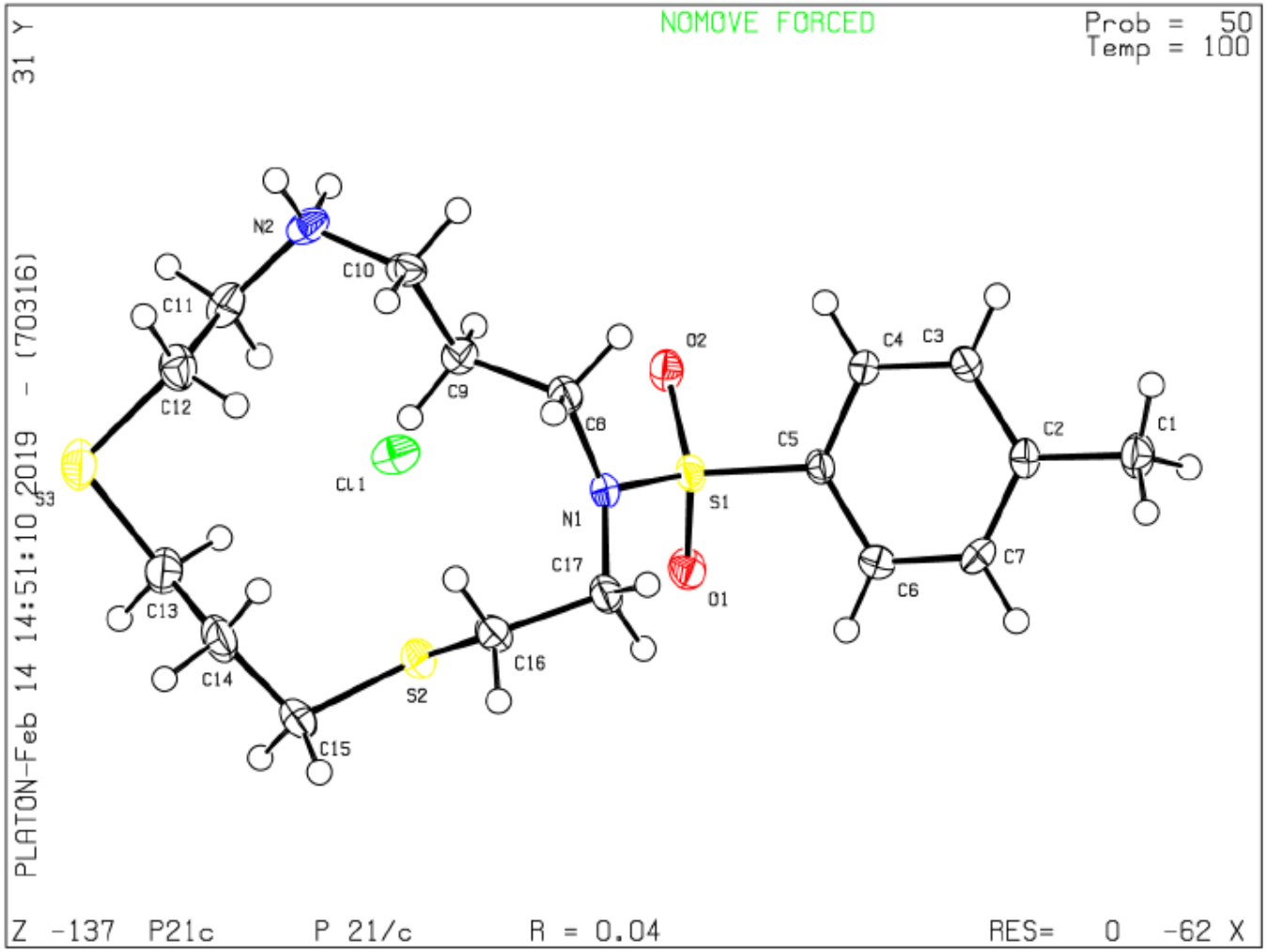


Figure S5. Crystal Structure for cyclized *mono*-sulfonamide **10**

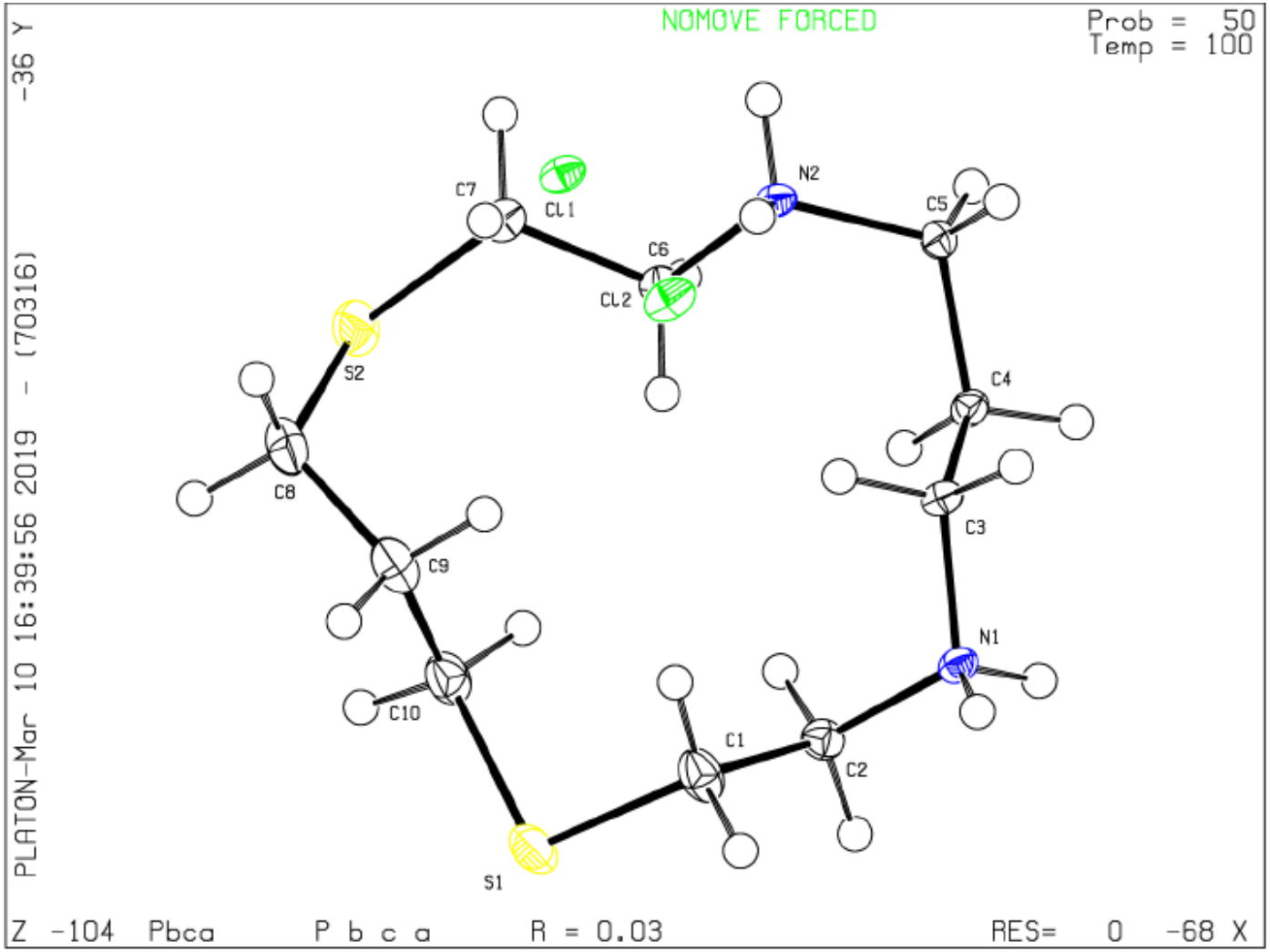


