Electronic Supplementary Material (ESI) for Green Chemistry.

Trihalide ionic liquids as non-volatile oxidizing solvents for metals

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Electronic supplementary information

Chlorine reaction setup and procedure

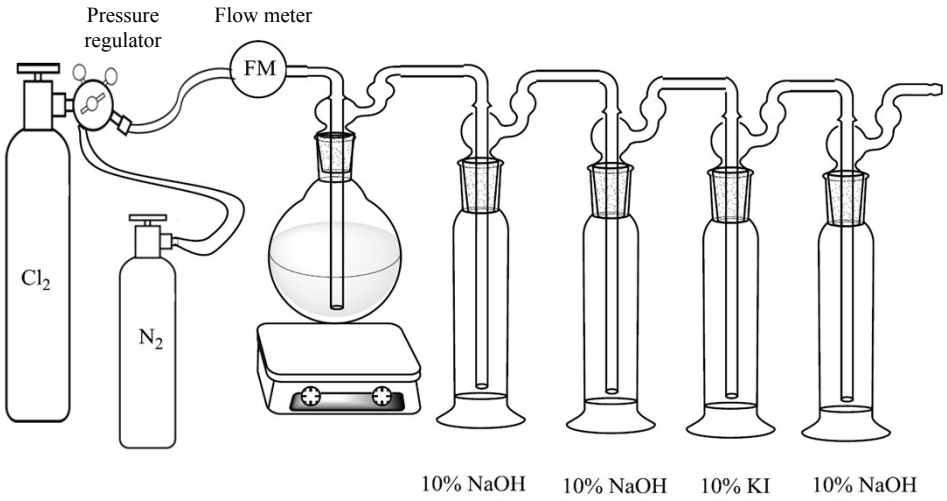


Figure S 1: Schematic overview of the chlorine reaction setup.

A sealed and controllable setup for the addition of chlorine was used, a detector for chlorine gas (with a threshold of 0.5 ppm) was present inside the fume hood monitoring the chlorine level. The chlorine bottle was connected to a flow meter to control the amount of chlorine flowing through the flask. A piece of glassware was designed to bubble the chlorine flow through the IL before being washed by two washing bottles containing a 10 wt% NaOH solution. Another washing bottle containing a KI solution was attached so any remaining chlorine could be detected by a color change of the solution (when chlorine oxidizes iodide, forming the brown colored triiodide anion). This was followed by an additional washing bottle with a 10 wt% NaOH solution.

The IL was dried on a Schlenk line in a round bottom flask while stirring with a stirring bar. Afterwards, the flask was attached to the chlorine setup and nitrogen (2 bar, 20 g/h) was used to purge the system for 30 minutes.[28] The flask was covered with aluminum foil in order to block incident light that can cleave the halide bonds, forming reactive radicals. Then, the nitrogen flow was replaced by chlorine gas (2 bar, 2.1 g/h), which was absorbed by the IL, since no bubbles escaped the IL. After the required amount of chlorine was added, nitrogen was used again to drive all the remaining chlorine gas in the tubing into the IL. This was done for 30 minutes (2 bar, 2.1 g/h).

Pictures

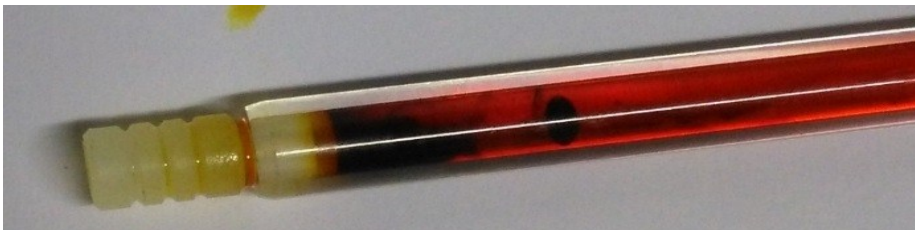


Figure S 2: Reacted viscometer sample containing $[P_{44410}][Br_3]$ and a gold coated stainless steel ball showing signs of corrosion.

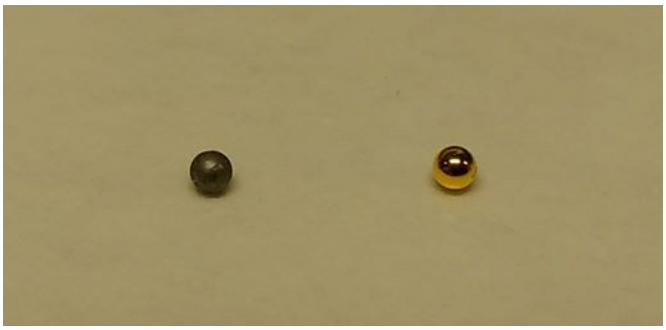


Figure S 3: Corrosion of the gold coated stainless steel ball which was left overnight (left) and an unused ball (right) for viscosity measurements.

Characterization

Monohalide ionic liquids

$[P_{44410}]Cl$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.47 (m, 8H, 4 CH_2), 1.54 (m, 16H, 8 CH_2), 1.26 (m, 12H, 6 CH_2), 0.98 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.84-18.75 (18 CH_2), 14.05 (1 CH_3), 13.51 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.11. Yield: 85%, 16.18 g. Water content: 1423 ppm. Viscosity: 8167 mPa·s (25 °C). Density: 0.917 g/cm^3 (25 °C).

$[P_{44410}]Br$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.47 (m, 8H, 4 CH_2), 1.55 (m, 16H, 8 CH_2), 1.26 (m, 12H, 6 CH_2), 0.98 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.83-18.87 (18 CH_2), 14.10 (1 CH_3), 13.52 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 32.75. Yield: 44%, 9.34 g. Water content: 348 ppm. Viscosity: 7317 mPa·s (25 °C). Density: 1.006 g/cm^3 (25 °C).

$[P_{44410}]I$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.44 (m, 8H, 4 CH_2), 1.56 (m, 16H, 8 CH_2), 1.26 (m, 12H, 6 CH_2), 0.99 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.82-19.02 (18 CH_2), 14.10 (1 CH_3), 13.54 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 32.95. Yield: 82%, 19.35 g. Water content: 98 ppm. Viscosity: 5219 mPa·s (25 °C). Density: 1.090 g/cm^3 (25 °C).

$[P_{66614}]Cl$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.47 (m, 8H, 4 CH_2), 1.51 (m, 16H, 8 CH_2), 1.26 (m, 32H, 16 CH_2), 0.89 (m, 12H, 4 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.93-29.01 (16 CH_2), 22.70-19.12 (12 CH_2), 14.13 (1 CH_3), 13.94 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.61. Yield: 42%, 4.18 g. Water content: 782 ppm. Viscosity: 2841 mPa·s (25 °C). Density: 0.890 g/cm^3 (25 °C).

$[N_{44410}]Br$

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 3.39 (m, 8H, 4 CH_2), 1.69 (m, 8H, 4 CH_2), 1.47 (m, 8H, 4 CH_2), 1.26 (m, 12H, 6 CH_2), 1.01 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 59.14 (4 CH_2-N), 31.84-19.81 (14 CH_2), 14.12 (1 CH_3), 13.74 (3 CH_3). Yield: 95%, 19.23 g. Melting point: 51 °C.

$[C_{10}(P_{444})_2][(Br)_2]$

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.55 (m, 4H, 2 CH_2), 2.44 (m, 12H, 6 CH_2), 1.55 (m, 32H, 16 CH_2), 1.37 (m, 8H, 4 CH_2), 0.98 (m, 18H, 6 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 30.55-28.16 (6 CH_2), 23.87 (12

CH_2), 21.69 (2 CH_2), 19.70-18.89 (8 CH_2), 13.55 (6 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 32.88 (2 PR_4). Yield: 91%, 14.14 g. Melting temperature: 75.1 °C.

Tributyldecylphosphonium trihalide ionic liquids:

$[P_{44410}][Cl_3]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.39 (m, 8H, 4 CH_2), 1.56 (m, 16H, 8 CH_2), 1.26 (m, 32H, 16 CH_2), 0.99 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.85-28.98 (16 CH_2), 24.01-18.78 (12 CH_2), 14.11 (1 CH_3), 13.51 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.07 (1 PR_4). Yield: 99%, 7.26 g. Viscosity: 400 mPa·s (25 °C). Density: 0.996 g/cm^3 (25 °C).

$[P_{44410}][BrCl_2]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.28 (m, 8H, 4 CH_2), 1.58 (m, 16H, 8 CH_2), 1.28 (m, 12H, 6 CH_2), 1.01 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.85-18.75 (18 CH_2), 14.12 (1 CH_3), 13.49 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.29 (1 PR_4). Yield: 100%, 9.89 g. Viscosity: 303 mPa·s (25 °C). Density: 1.094 g/cm^3 (25 °C).

$[P_{44410}][ClBr_2]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.29 (m, 8H, 4 CH_2), 1.59 (m, 16H, 8 CH_2), 1.28 (m, 12H, 6 CH_2), 1.01 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.86-18.86 (18 CH_2), 14.13 (1 CH_3), 13.53 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.01 (1 PR_4). Yield: 100%, 12.94 g. Viscosity: 376 mPa·s (25 °C). Density: 1.169 g/cm^3 (25 °C).

$[P_{44410}][Br_3]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.28 (m, 8H, 4 CH_2), 1.60 (m, 16H, 8 CH_2), 1.28 (m, 12H, 6 CH_2), 1.02 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.87-18.85 (18 CH_2), 14.14 (1 CH_3), 13.56 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.39 (1 PR_4). Yield: 100%, 11.71 g. Viscosity: 382 mPa·s (25 °C). Density: 1.253 g/cm^3 (25 °C).

$[P_{44410}][IBr_2]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.27 (m, 8H, 4 CH_2), 1.60 (m, 16H, 8 CH_2), 1.28 (m, 12H, 6 CH_2), 1.03 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.87-19.07 (18 CH_2), 14.14 (1 CH_3), 13.57 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.08 (1 PR_4). Yield: 99%, 9.90 g. Viscosity: 381 mPa·s (25 °C). Density: 1.325 g/cm^3 (25 °C).

$[P_{44410}][BrI_2]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.27 (m, 8H, 4 CH_2), 1.60 (m, 16H, 8 CH_2), 1.28 (m, 12H, 6 CH_2), 1.03 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.88-19.07 (18 CH_2), 14.16 (1 CH_3), 13.66 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.09 (1 PR_4). Yield: 100%, 11.74 g. Viscosity: 358 mPa·s (25 °C). Density: 1.433 g/cm^3 (25 °C).

$[P_{44410}][I_3]$:

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.27 (m, 8H, 4 CH_2), 1.62 (m, 16H, 8 CH_2), 1.29 (m, 12H, 6 CH_2), 1.04 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.88-19.31 (18 CH_2), 14.16 (1 CH_3), 13.70 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.15 (1 PR_4). Yield: 100%, 14.49 g. Viscosity: 371 mPa·s (25 °C). Density: 1.469 g/cm^3 (25 °C).

Trihalide ILs with other cations

$[P_{66614}][Cl_3]$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.46 (m, 8H, 4 CH_2), 1.51 (m, 16H, 8 CH_2), 1.26 (m, 32H, 16 CH_2), 0.90 (m, 12H, 4 CH_3) ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.91-18.98 (28 CH_2), 14.12 (1 CH_3), 13.94 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.22 (1 PR_4). Yield: 99%, 10.88 g. Viscosity: 590 mPa·s (25 °C). Density: 0.954 g/cm^3 (25 °C).

$[P_{66614}][ClBr_2]$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.29 (m, 8H, 4 CH_2), 1.55 (m, 16H, 8 CH_2), 1.26 (m, 32H, 16 CH_2), 0.91 (m, 12H, 4 CH_3) ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 31.93-19.10 (28 CH_2), 14.13 (1 CH_3), 14.00 (3 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 33.10 (1 PR_4). Yield: 100%, 10.19 g. Viscosity: 420 mPa·s (25 °C). Density: 1.080 g/cm^3 (25 °C).

$[N_{44410}][Br_3]$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 3.30 (m, 8H, 4 CH_2), 1.72 (m, 8H, 4 CH_2), 1.50 (m, 8H, 4 CH_2), 1.27 (m, 12H, 6 CH_2), 1.05 (m, 9H, 3 CH_3), 0.88 (m, 3H, 1 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 59.17 (4 CH_2-N), 31.86-19.89 (14 CH_2), 14.14 (1 CH_3), 13.80 (3 CH_3). Yield: 100%, 8.50 g. Viscosity: 1201 mPa·s (25 °C). Density: 1.255 g/cm^3 (25 °C).

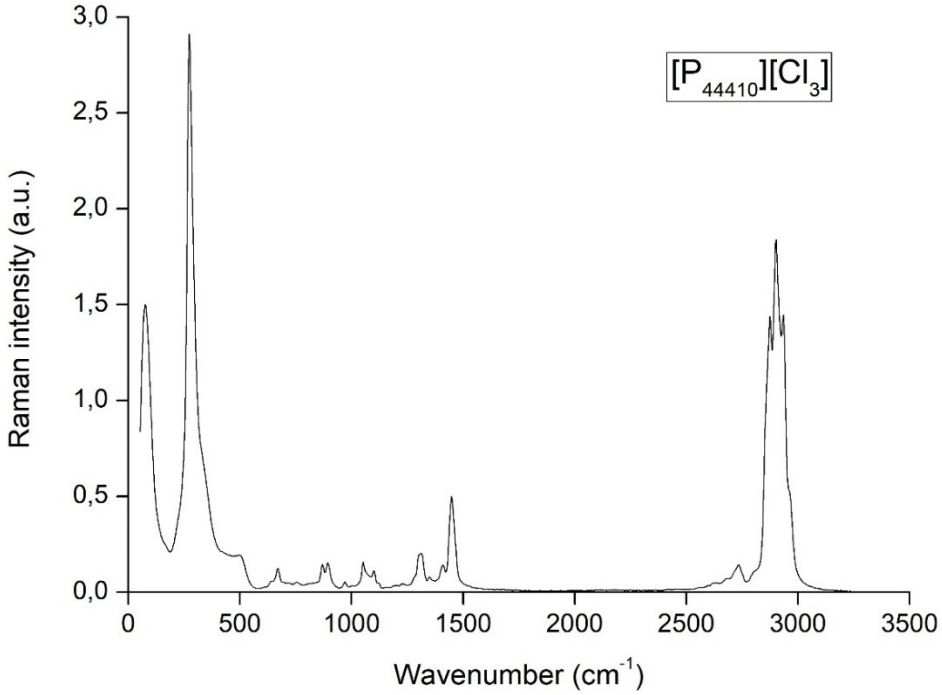
$[C_{10}(P_{444})_2][(Br_3)_2]$:

^{1}H NMR: (300 MHz, $CDCl_3$, δ/ppm): 2.29 (m, 16H, 8 CH_2), 1.59 (m, 32H, 16 CH_2), 1.38 (m, 8H, 4 CH_2), 1.01 (m, 18H, 6 CH_3). ^{13}C NMR: (75 MHz, $CDCl_3$, δ/ppm): 30.53-28.05 (6 CH_2), 24.00 (12 CH_2), 21.69 (2 CH_2), 19.71-18.92 (8 CH_2), 13.58 (6 CH_3). ^{31}P NMR: (162 MHz, $CDCl_3$, δ/ppm): 32.98 (2 PR_4). Yield: 100%, 10.24 g. Melting temperature: 65.6 °C

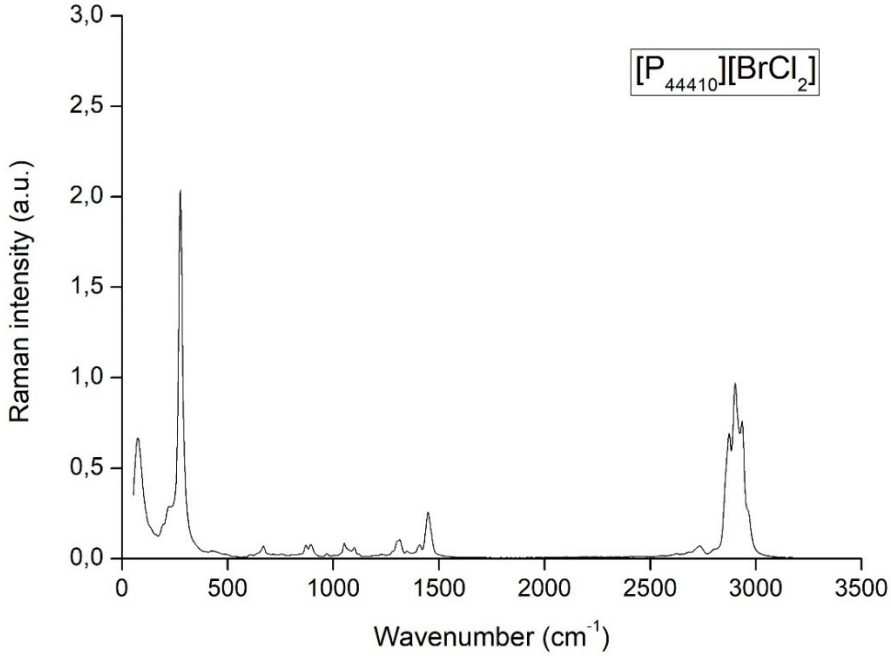
Raman spectra

All the Raman spectra were recorded on the pure ILs, but due to the increasing signal scattering with heavier halogen atoms, the laser power had to be lowered. Below the spectra and an overview of the distinctive trihalide signals can be found, together with the used laser power.

