Supporting Information

Design and Synthesis of a Bombesin Peptide-conjugated Tripodal Phosphino Dithioether Ligand Topology for the Stabilization of the *fac*-$[M(CO)_3]^+$ Core (M = ^{99m}Tc or Re)

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1. C-13 NMR data

$(EtO)_2P(O)CH_2CH_2SCH_2CH_2SH$ (1a): ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 61.70 (d, $P(O)CH_2CH_3$), 35.94 (s, SCH_2CH_2S), 26.71 (d, J_{P-C}= 136.80 Hz, P-CH_2), 24.71 (d, $^2J_{P-C}$ = 3.69 Hz, PCH_2CH_2S), 24.34 (S, CH_2), 16.32 (d, $P(O)CH_2CH_3$).

$H_2PCH_2CH_2SCH_2CH_2SH$ (2): $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): δ 35.84 (s, SCH_2), 34.97 (s, CH_2), 24.61 (s, $HSCH_2$), 14.83 (d, JP-C = 11. 45 Hz, P-CH_2)

$H_2PCH_2CH_2SCH_2CH_2SCH_3$ (3): ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 35.14 (s, SCH_2), 34.03 (s, CH_2), 31.34(s, SCH_2), 15.40 (s, SCH_3), 14.77 (d, J_{P-C} = 11. 20 Hz, P-CH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) : δ -141.13 (s).

$[(HOCH_2)_3PCH_2CH_2SCH_2CH_2SCH_3]Cl$ (4a): ^{13}C $\{^1H\}$ NMR (D_2O, 75 MHz): δ 50.21 (d, J_{P-C} = 53.74 Hz, P-CH_2), 32.58 (s, SCH_2), 30.25 (s, CH_2), 22.74 (d, J_{P-C} = 5.24 Hz, SCH_2CH_2P), 14.87 (d, J_{P-C} = 38.19 Hz, SCH_2CH_2P), 13.85 (s, SCH_3).

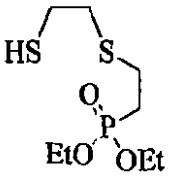
$H_2PCH_2CH_2SCH_2CH_2SCH_2COO^tBu$ (7): $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): δ 169.30 (s, *C*OO^tBu), 81.32 (S, COO*C*(CH3)3), 34.92 (s, SCH_2CO), 34.56 (s, SCH_2), 32.18 (s, SCH_2), 27.80 (s, SCH_2), 14.71 (d, JP-C = 11. 25 Hz, P-CH_2).

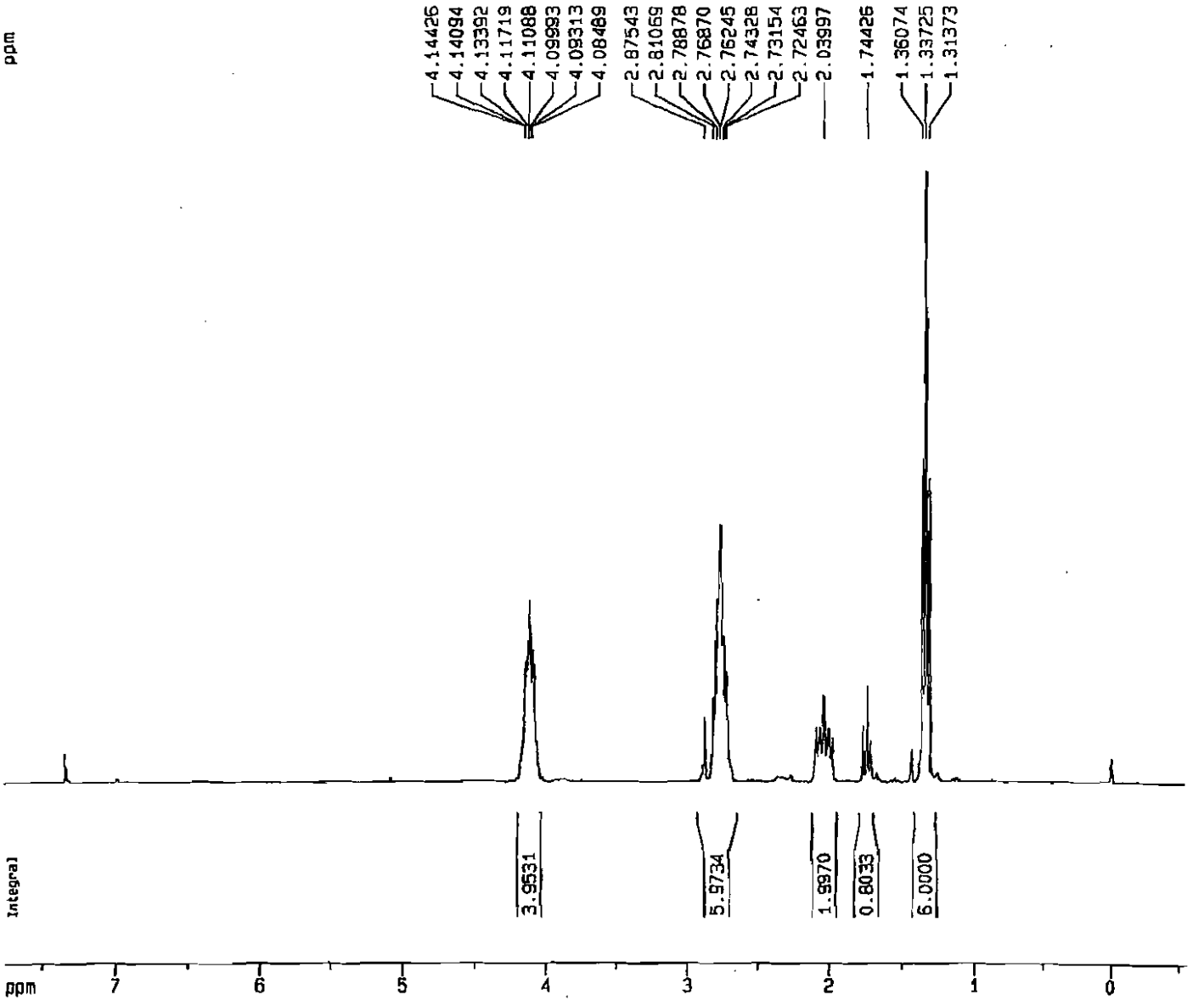
$H_2PCH_2CH_2SCH_2CH_2SCH_2COOH$ (8): ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 175.62 (s, COOH), 35.06 (s, SCH_2CO), 32.45 (s, SCH_2), 31.14 (s, SCH_2), 27.84 (s, SCH_2), 14.71 (d, JP-C = 11. 25 Hz, P-CH_2).

2. ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ and ^{31}P NMR Spectra of compounds synthesized in the present study:

^{31}P NMR

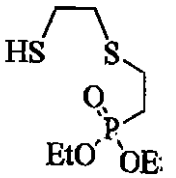
($CDCl_3$, 300 MHz)

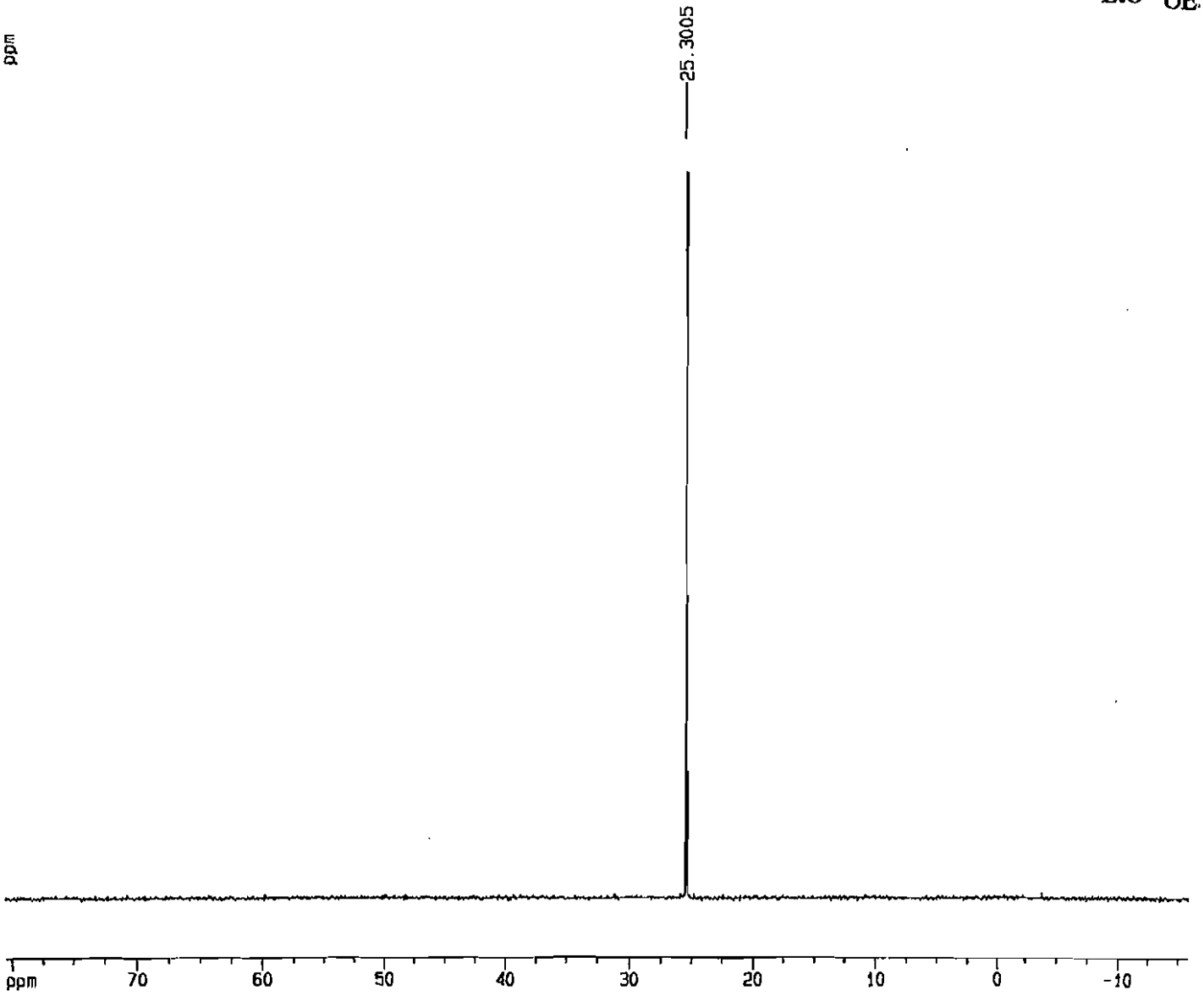




$^{31}P\{^{1}H\}$ NMR

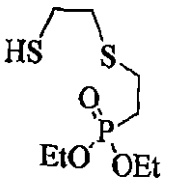
($CDCl_3$, 121 MHz)

