Supplementary Information for:

Regioselective β-Pyrrolic Electrophilic Substitution of Hydrodipyrrin–Dialkylboron Complexes Facilitates Access to Synthetic Models for Chlorophyll *f*

Mengran Liu, Marcin Ptaszek, Olga Mass, Daniel Minkler, Roger D. Sommer, Jayeeta Bhaumik and Jonathan S. Lindsey

Table of Contents

1. NMR Characterization of Dibutylboron Formyltetrahydrodipyrrins.

The resonances observed for protons in dibutylboron formyltetrahydrodipyrrins **1-F^{7}BBu$_2$**, **1-F^{8}BBu$_2$** and **1-F^{9}BBu$_2$** were assigned (Table S1). In **1-F^{9}BBu$_2$** the formyl proton exhibited two cross peaks with a butyl group and H^8. In **1-F^{8}BBu$_2$** the formyl proton has two NOE with H^9 and H^7. And in **1-F^{7}BBu$_2$** the formyl proton has two cross peaks with H^8 and a methine proton. The observed NOE of the pyrrolic protons in formyltetrahydrodipyrrin–dibutylboron complexes also strongly supported the assigned structures (Figure S1).

Table S1. ^{1}H NMR chemical shifts of dibutylboron formyltetrahydrodipyrrins.

Compound	H-formyl	H^7	H^8	H^9
1-F^{7}BBu$_2$	9.77	–	6.55	6.62
1-F^{8}BBu$_2$	9.68	6.37	–	7.29
1-F^{9}BBu$_2$	9.81	6.02	7.14	–

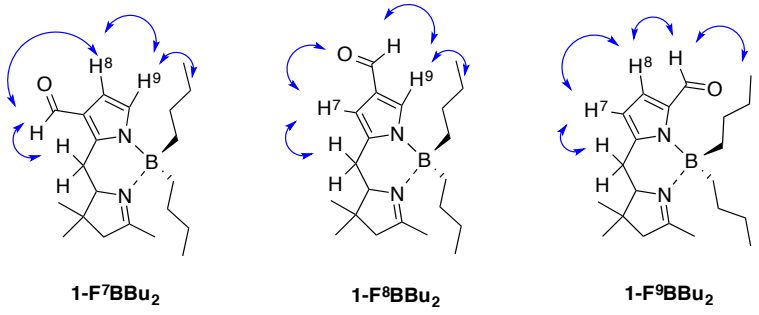


Figure S1. NOEs observed with tetrahydrodipyrrin–dialkylboron complexes.

The position of the formyl group in **1-F^{7}BBu$_2$** was established by ^{1}H NMR spectroscopy with observation of the following NOE signals: (1) the NOE signal between the formyl proton and one of the methylene group protons (note the chemical shift change of one of the methylene group protons is pronounced upon formylation, from 2.82–2.85 ppm to 3.57–3.63 ppm); (2) the NOE signal between the formyl proton and the β-pyrrolic proton; (3) the NOE signal between the α-pyrrolic proton and the butyl group; and (4) the NOE signal between the α- and β-pyrrolic protons.

2. X-ray Data.

Table S2. Summary of Crystal Data for **1-BBu$_2$**, **1-Br^{8}BBu$_2$**, **2-BBu$_2$**, and **1-Br^{8}F^{7}BBu$_2$**.

	1-BBu$_2$	**1-Br^{8}BBu$_2$**	**2-BBu$_2$**	**1-Br^{8}F^{7}BBu$_2$**
CCDC registry	974409	974410	974412	974411
Formula	$C_{20}H_{35}BN_2$	$C_{20}H_{34}BBrN_2$	$C_{27}H_{39}BN_2$	$C_{21}H_{34}BBrN_2O$
Formula Weight (*g/mol*)	314.32	393.21	402.41	421.22
Crystal Dimensions (*mm*)	0.32 × 0.20 × 0.09	0.45 × 0.30 × 0.20	0.36 × 0.26 × 0.08	0.50 × 0.37 × 0.09
Crystal System	monoclinic	monoclinic	monoclinic	orthorhombic
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Temperature, K	110	110	173	110
a, Å	15.8194(3)	8.8715(3)	9.077(2)	17.5208(3)
b, Å	7.93900(10)	26.3874(12)	16.466(6)	16.5255(3)
c, Å	16.6596(3)	9.8079(4)	18.163(6)	15.1765(3)
α, deg	90	90	90	90
β, deg	110.7227(8)	115.588(2)	109.714(8)	90
γ, deg	90	90	90	90
V, Å$_3$	1956.92(6)	2070.80(15)	2555.6(14)	4394.20(14)
Number of reflections to determine final unit cell	9052	503	8126	9969
Min and Max 2θ for cell determination (deg)	4.4, 44.38	4.85, 51.95	4.76, 42.28	5.26, 62.01
Z	4	4	4	8
F(000)	696.32	832	880	1776
ρ (*g/cm*)	1.067	1.261	1.046	1.273
λ, Å, (MoKα)	0.71073	0.71073	0.71073	0.71073
μ, (cm^{-1})	0.06	1.989	0.06	1.883
Max 2θ for data collection (deg)	53.32	56.56	52.82	54.64
Measured fraction of data	0.999	0.999	0.999	0.999
Number of reflections measured	110726	29325	54612	77149
Unique reflections measured	4114	5130	5249	9523
R_{merge}	0.031	0.0377	0.0461	0.0377
Number of parameters in least-squares	349	222	277	500
R_1	0.052	0.0643	0.0696	0.0456
wR_2	0.079	0.1295	0.191	0.1098
R_1 (all data)	0.074	0.0771	0.1097	0.0497
wR_2 (all data)	0.157	0.1343	0.222	0.1119

Compound **1-Br^{8}F^{7}BBu$_2$** crystallizes in the chiral space group. The absolute structure parameter for **1-Br^{8}F^{7}BBu$_2$** was refined using TWIN/BASF commands to accommodate for a small amount of racemic twinning. Electron density peaks in the difference map of **1-Br^{8}F^{7}BBu$_2$** revealed disorder in the position of the bromine atom (Br1, Br1A; Br2, Br2A) on both of the molecules in the asymmetric unit (at the respective positions C8, C9 and C29, C30). The two enantiomers of **1-Br^{8}F^{7}BBu$_2$** are displayed in Figure S2. In addition, the two ball-and-stick models show the composite electron density for the presence of **1-Br^{8}F^{7}BBu$_2$** and **1-Br^{9}F^{7}BBu$_2$** in 97:3 ratio.

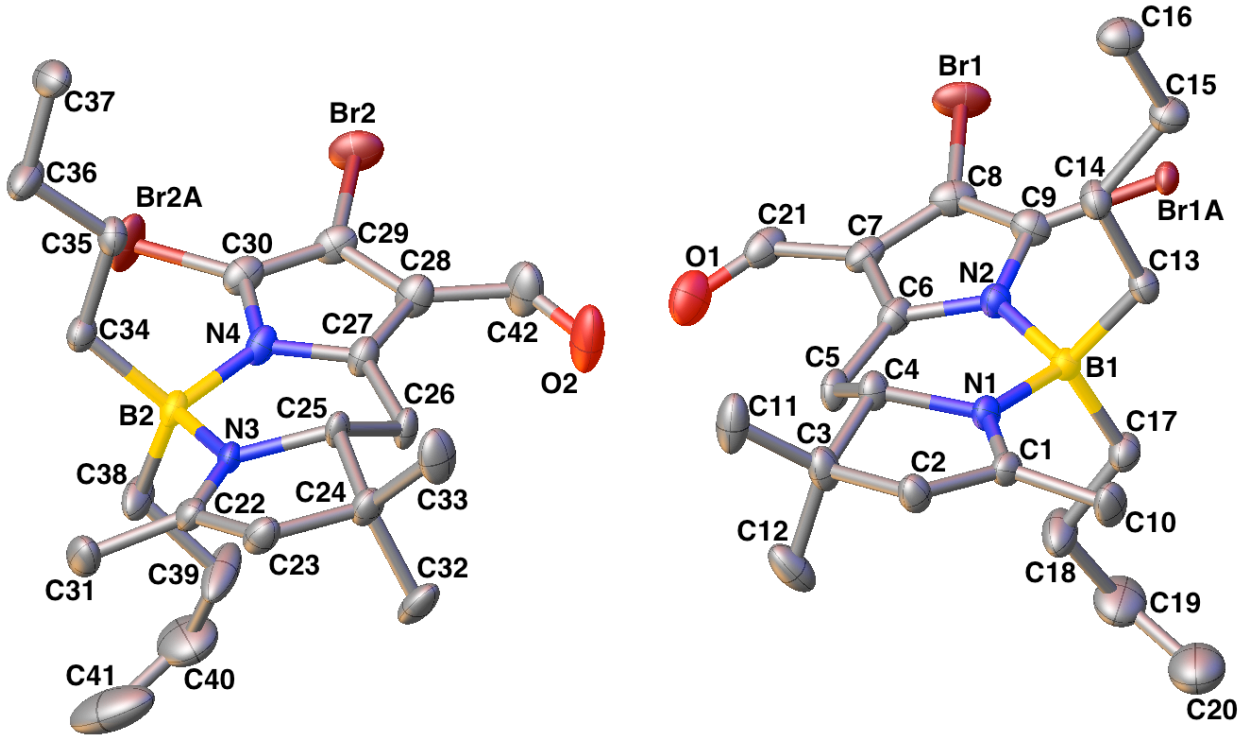


Figure S2. Enantiomers of **1-Br^{8}F^{7}BBu$_2$** also showing the disorder of the bromo position.

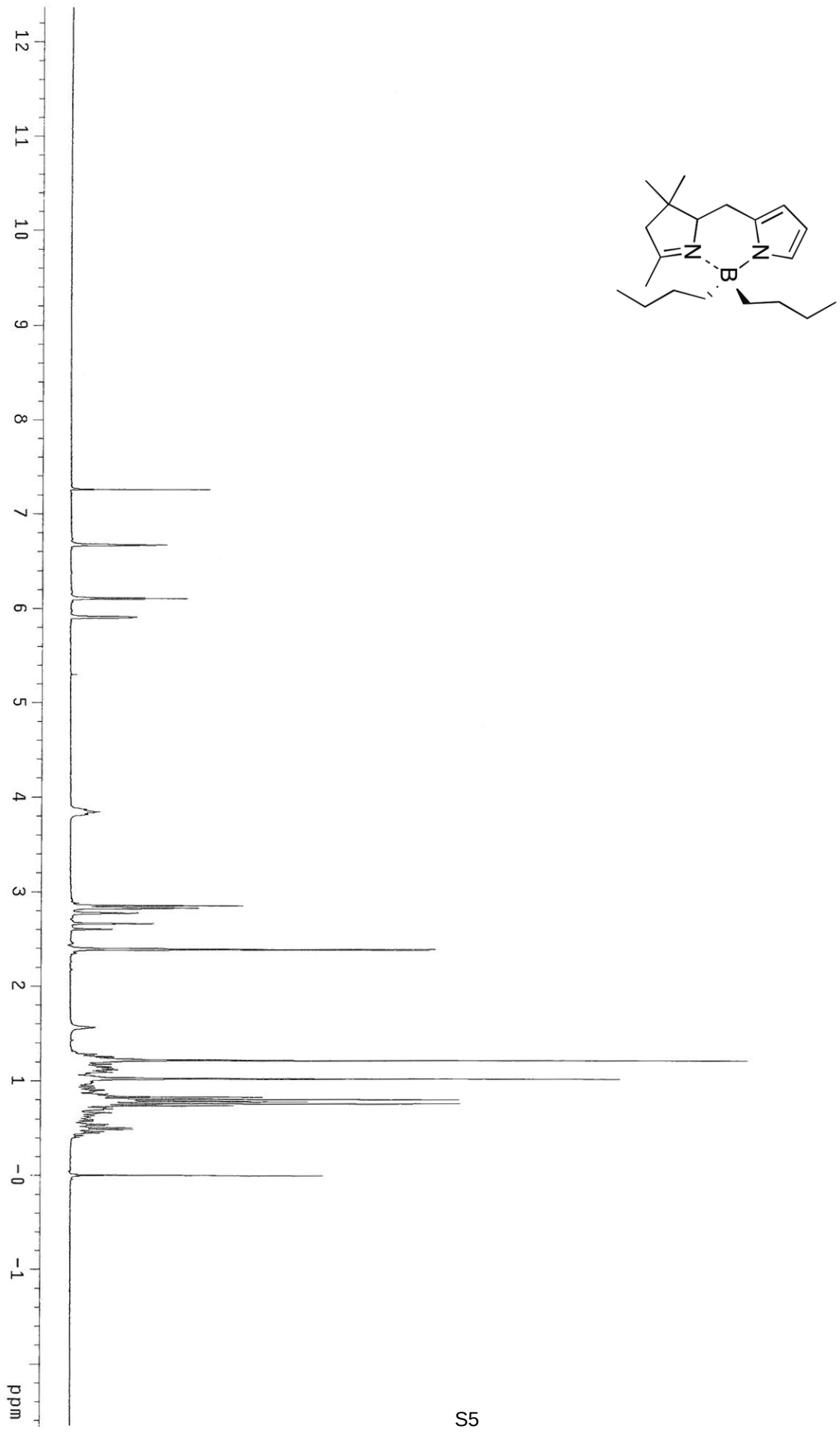
3. Decomplexation Results

Table S3. Conditions for decomplexation of **1-BR$_2$**.

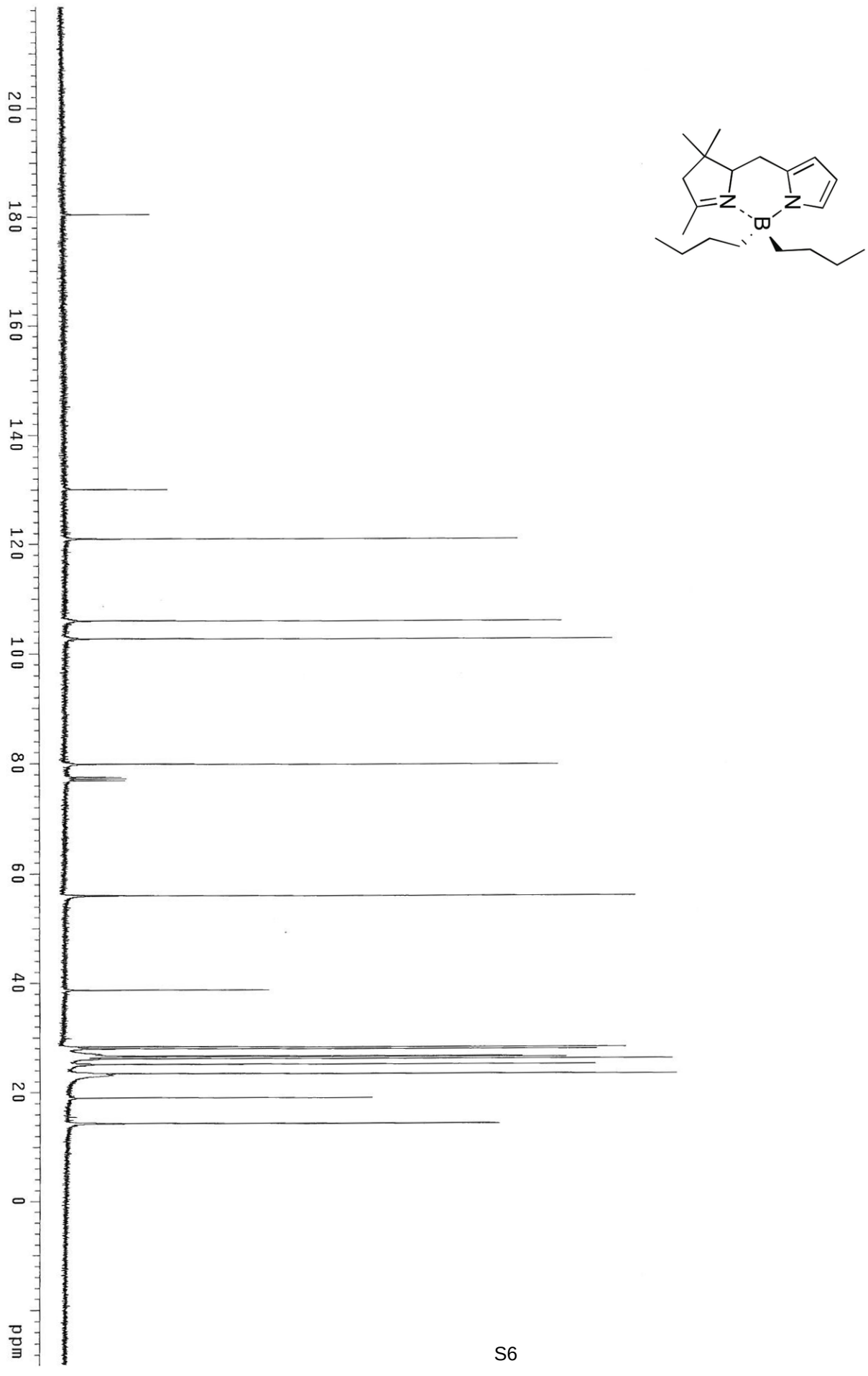
Entry	Reagent	Solvent	Temp., Time	Result[a]
1	Propylamine	Propylamine	Reflux, 1 h	**1-BBu$_2$** (intact), **1** (none)
2	Glycine	THF/MeOH, 1:1	Reflux, 1 h	**1-BBu$_2$** (major), **1** (minor)
3	DTT, Pyridine	THF	Reflux, 1 h	**1-BBu$_2$** (none), **1** (none), extensive byproducts
4[b]	TFA, 450 mM	CH_2Cl_2	RT, 10 min	**1** (~50%), unknown (~50%)
5[b]	Pentanol	Pentanol	Reflux, 2 h	**1-BBu$_2$** (trace), **1** (~quant.)
6	PhOH, K_2CO_3	CH_3CN	Reflux, 2 h	**1-BBu$_2$** (trace), **1** (~quant.)
7	$N_2H_4 \cdot H_2O$	THF	Reflux, 1 h	**1-BBu$_2$** (none), **1** (~quant.)
8	KOH (excess)	THF/MeOH, 1:1	Reflux, 1 h	**1-BBu$_2$** (none), **1** (~quant.)