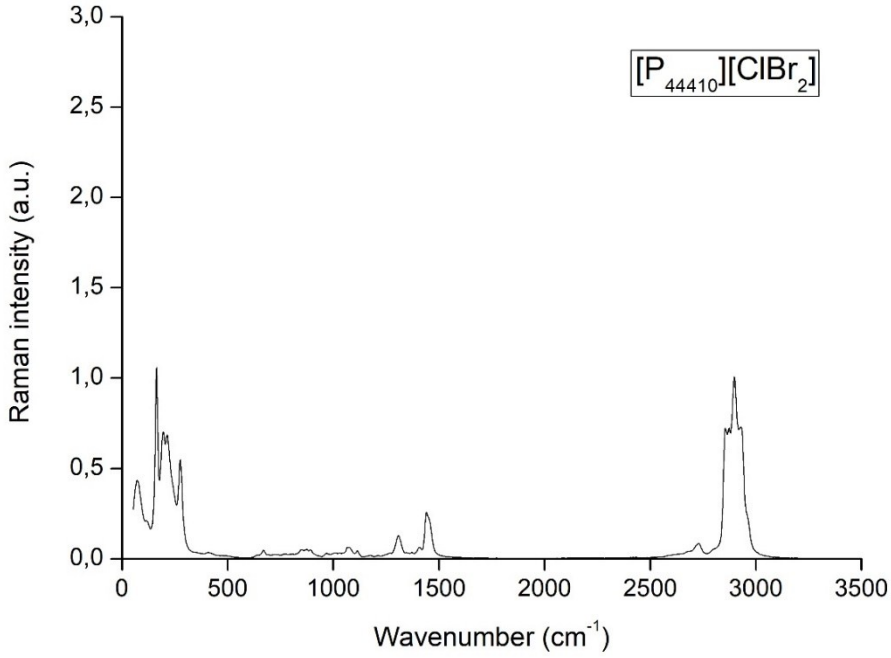
$[P_{44410}][Cl_3]$: 300 mW



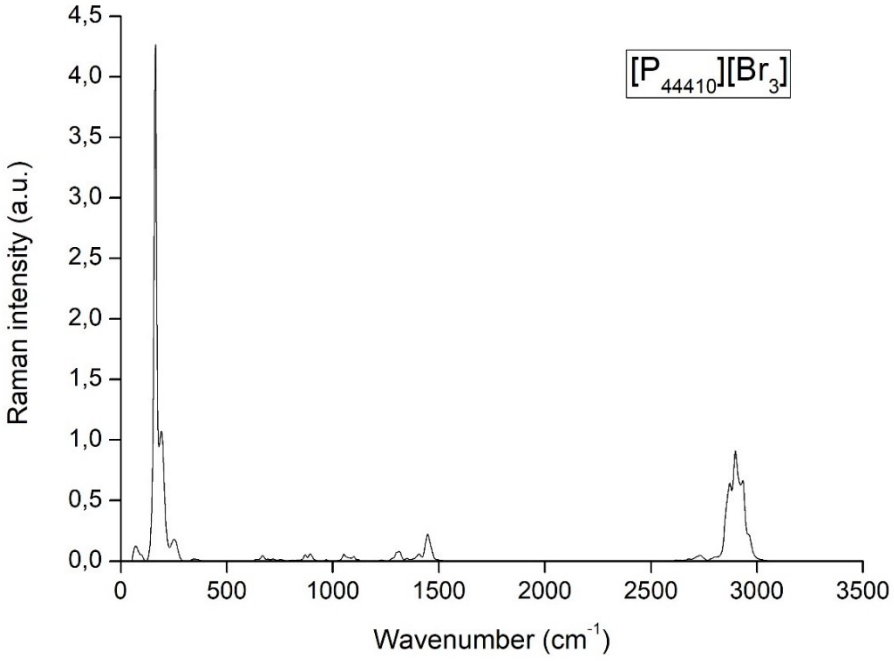
$[P_{44410}][BrCl_2]$: 500 mW



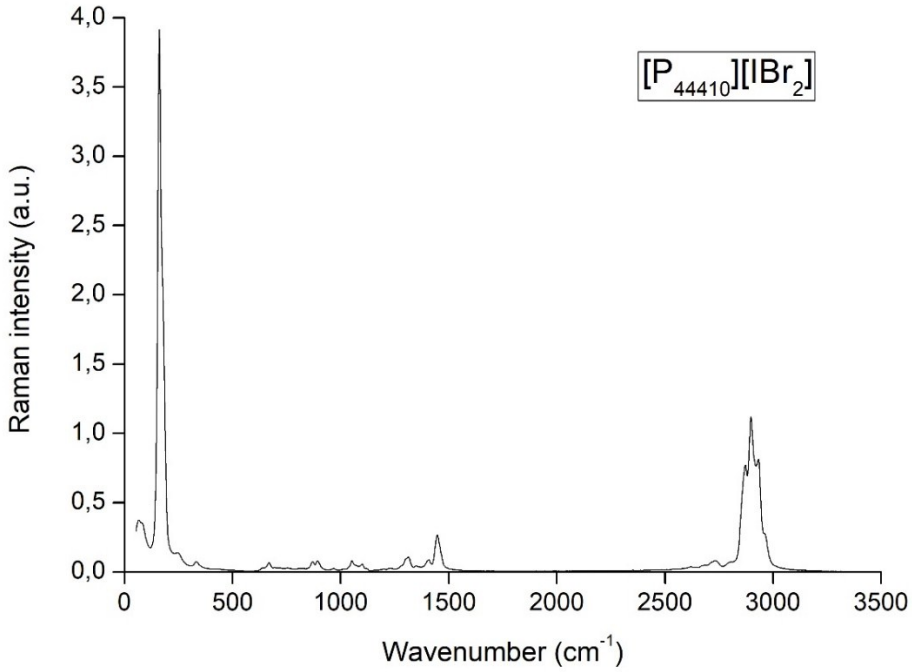
$[P_{44410}][ClBr_2]$: 500 mW



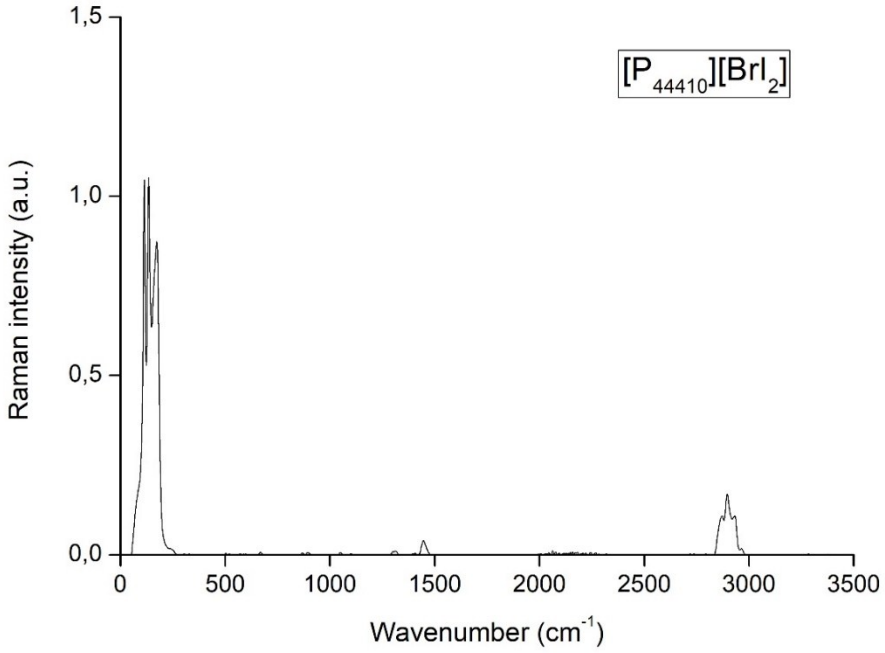
$[P_{44410}][Br_3]$: 500 mW



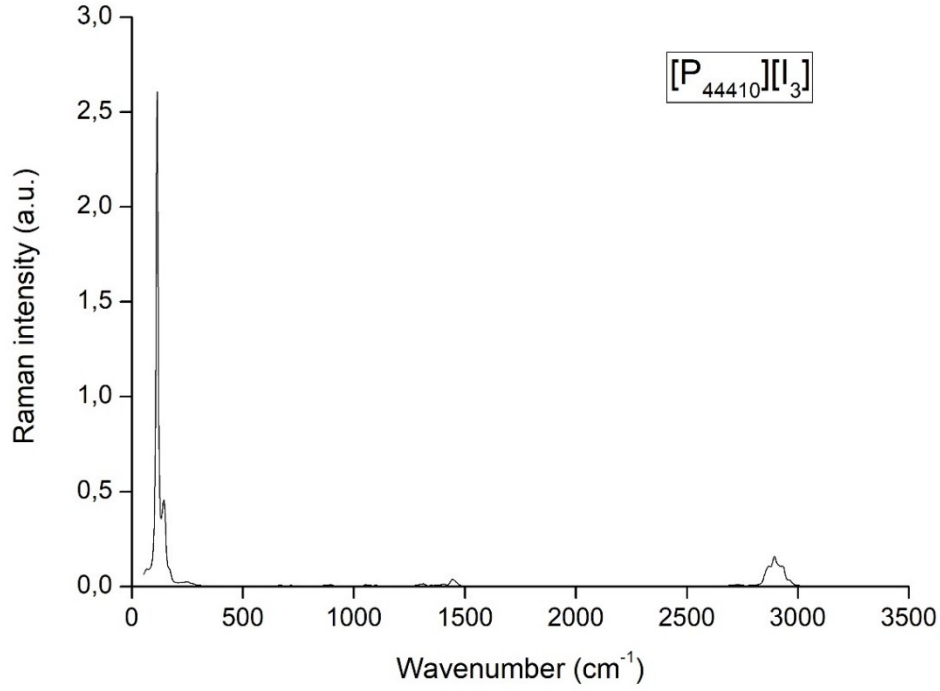
$[P_{44410}][IBr_2]$: 250 mW



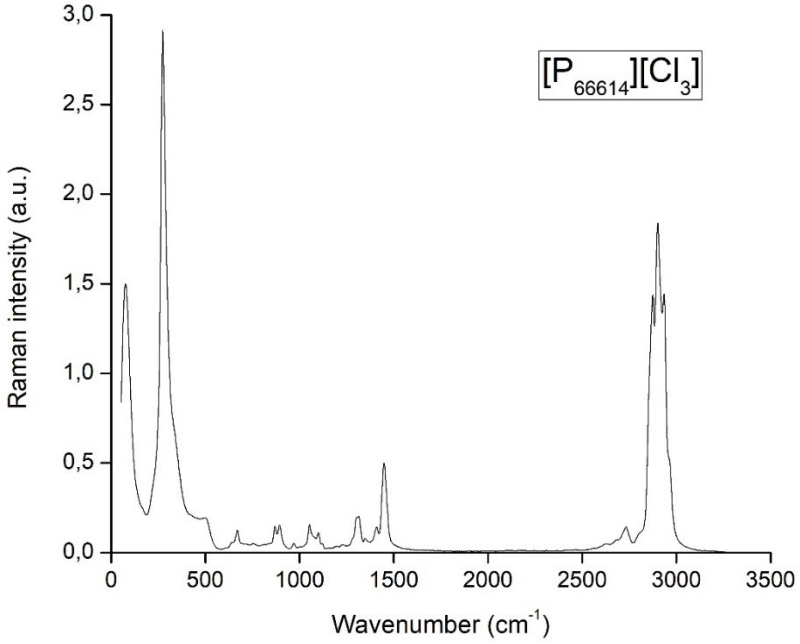
$[P_{44410}][BrI_2]$: 100 mW



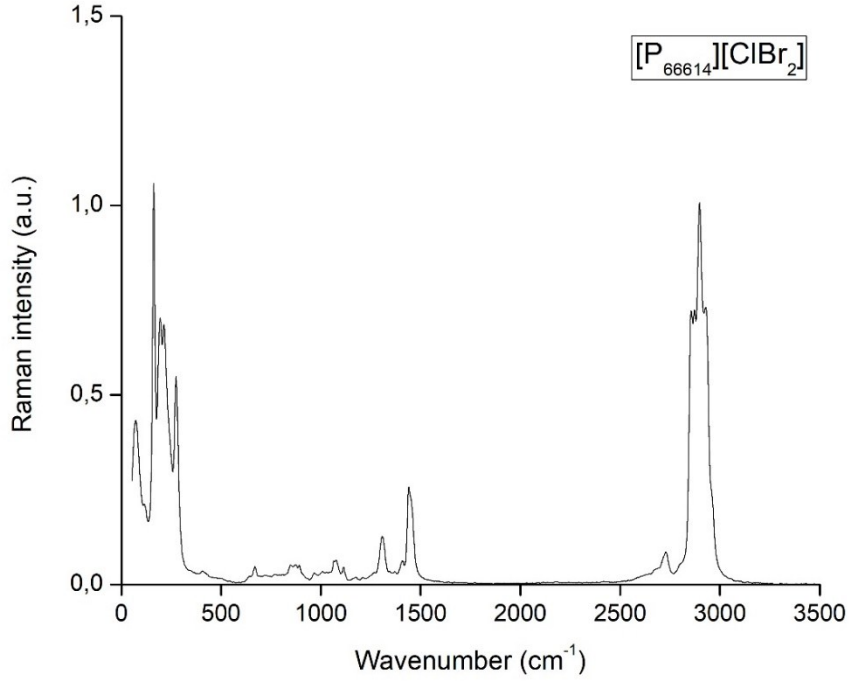
$[P_{44410}][I_3]$: 50 mW



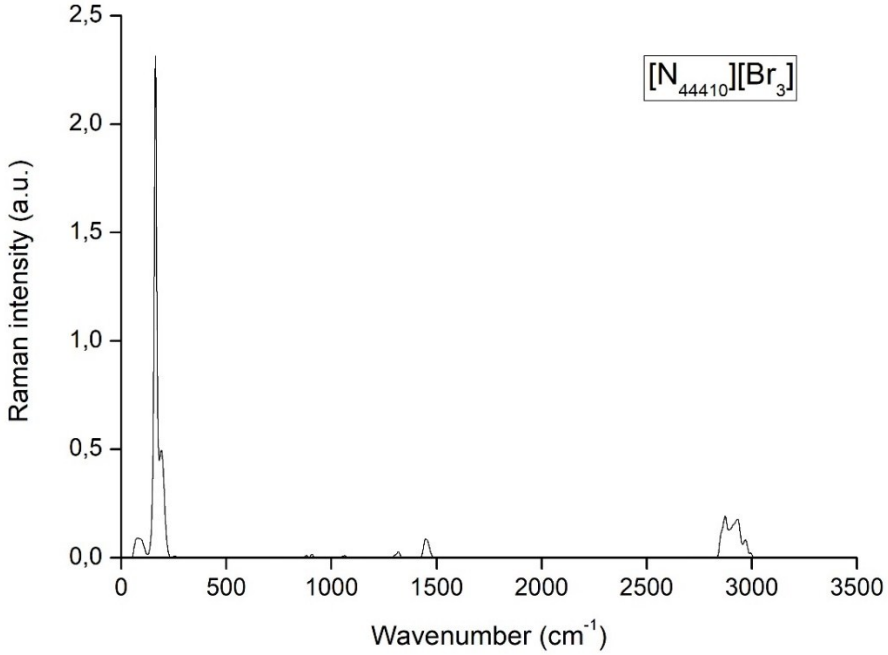
$[P_{66614}][Cl_3]$: 500 mW



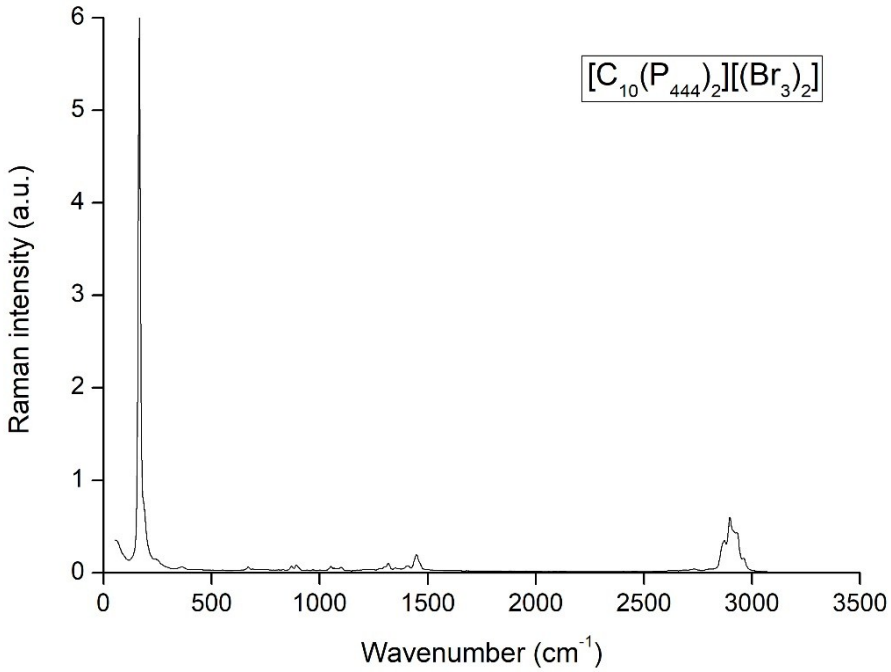
$[P_{66614}][ClBr_2]$: 500 mW



$[N_{44410}][Br_3]$: 500 mW



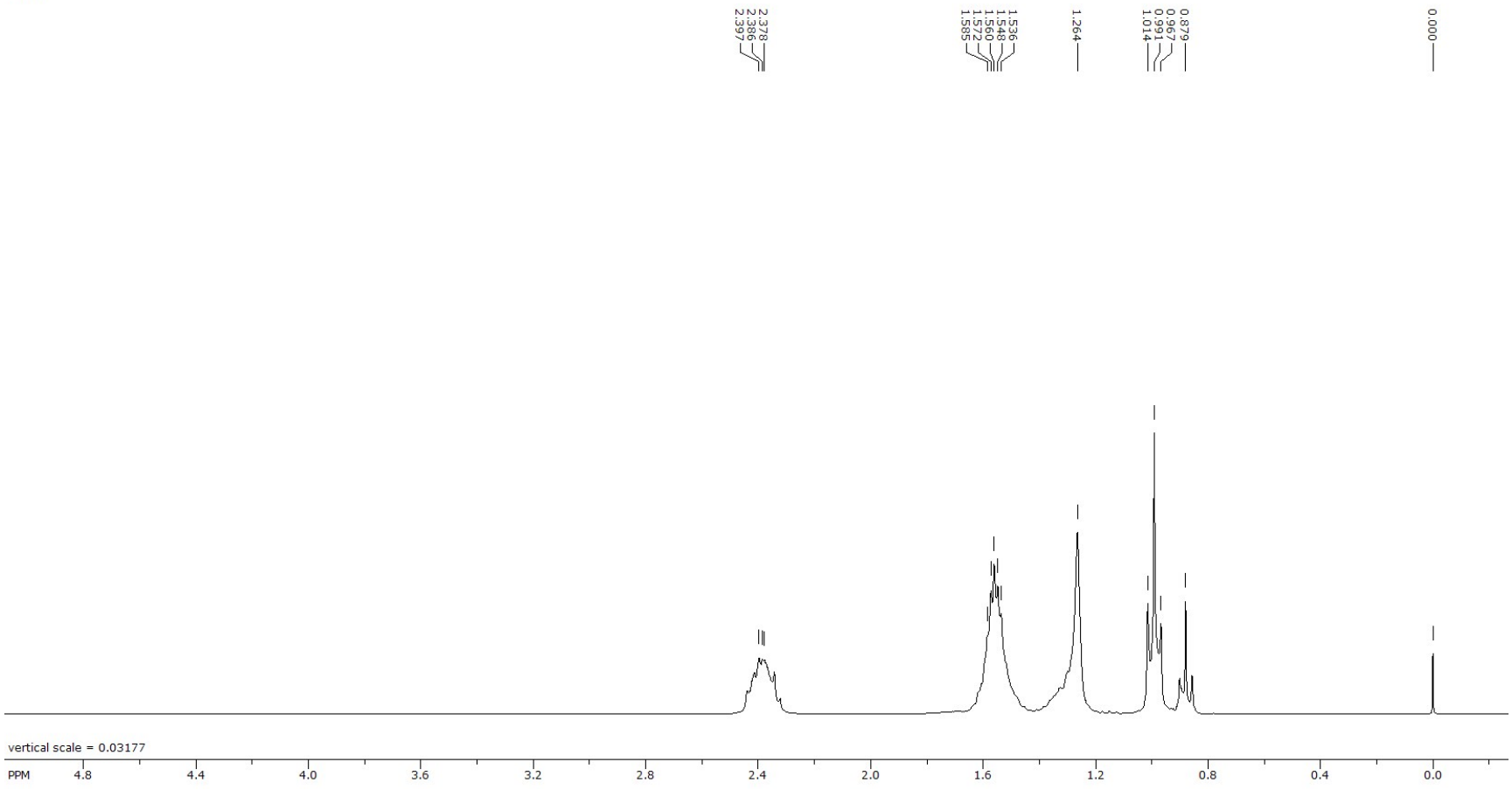
$[C_{10}(P_{444})_2][(Br_3)_2]$: 500 mW



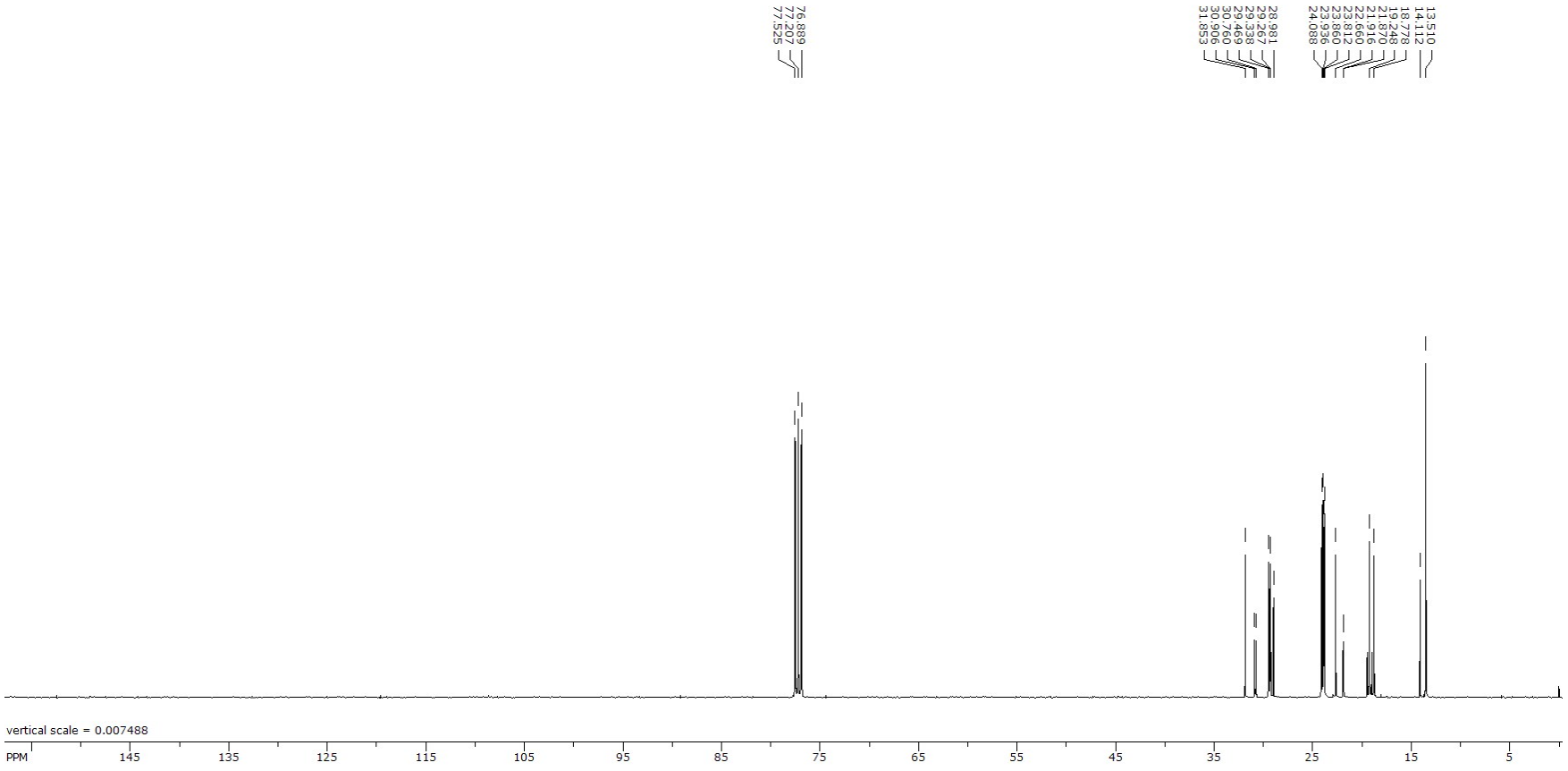
NMR spectra