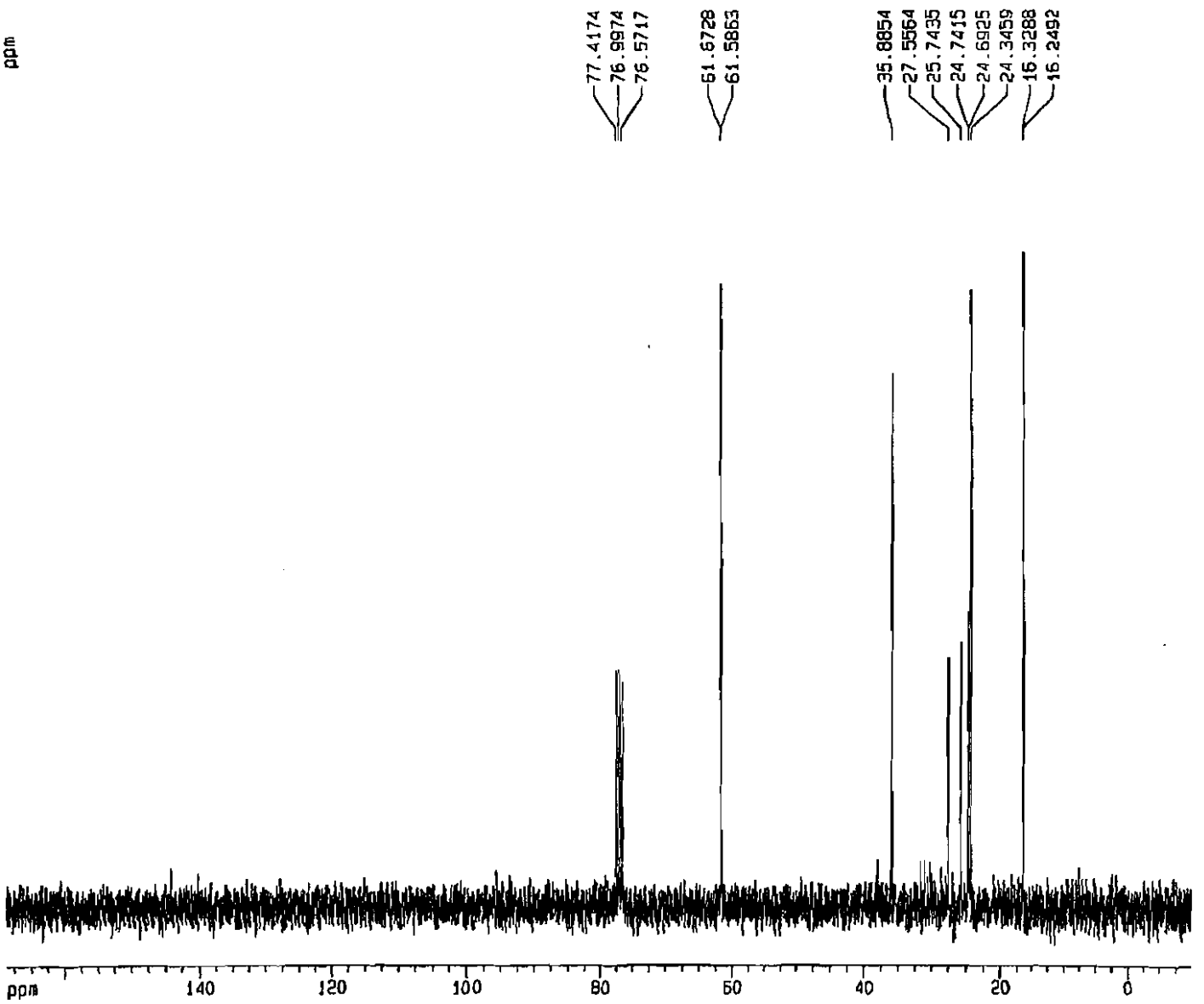




^{13}C NMR

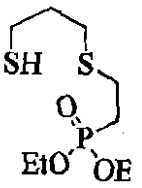
($CDCl_3$, 75MHz)