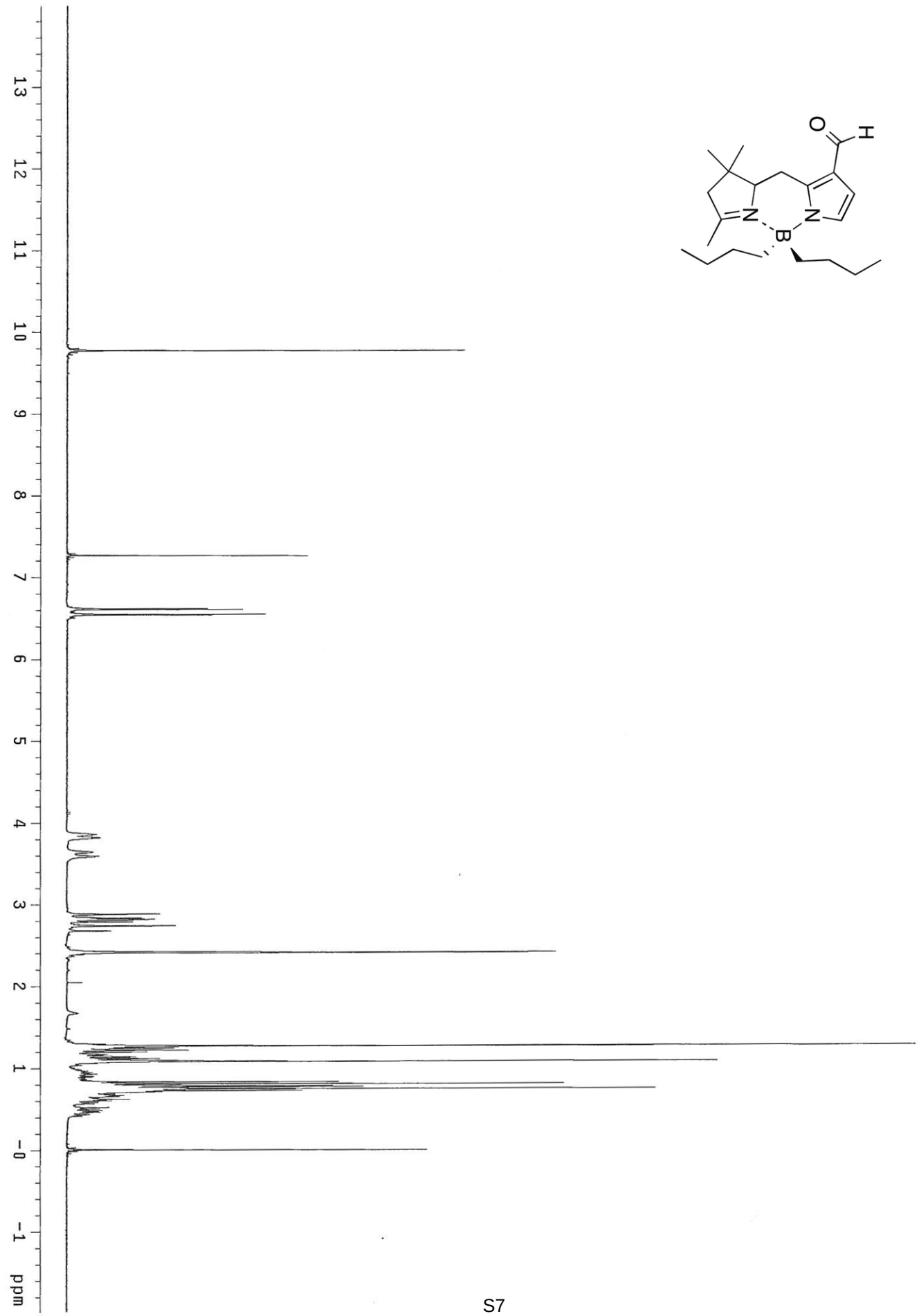
[a]The product distribution was estimated on the basis of TLC analysis with visual inspection.
[b]Application of the same conditions to **1-BMe$_2$** afforded the corresponding product distribution.

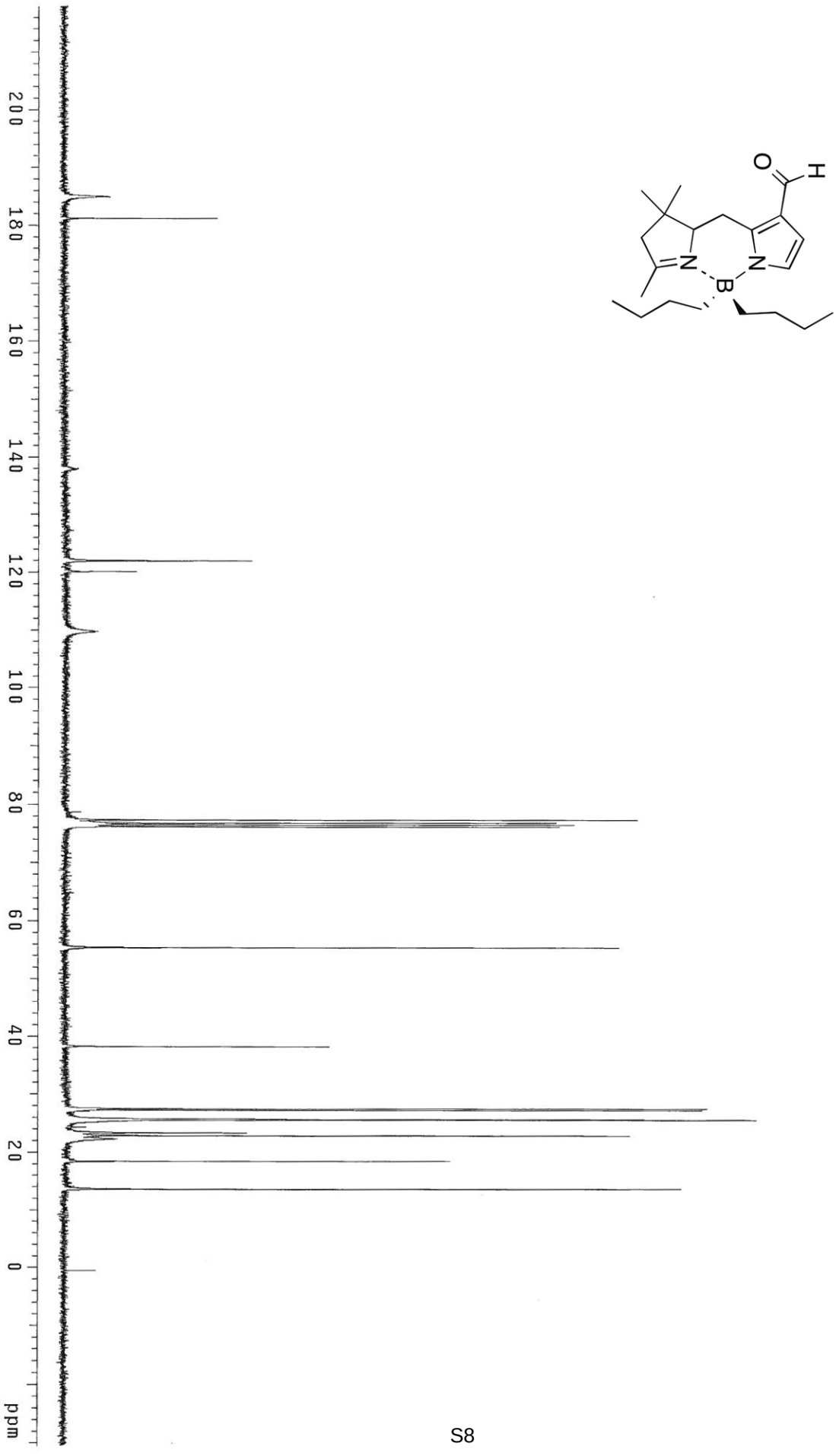
4. Spectral Data.