Figure S6. Crystal Structure for *bis*-protonated ligand **L1-HCl**

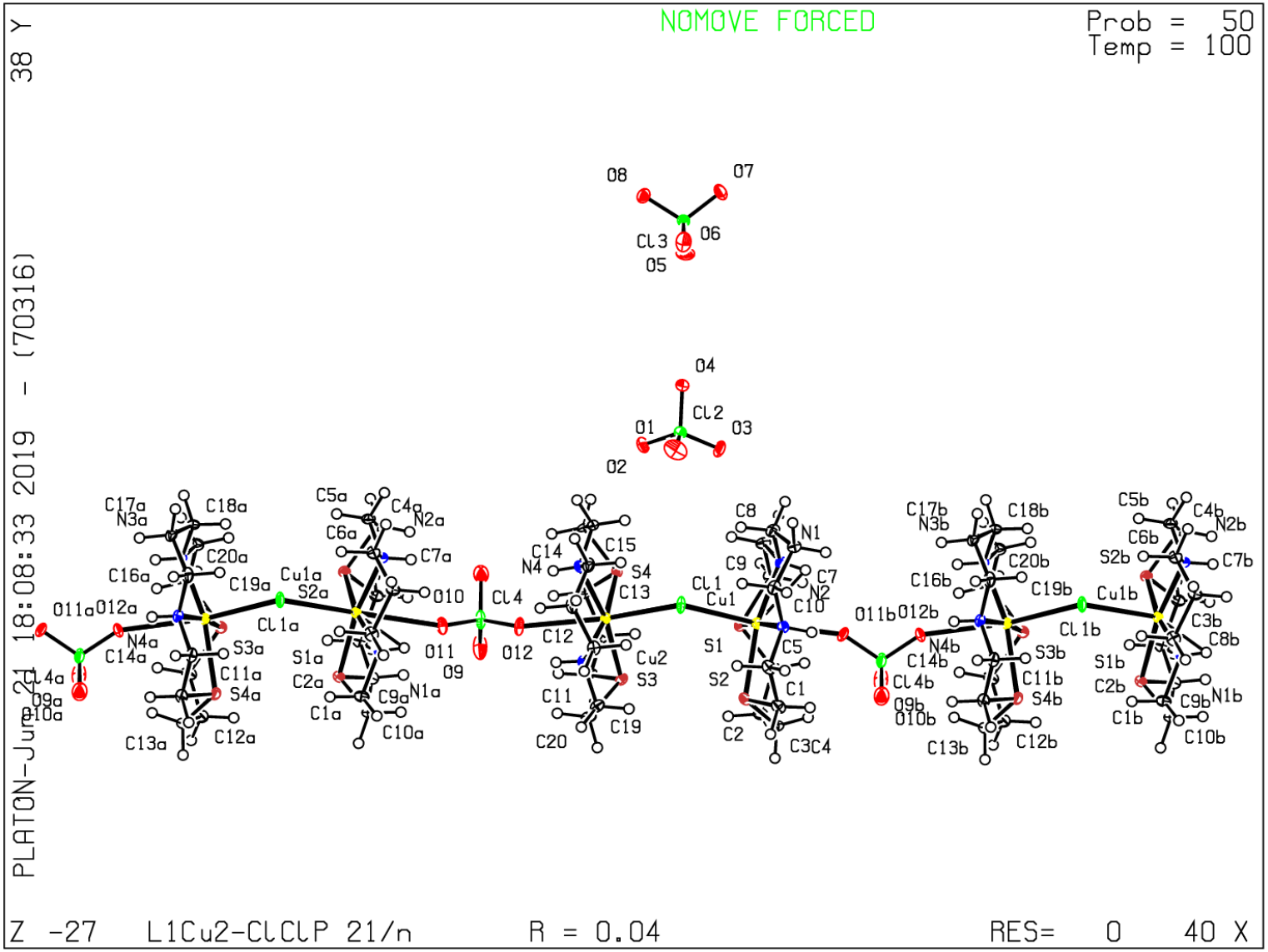


Figure S7. Crystal Structure for **[(L1Cu)$_2$μ-Cl](ClO$_4$)$_3$**