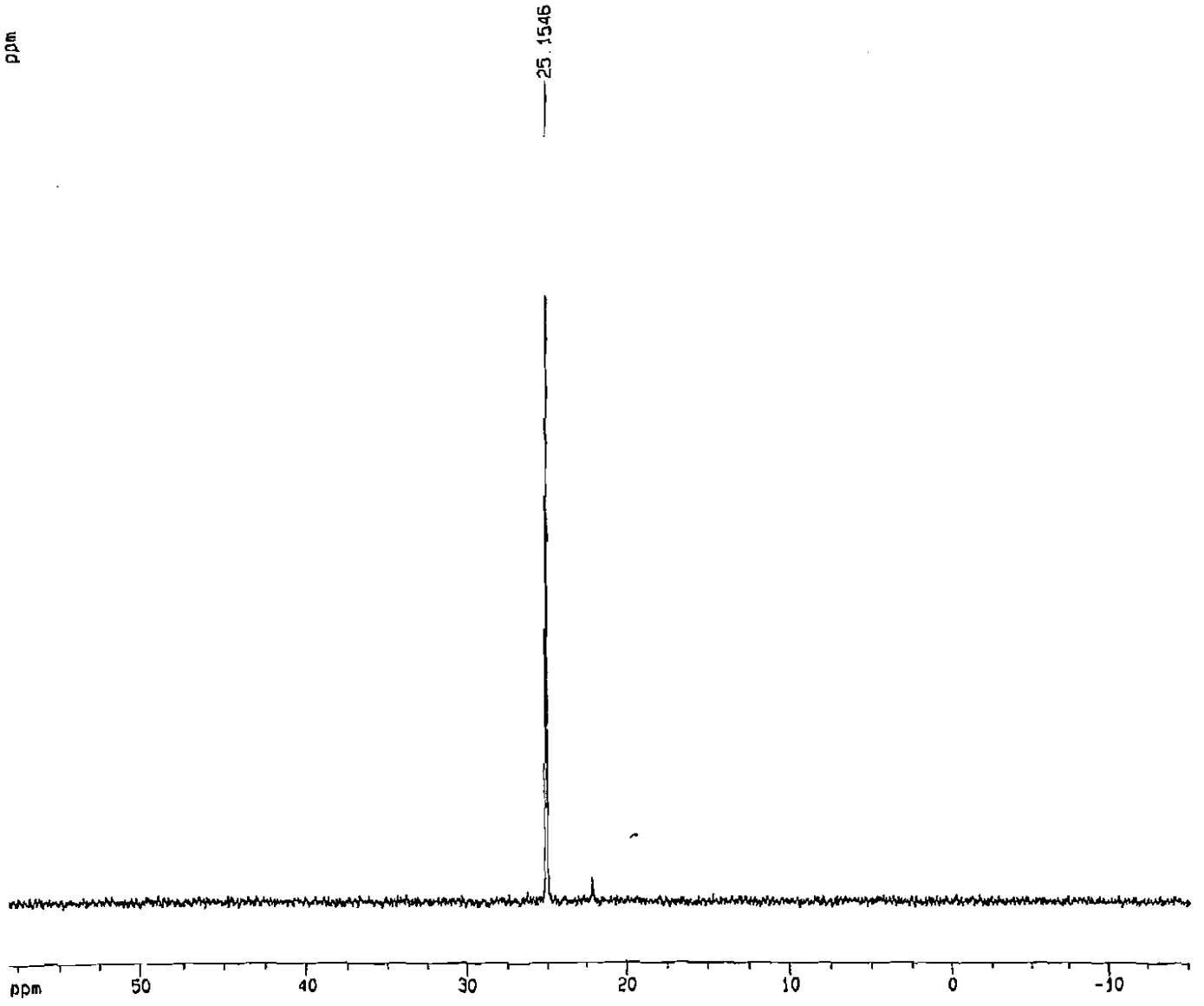




$^{31}P\{^{1}H\}$ NMR

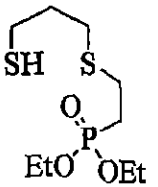
$CDCl_3$, 121 MHz

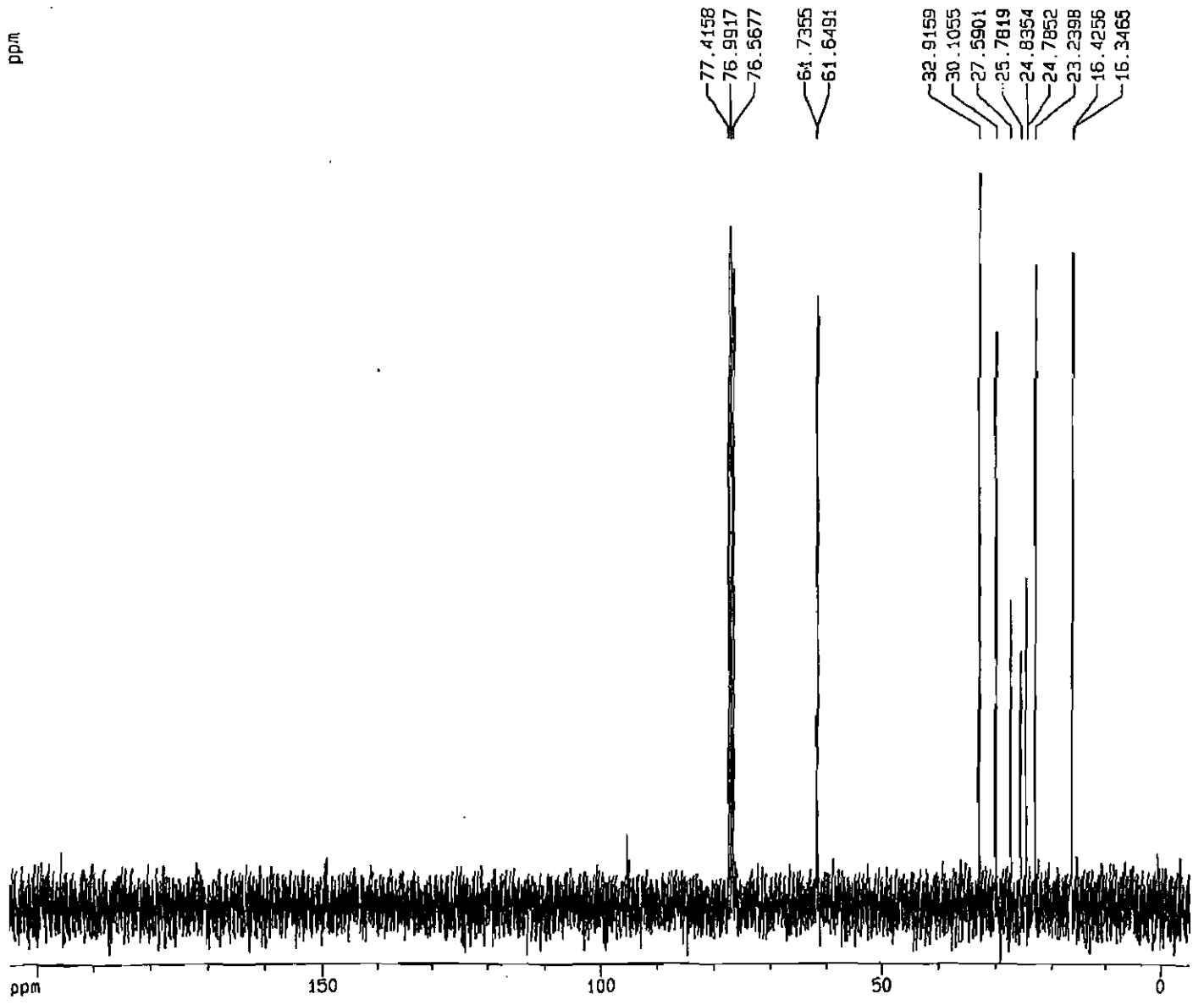


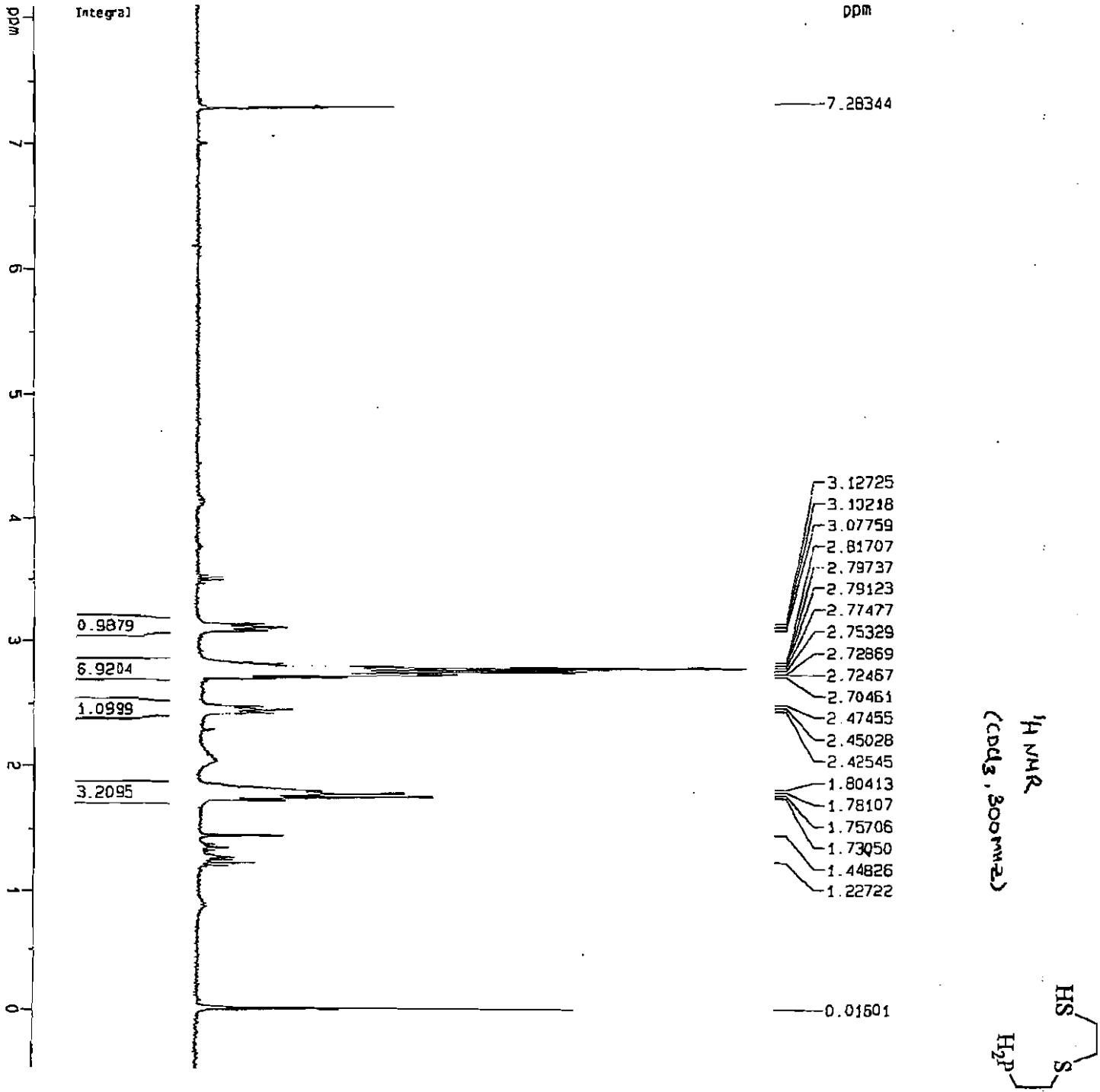


^{13}C NMR

$CDCl_3$, 75MHz





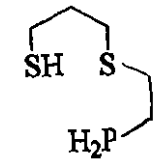


^1H NMR
($CDCl_3$, 300MHz)

ppm
200
150
100
50
0
ppm
^{13}C NMR
($CDCl_3$, 75 MHz)
PH_2
S
SH
77.4201
76.9948
76.5716
35.8426
34.9789
24.6153
14.9080
14.7563

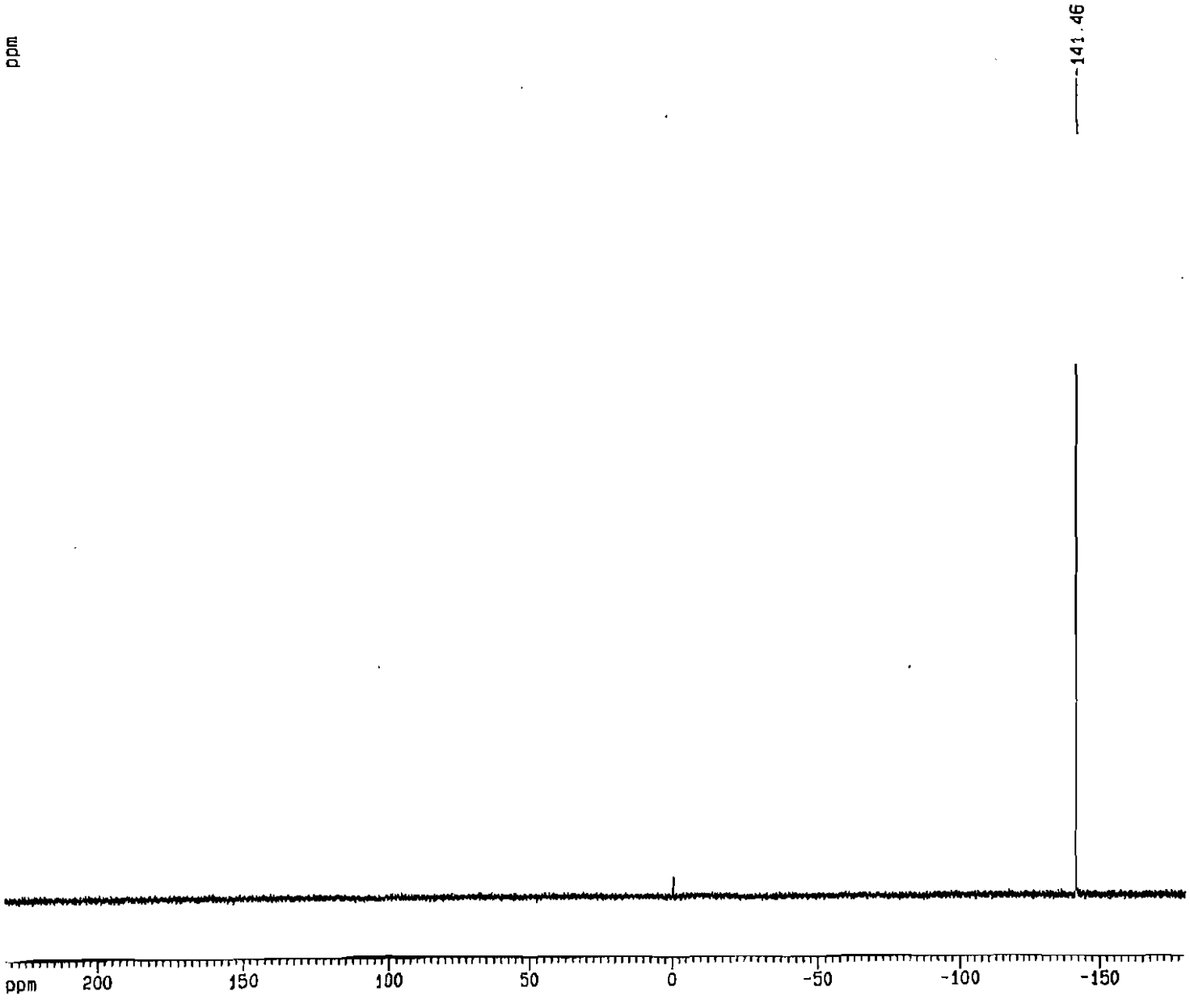
^{31}P NMR

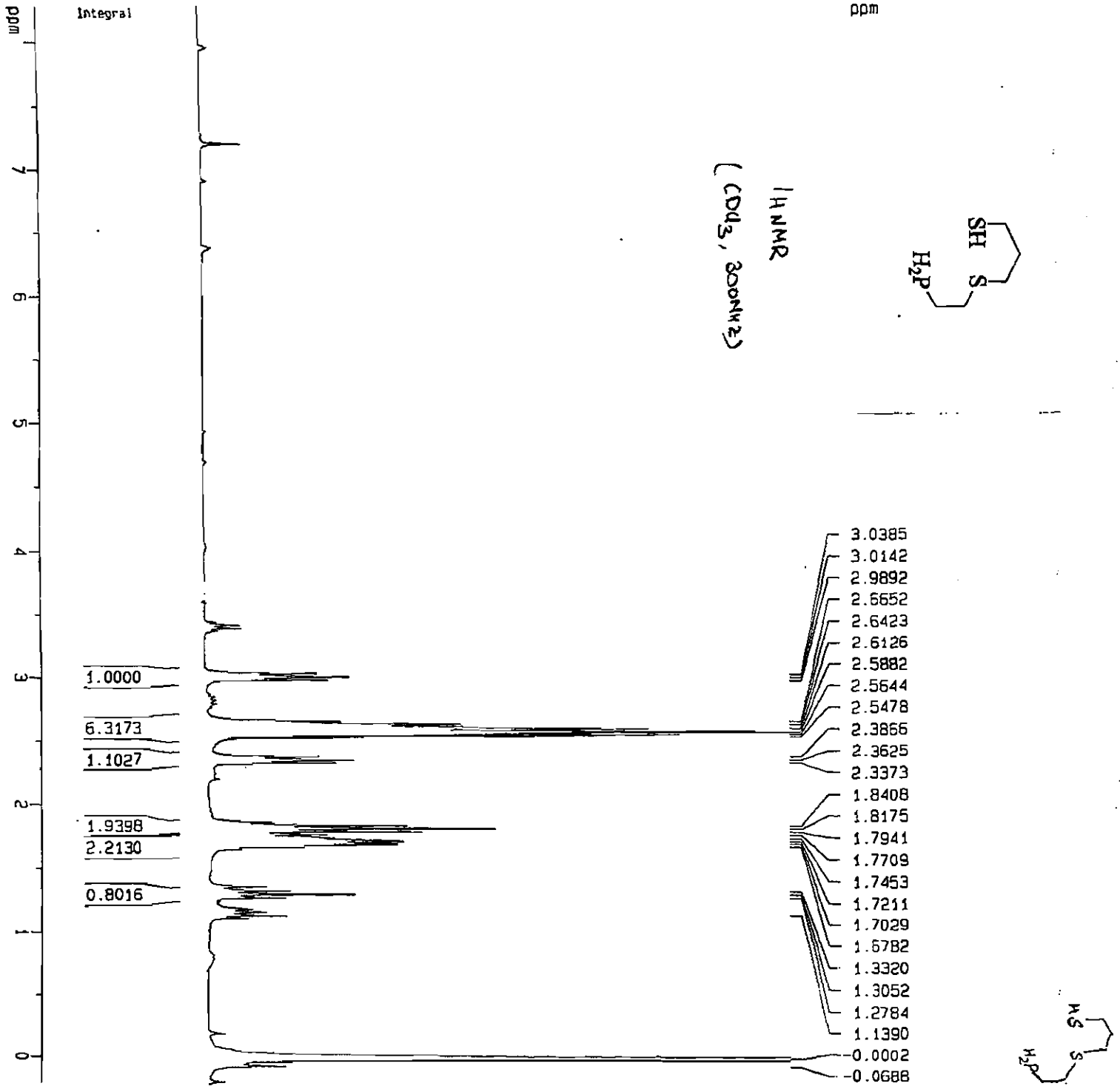
($CDCl_3$, 121 MHz)