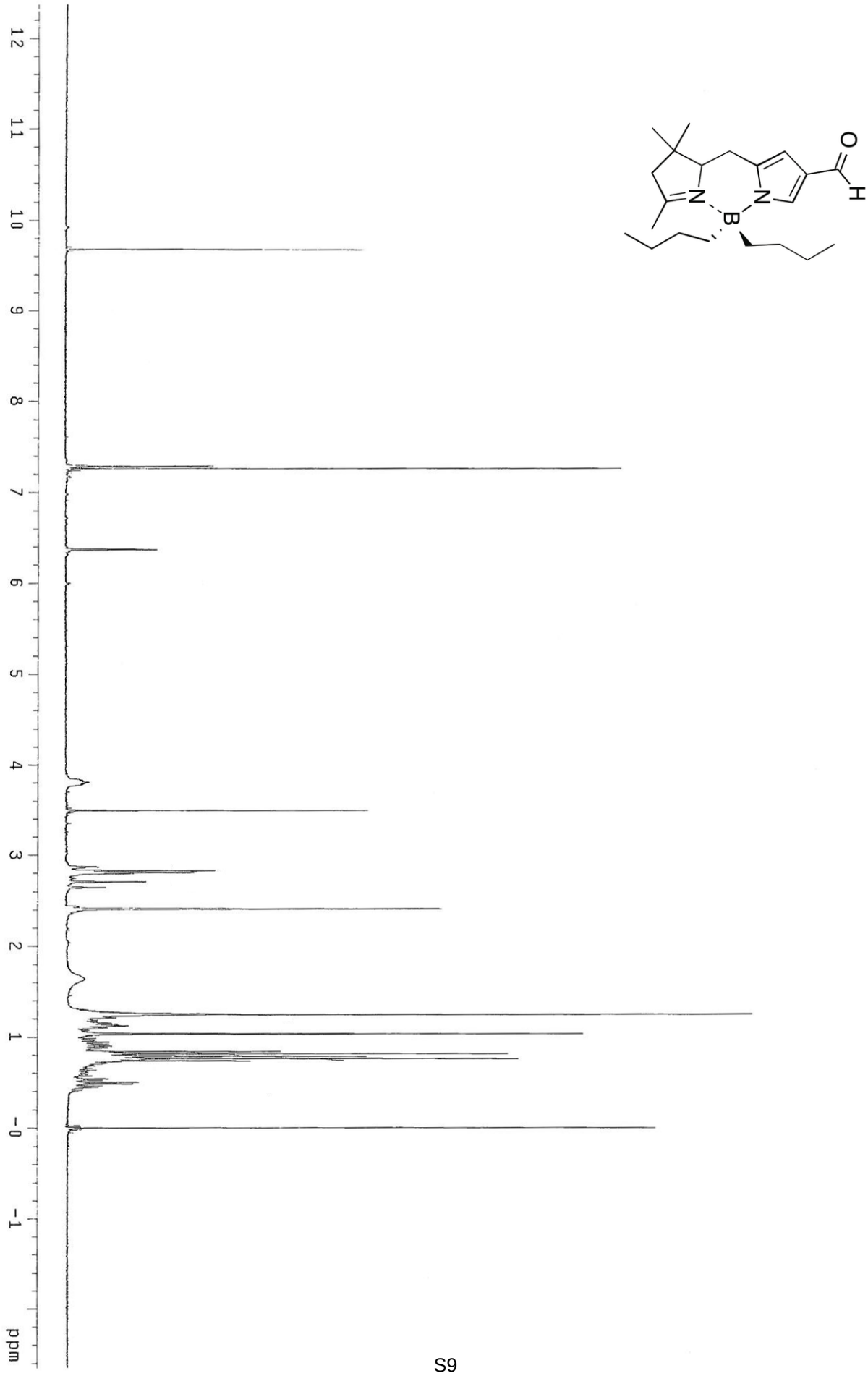

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

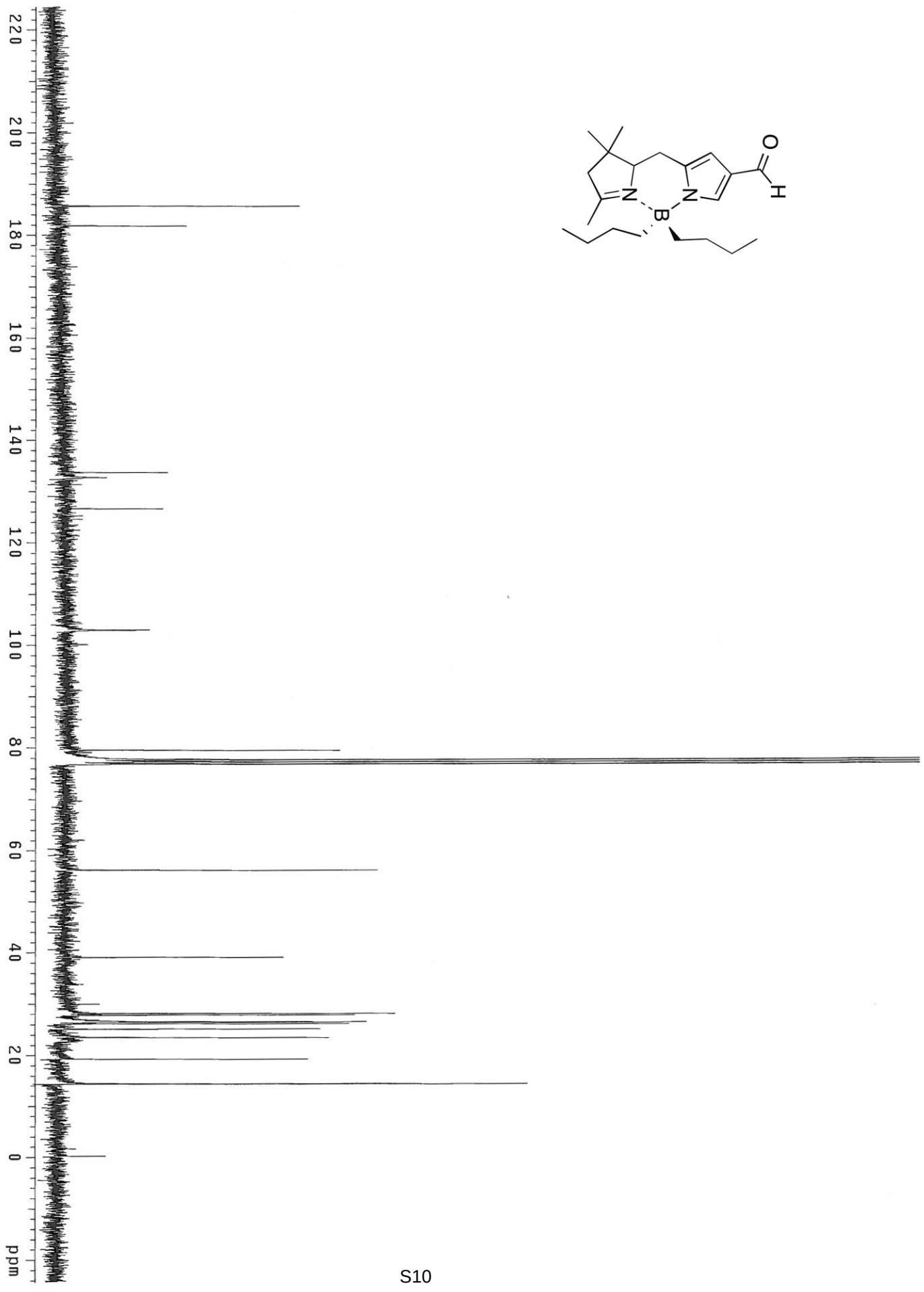
N
N
B

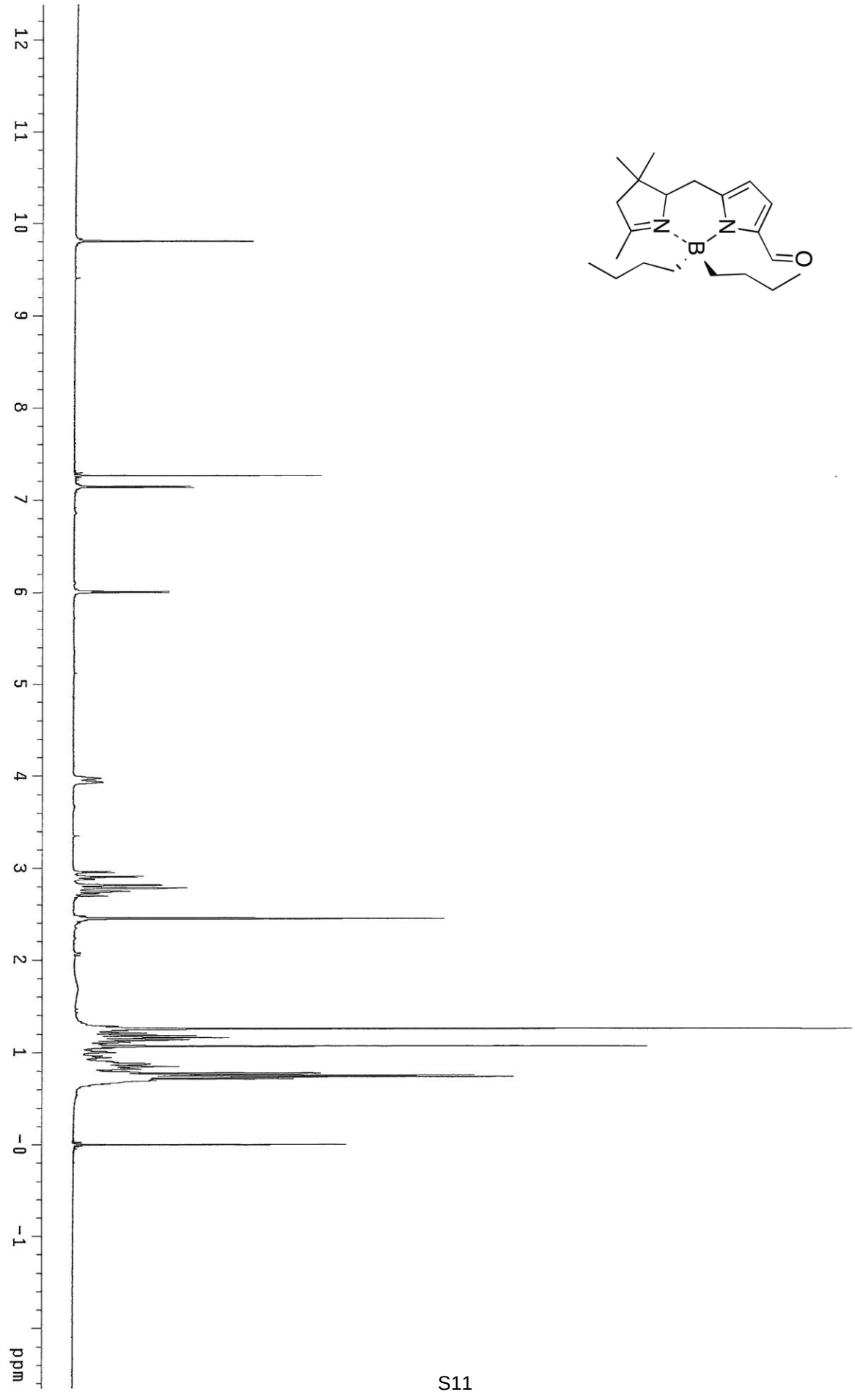

200
180
160
140
120
100
80
60
40
20
0
ppm
N
N
B

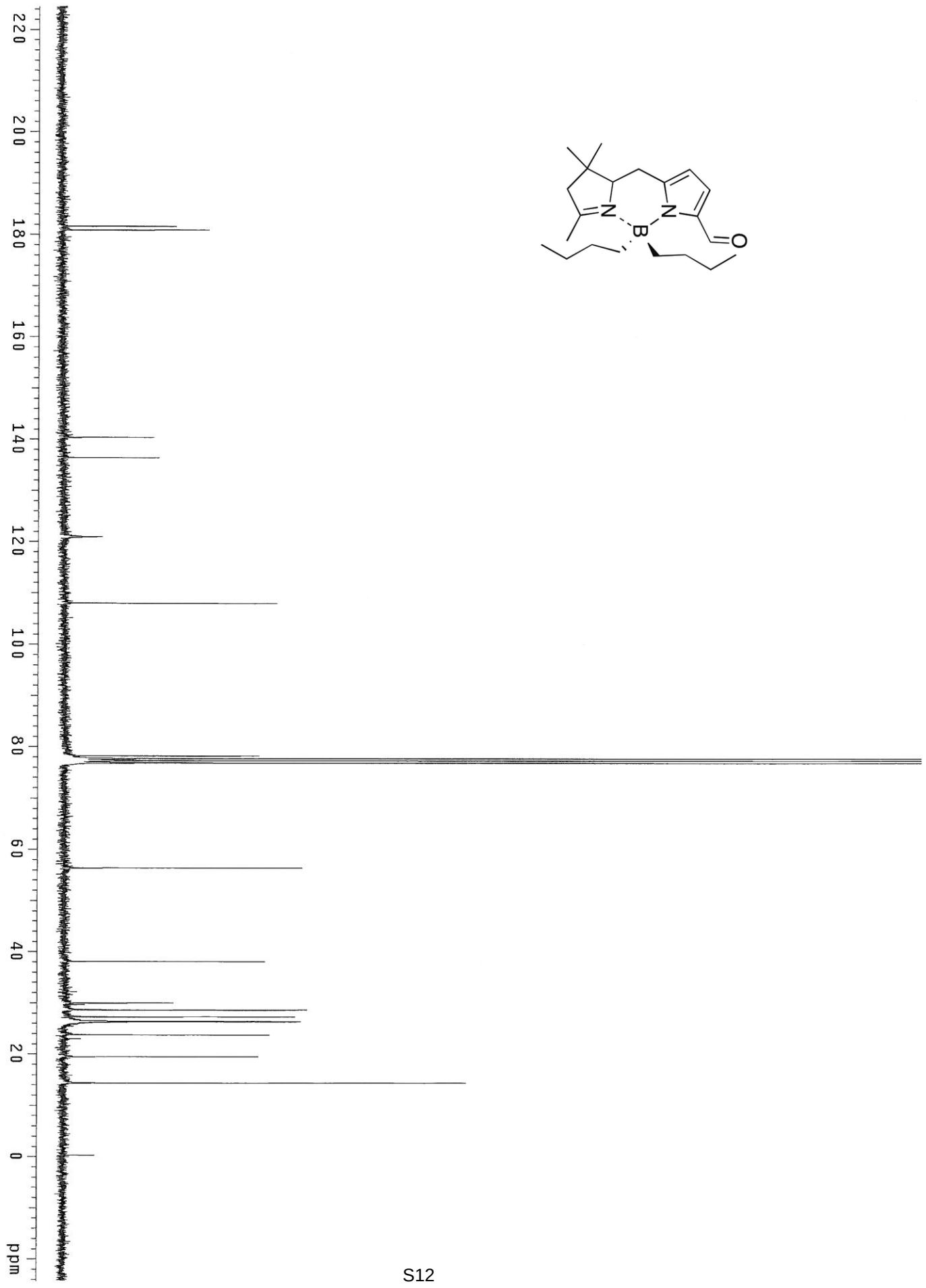

13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
O
H
N
N
B

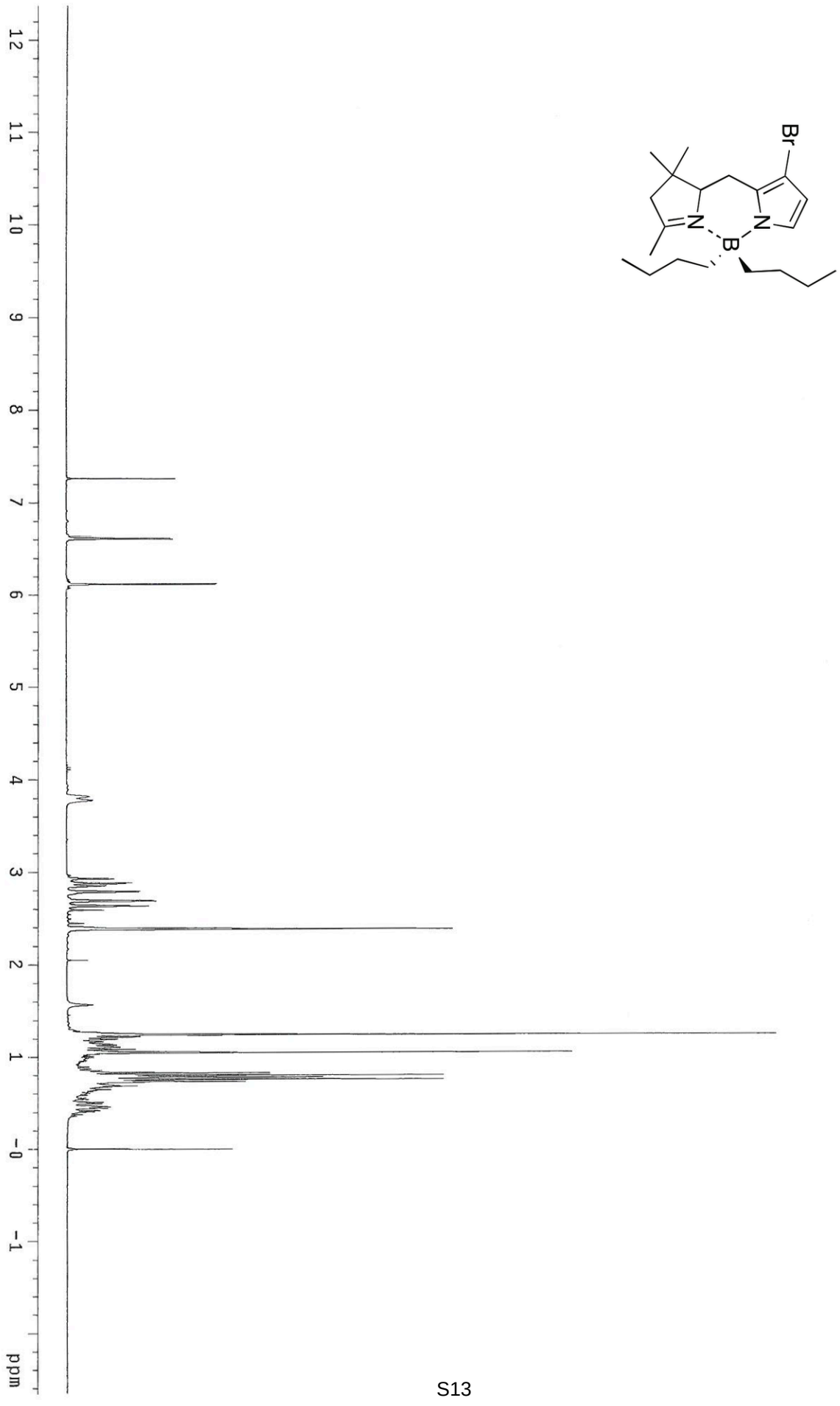

O
H
N
N
B
200
180
160
140
120
100
80
60
40
20
0
ppm

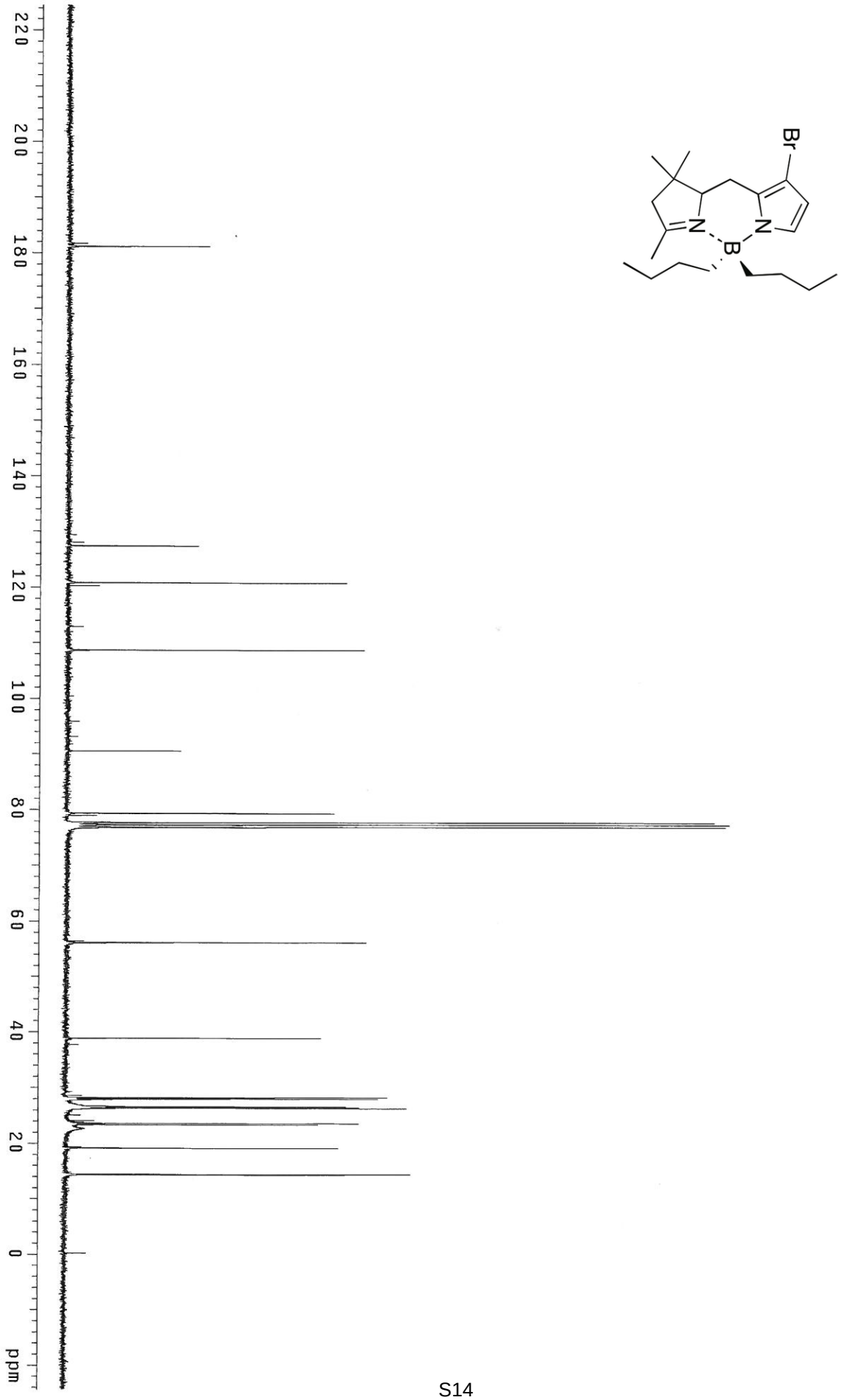

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
O
H
N
N
B

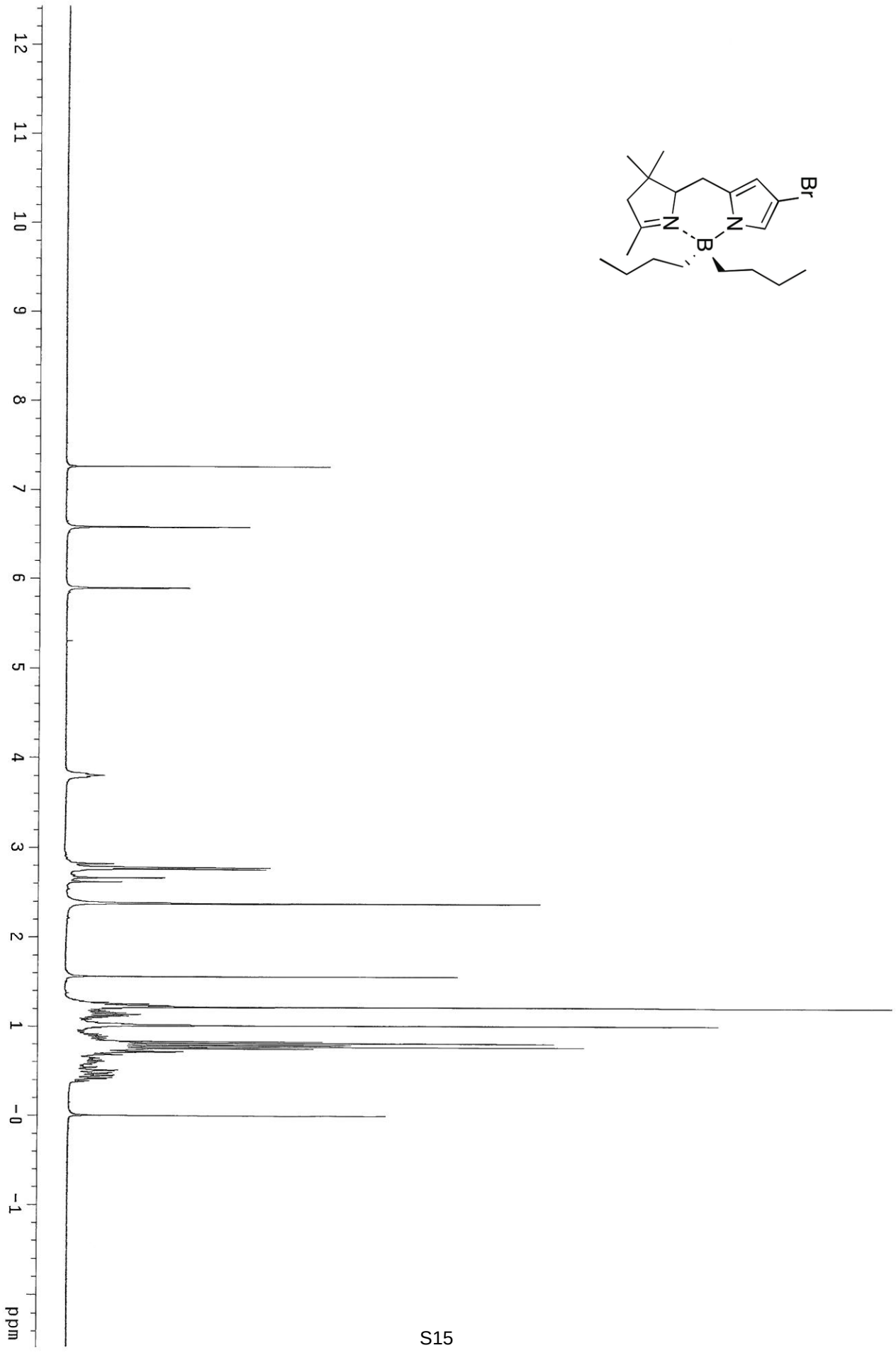

220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