$[P_{44410}][Cl_3]$

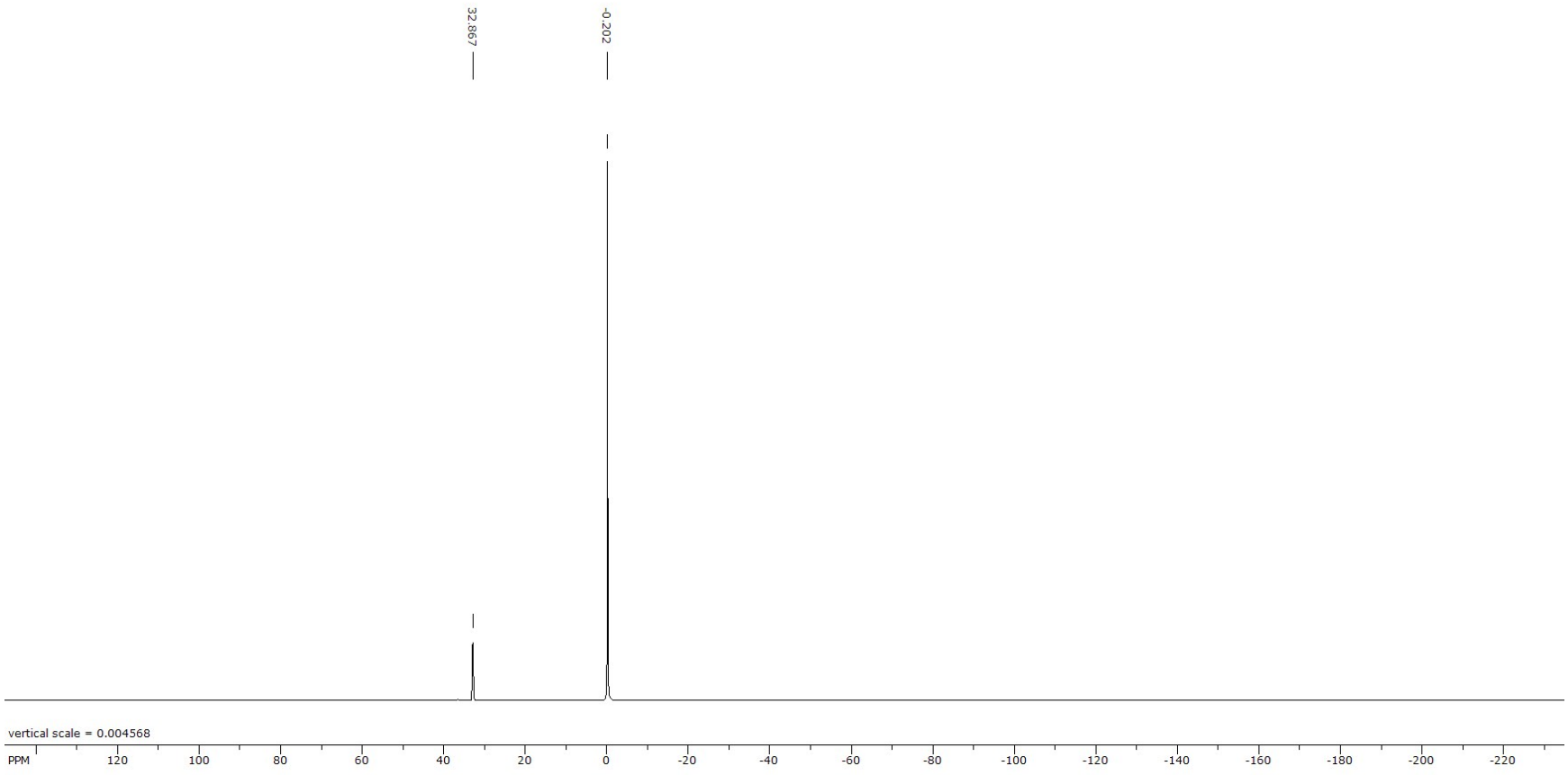
^1H NMR



^{13}C NMR

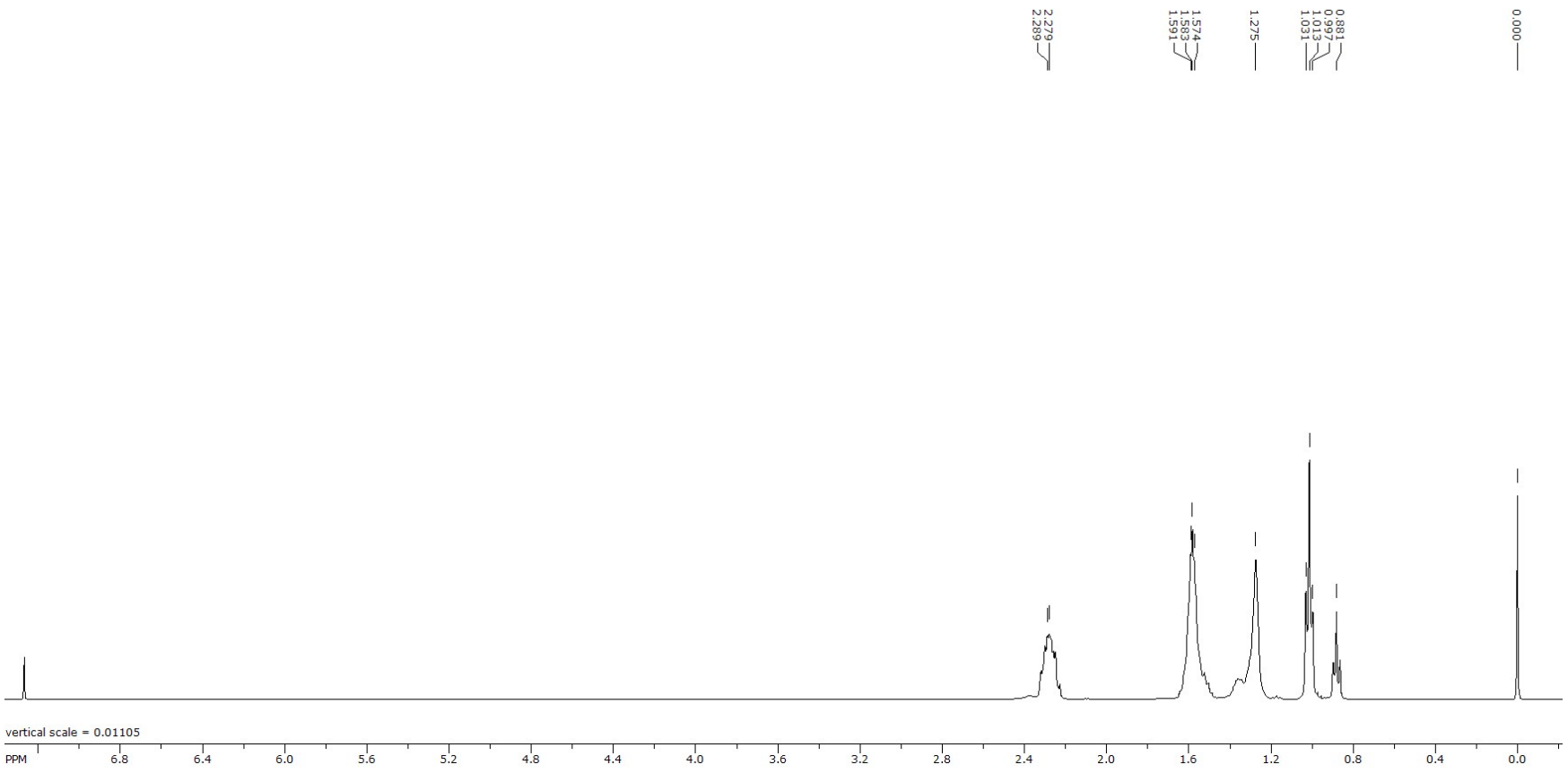

76.889
77.207
77.525
31.853
30.906
30.760
29.469
29.338
29.267
28.981
24.088
23.936
23.860
23.812
21.946
21.870
19.248
18.778
14.112
13.510
vertical scale = 0.007488
PPM
145
135
125
115
105
95
85
75
65
55
45
35
25
15
5

^{31}P NMR

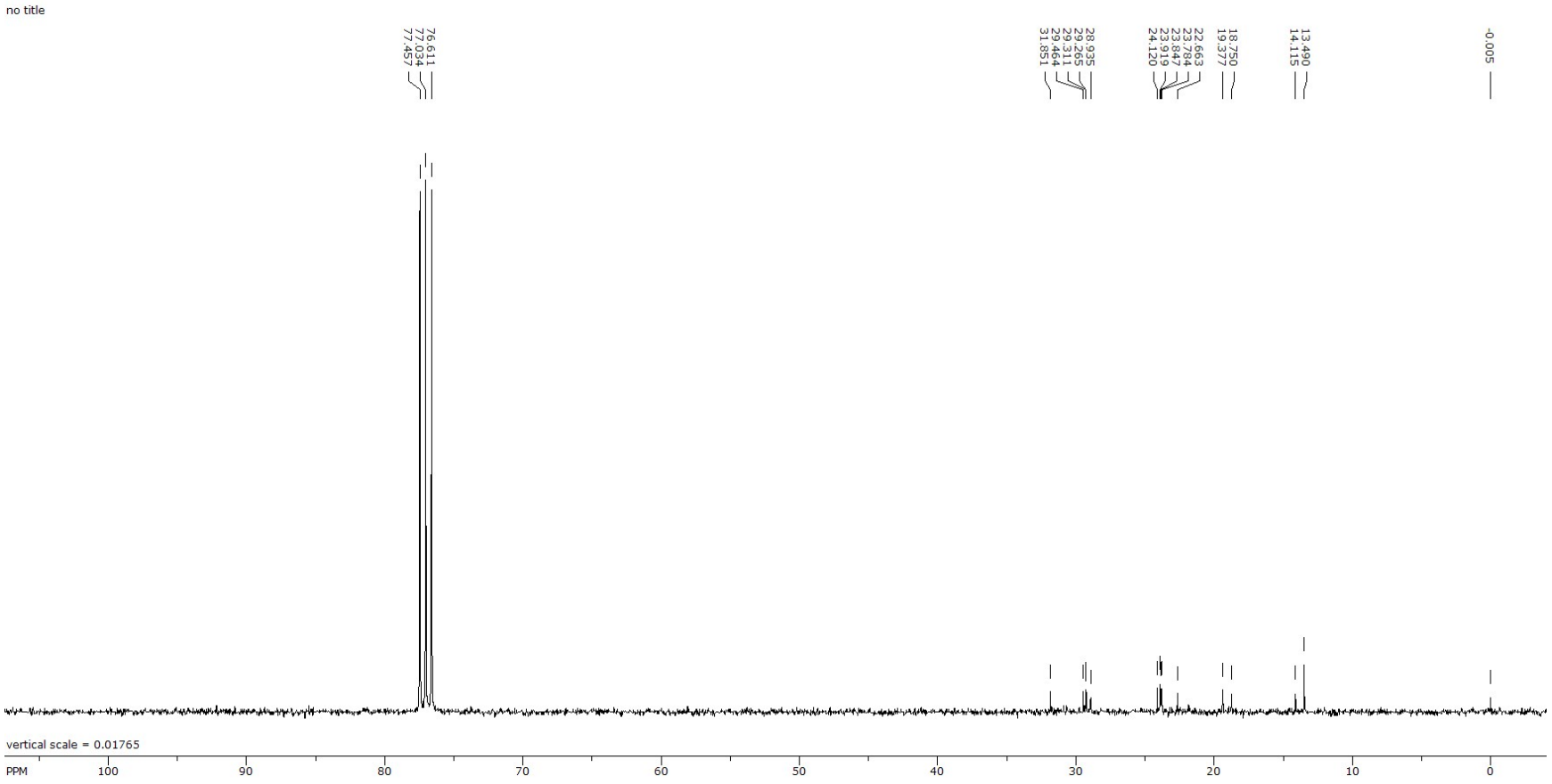

32.867
-0.202
vertical scale = 0.004568
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[P_{44410}][BrCl_2]$

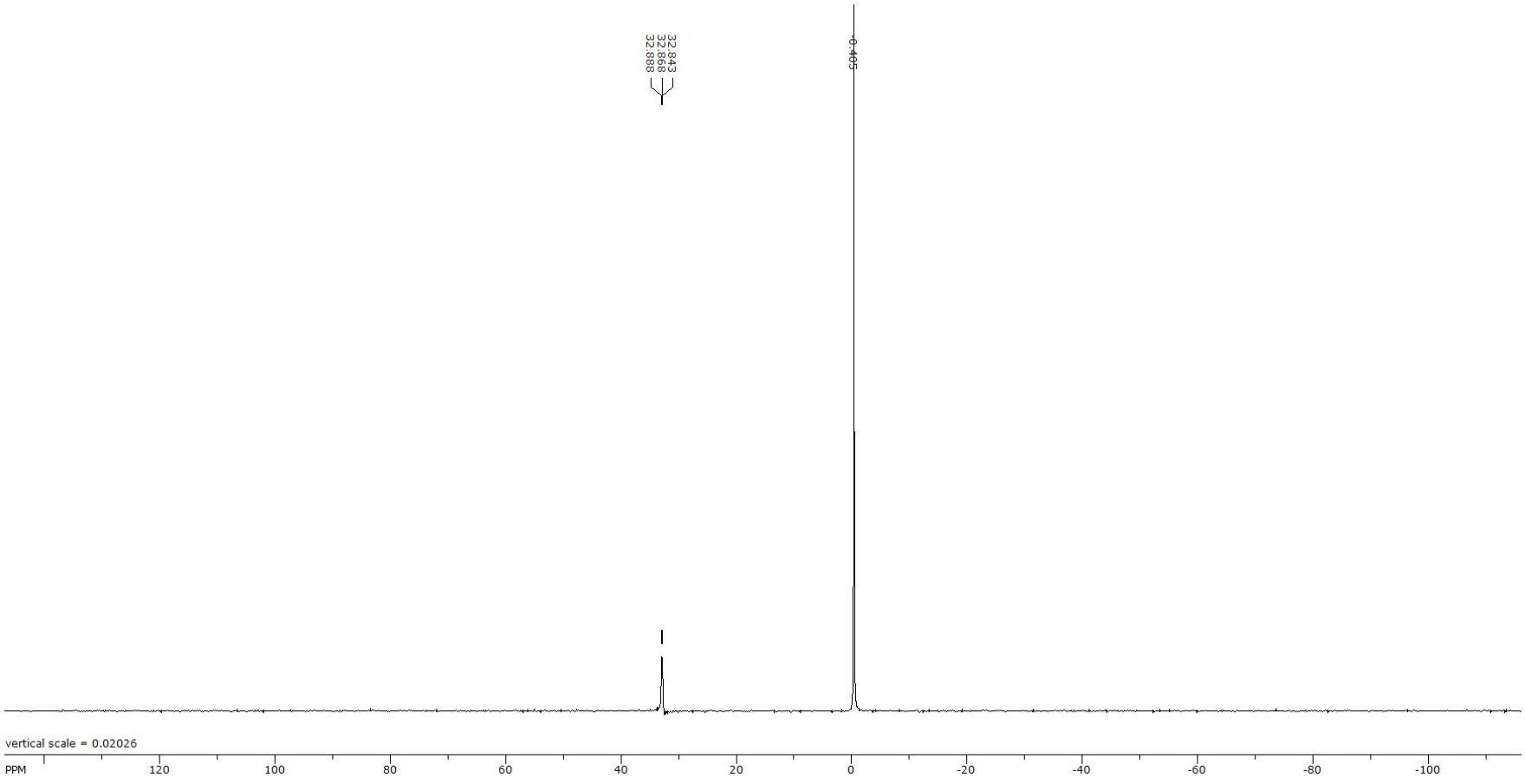
^1H NMR



^{13}C NMR

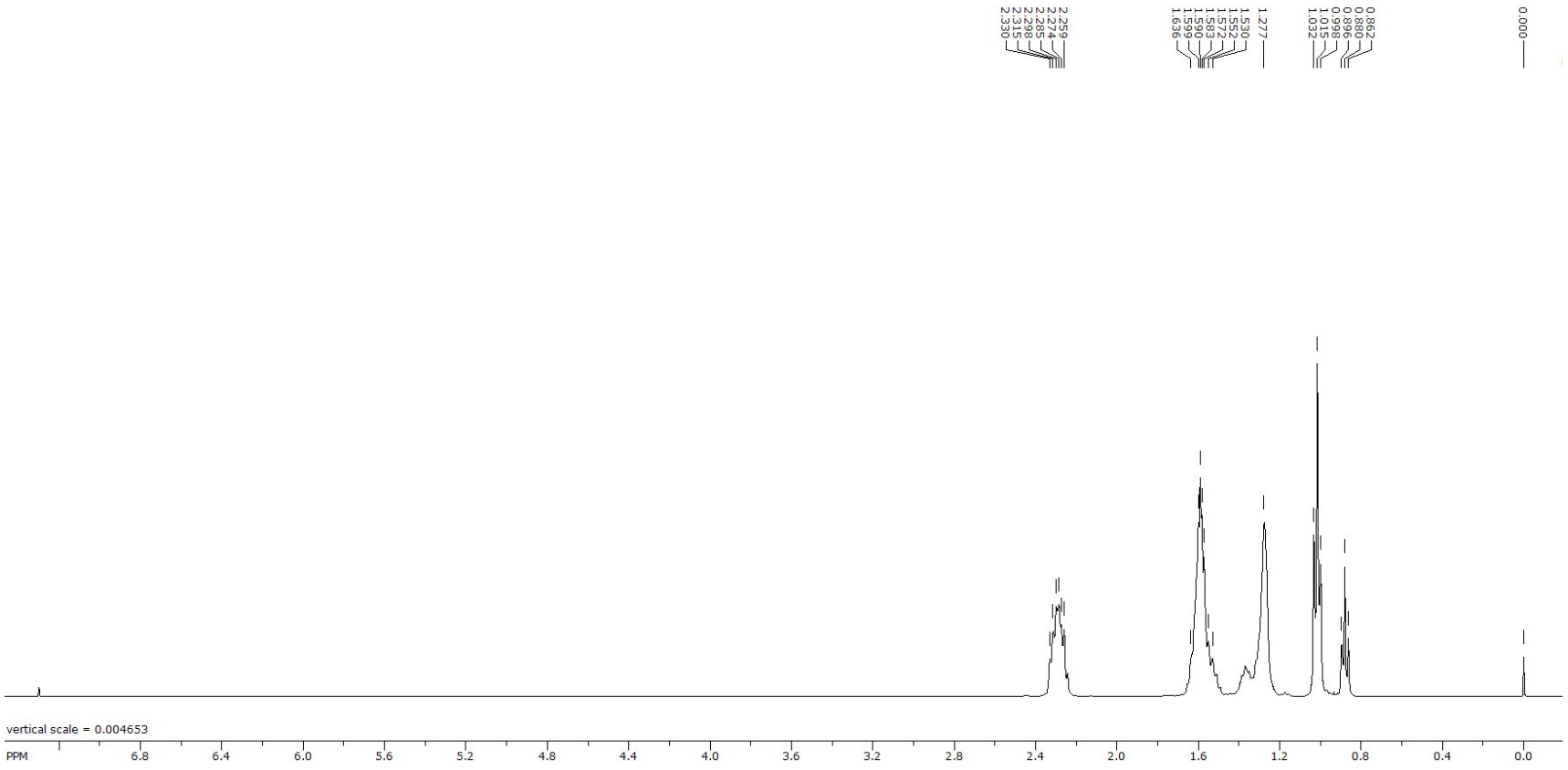

no title
77.457
77.054
76.611
31.851
29.484
29.311
29.265
28.935
24.120
23.919
23.847
23.784
22.663
19.377
18.750
14.115
13.490
-0.005
vertical scale = 0.01765
PPM
100
90
80
70
60
50
40
30
20
10
0