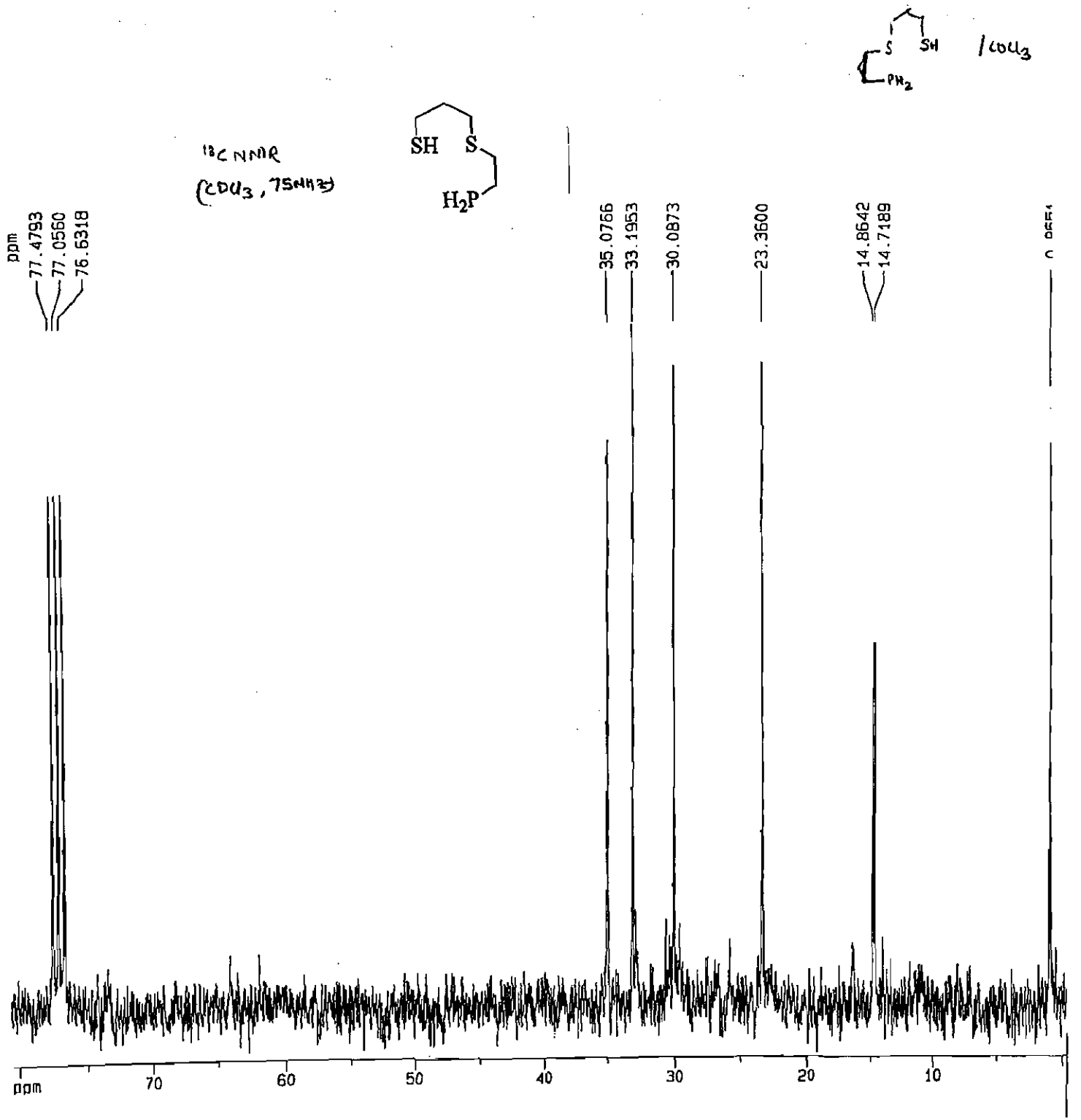


$^{31}P\{^1H\}$ NMR

($CDCl_3$, 121.5 MHz)

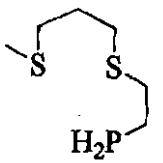


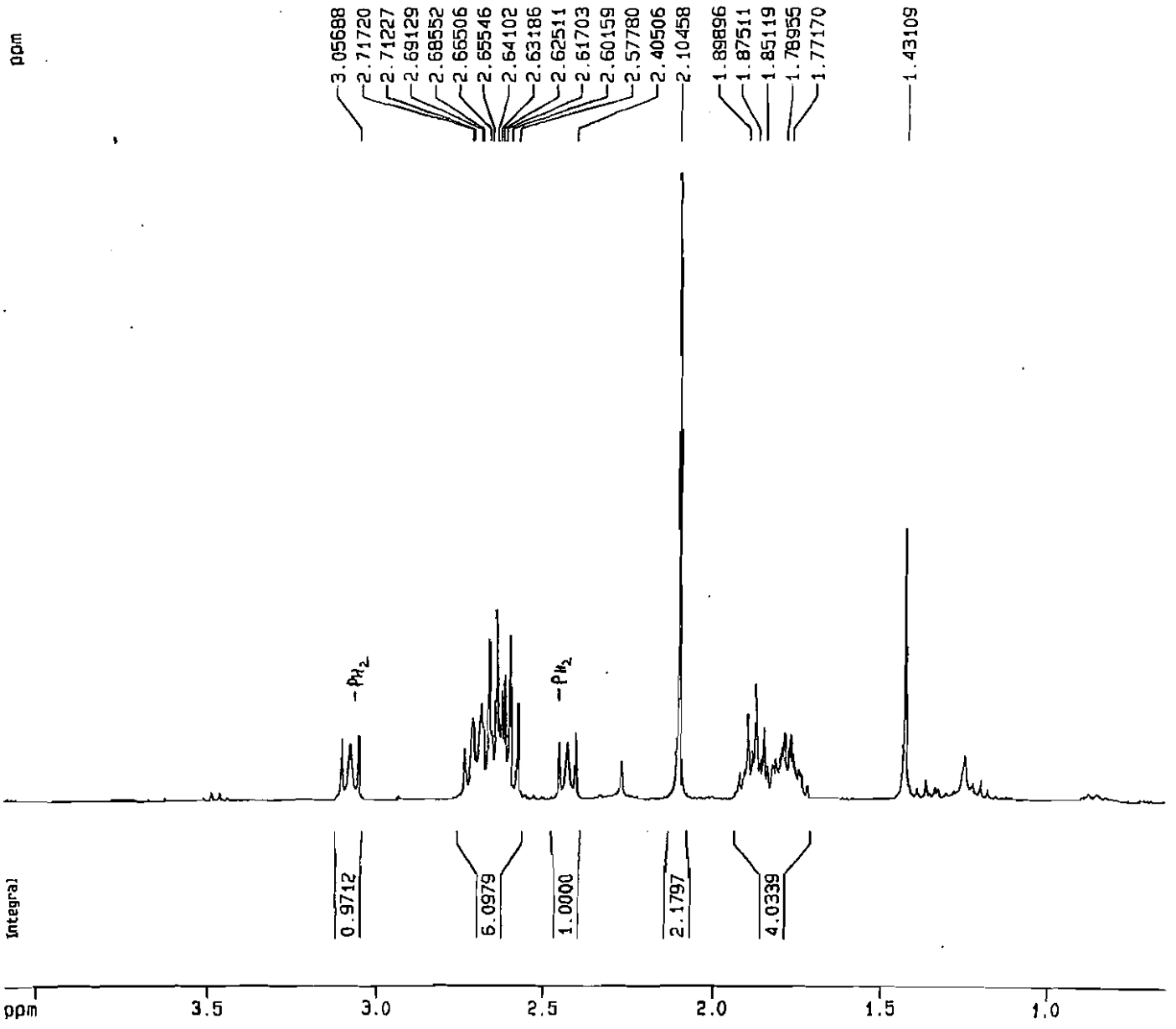

Integral
ppm
1H NMR
(CDCl3, 300MHz)
SH
S
H2P
1.0000
6.3173
1.1027
1.9398
2.2130
0.8016
3.0385
3.0142
2.9892
2.6652
2.6423
2.6126
2.5882
2.5644
2.5478
2.3866
2.3625
2.3373
1.8408
1.8175
1.7941
1.7709
1.7453
1.7211
1.7029
1.6782
1.3320
1.3052
1.2784
1.1390
-0.0002
-0.0688


ppm
77.4793
77.0560
76.6318
35.0766
33.1953
30.0873
23.3600
14.8642
14.7189
ppm
70
60
50
40
30
20
10

^1H NMR

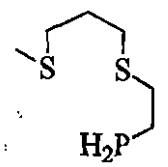
($CDCl_3$, 300 MHz)