H
N
N
B

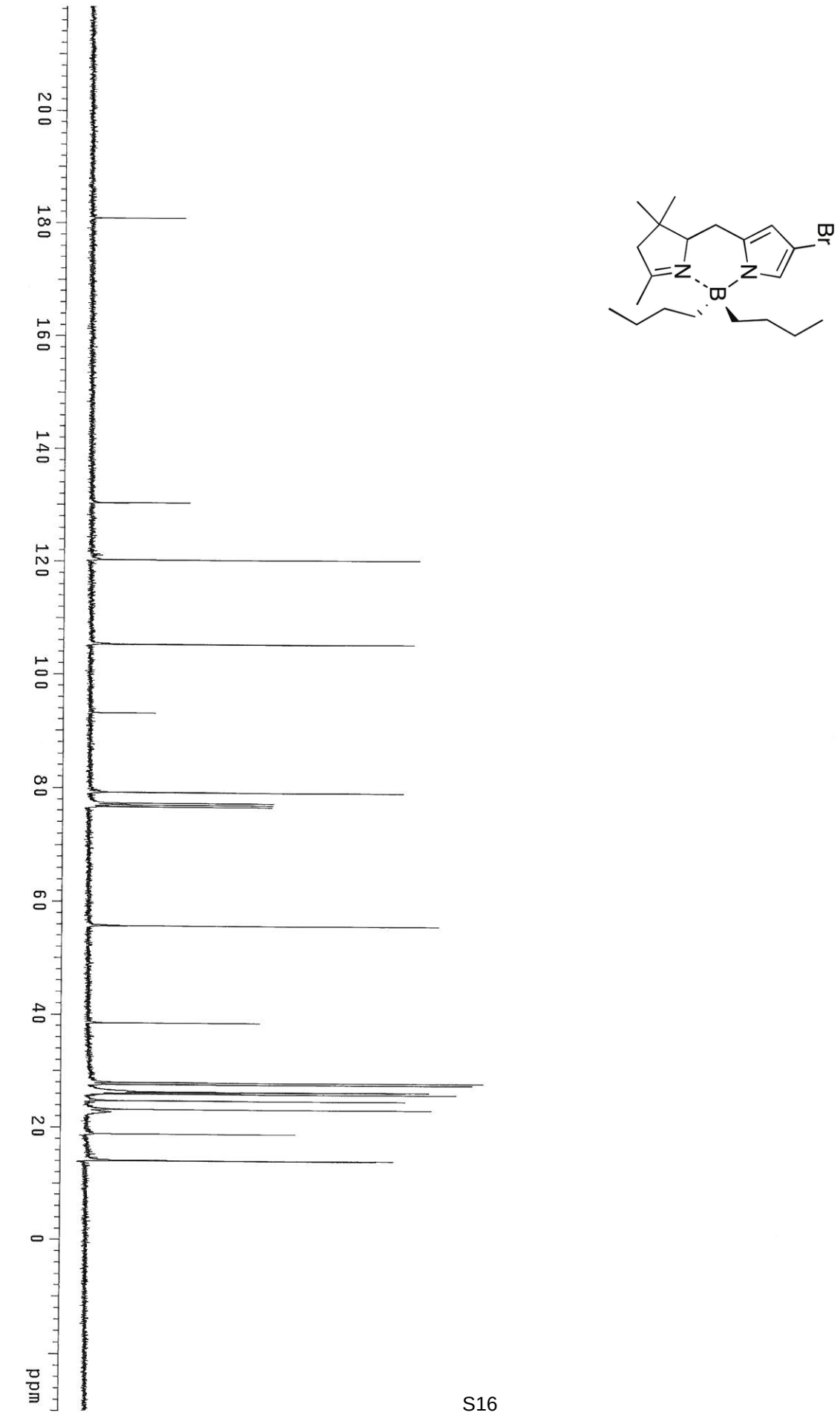

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
N
N
B
O


220
200
180
160
140
120
100
80
60
40
20
0
ppm
N
N
B
O

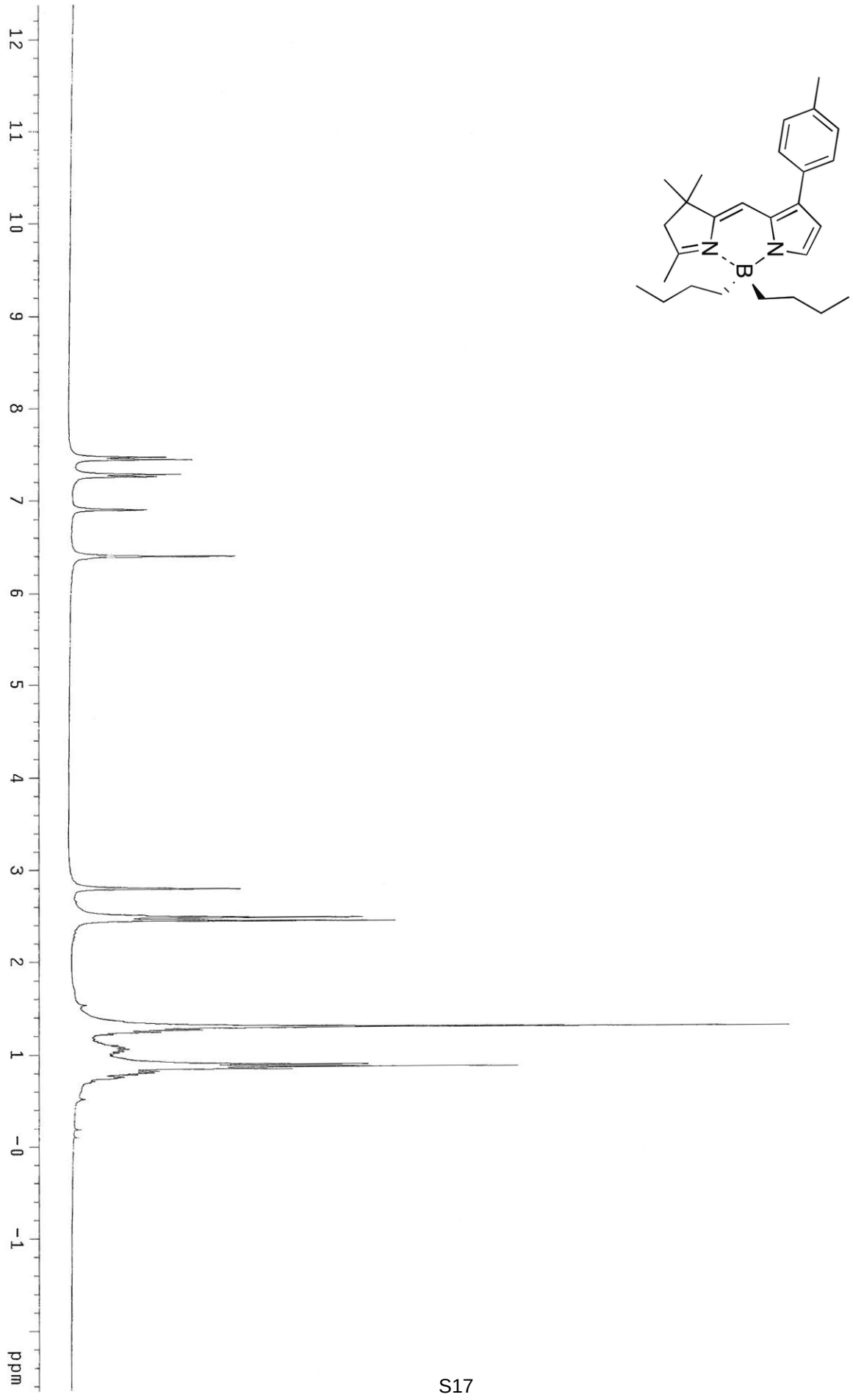

Br
N
N
B
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

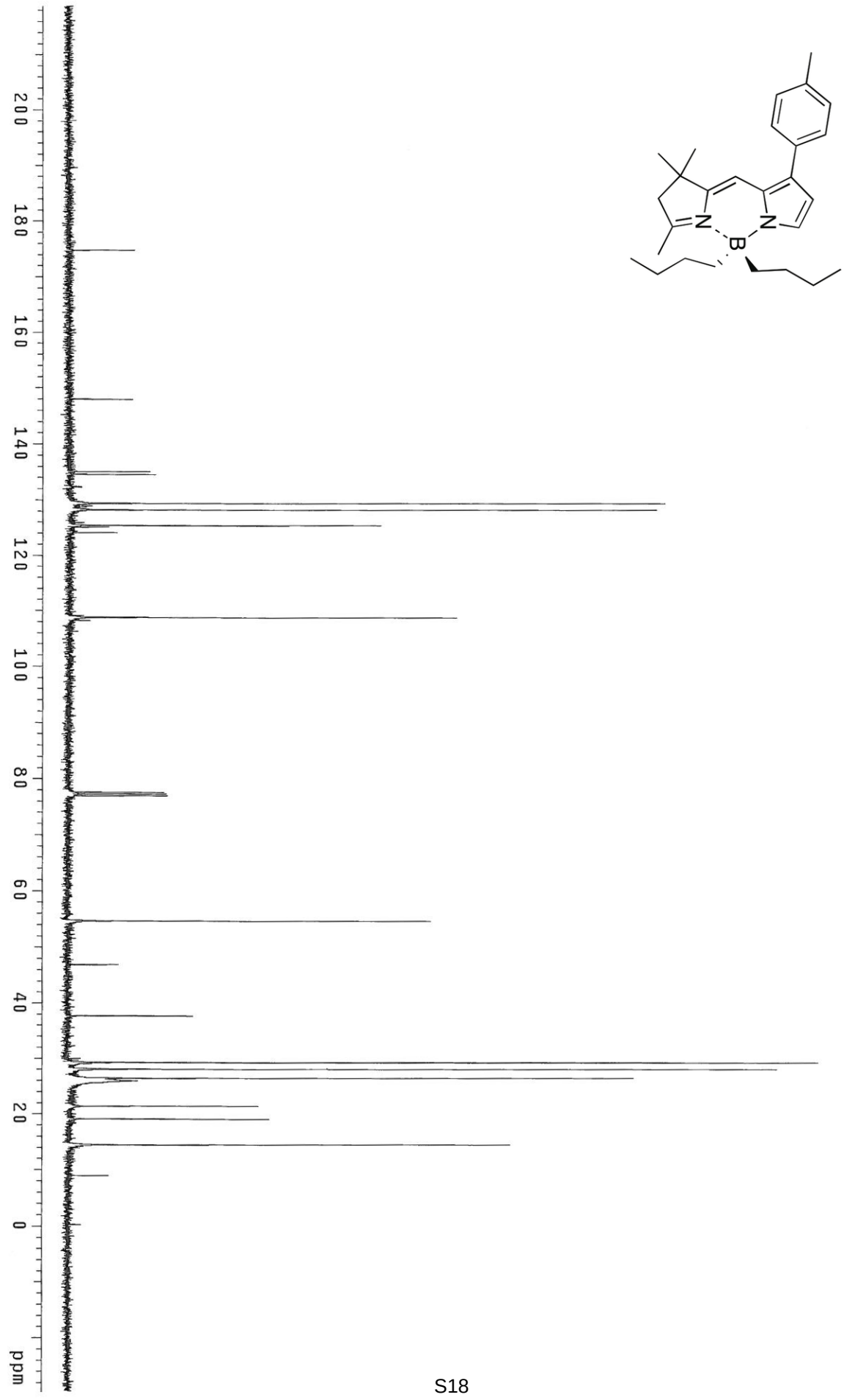

Br
N
N
B
220
200
180
160
140
120
100
80
60
40
20
0
ppm

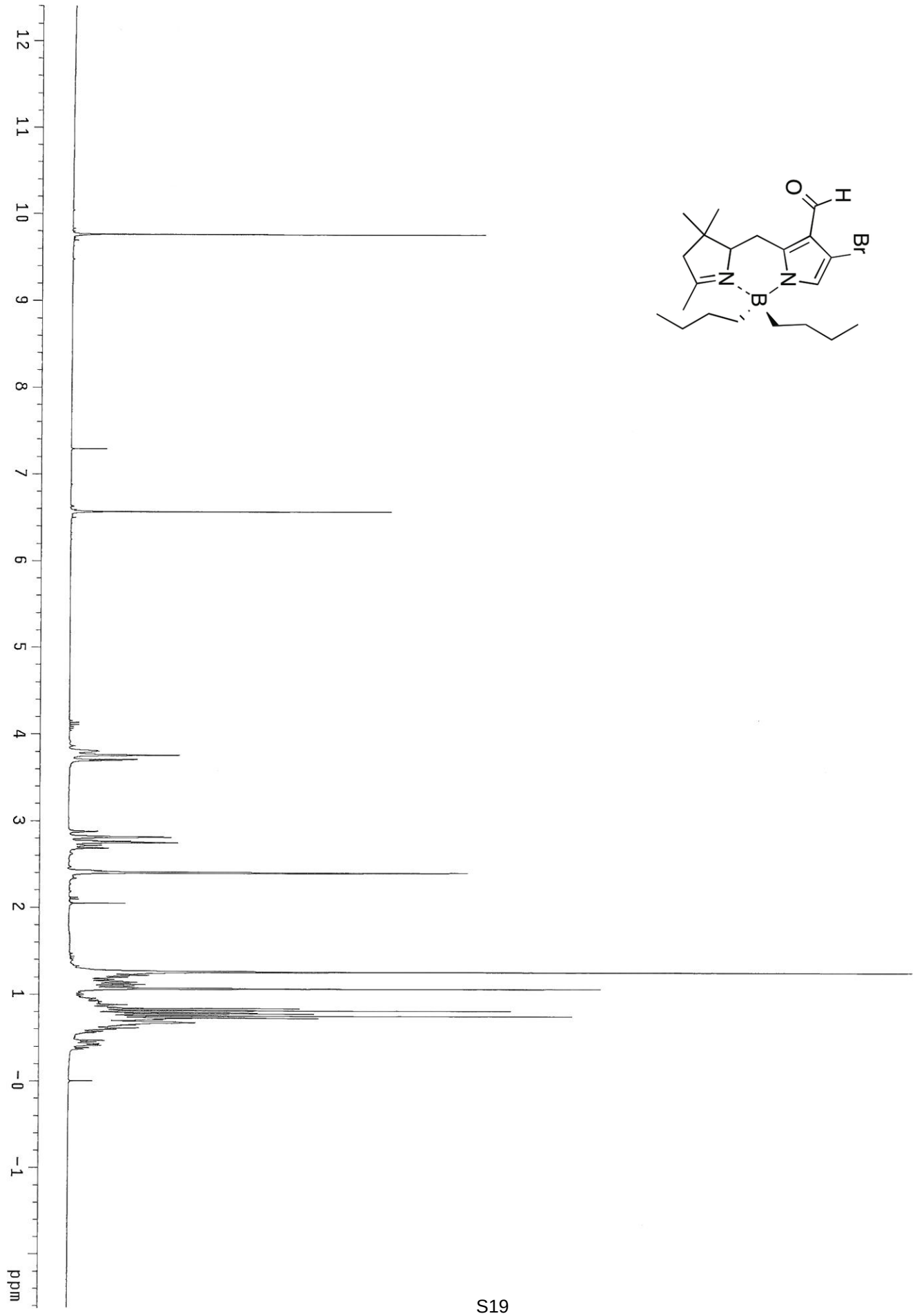

Br
N
N
B
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


200
180
160
140
120
100
80
60
40
20
0
ppm

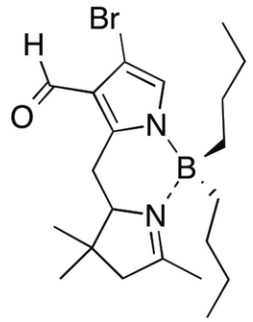
Br
N
N
B

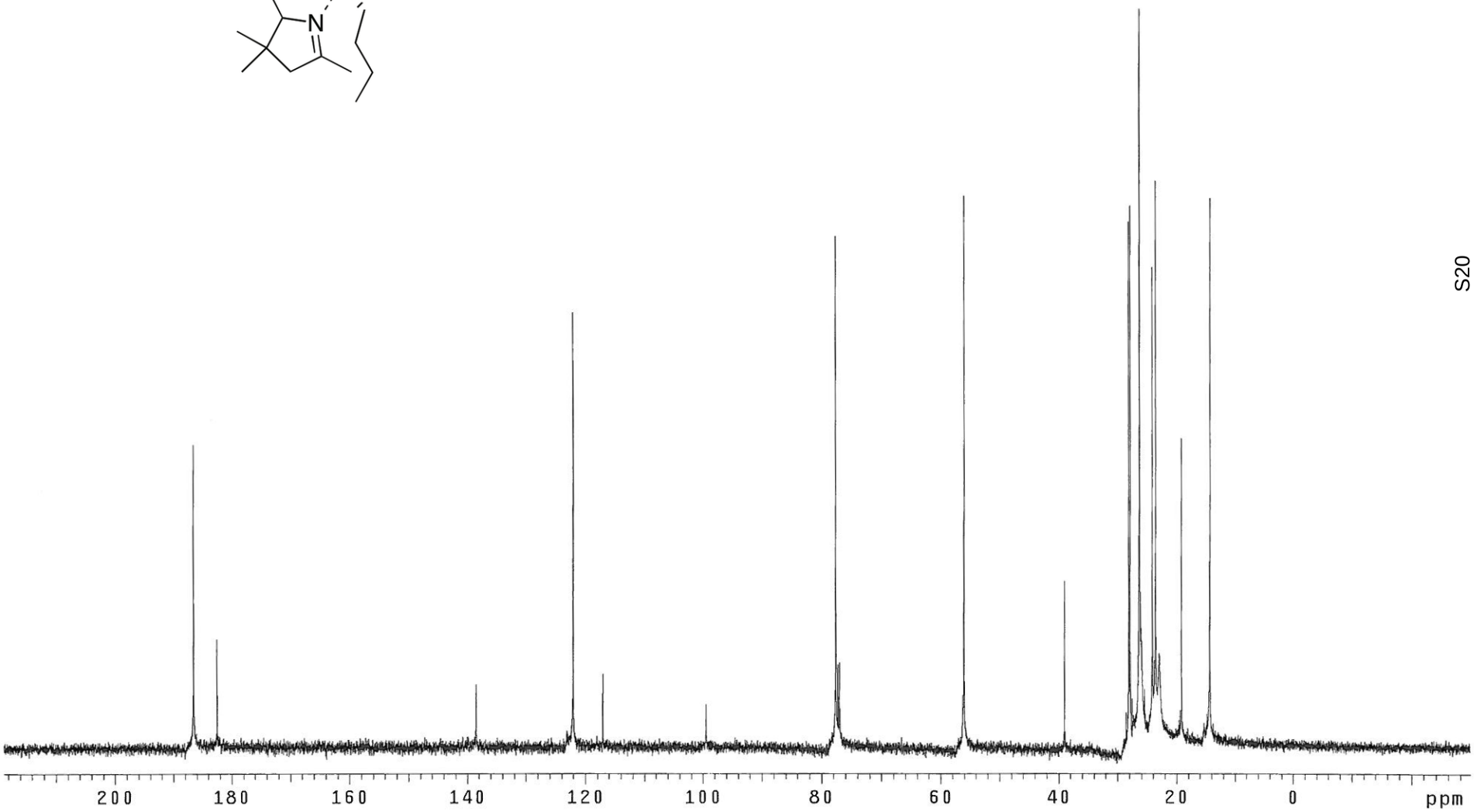