^{31}P NMR

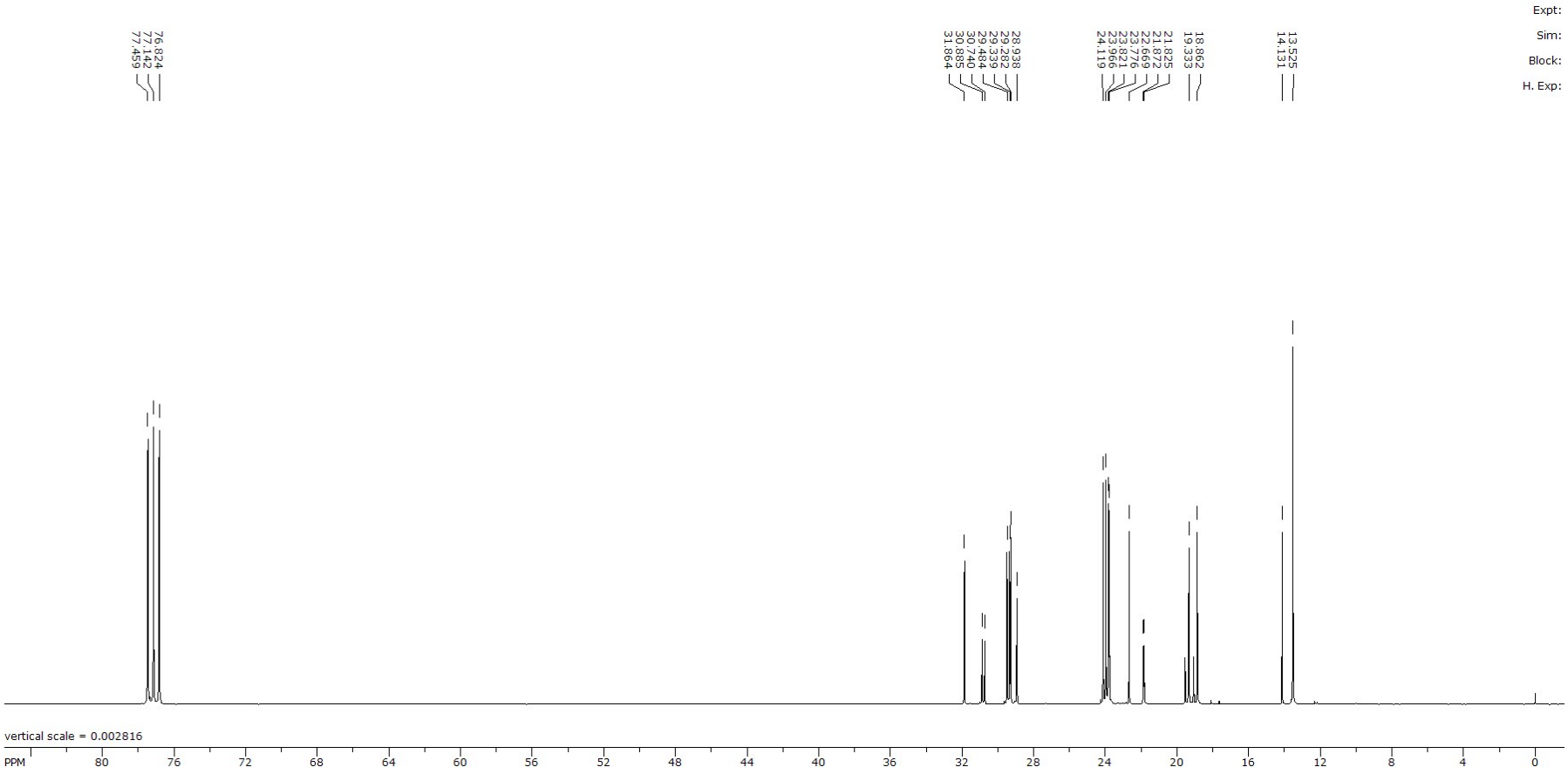

32.843
32.868
32.888
-0.405
vertical scale = 0.02026
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

$[P_{44410}][ClBr_2]$

^1H NMR



^{13}C NMR


Expt:
Sim:
Block:
H. Exp:
76.824
77.142
77.459
31.864
30.885
30.749
29.484
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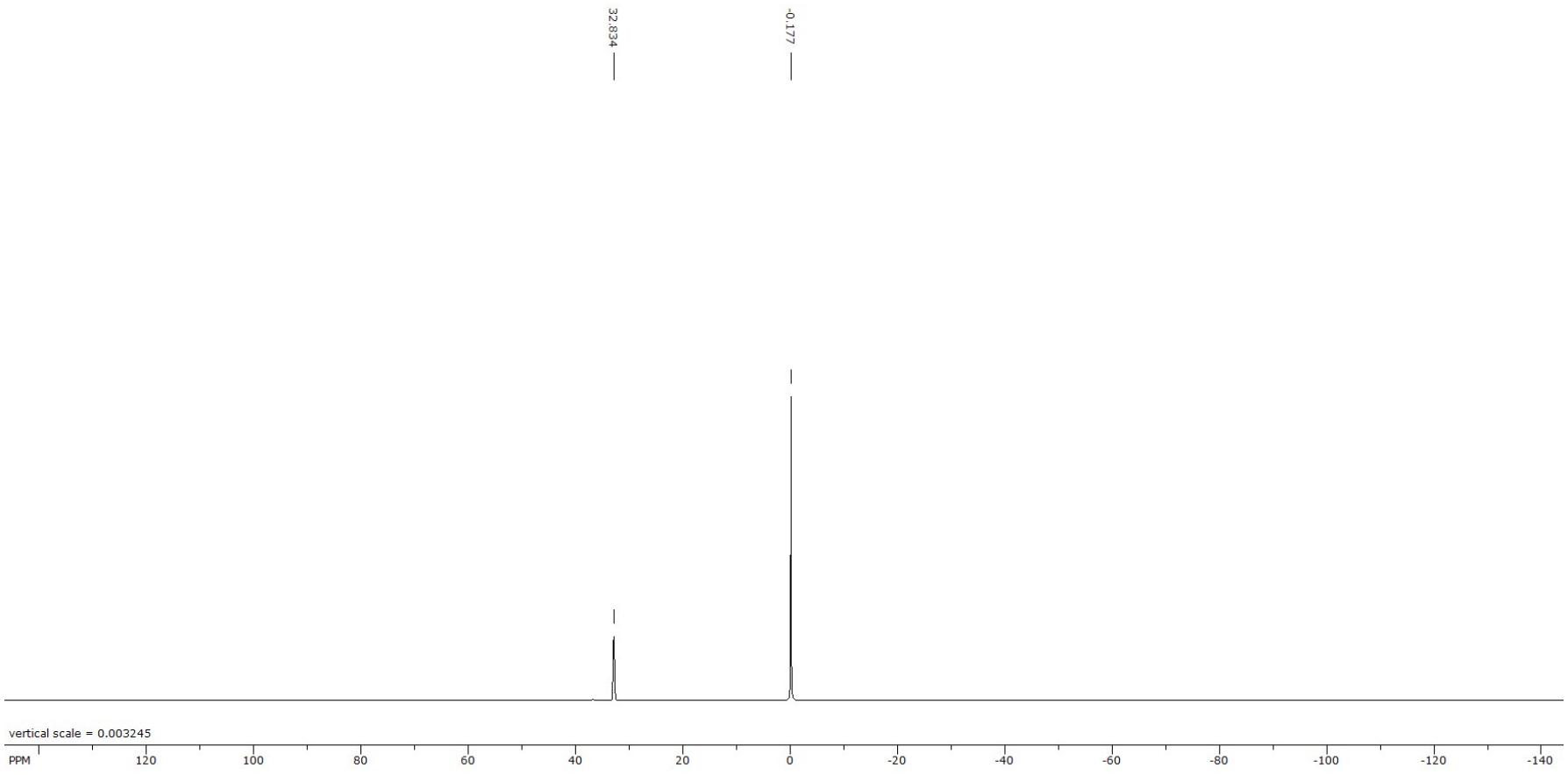
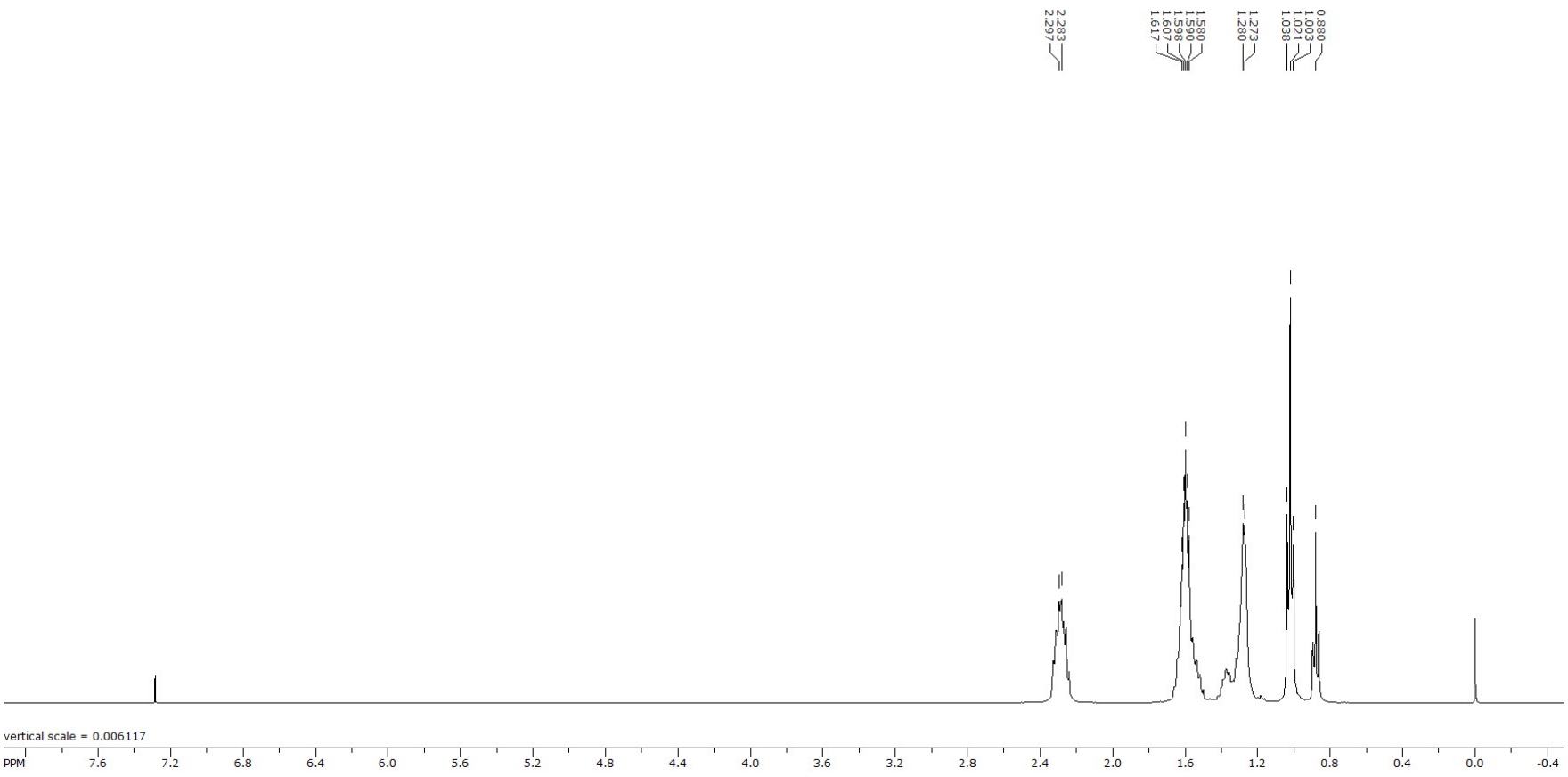
29.282
28.938
24.119
23.966
23.821
23.776
22.669
21.872
21.825
19.333
18.862
14.131
13.525
vertical scale = 0.002816
PPM
80
76
72
68
64
60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
0

^{31}P NMR

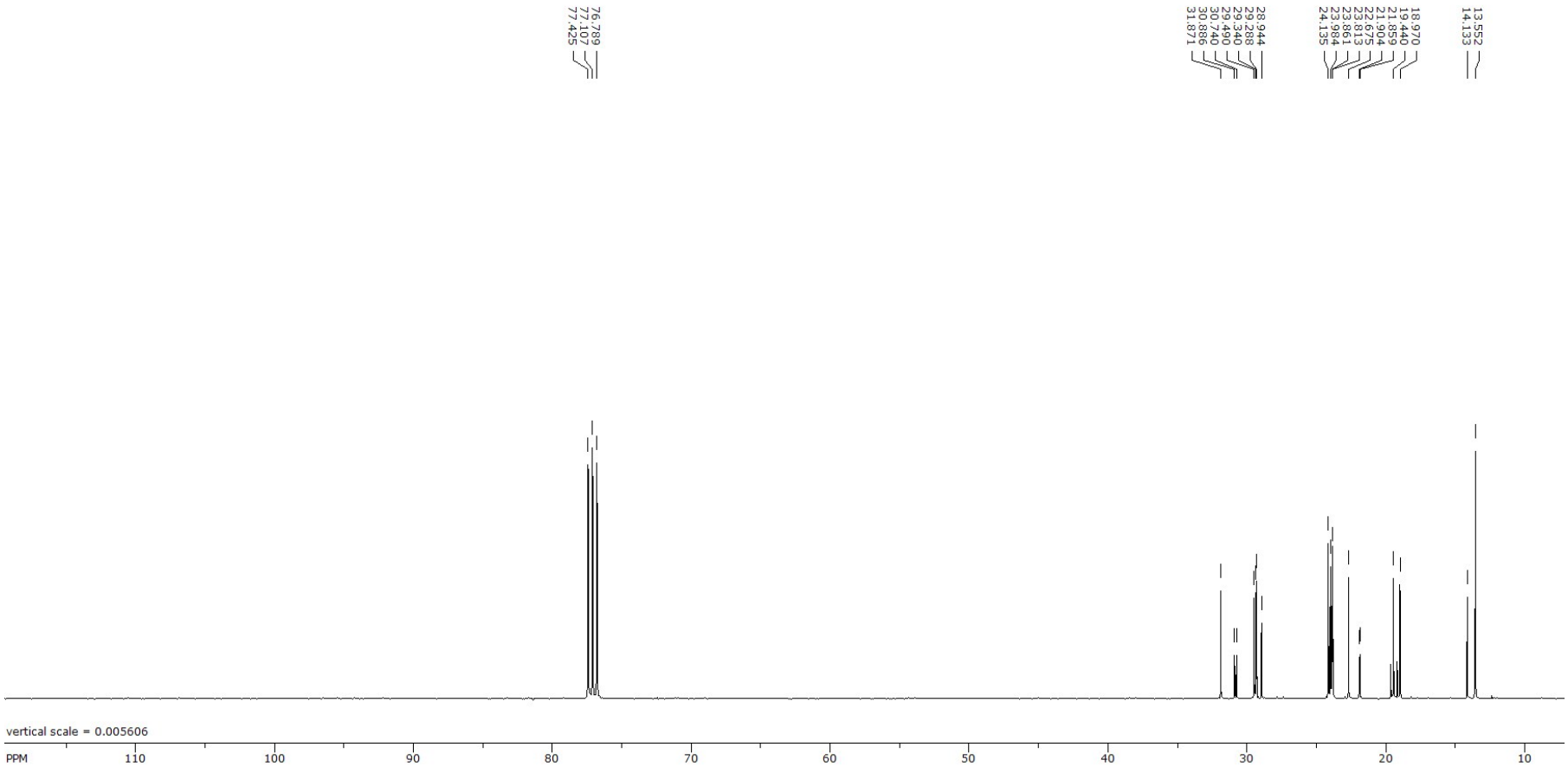

32.834
-0.177
vertical scale = 0.003245
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140