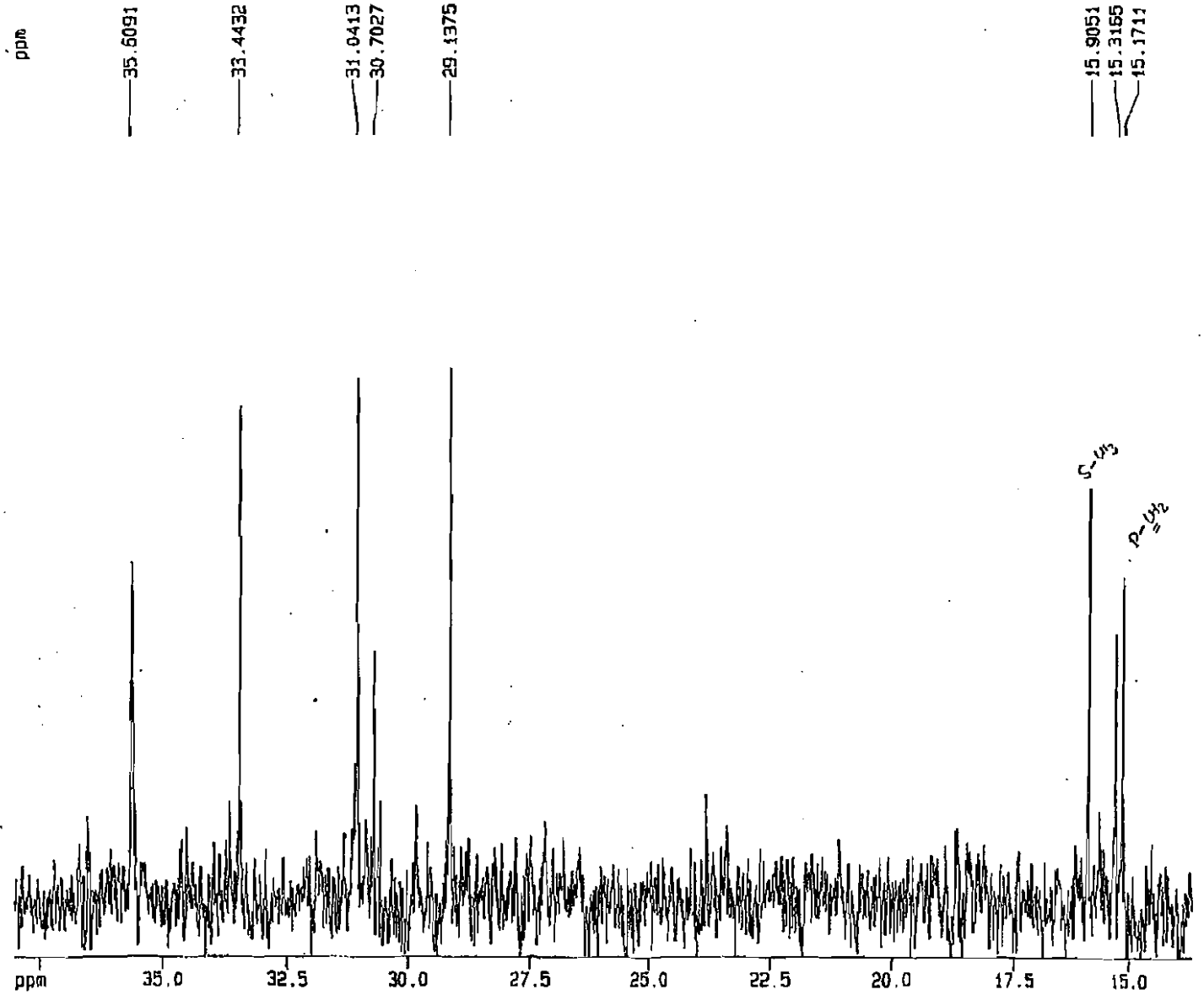




^{13}C NMR

($CDCl_3$, 75 MHz)





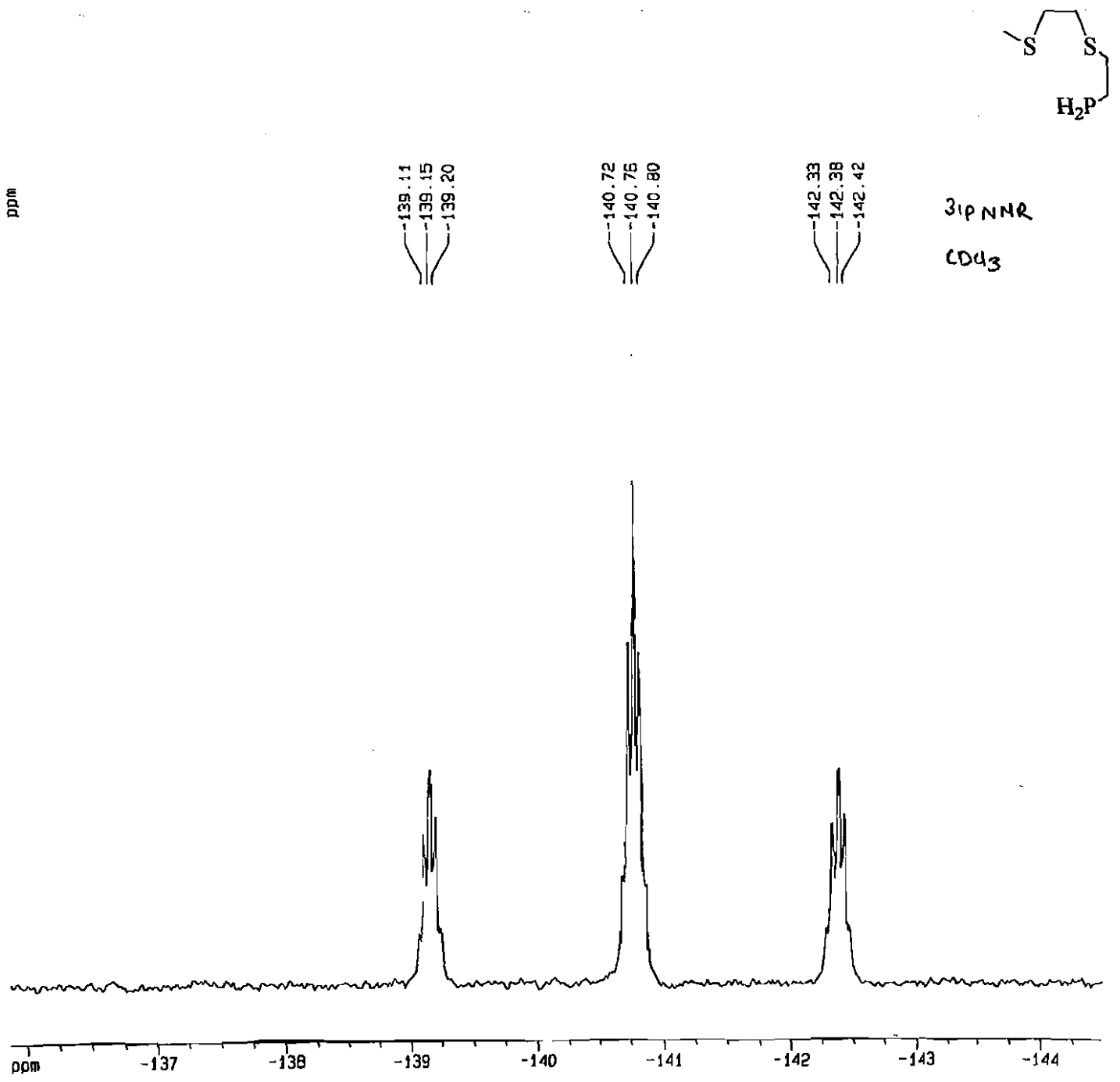
ppm
200
100
0
-100
-200
ppm
-144.31
31P{1H} NMR
CDCl3, 121.5 MHz
S
S
H2P

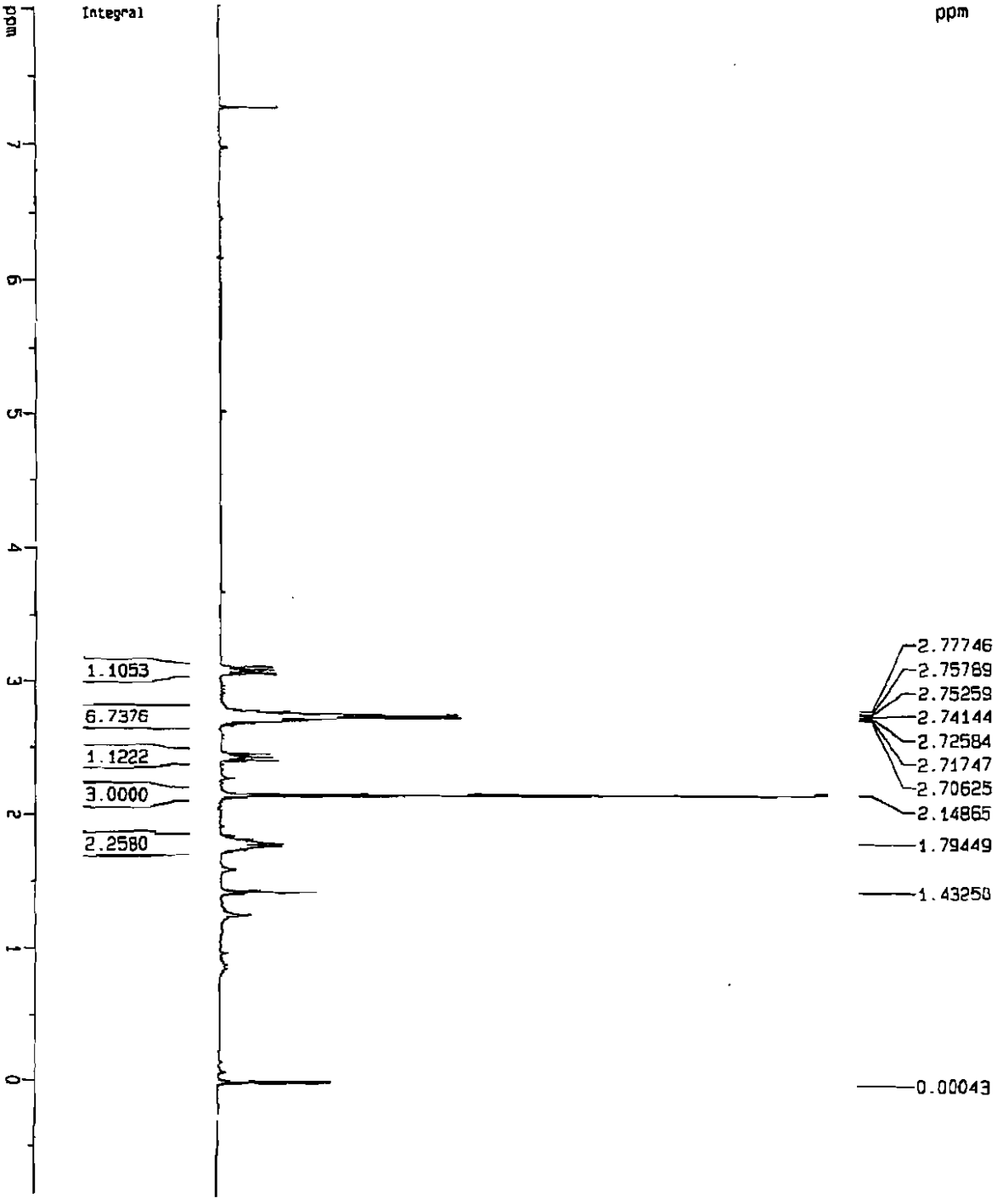
ppm

^{31}P NMR

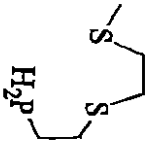
(109 MHz, H_2O)