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
N
N
B

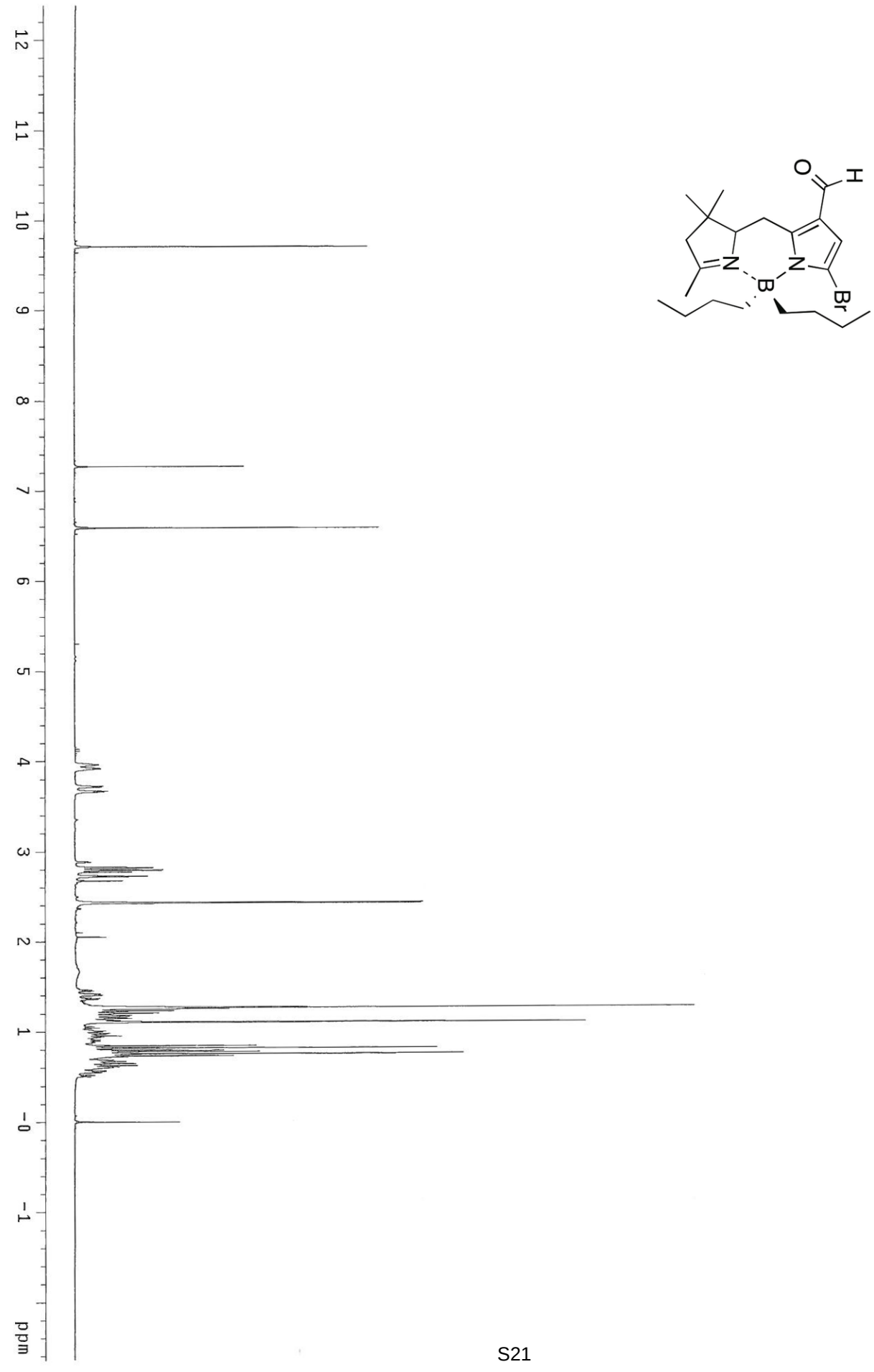

200
180
160
140
120
100
80
60
40
20
0
ppm
N
N
B

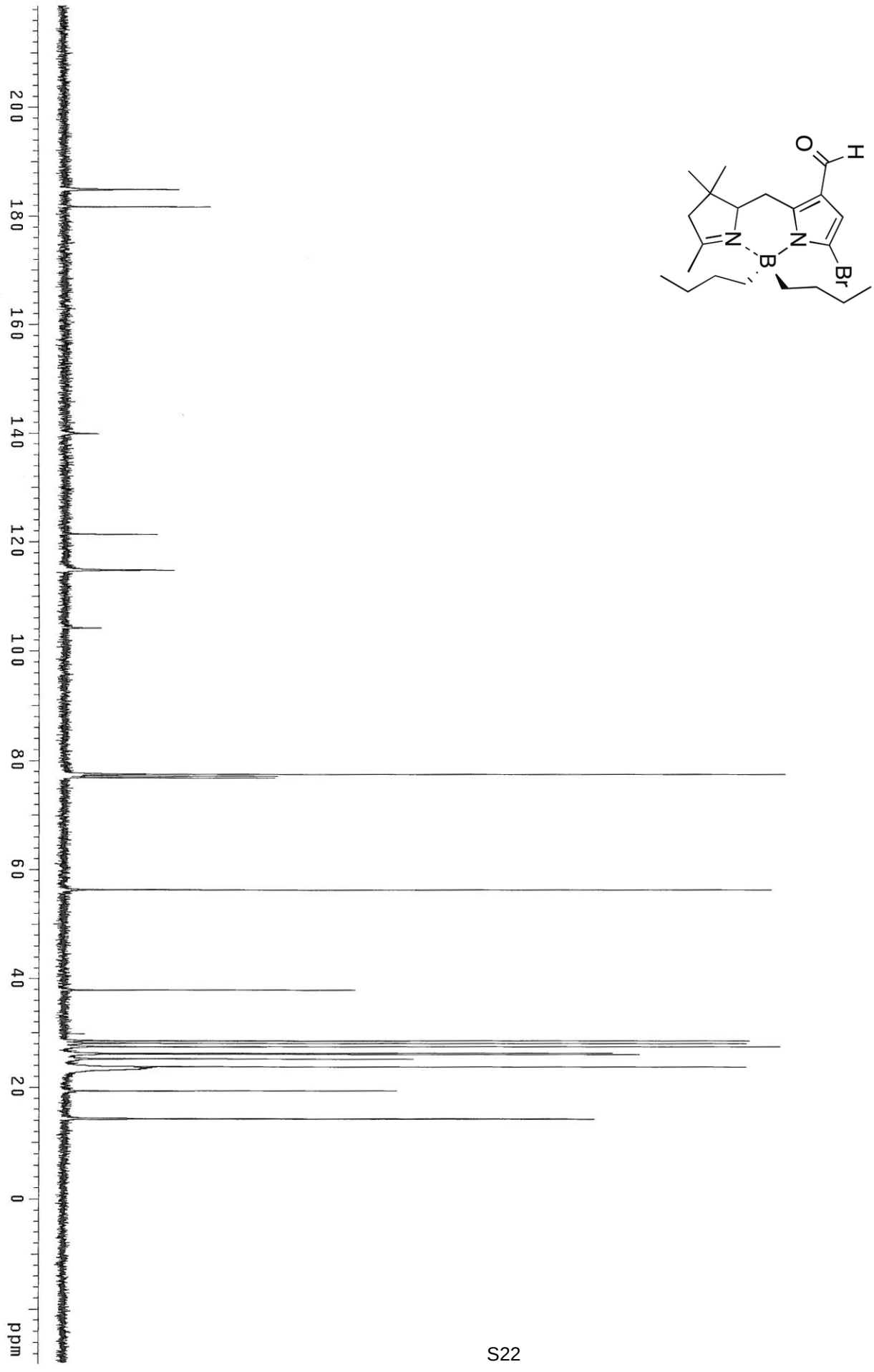

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

O
H
Br
N
N
B

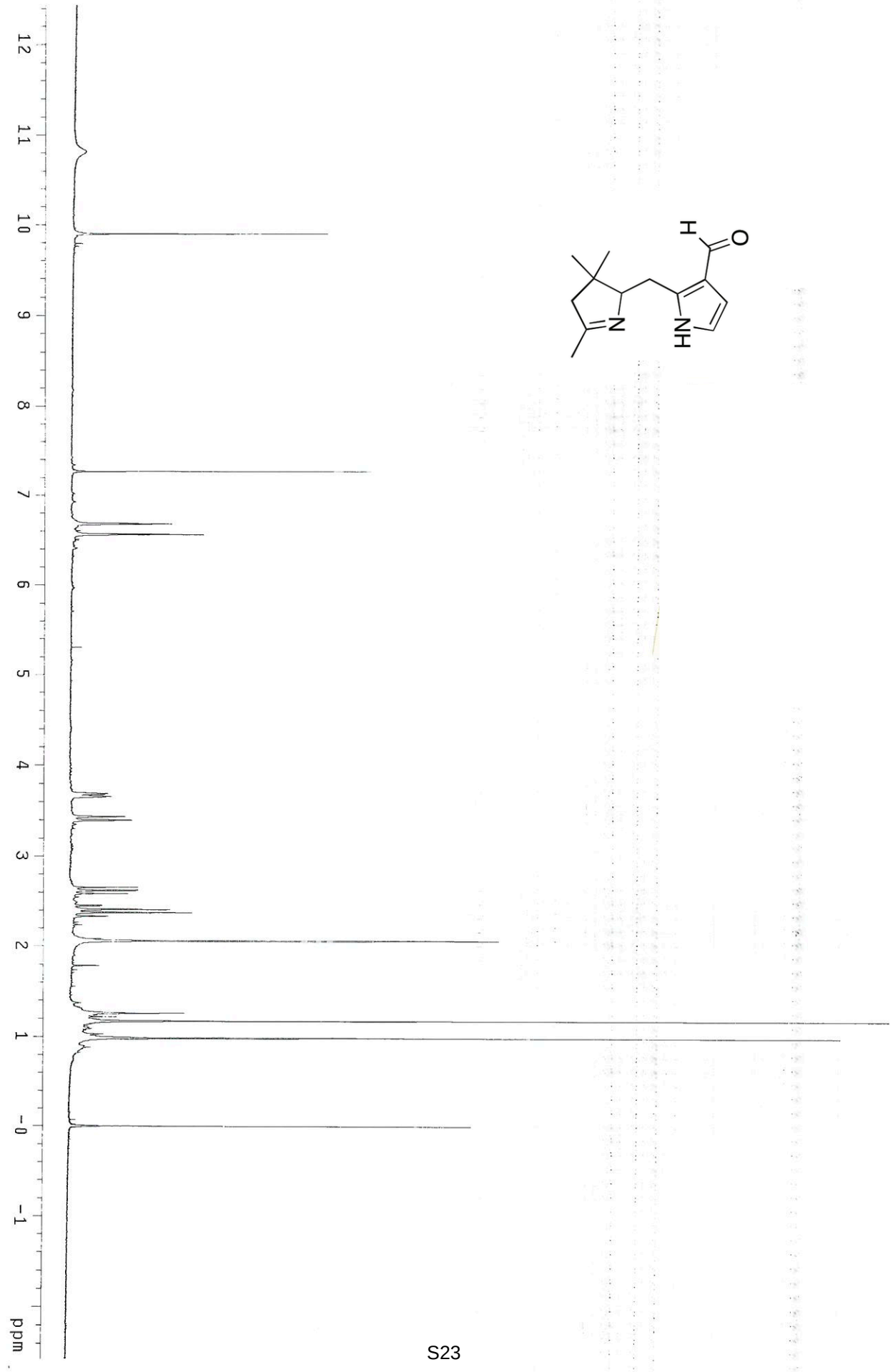

Br
H
O
N
B
N

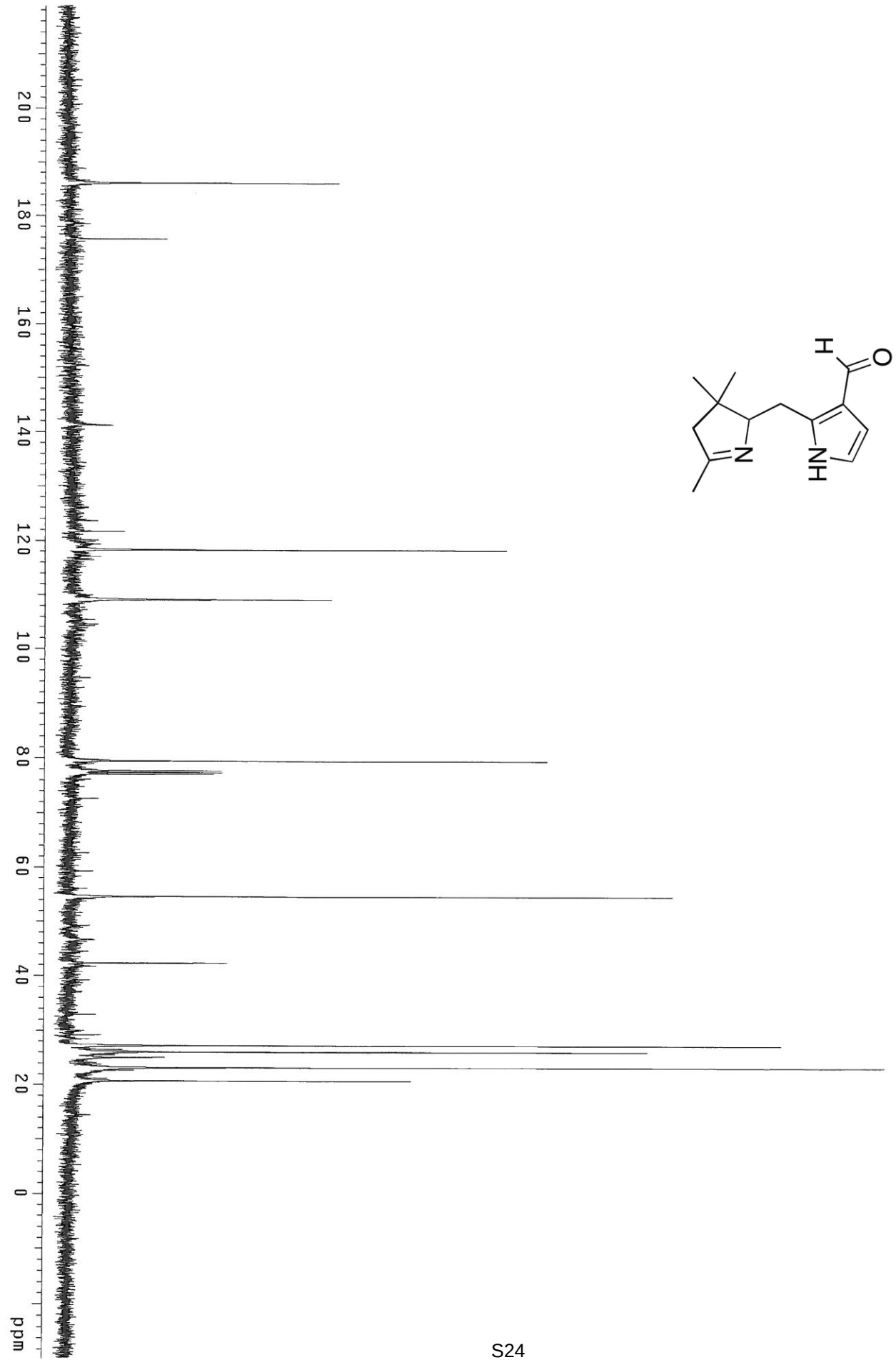

200
180
160
140
120
100
80
60
40
20
0
ppm

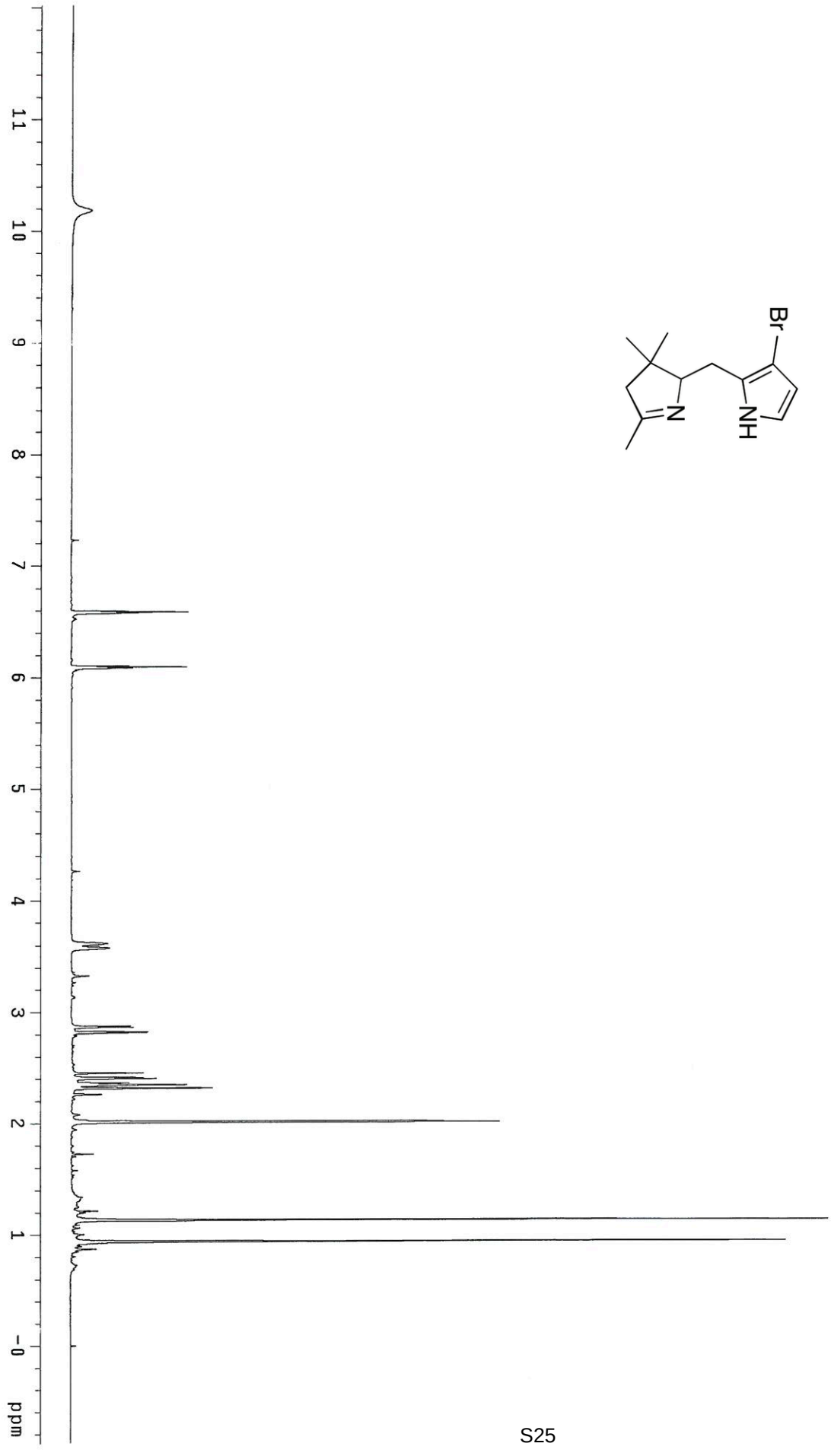

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
O
H
N
N
B
Br

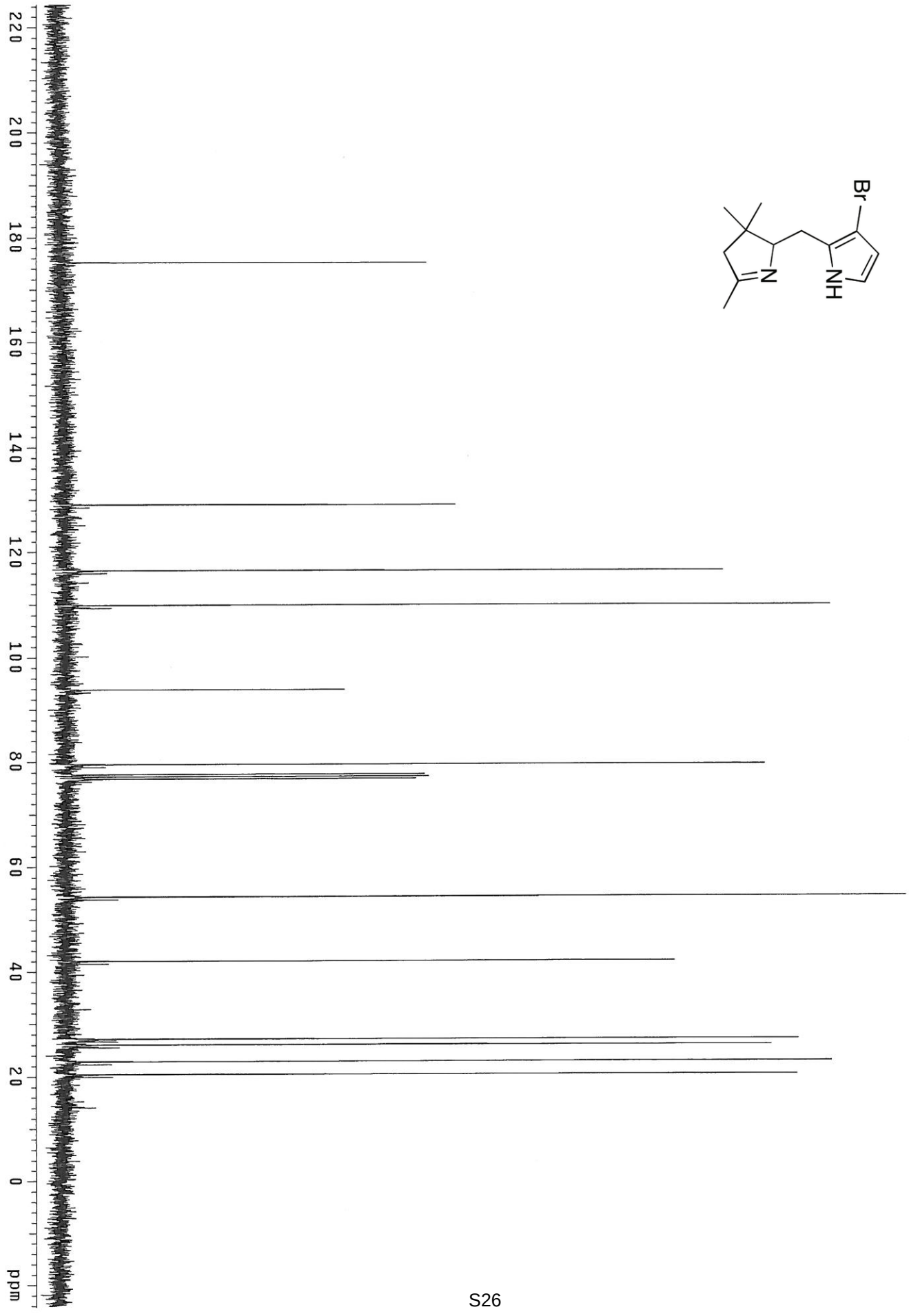

200
180
160
140
120
100
80
60
40
20
0
ppm

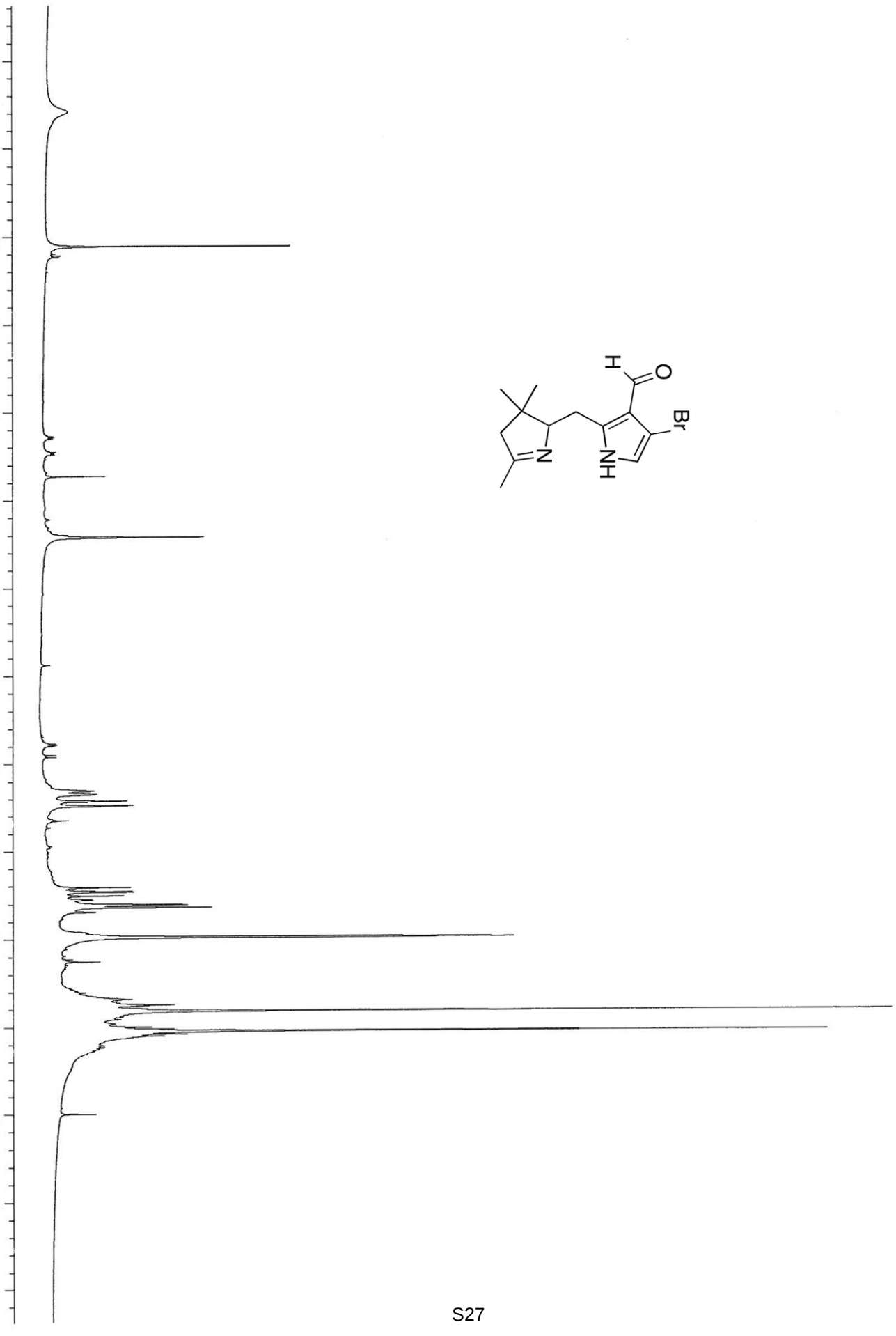
O
H
N
N
B