$[P_{44410}][Br_3]$

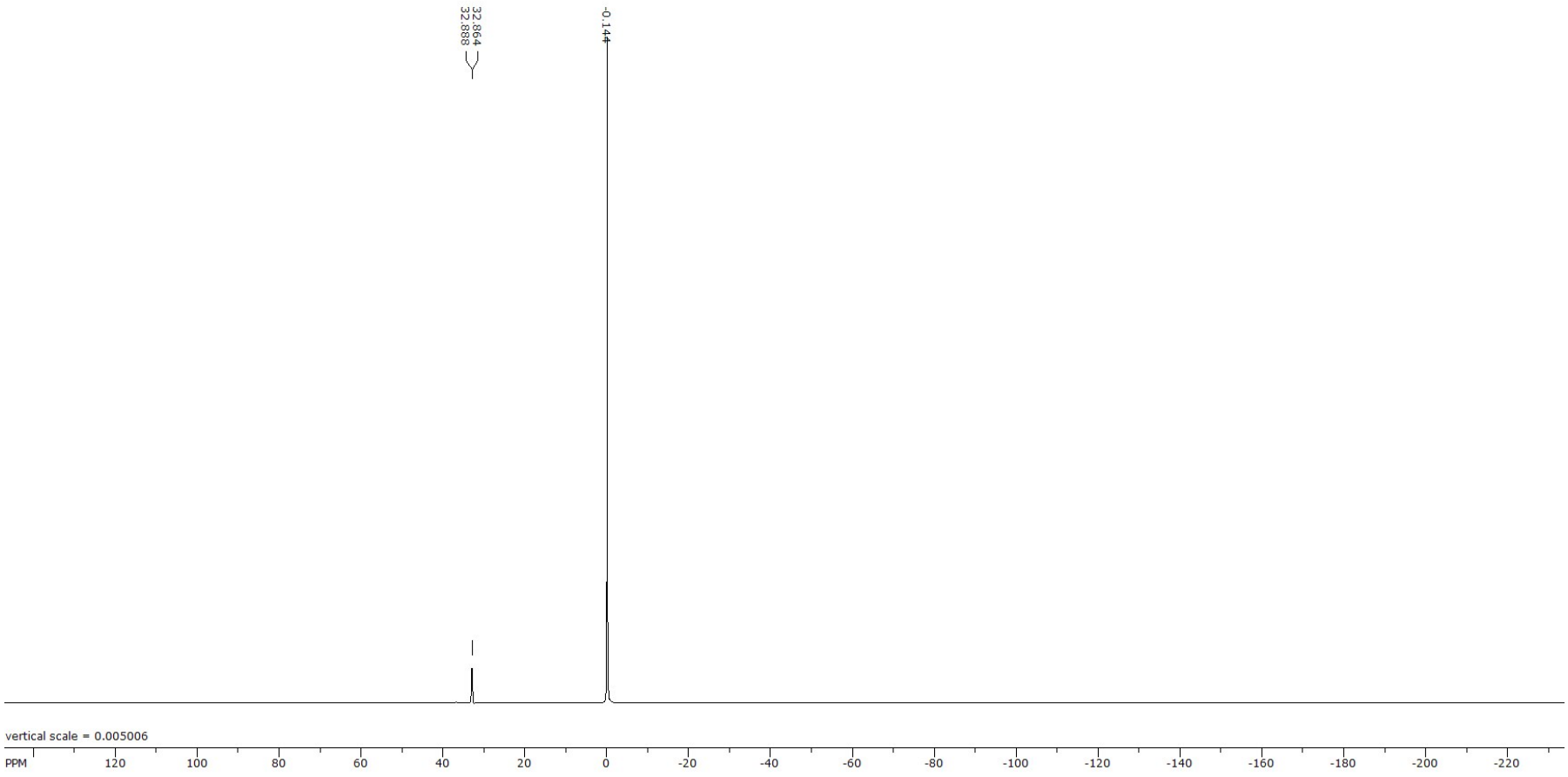
^1H NMR



^{13}C NMR

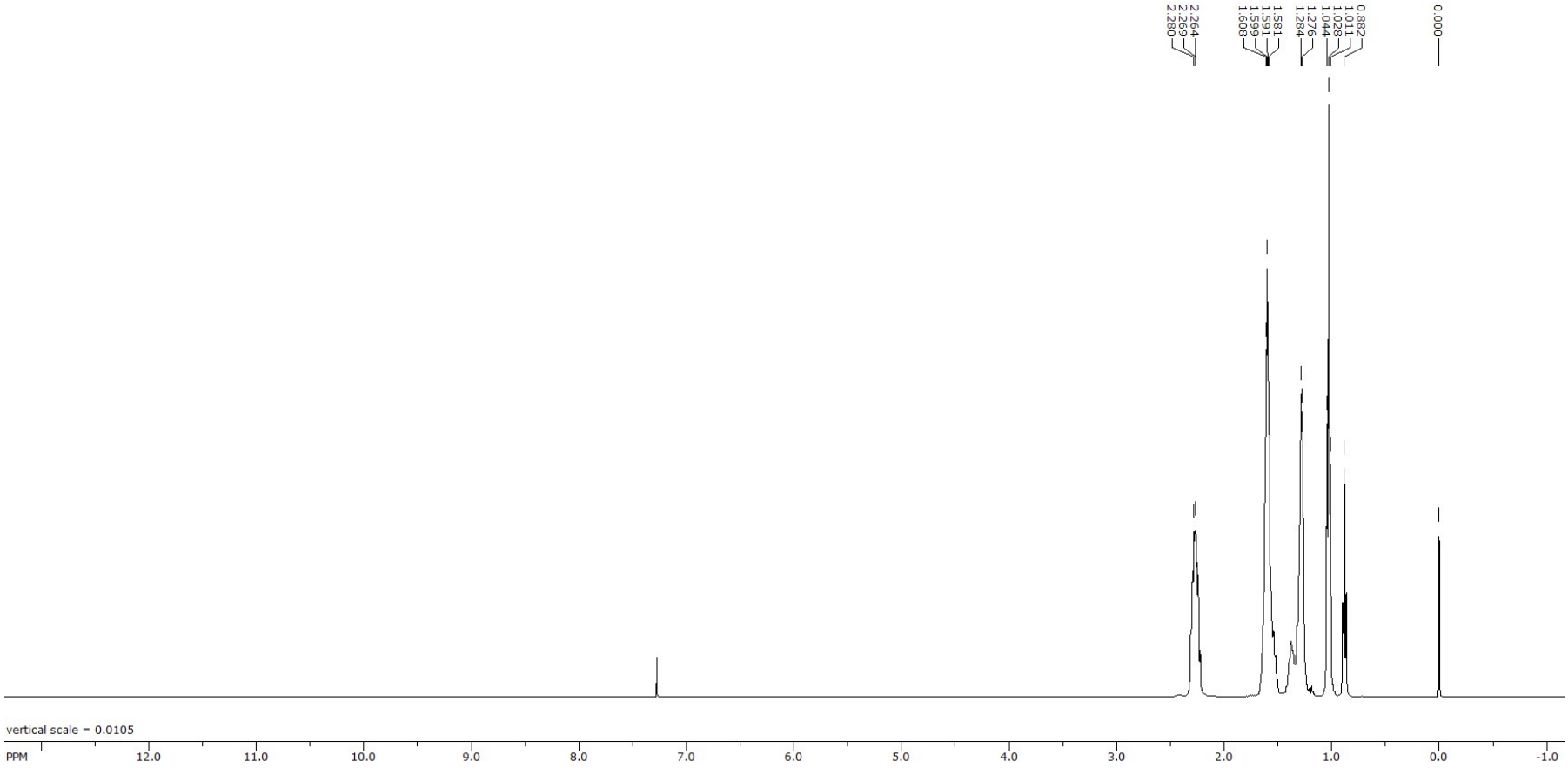

76.789
77.107
77.425
31.871
30.886
30.740
29.490
29.340
29.268
28.944
24.135
23.984
23.861
23.813
22.675
21.904
21.859
19.440
18.970
14.133
13.552
vertical scale = 0.005606
PPM
110
100
90
80
70
60
50
40
30
20
10

^{31}P NMR

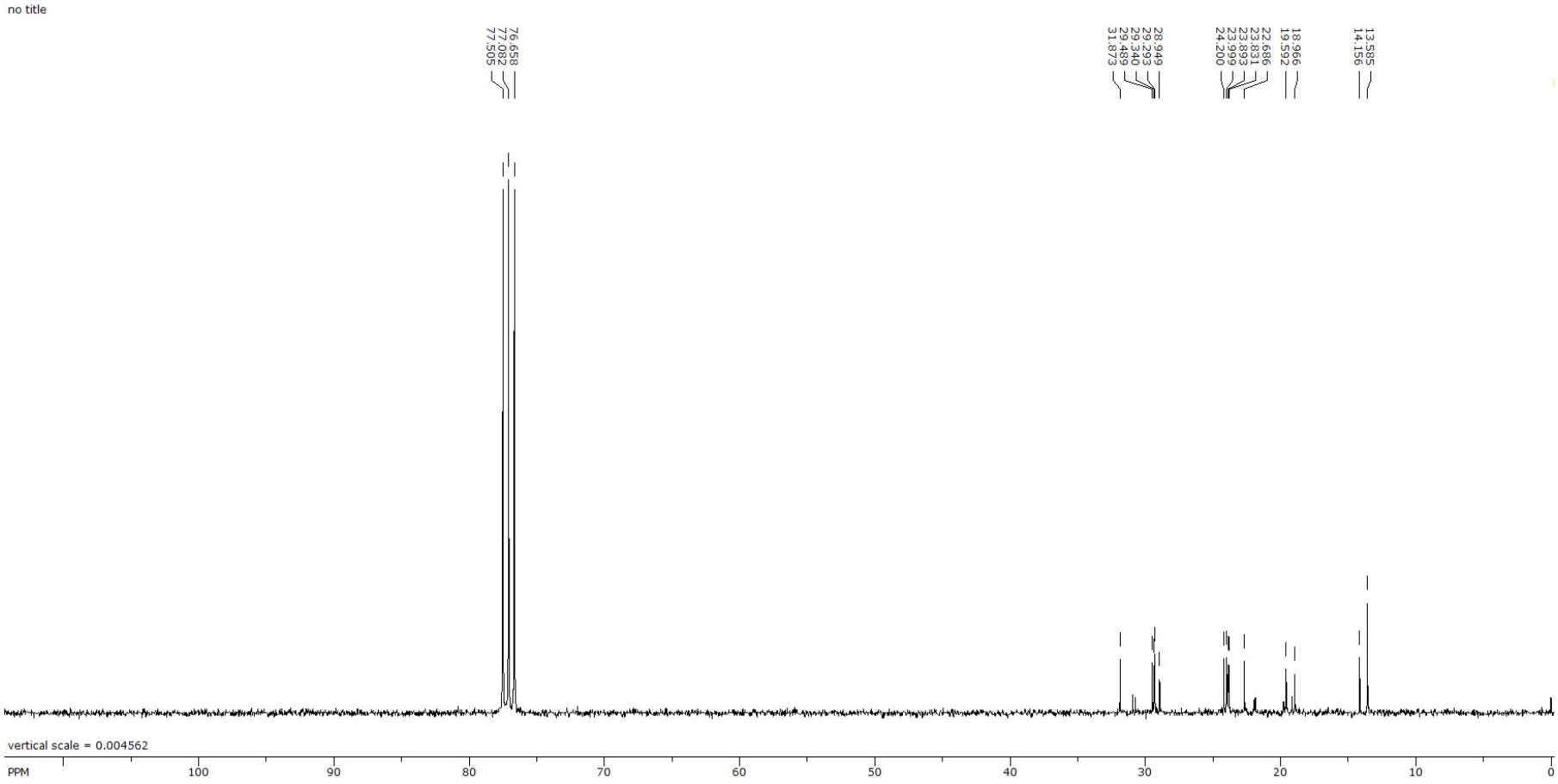

32.864
32.888
-0.144
vertical scale = 0.005006
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[P_{44410}][IBr_2]$

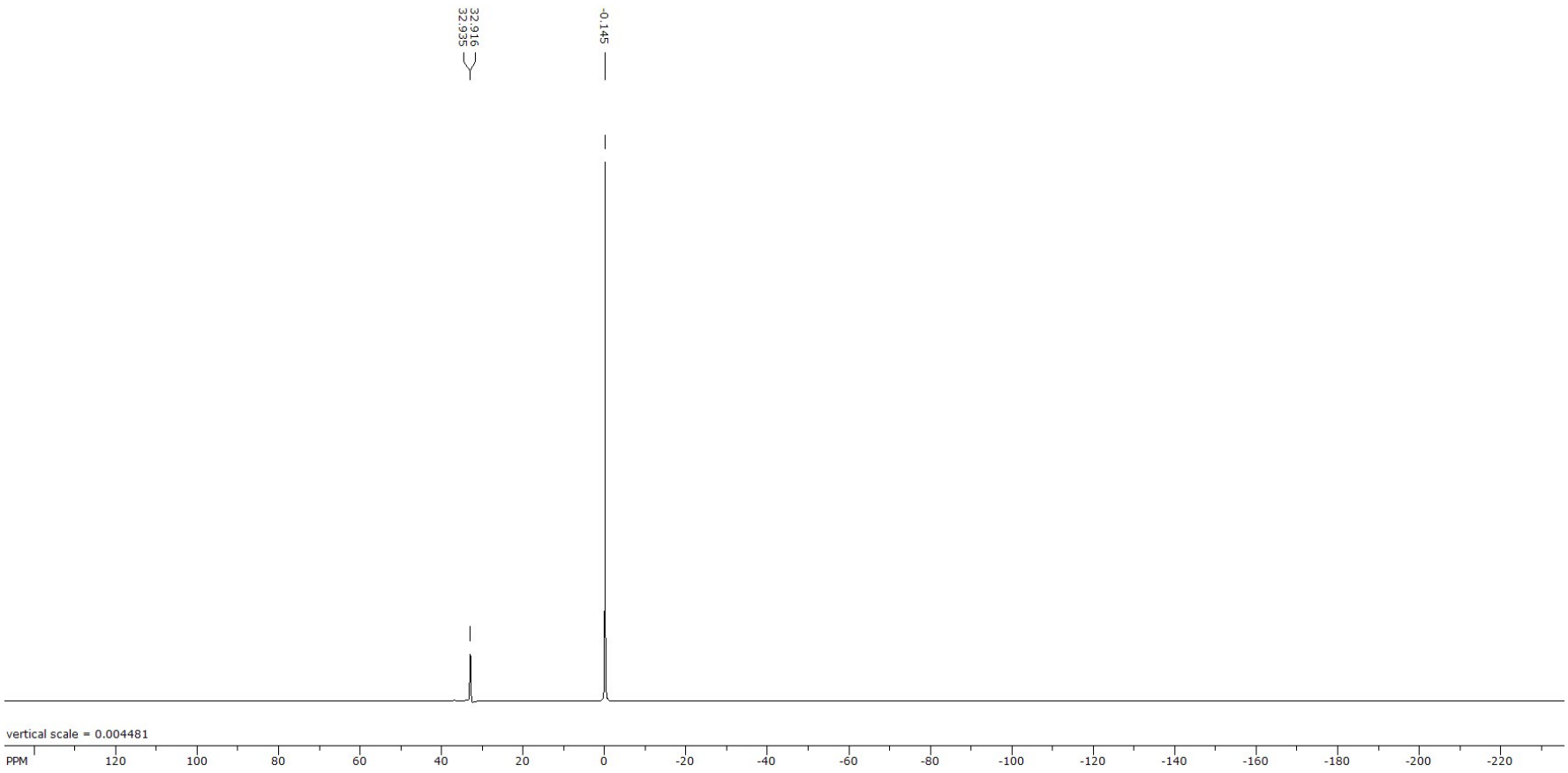
^1H NMR



^{13}C NMR

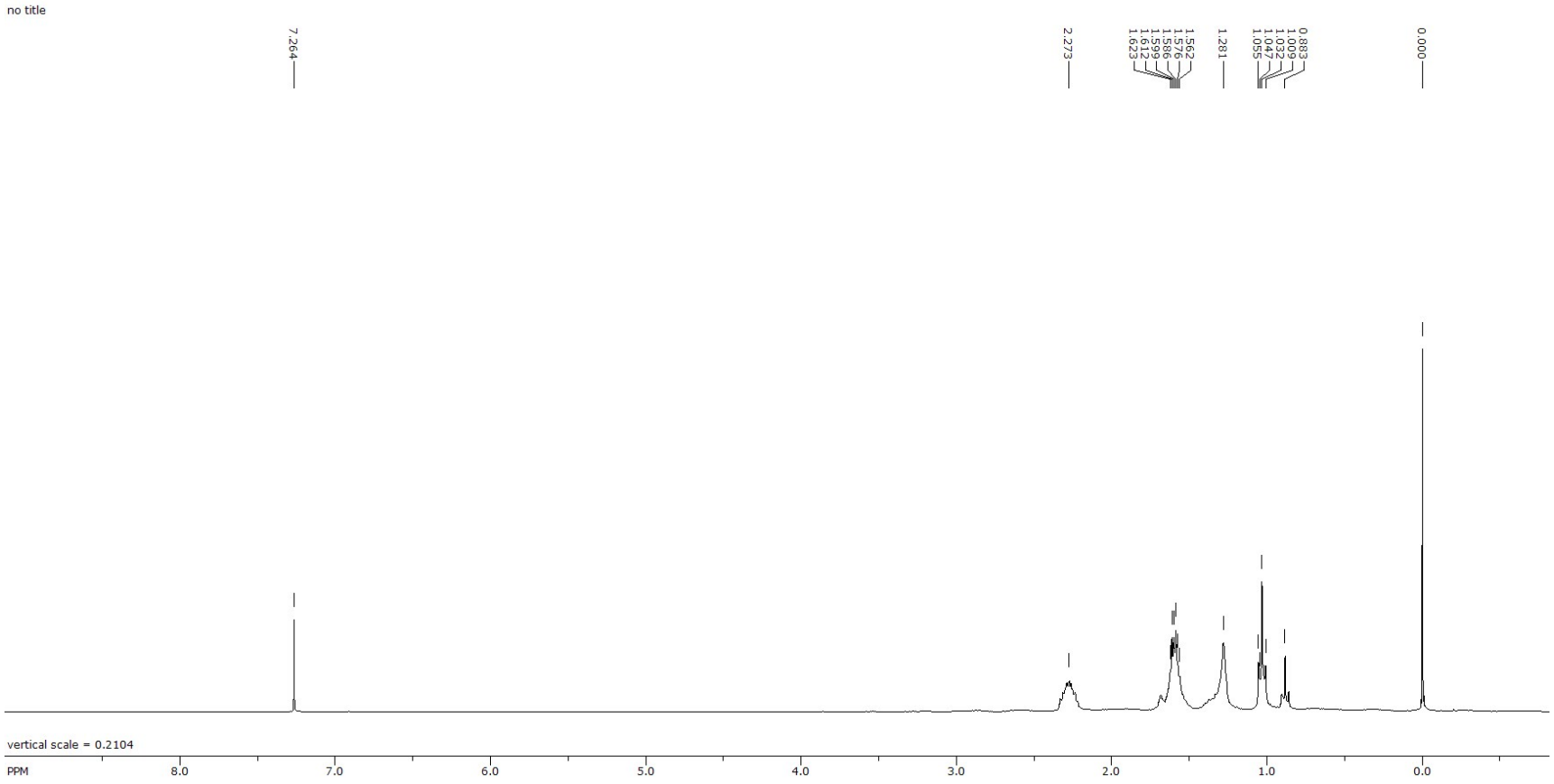

no title
77.505
77.082
76.658
31.873
29.489
29.340
29.293
28.949
24.200
23.999
23.893
23.831
22.686
19.592
18.966
14.156
13.585
vertical scale = 0.004562
PPM
100
90
80
70
60
50
40
30
20
10
0

^{31}P NMR

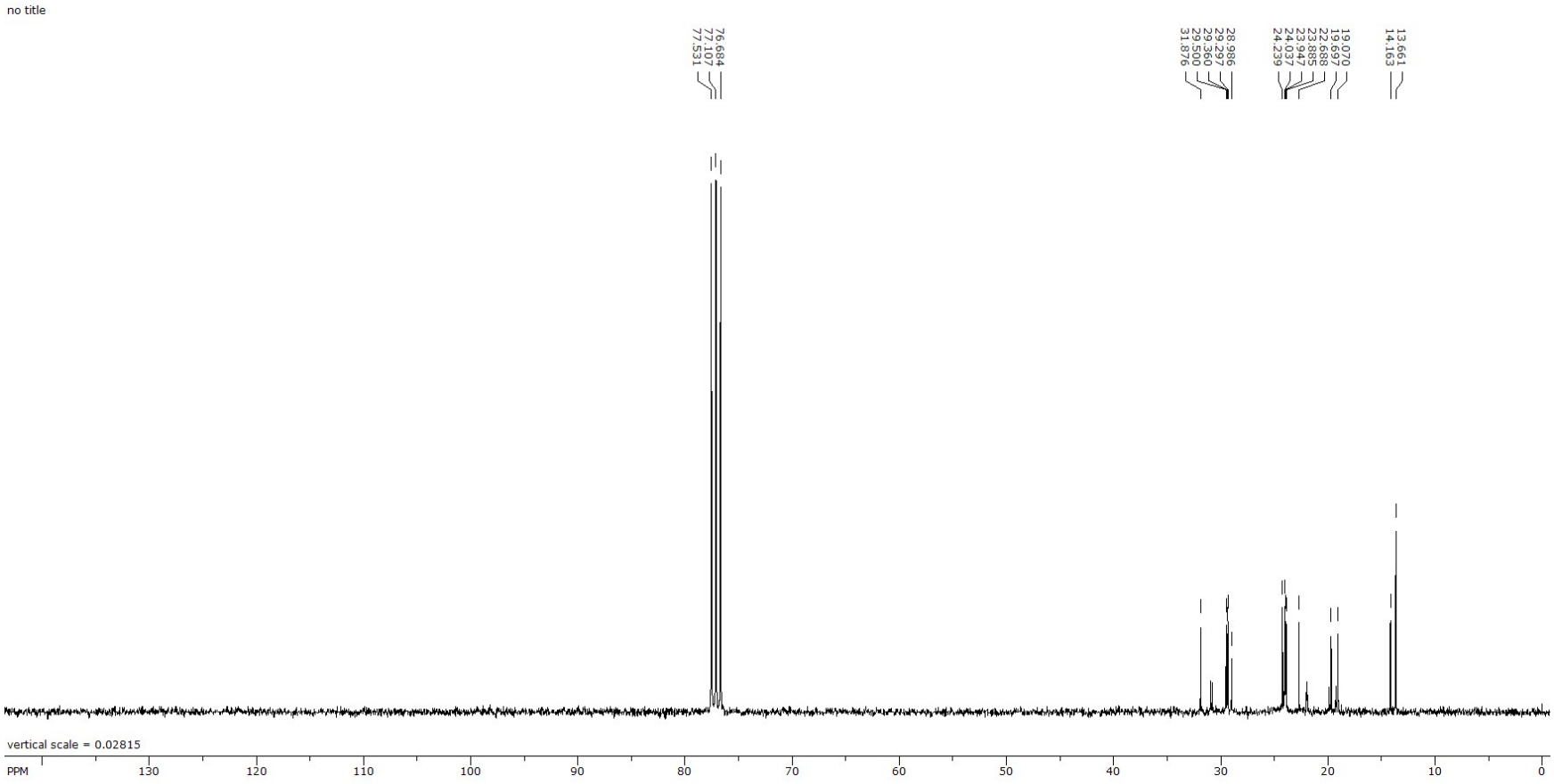

32.916
32.935
-0.145
vertical scale = 0.004481
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[P_{44410}][BrI_2]$