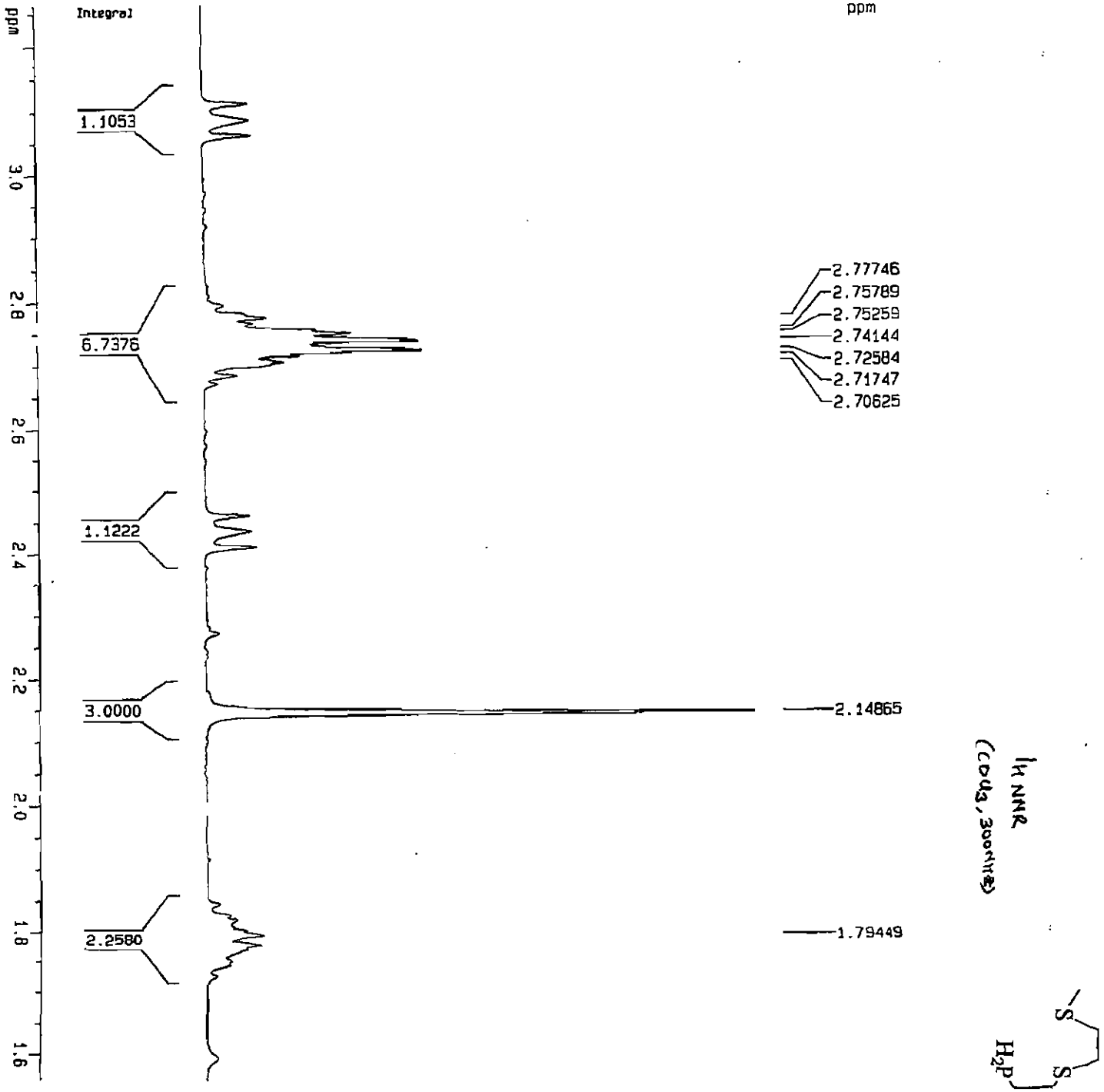
-139.11
-139.15
-139.20
-140.72
-140.76
-140.80
-142.33
-142.38
-142.42


S
S
H2P
ppm
-139.11
-139.15
-139.20
-140.72
-140.76
-140.80
-142.33
-142.38
-142.42
31P NMR
CDCl3
ppm
-137
-138
-139
-140
-141
-142
-143
-144



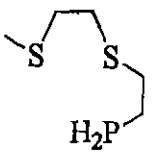
^{1}H NMR
($CDCl_3$, 300MHz)

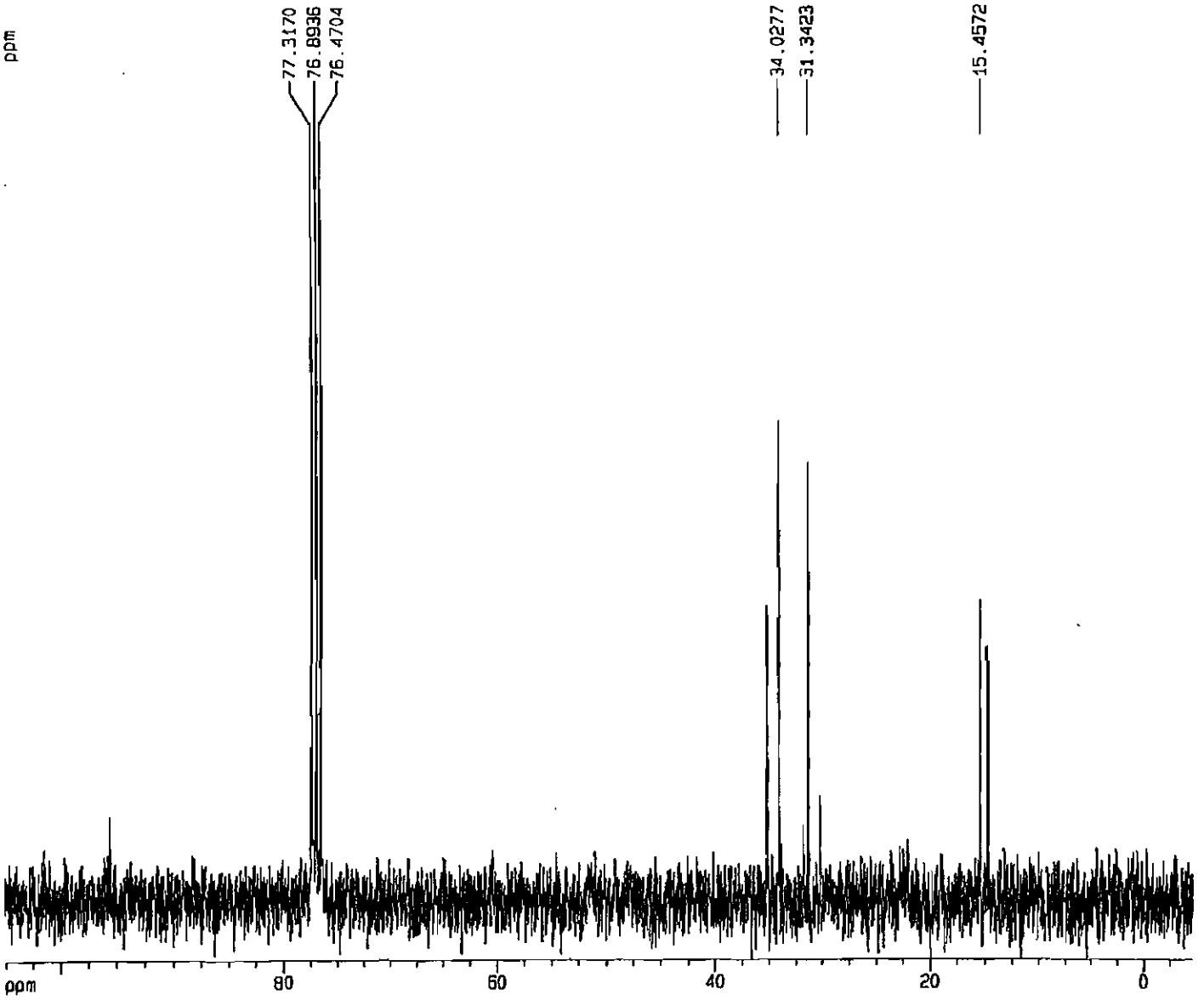


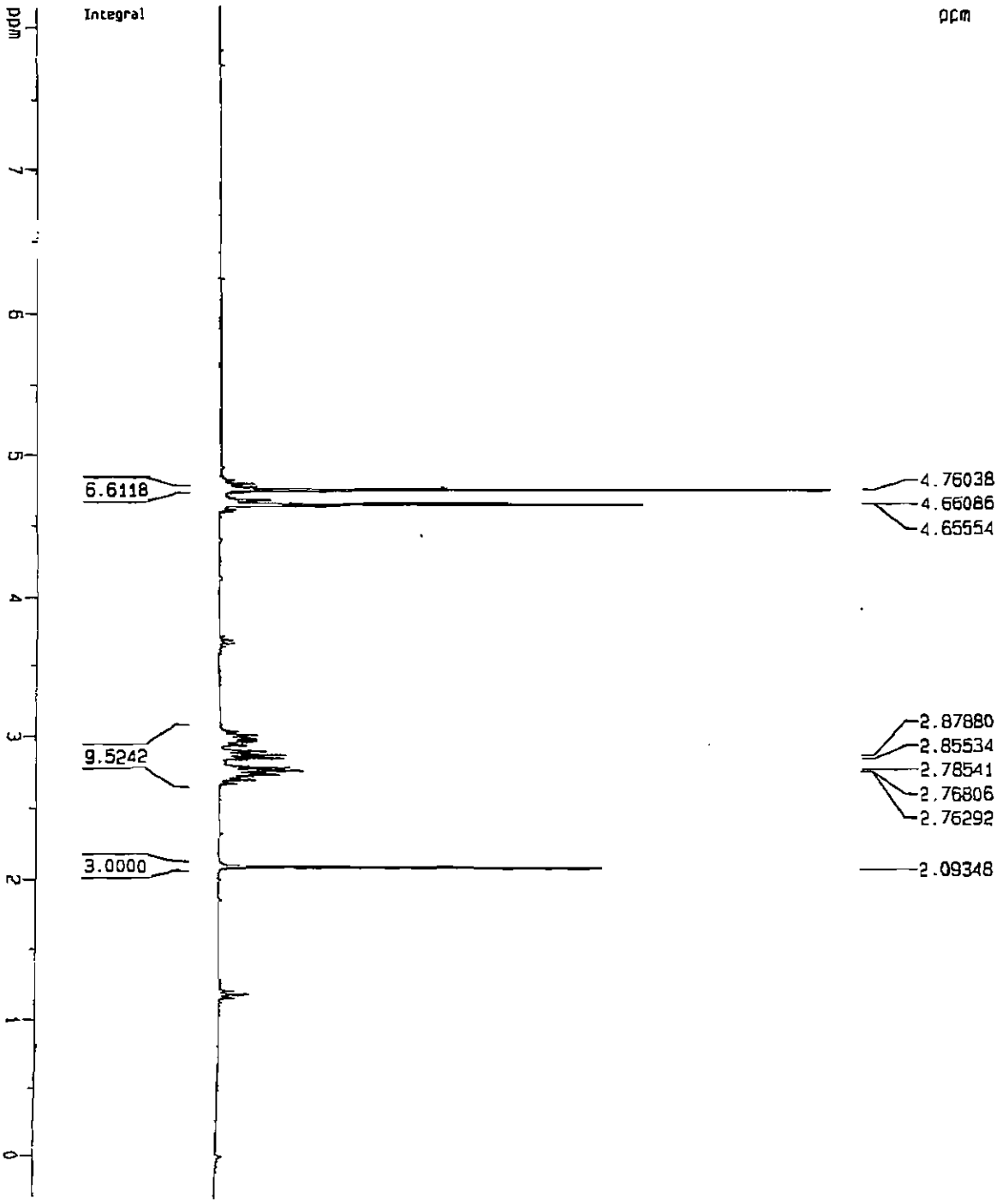

ppm
Integral
1.1053
6.7376
1.1222
3.0000
2.2580
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
ppm
2.77746
2.75789
2.75259
2.74144
2.72584
2.71747
2.70625
2.14865
1.79449
^1H NMR
(CDCl3, 300MHz)
S
S
H_2P