Br

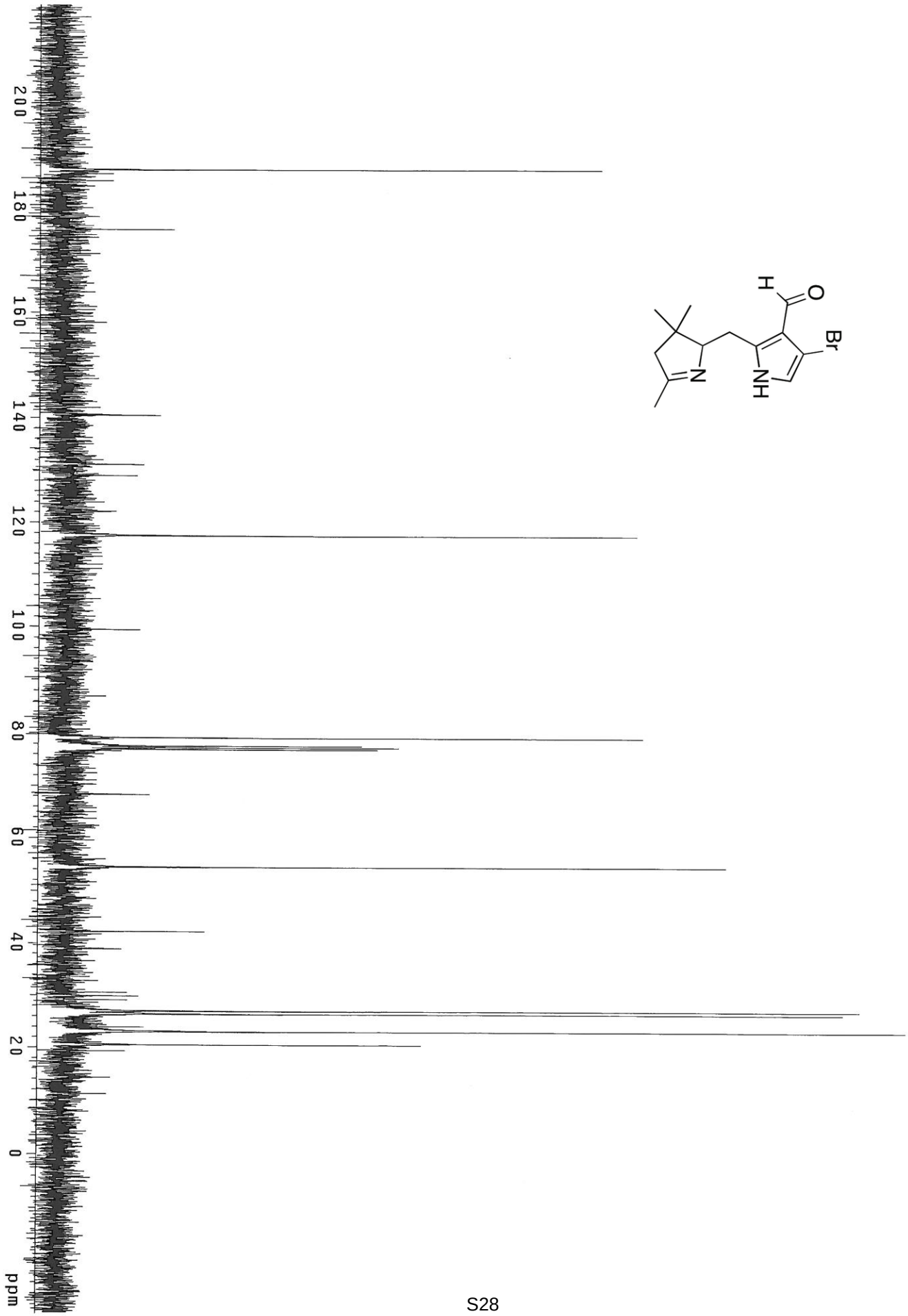

12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
O
H
N
NH

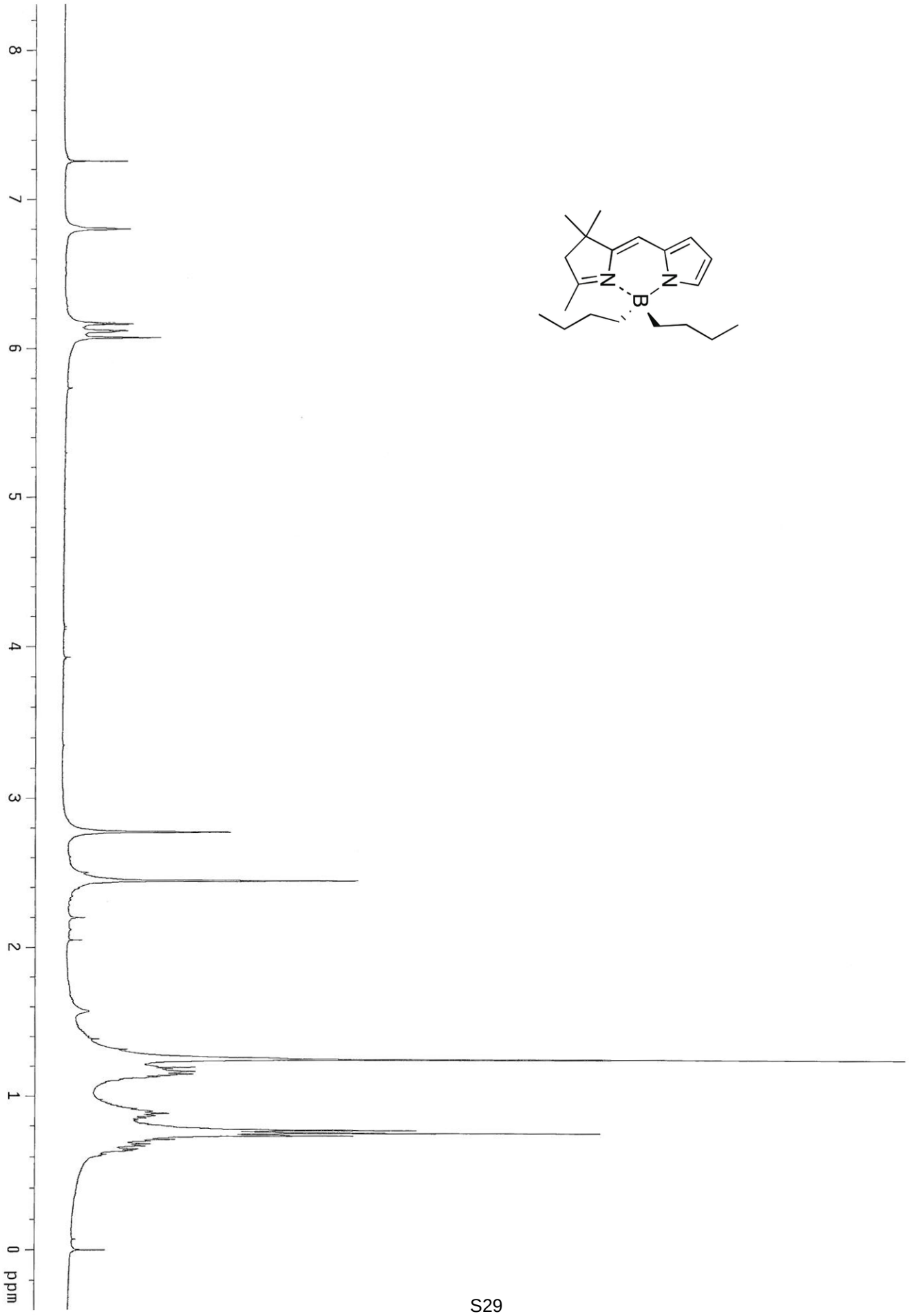

200
180
160
140
120
100
80
60
40
20
0
ppm
H
O
N
NH


11
10
9
8
7
6
5
4
3
2
1
−0
ppm
Br
N
NH

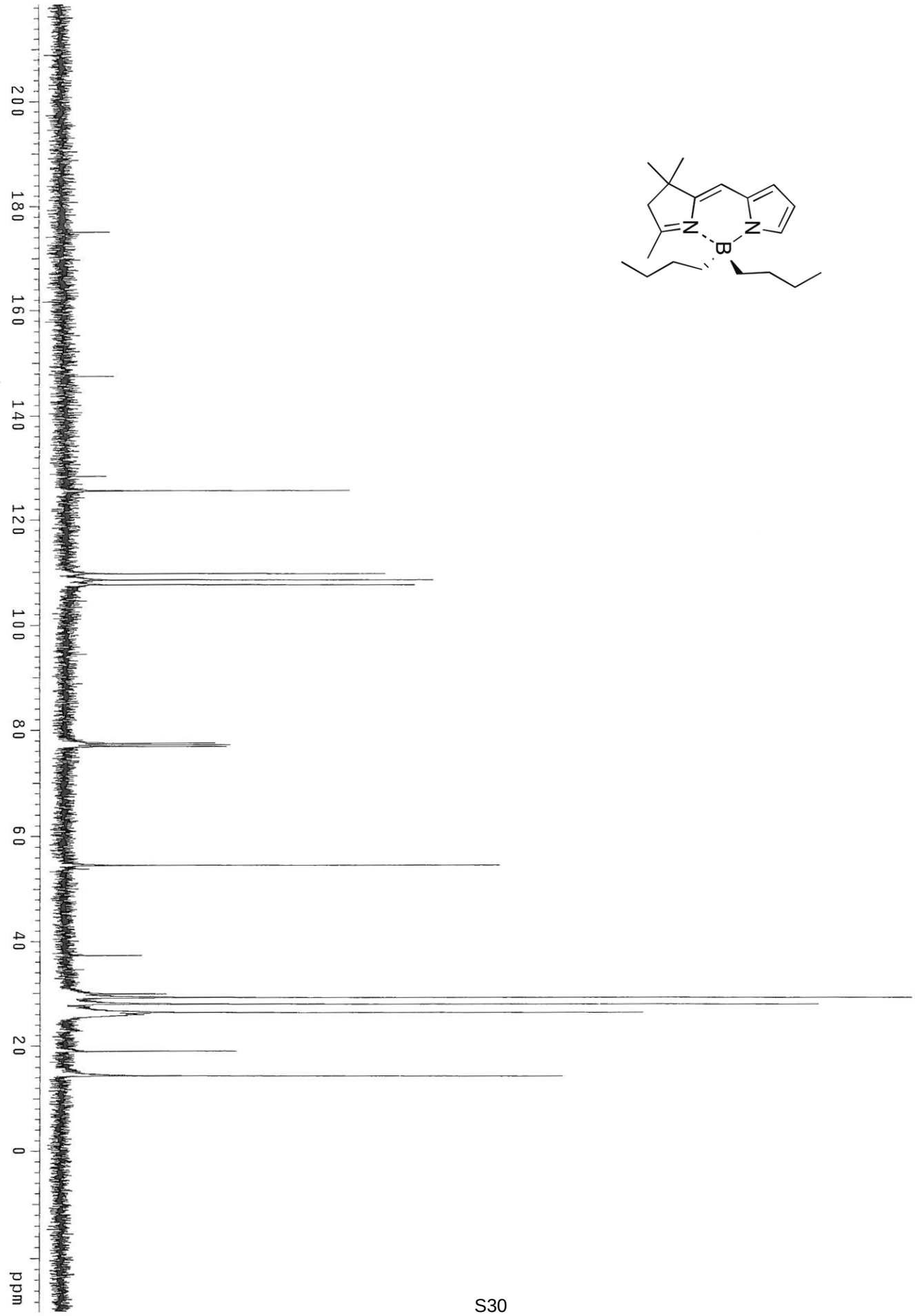

220
200
180
160
140
120
100
80
60
40
20
0
ppm
Br
N
NH


12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
H
O
Br
N
NH

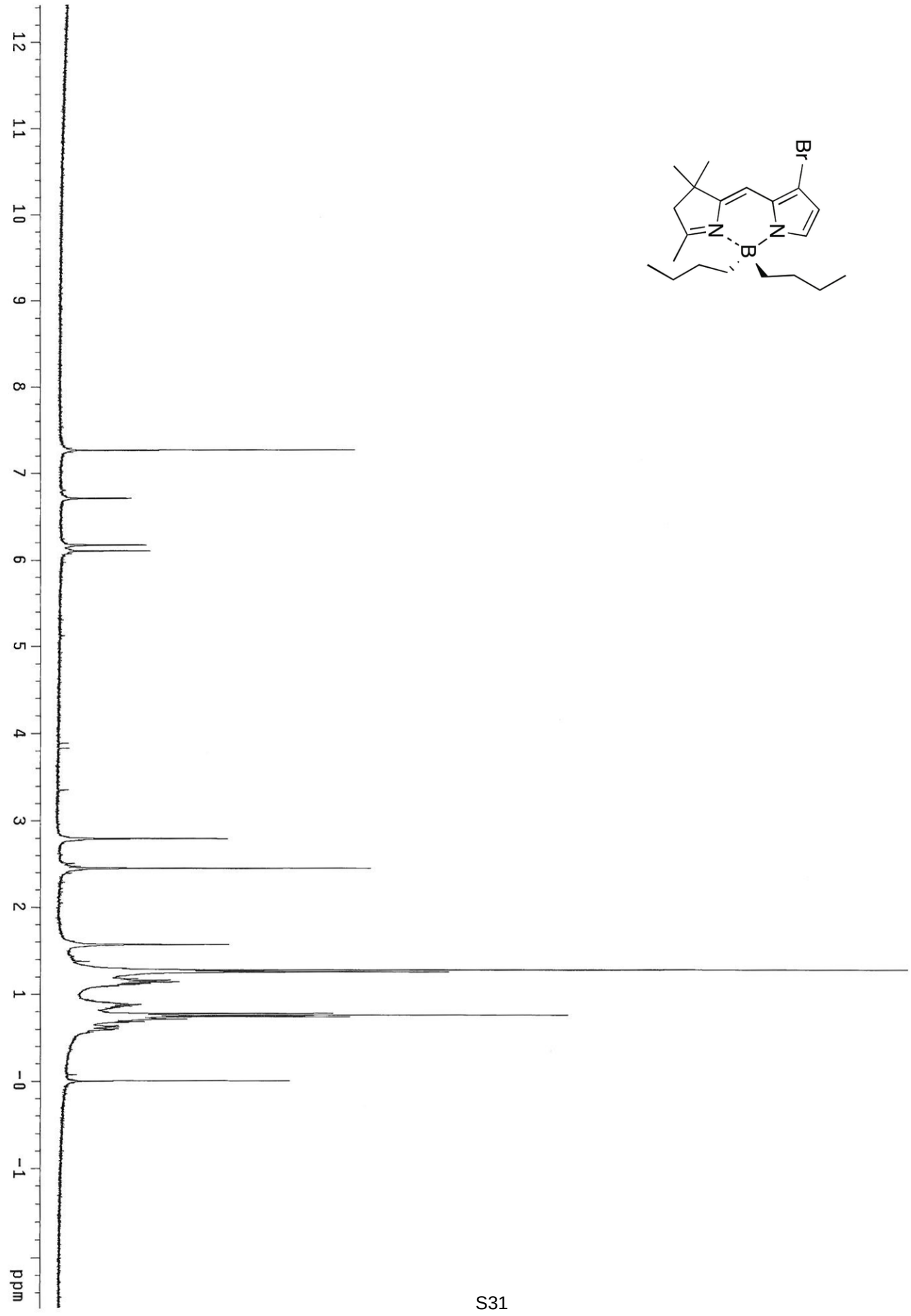

200
180
160
140
120
100
80
60
40
20
0
ppm
H
O
Br
N
NH

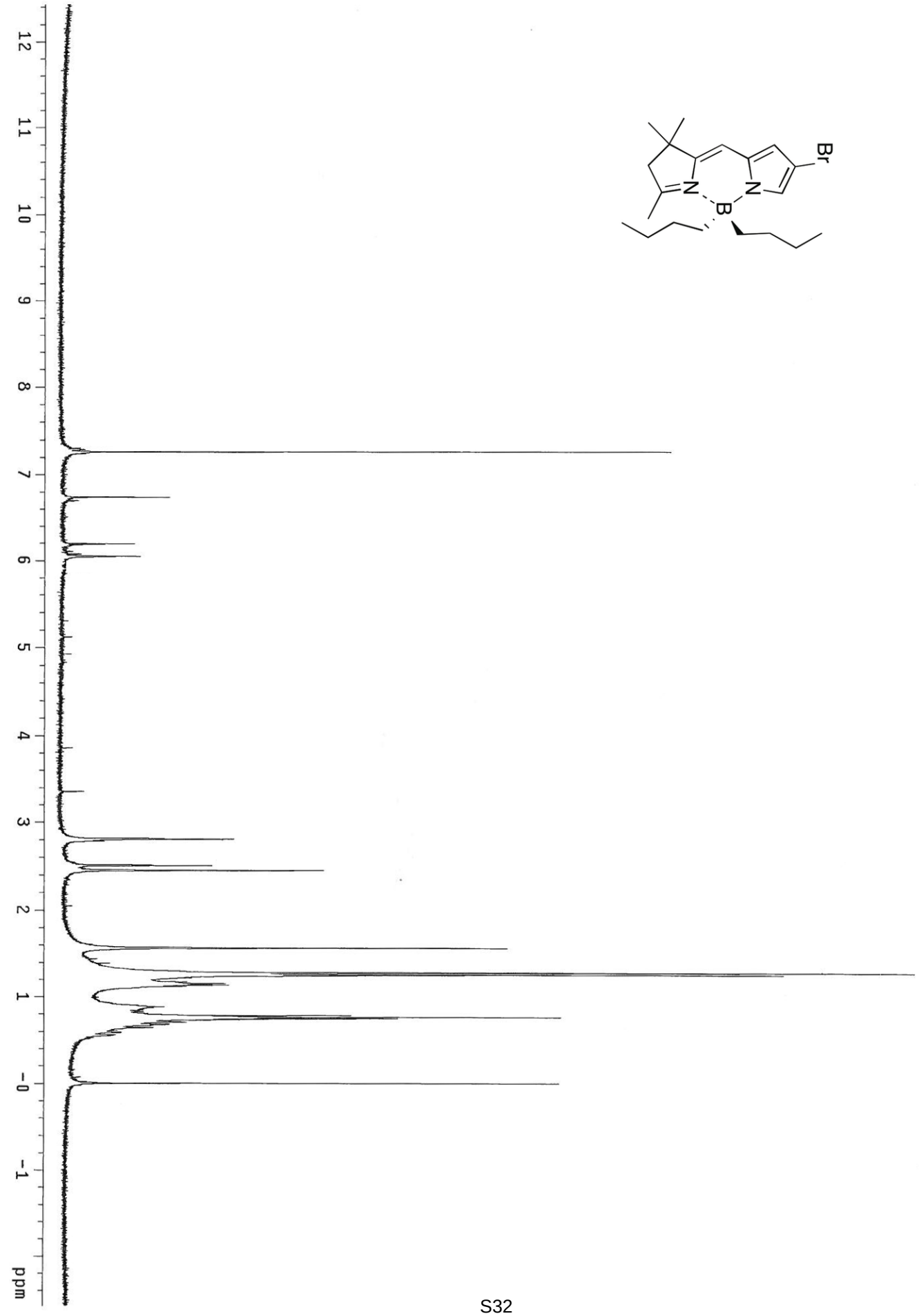

8
7
6
5
4
3
2
1
0
ppm

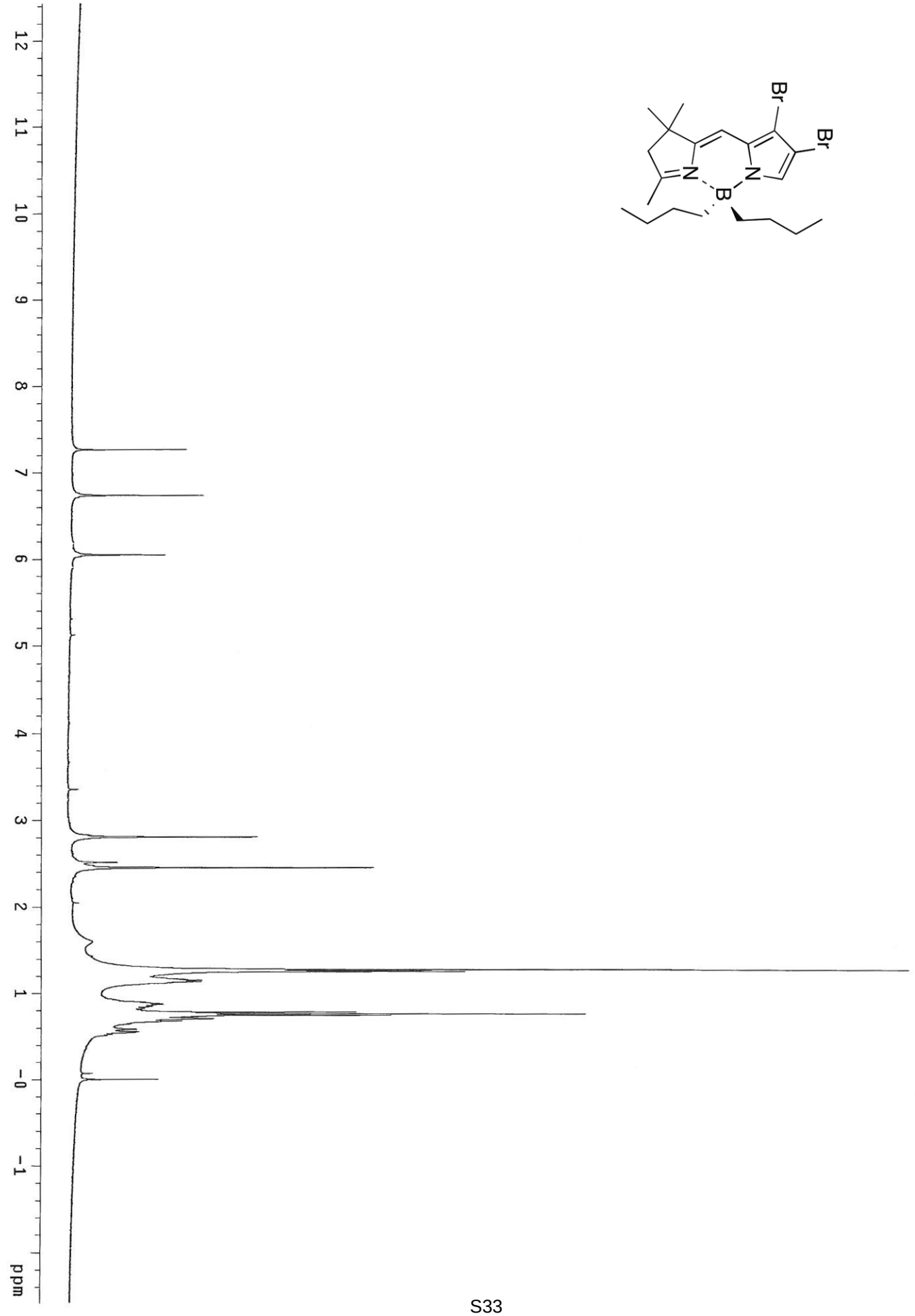
N
B
N