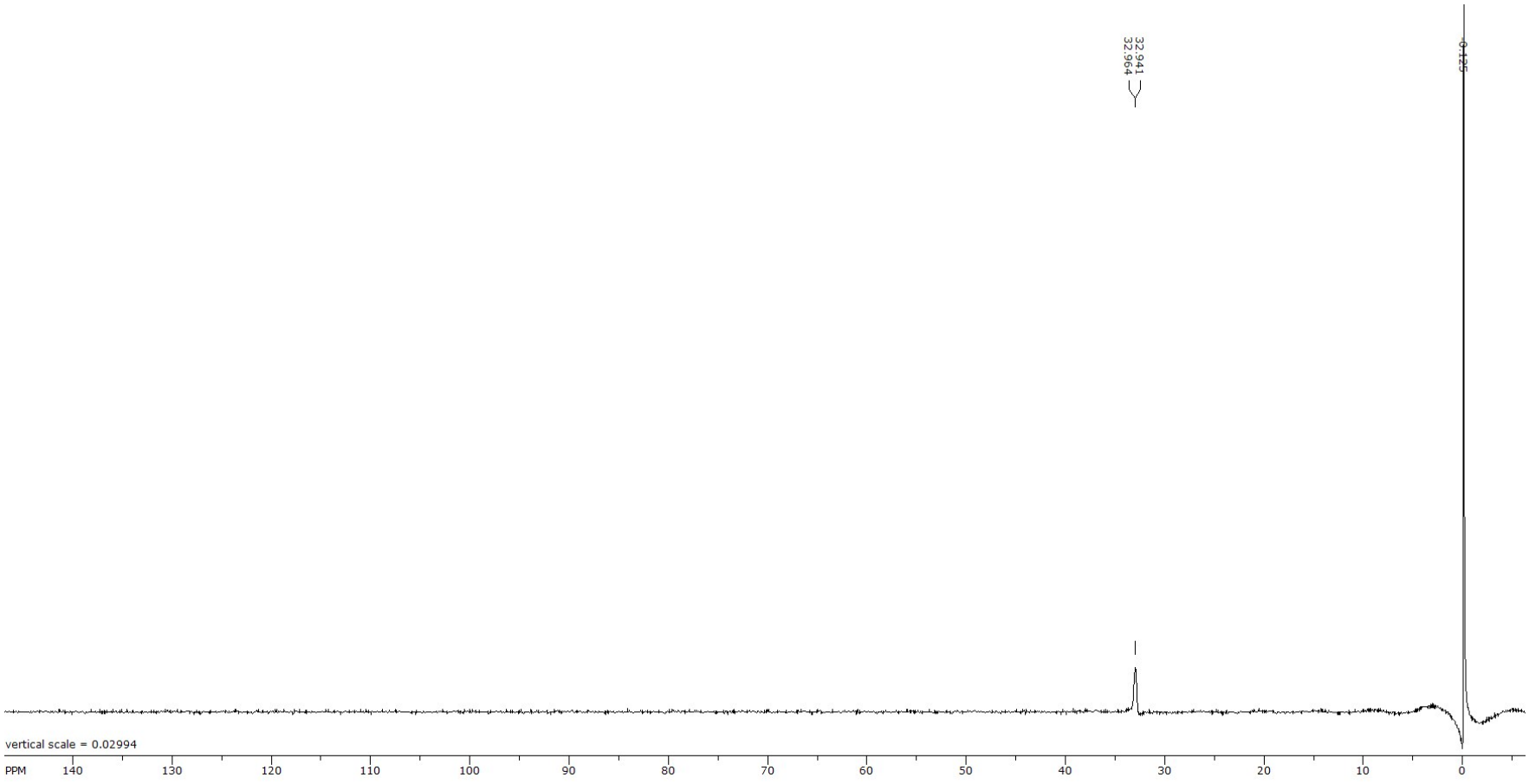
^1H NMR



^{13}C NMR

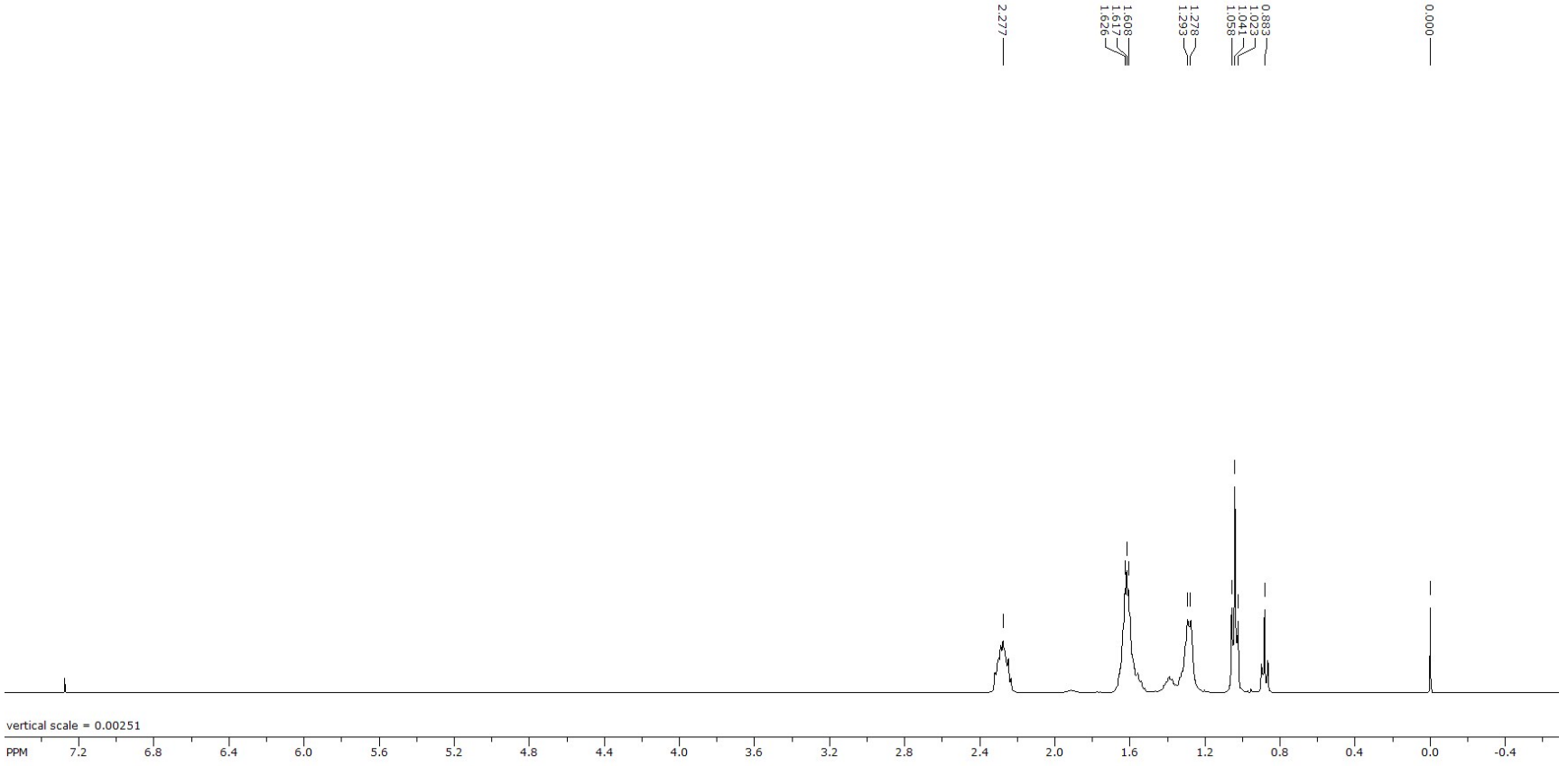

no title
76.684
77.107
77.531
28.986
29.287
29.360
29.500
31.876
19.070
19.697
22.688
23.885
23.947
24.037
24.239
13.661
14.163
vertical scale = 0.02815
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{31}P NMR

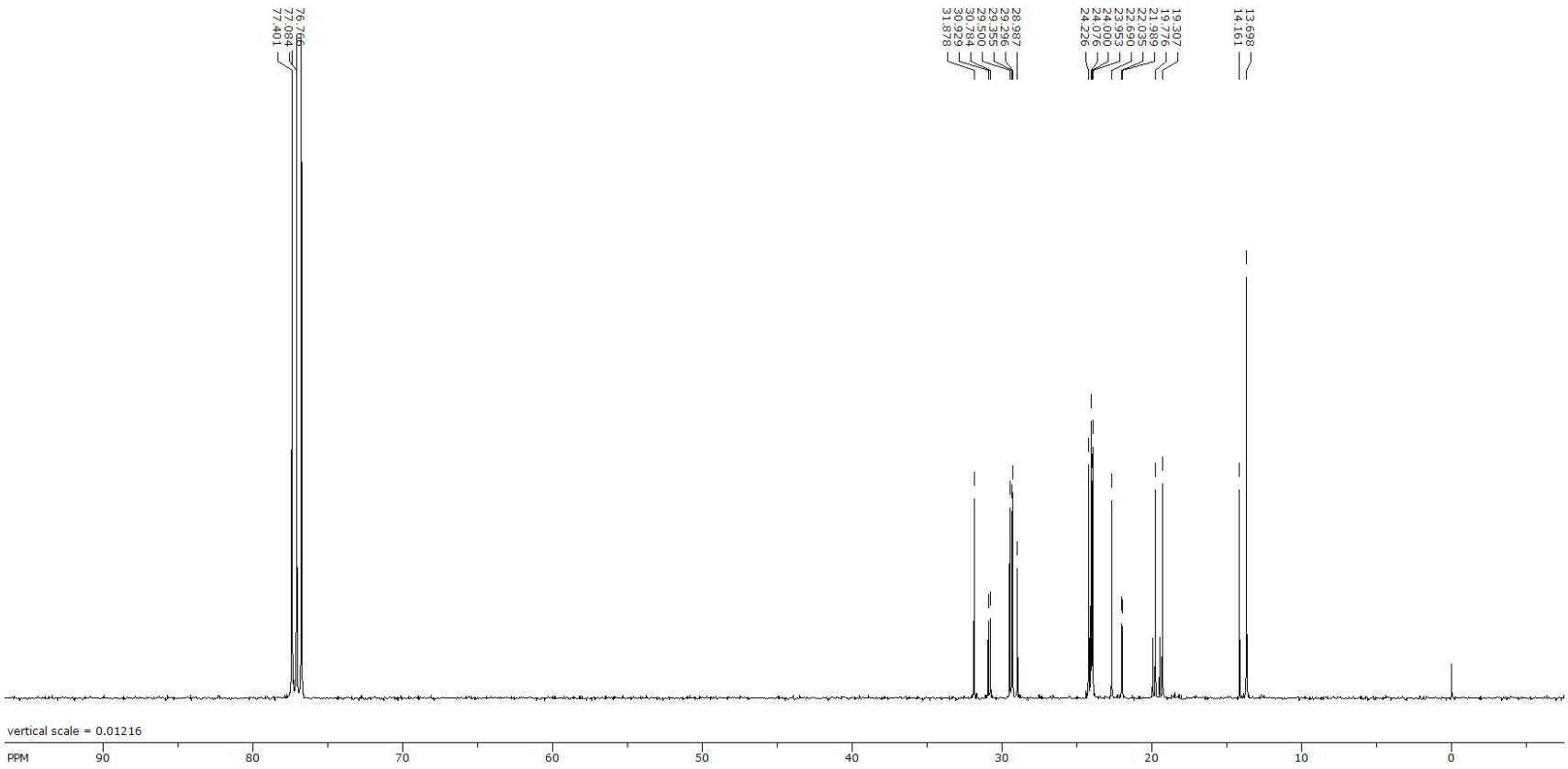

32.941
32.964
0.125
vertical scale = 0.02994
PPM
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

$[P_{44410}][I_3]$

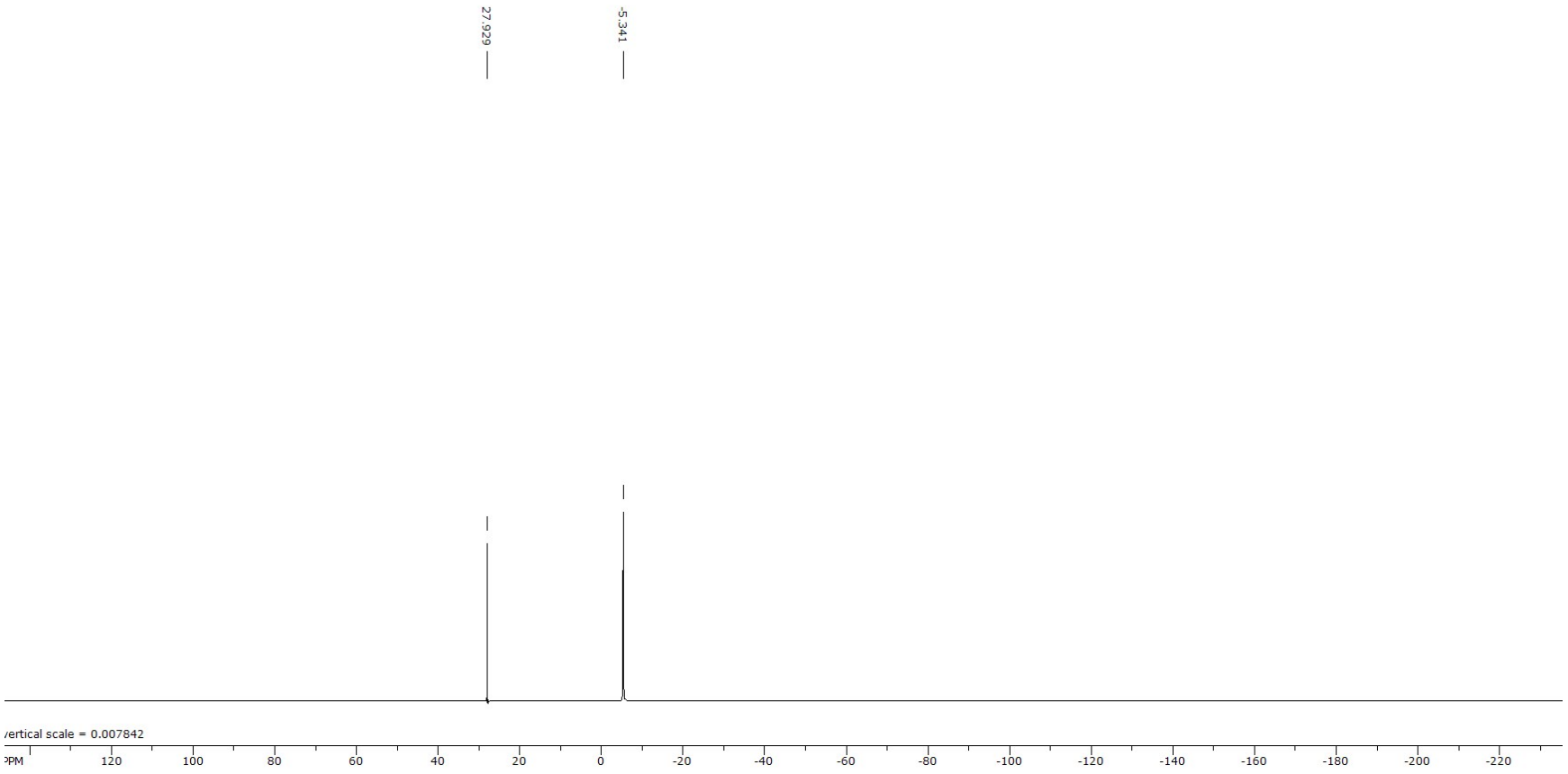
^1H NMR



^{13}C NMR

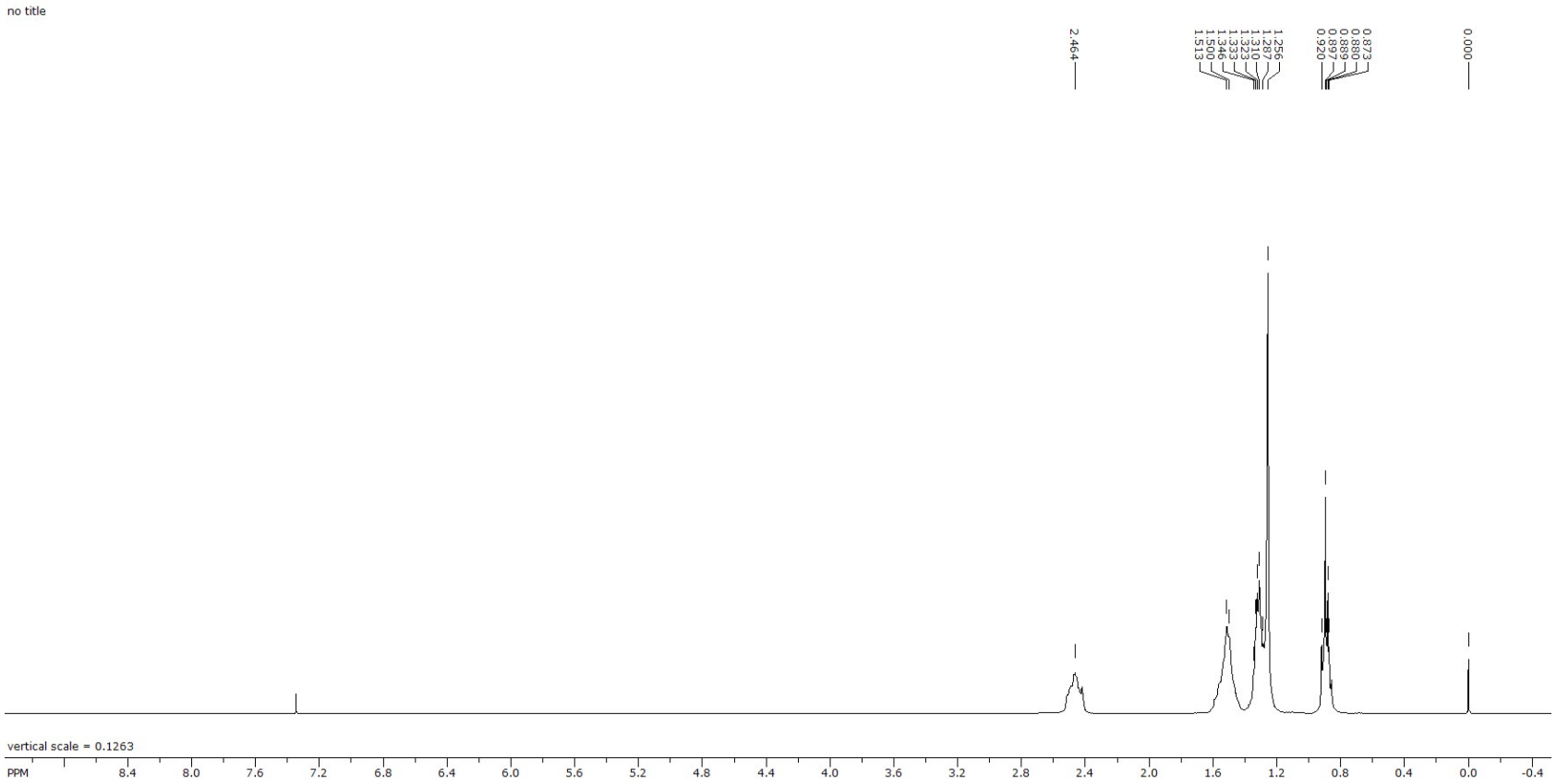

77.401
77.084
76.766
31.878
30.784
29.500
29.355
29.296
28.987
24.226
24.076
24.000
23.953
22.690
22.035
21.989
19.776
19.307
14.161
13.698
vertical scale = 0.01216
PPM
90
80
70
60
50
40
30
20
10
0