^{13}C NMR

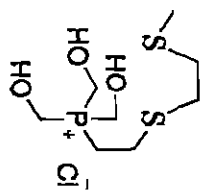
($CDCl_3$, 75 MHz)





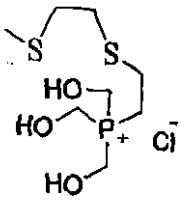


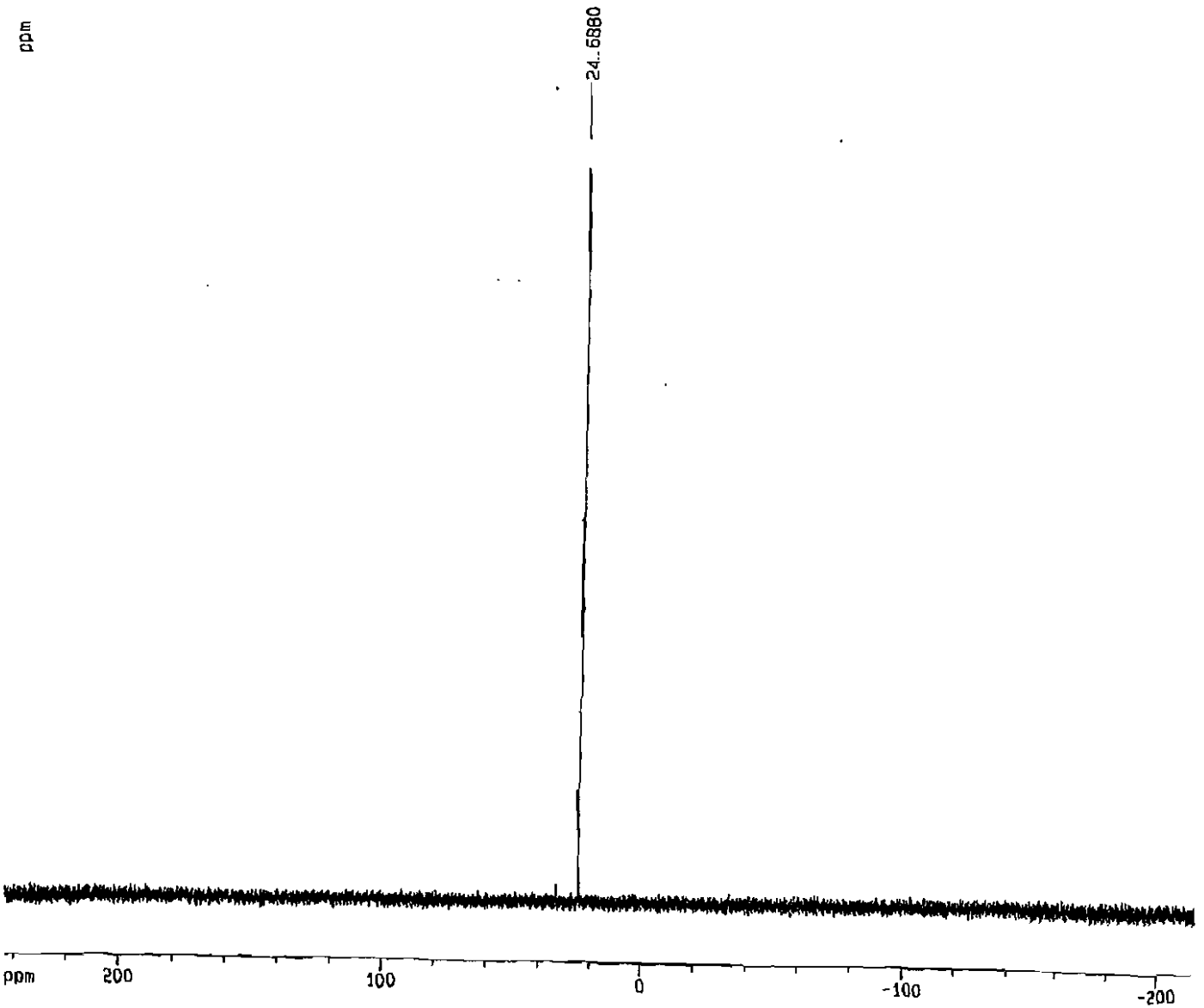
^{1}H NMR
(D_2O, 300 MHz)

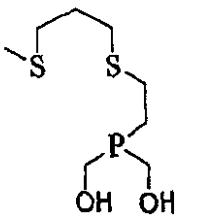


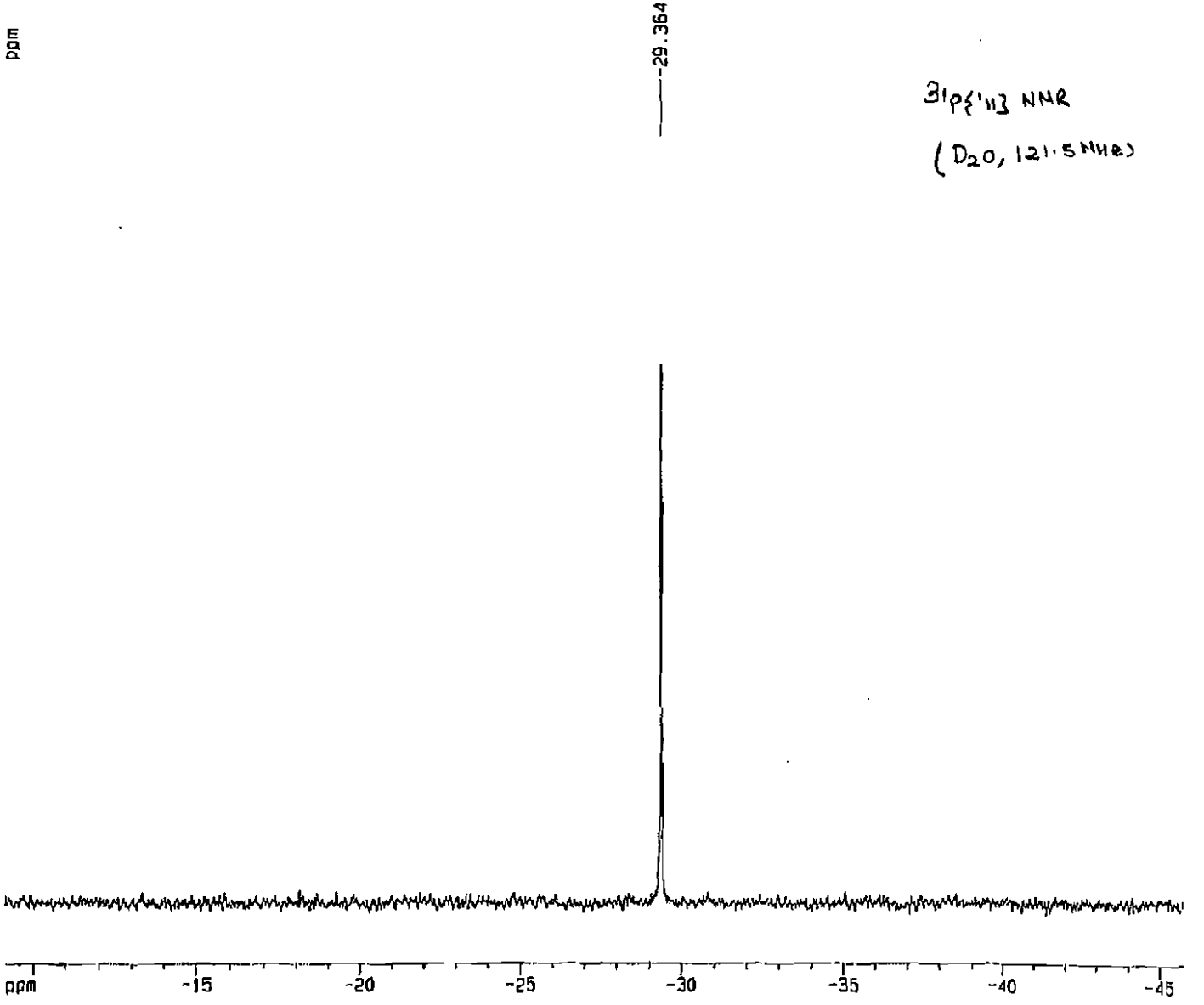
^{13}C NMR
(D_2O, 75 MHz)

^{31}PNMR
(D_2O, 121.5 MHz)