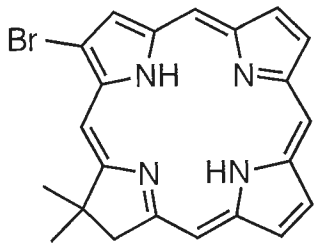

200
180
160
140
120
100
80
60
40
20
0
ppm

N
N
B

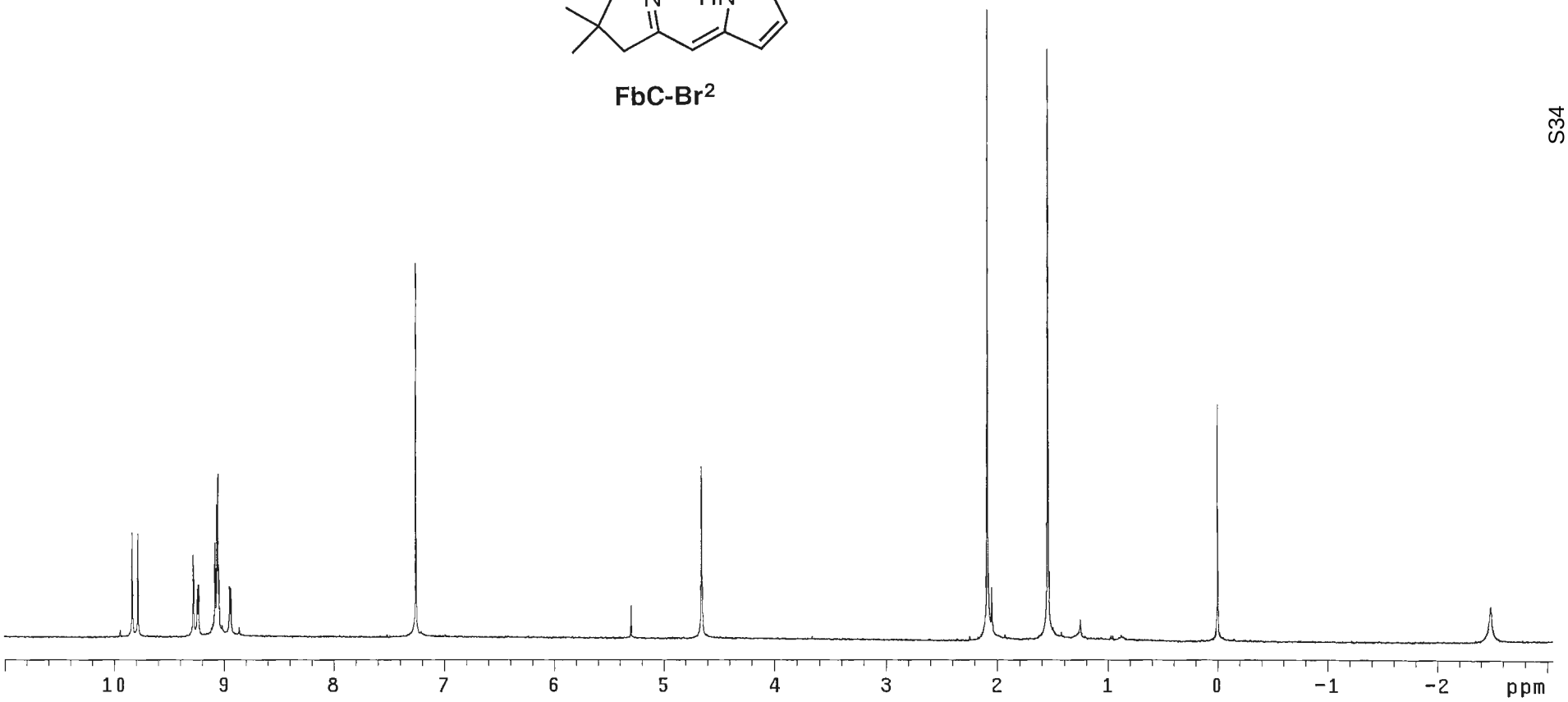

Br
N
N
B
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


Br
N
N
B
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

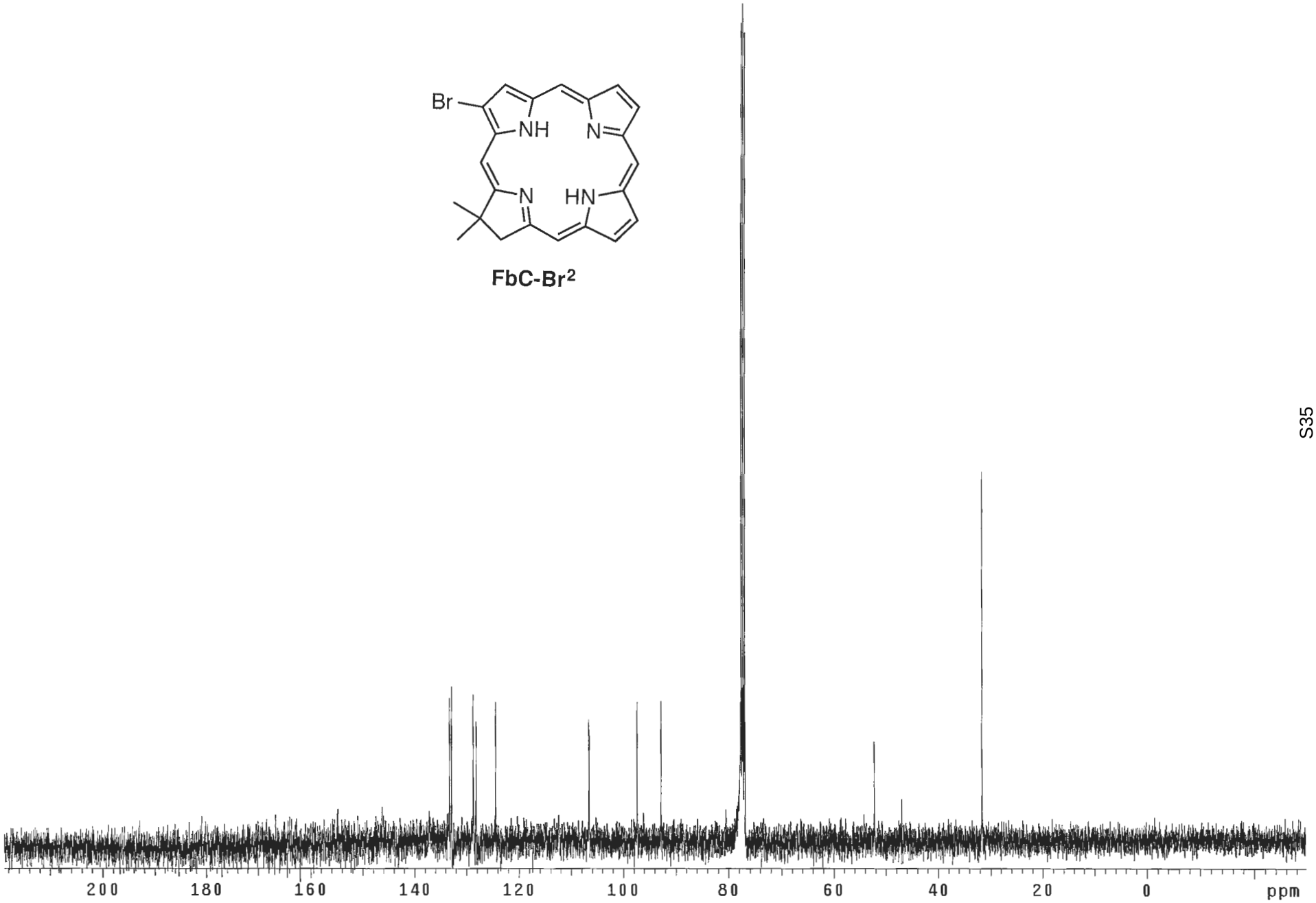

Br
Br
N
N
B
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm



FbC-Br^2

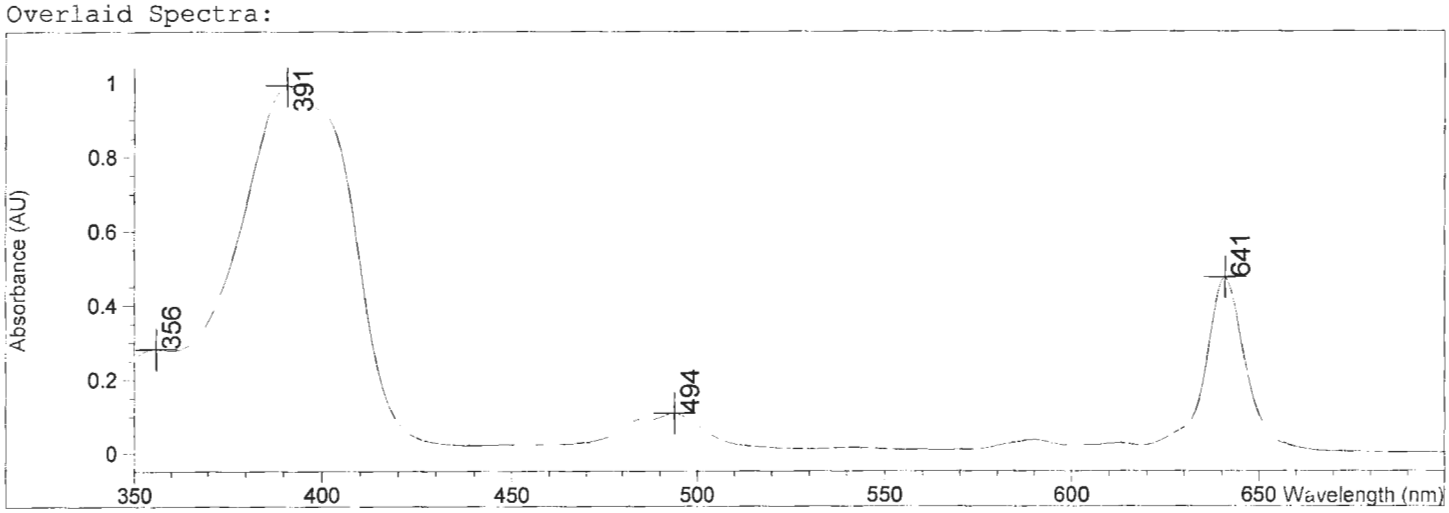


FbC-Br^2

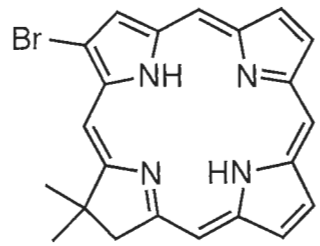


Method file : <untitled>
Information : Default Method
Data File : C:\Chem32\1\DATA\Mengran Liu\070513_2BRFBC_TOLUENE_2.SD Created : 7/5/13 10:34:20

Overlaid Spectra:



#	Name	Peaks(nm)	Abs(AU)
1		391.0	0.99278
1		641.0	0.47497
1		356.0	0.28198
1		494.0	0.10805

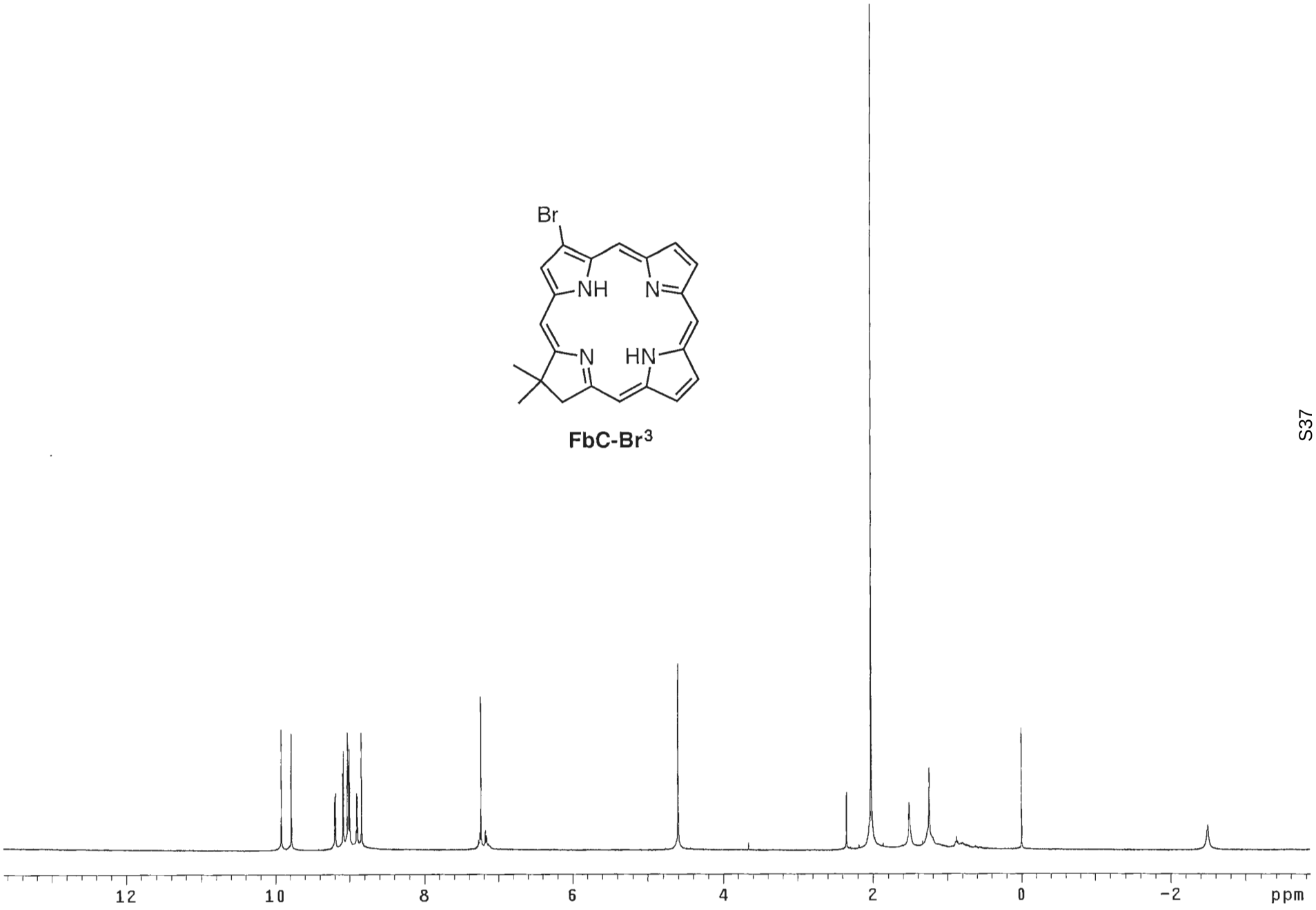


FbC-Br^2

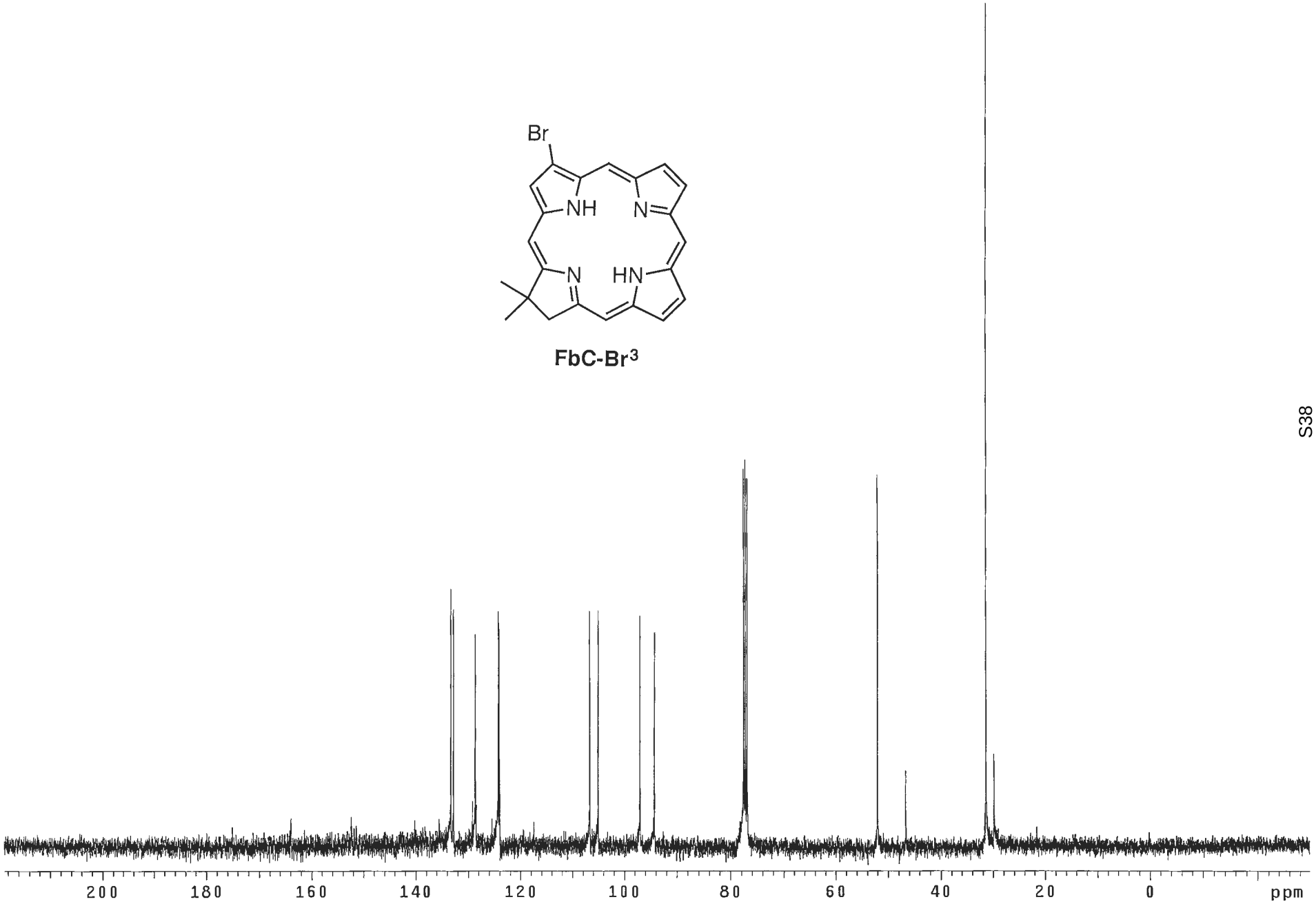
Report generated by : Lindsey Lab

*** End Spectrum/Peak Report ***

FbC-Br[3]

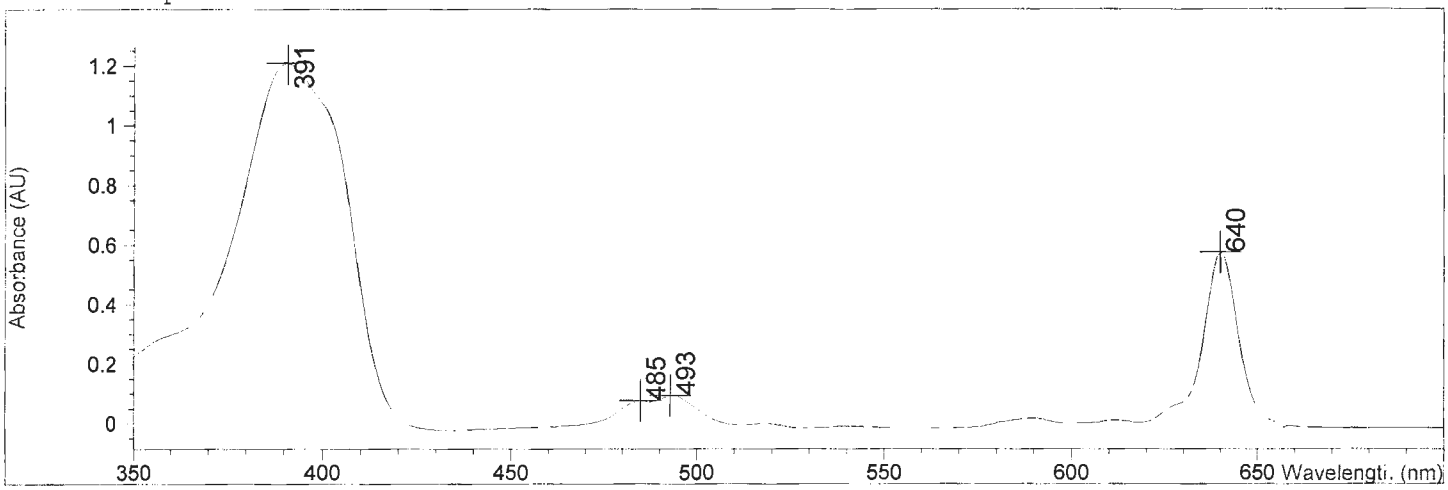


FbC-Br^3

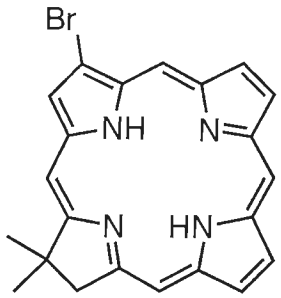


Method file : <untitled>
Information : Default Method
Data File : C:\Chem32\1\DATA\Mengran Liu\070513_3BRFBC_TOLUENE_2.SD Created : 7/5/13 10:41:19

Overlaid Spectra:



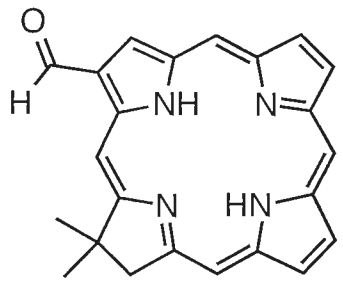
#	Name	Peaks(nm)	Abs(AU)
1		391.0	1.21000
1		640.0	0.57511
1		493.0	9.3338E-2
1		485.0	7.6340E-2



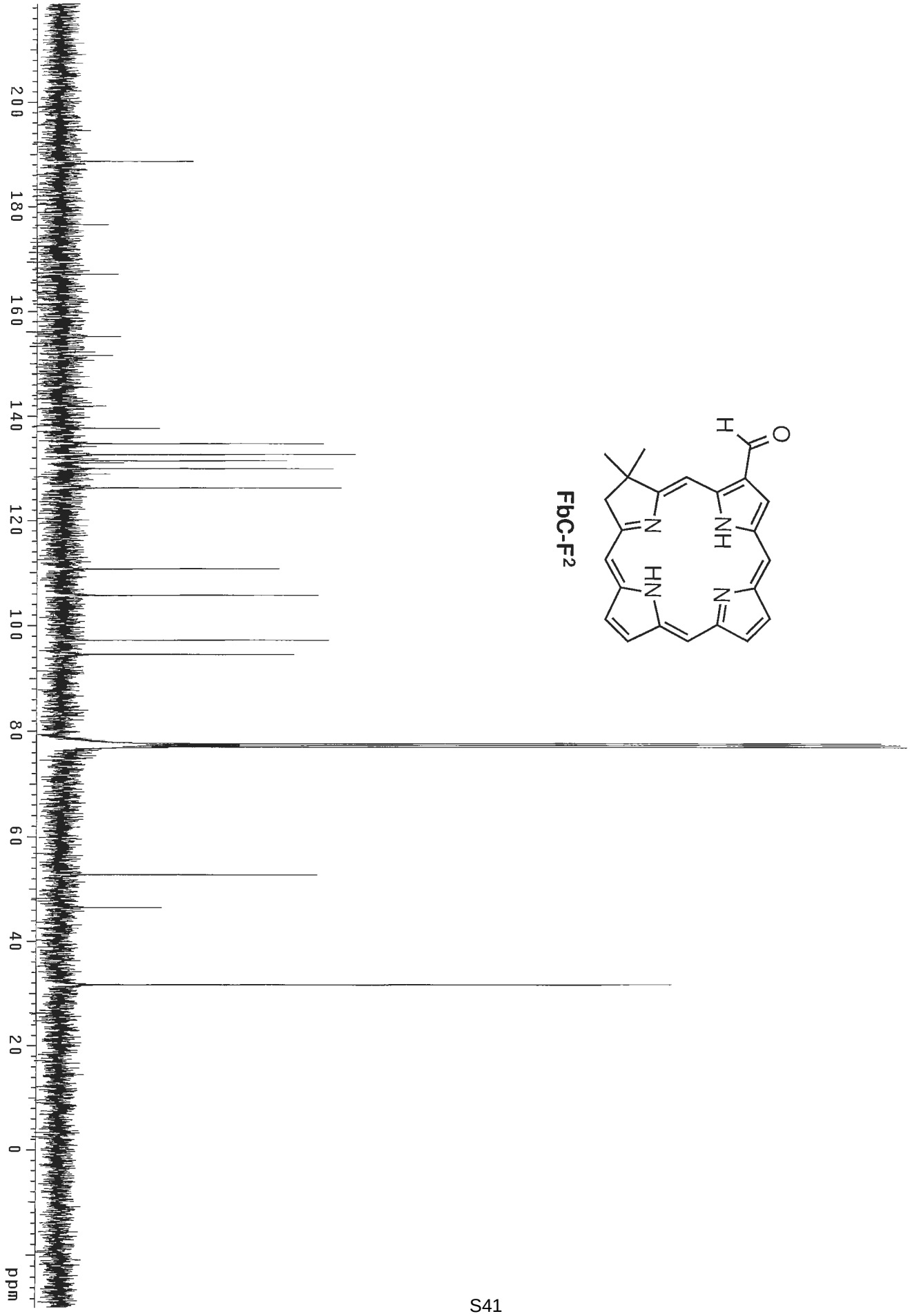
FbC-Br^3

Report generated by : Lindsey Lab .....

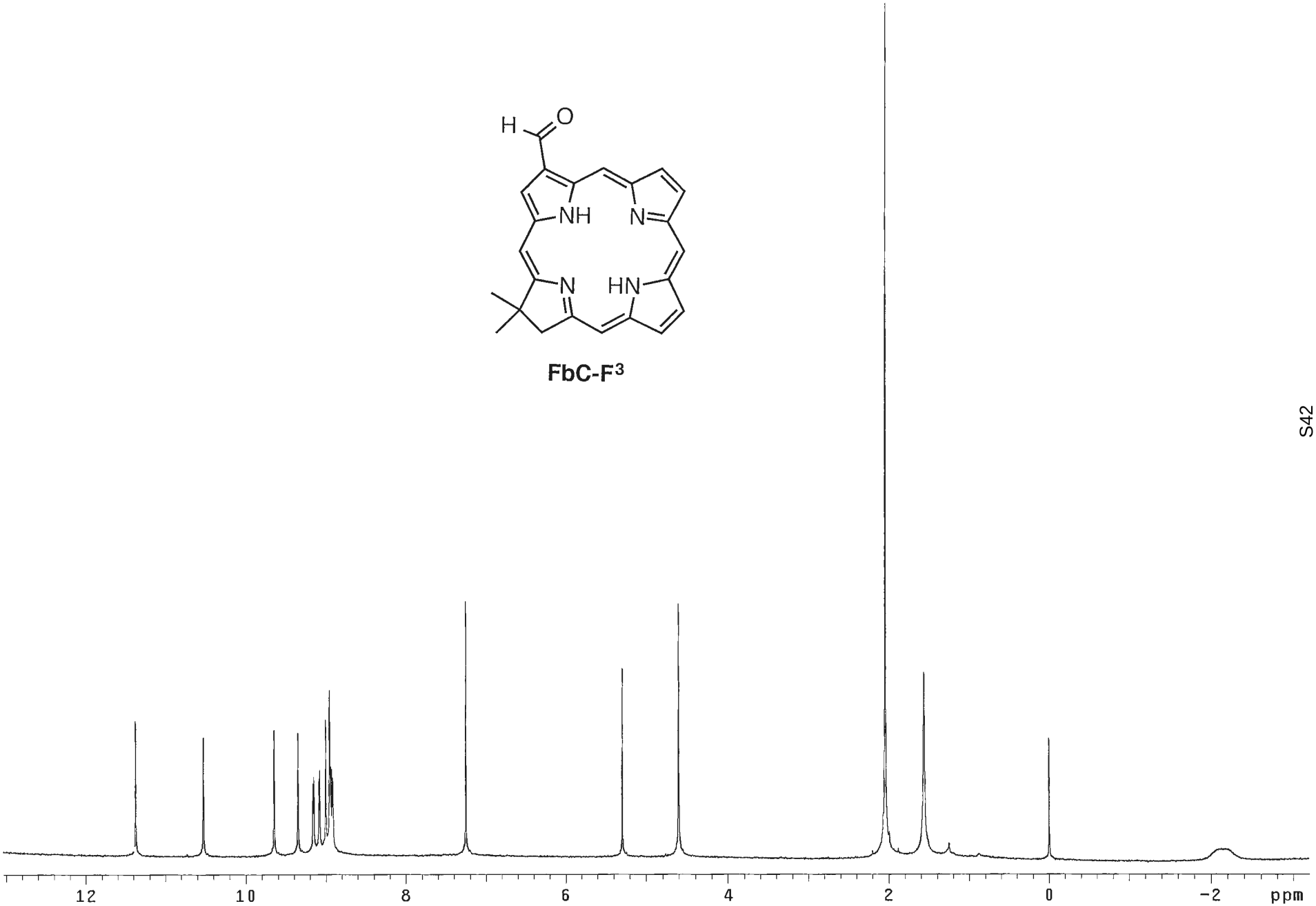
*** End Spectrum/Peak Report ***

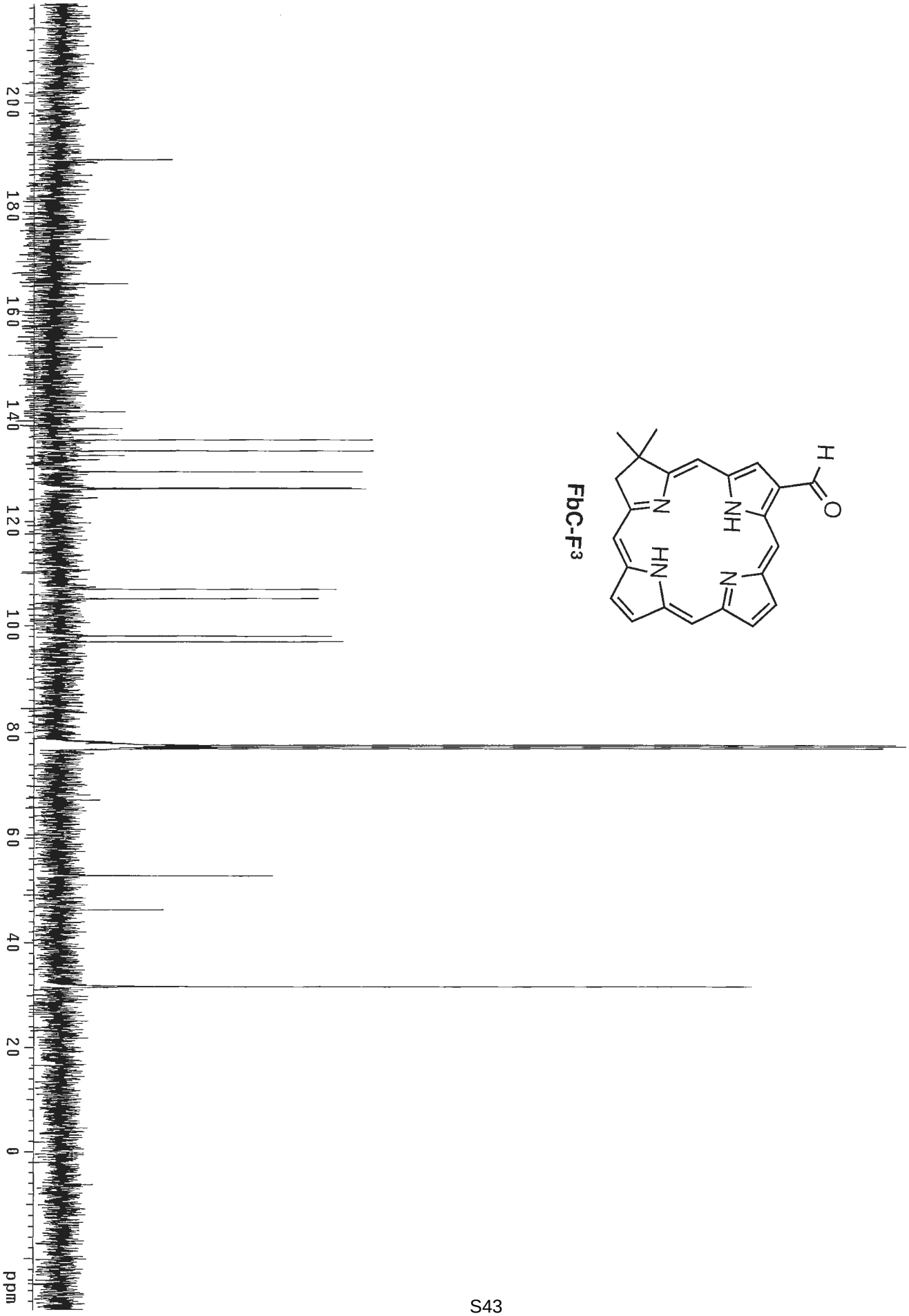


FbC-F^2


200
180
160
140
120
100
80
60
40
20
0
ppm
FbC-F2
H
O
N
NH
HN
N

FbC-F^3





FbC-F3