^{31}P NMR

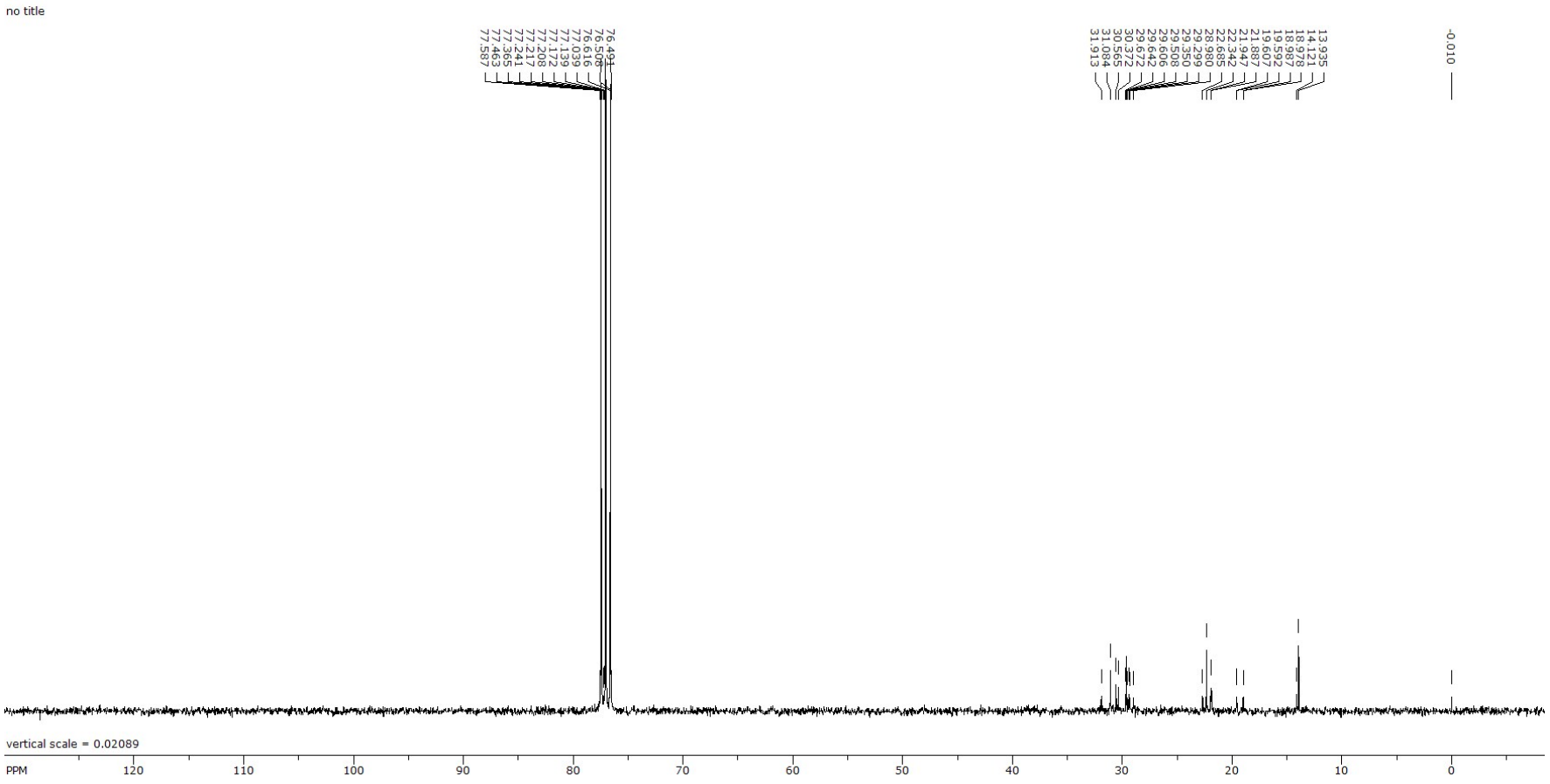

27.929
-5.341
vertical scale = 0.007842
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[P_{66614}][Cl_3]$

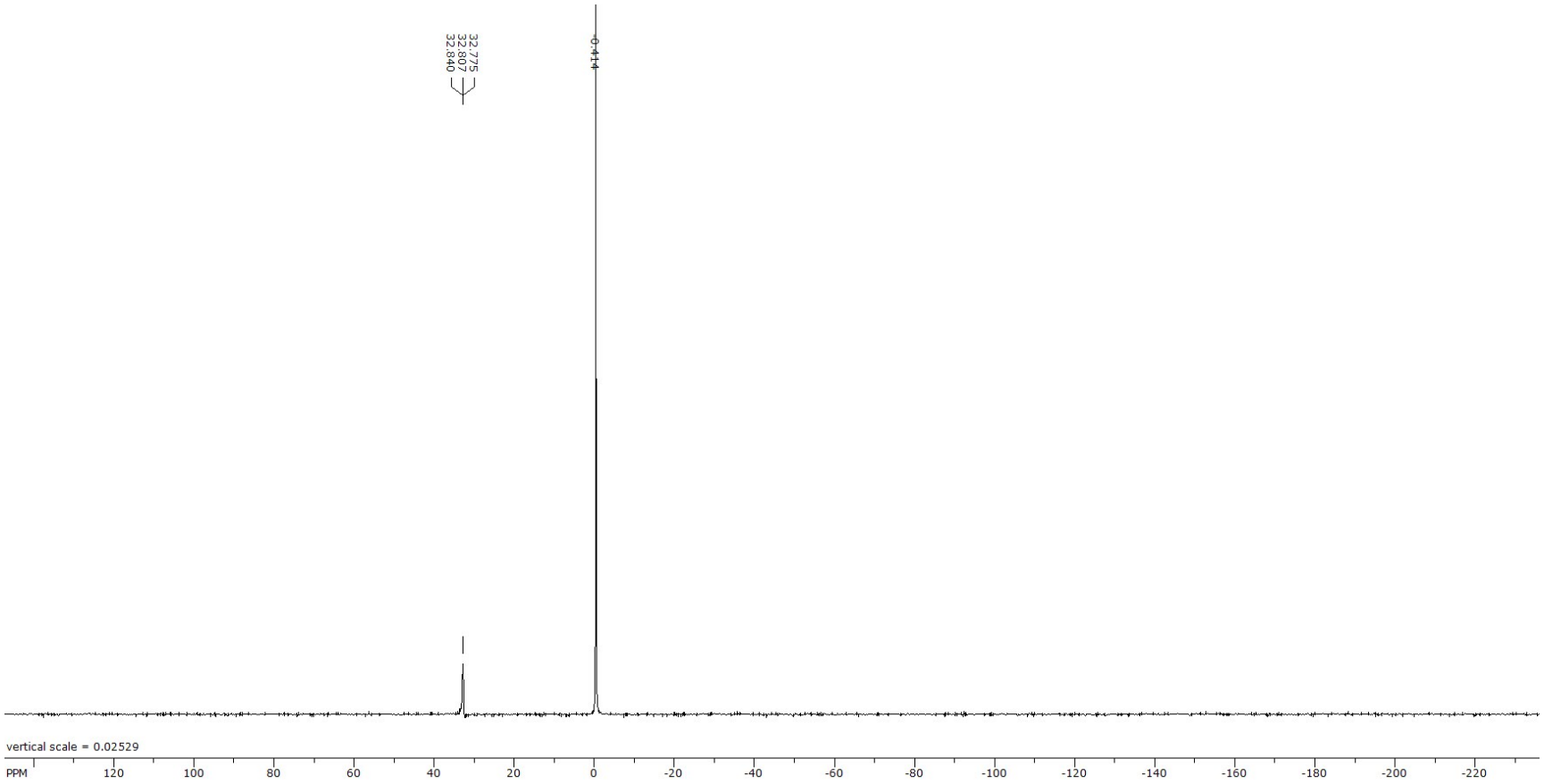
^1H NMR



^{13}C NMR

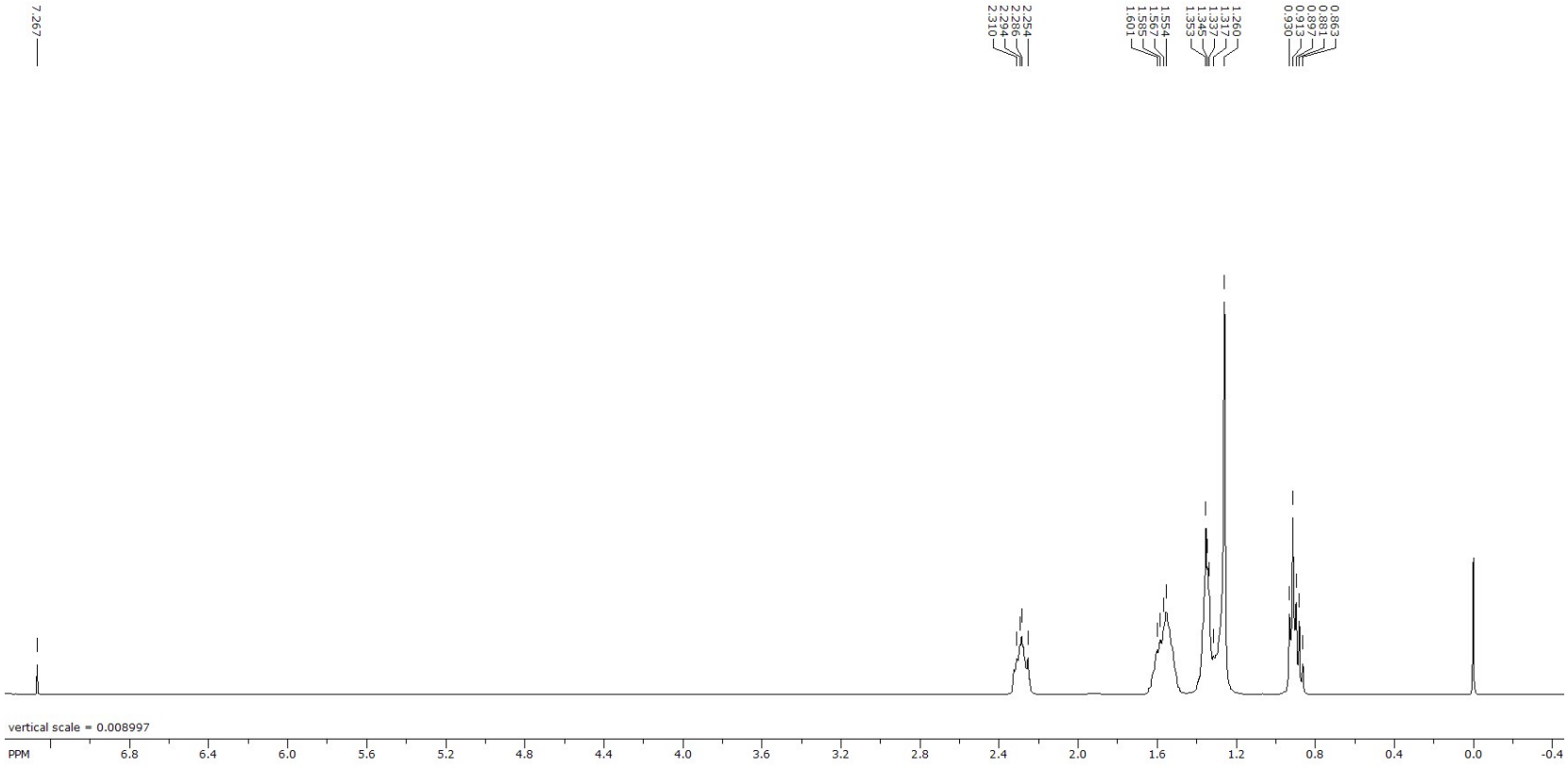

no title
77.587
77.483
77.385
77.241
77.217
77.208
77.172
77.139
77.039
76.616
76.508
76.491
31.913
31.084
30.565
30.372
29.672
29.642
29.606
29.508
29.350
29.299
28.980
22.685
22.342
21.887
19.607
19.592
18.987
18.978
14.121
13.935
-0.010
vertical scale = 0.02089
PPM
120
110
100
90
80
70
60
50
40
30
20
10
0

^{31}P NMR

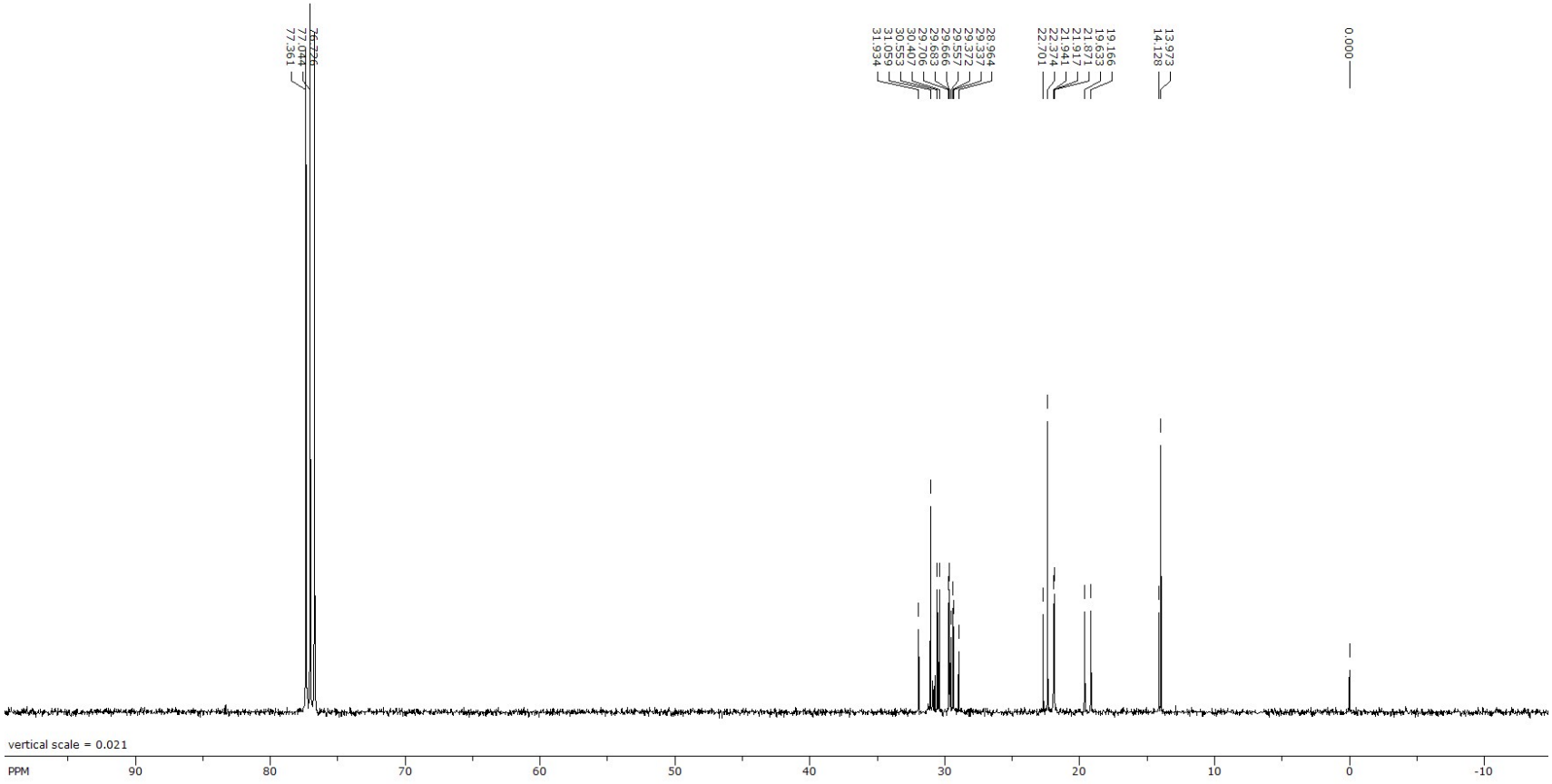

32.775
32.807
32.840
0.414
vertical scale = 0.02529
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[P_{66614}][ClBr_2]$