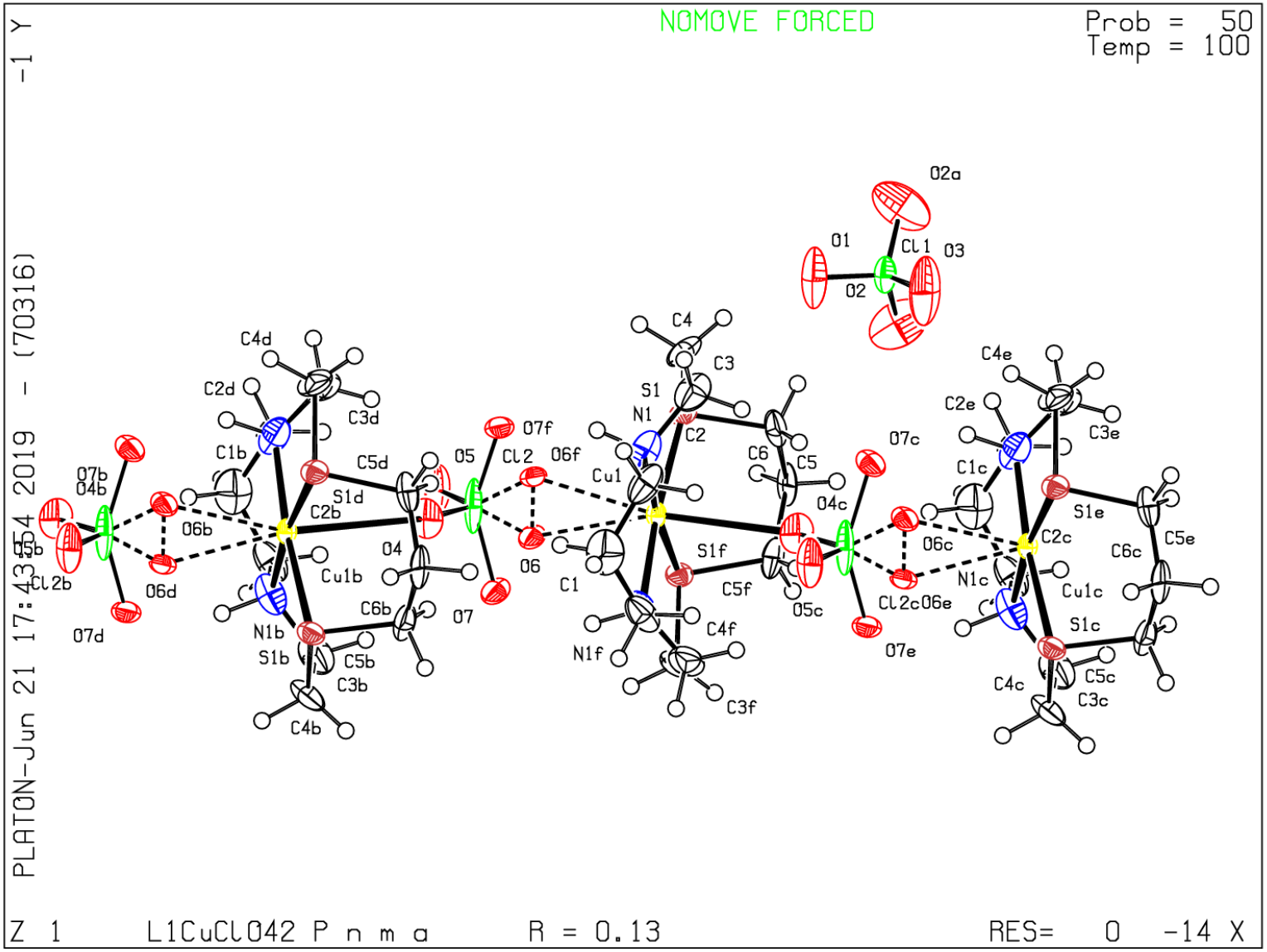
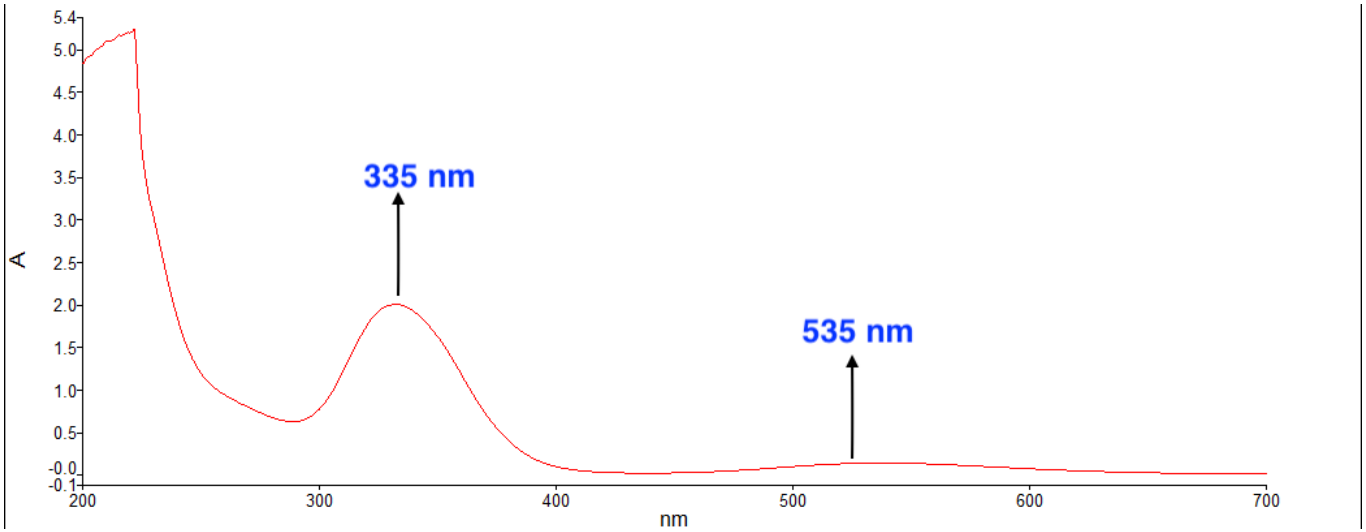


Figure S8. Crystal Structure for **L1Cu(ClO$_4$)$_2$**

UV-Data:

[**L1Cu(ClO$_4$)$_2$**]$_{aq}$ = 2.44 mM
Scan Range: 700-200 nm
Scan Speed: 480 nm/min
Data Interval: 1 nm
Cycle Count: 1
Cycle Time: 1 sec
Ordinate Type: A
Slit Width: 1 nm