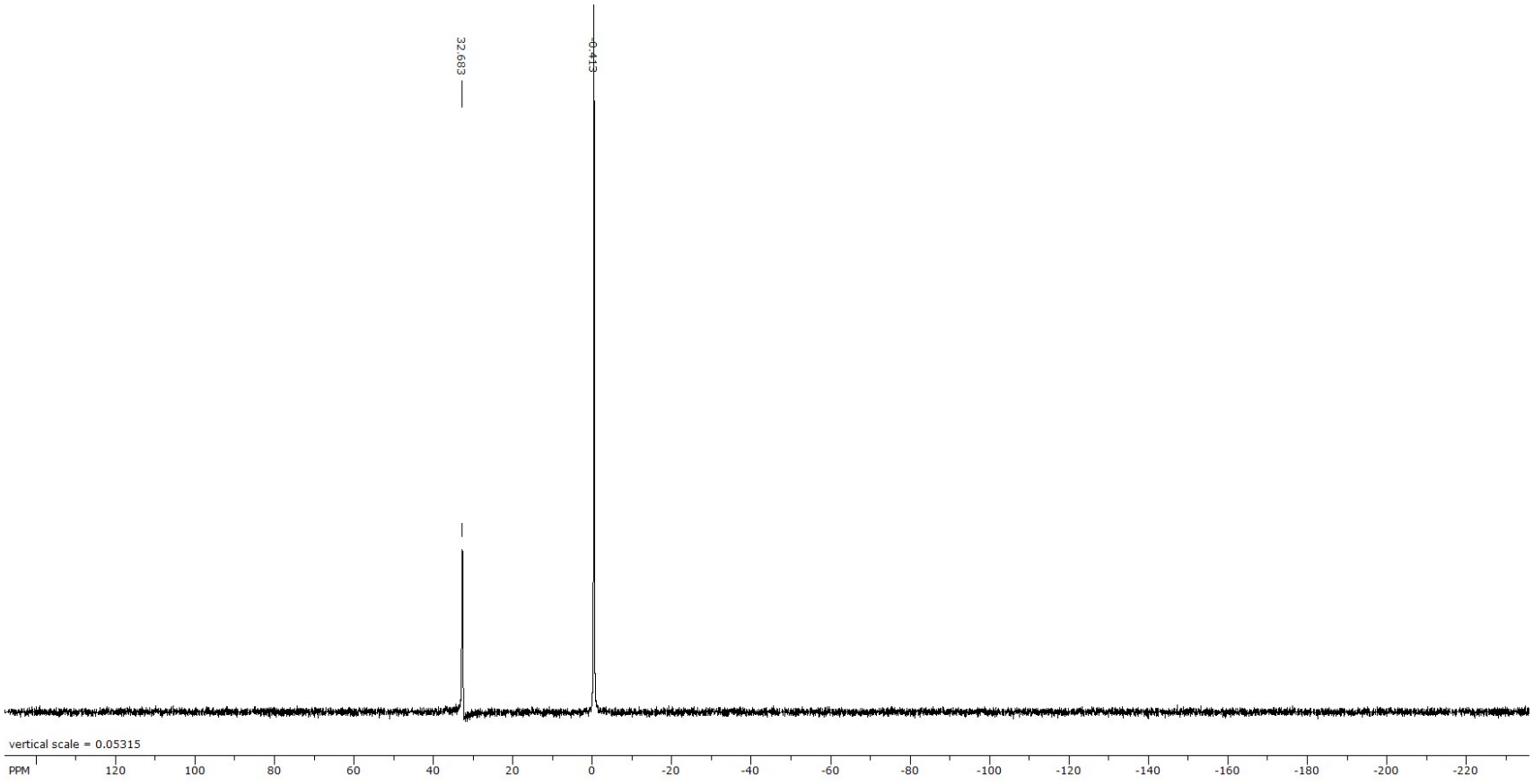
^1H NMR



^{13}C NMR

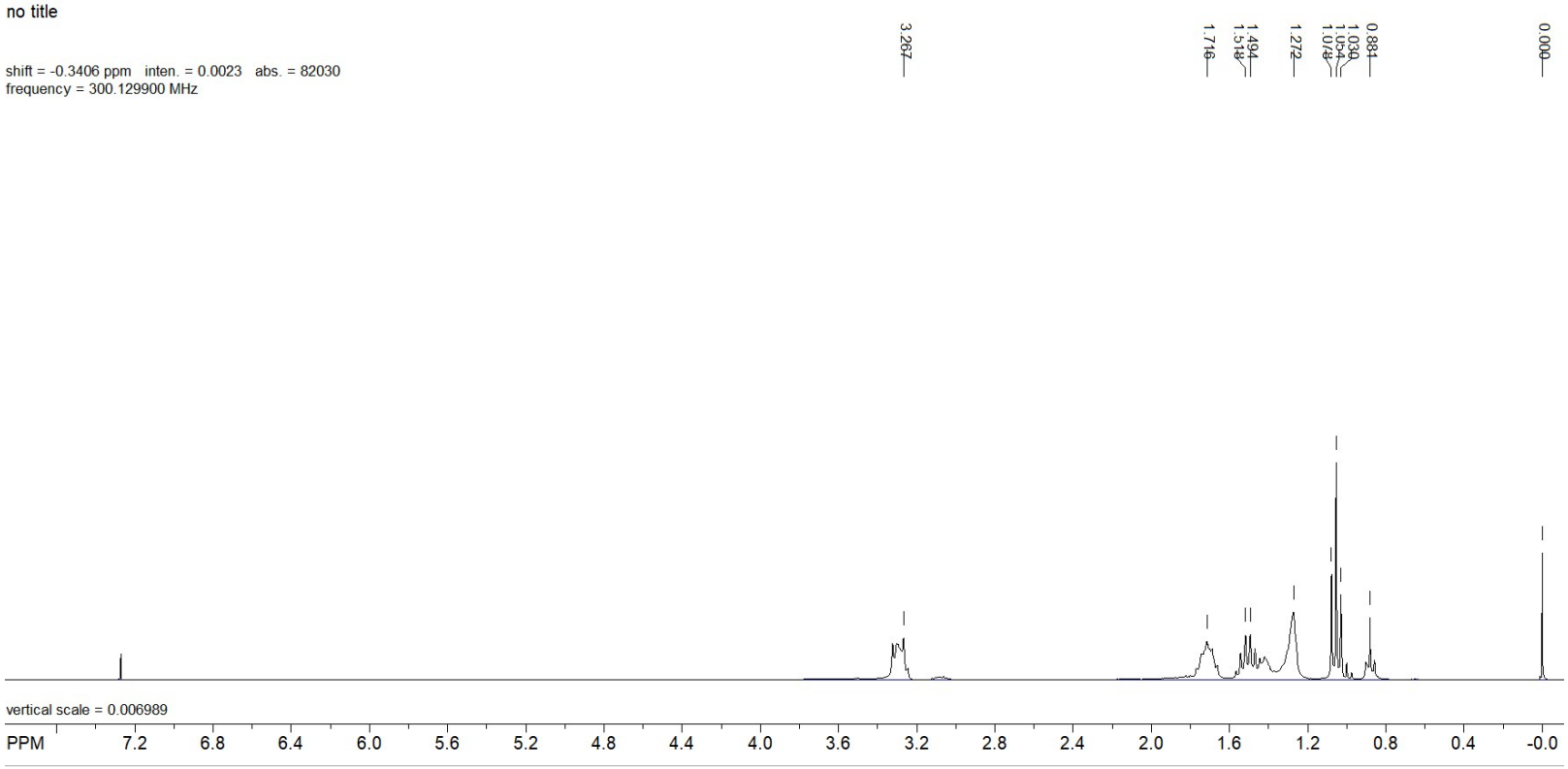

77.361
77.044
76.726
31.934
31.059
30.553
30.407
29.988
29.666
29.557
29.372
29.337
28.964
22.701
22.374
21.941
21.817
19.633
19.166
14.128
13.973
0.000
vertical scale = 0.021
PPM
90
80
70
60
50
40
30
20
10
0
-10

^{31}P NMR

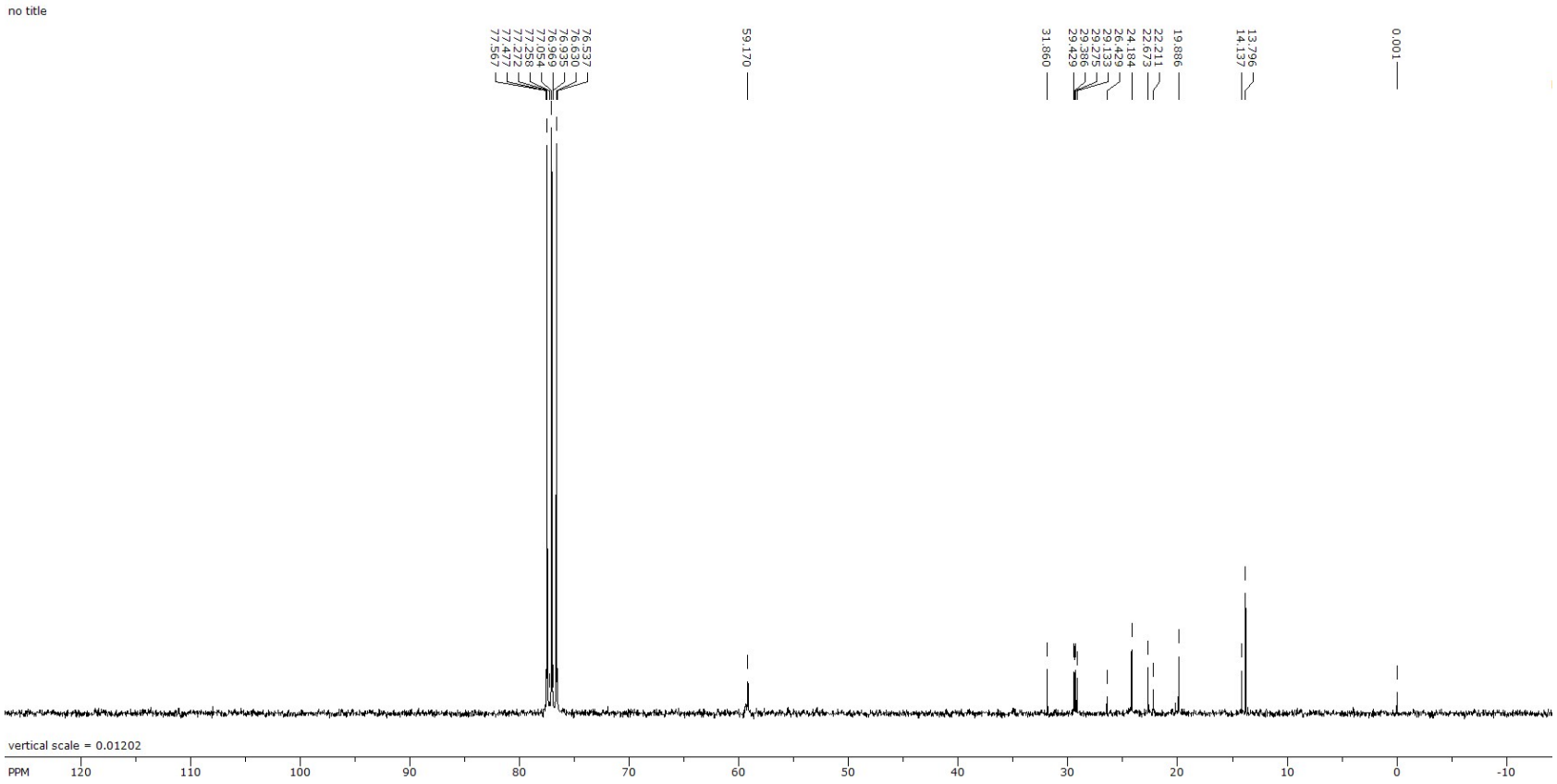

32.683
0.413
vertical scale = 0.05315
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220

$[N_{44410}][Br_3]$

^1H NMR

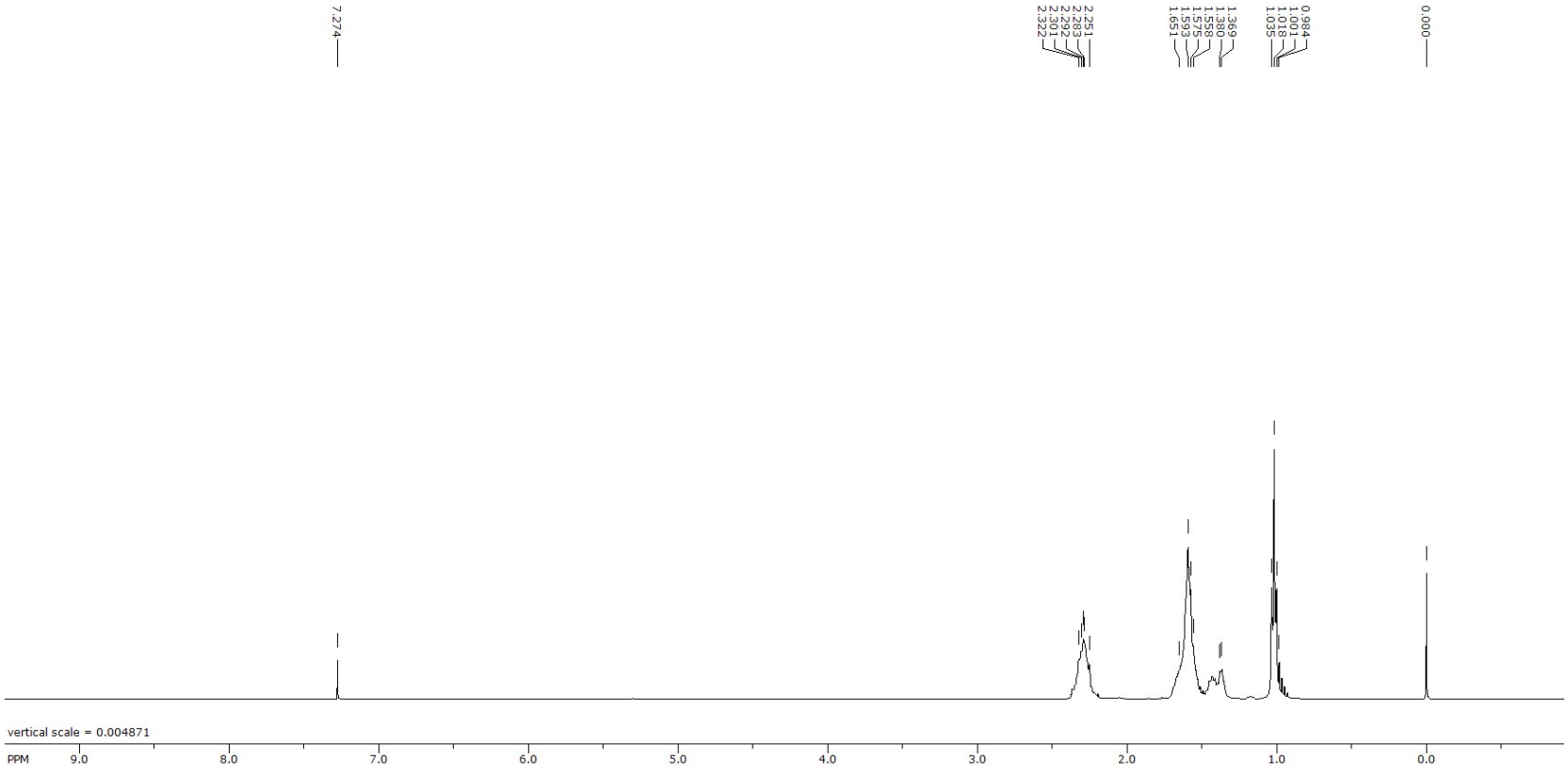


^{13}C NMR

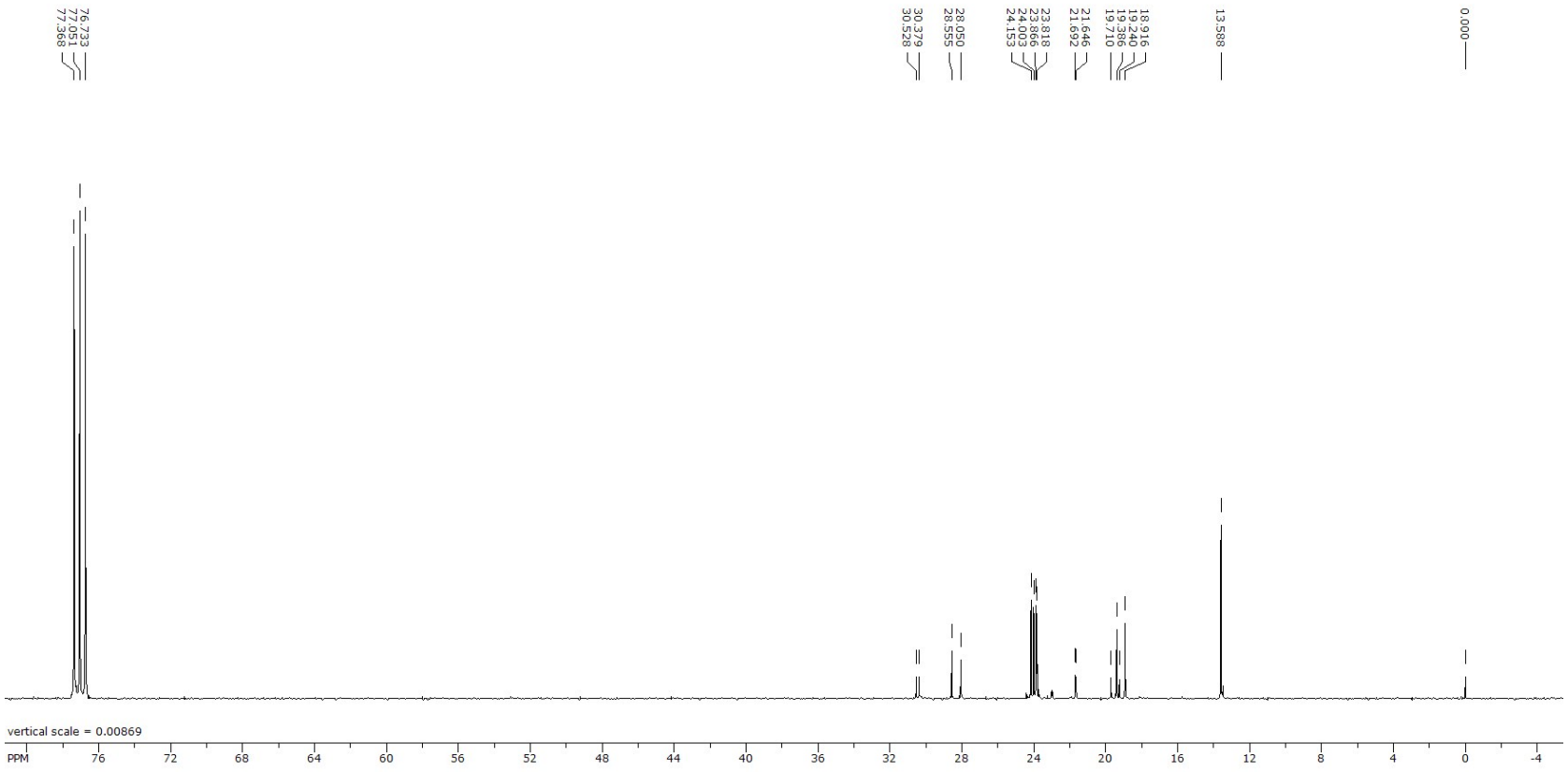

no title
77.567
77.477
77.272
77.054
76.965
76.630
76.537
59.170
31.860
29.429
29.386
29.275
26.429
24.184
22.673
22.211
19.886
14.137
13.796
0.001
vertical scale = 0.01202
PPM
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

$[C_{10}(P_{444})_2][(Br_3)_2]$

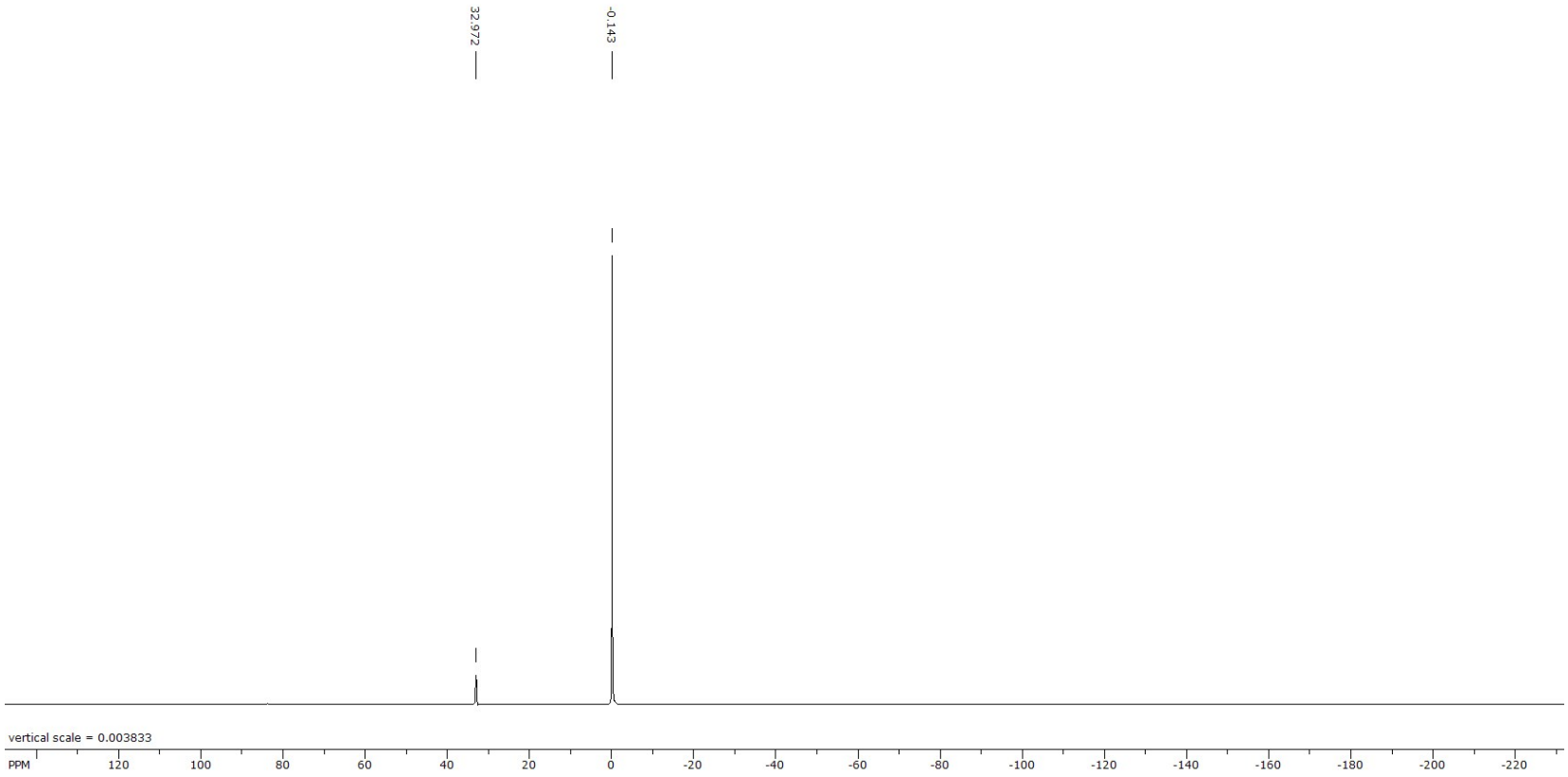
^1H NMR



^{13}C NMR


77.368
77.581
76.723
30.528
30.379
28.555
28.050
24.153
24.003
23.866
23.818
21.692
21.646
19.710
19.340
19.240
18.916
13.588
0.000
vertical scale = 0.00869
PPM
76
72
68
64
60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
0
-4

^{31}P NMR


32.972
-0.143
vertical scale = 0.003833
PPM
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220