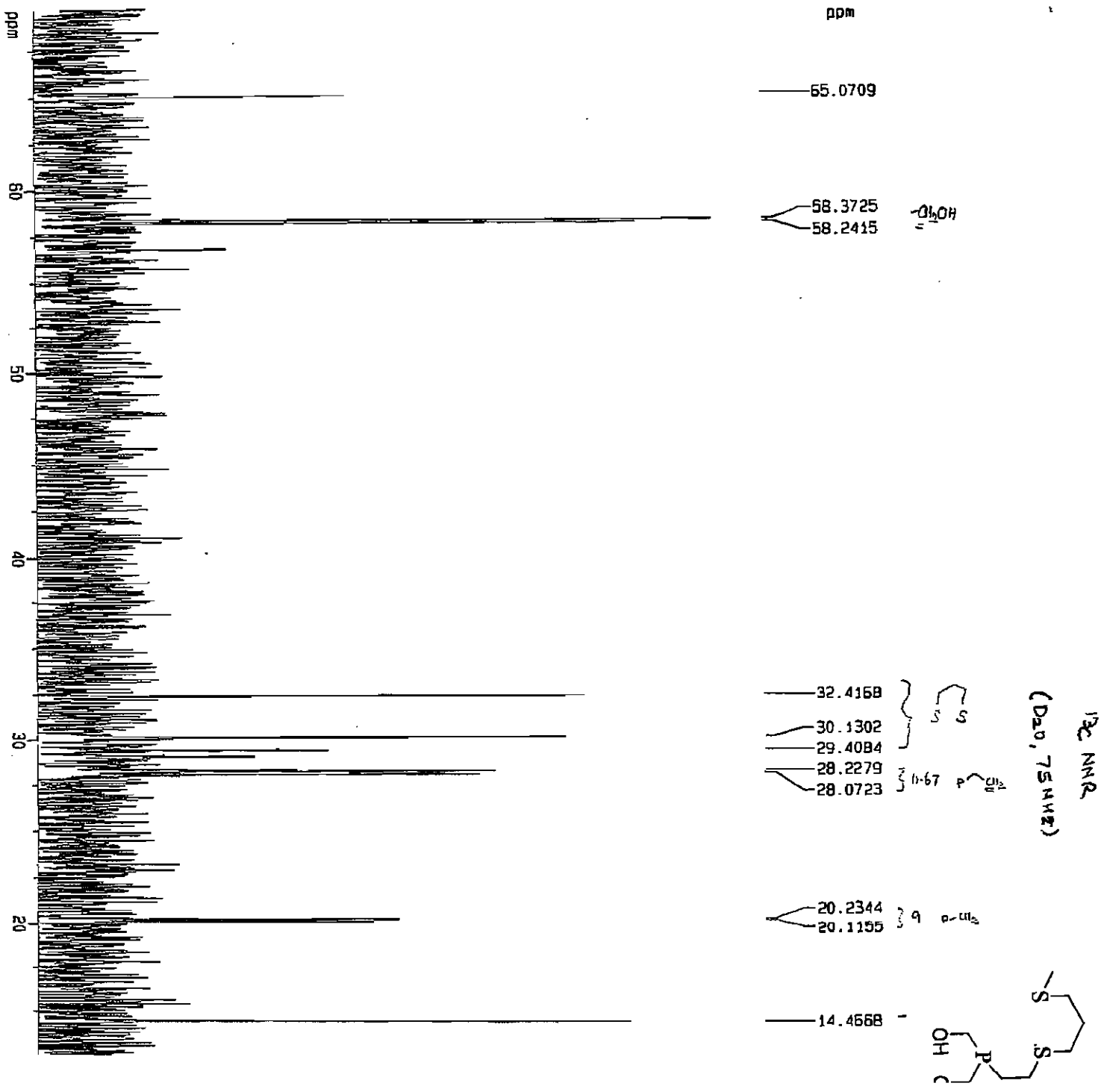


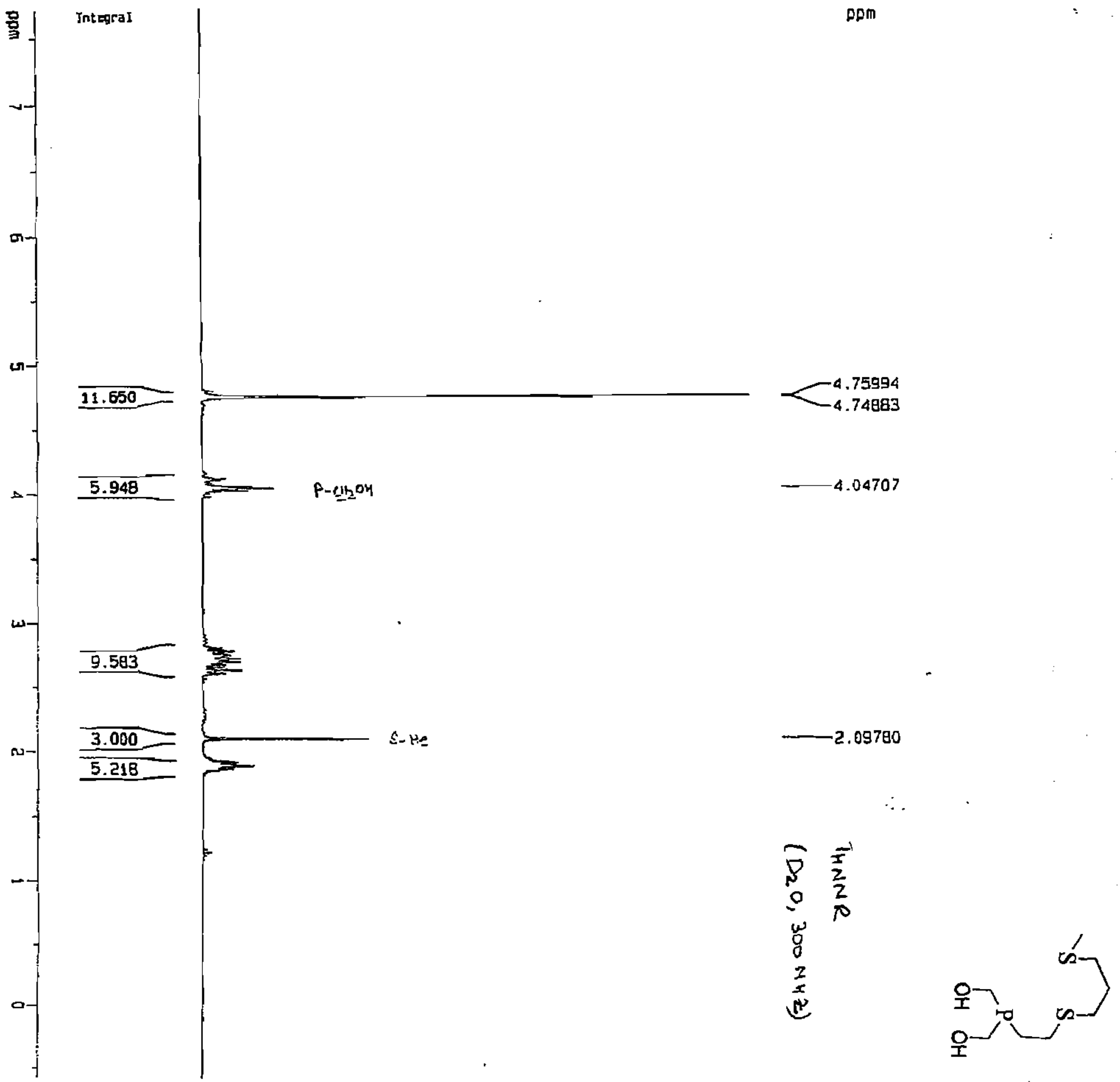


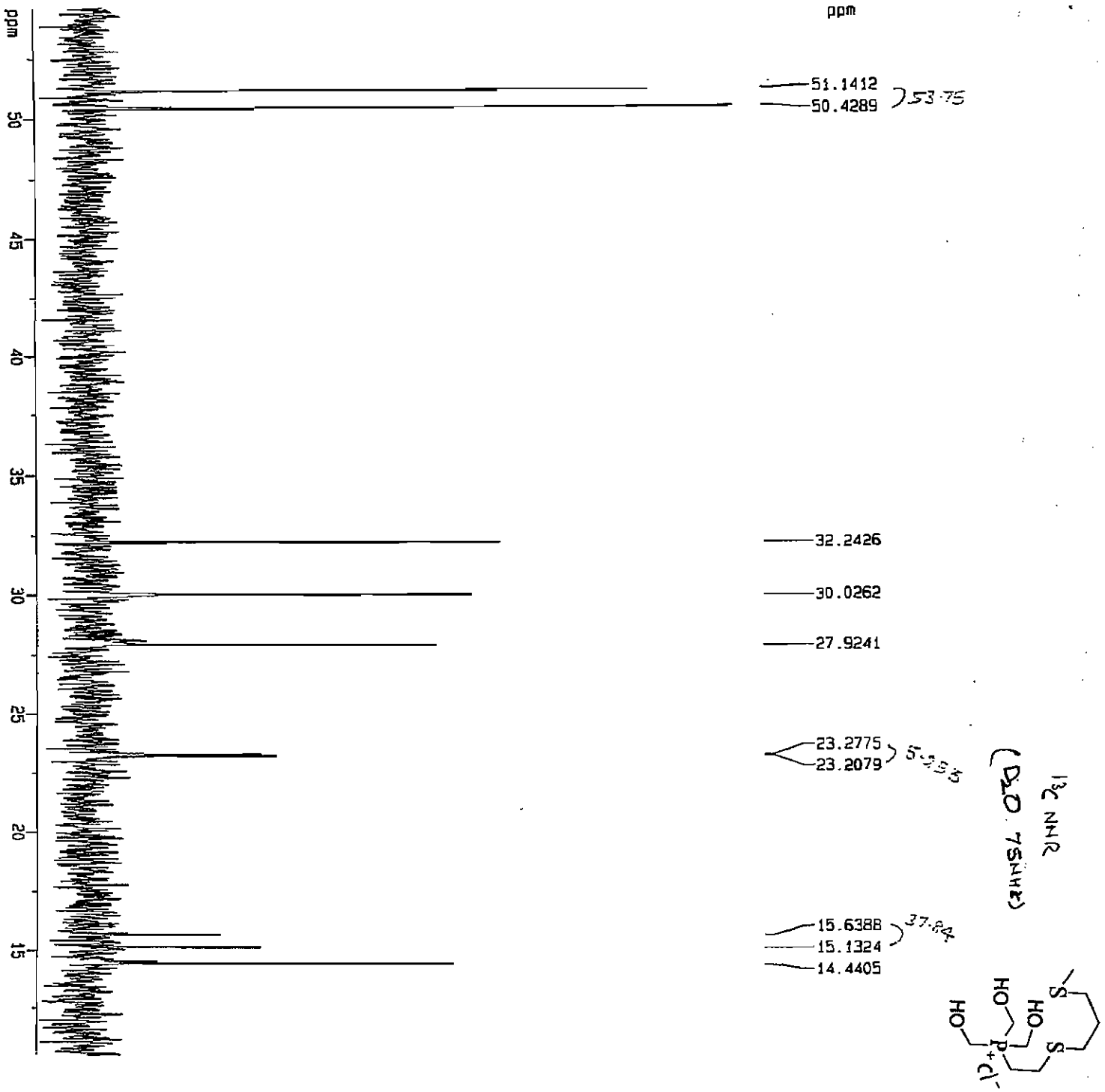


$^{31}P\{^1H\}$ NMR

(D_2O, 121.5 MHz)


ppm
60
50
40
30
20
65.0709
58.3725
58.2415
32.4168
30.1302
29.4084
28.2279
28.0723
20.2344
20.1155
14.4668
OH
P
S
S


ppm
Integral
ppm
11.650
5.948
9.583
3.000
5.218
P-CH2OH
S-Me
4.75994
4.74883
4.04707
2.09780
1H NMR
(D2O, 300 MHz)
S
S
P
OH
OH
7
6
5
4
3
2
1
0

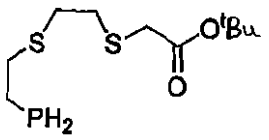

ppm
ppm
51.1412
50.4289
53.75
32.2426
30.0262
27.9241
23.2775
23.2079
15.6388
15.1324
14.4405
^{13}C NMR
(D_2O 75MHz)
HO
HO
HO
S
S
P^+Cl^-

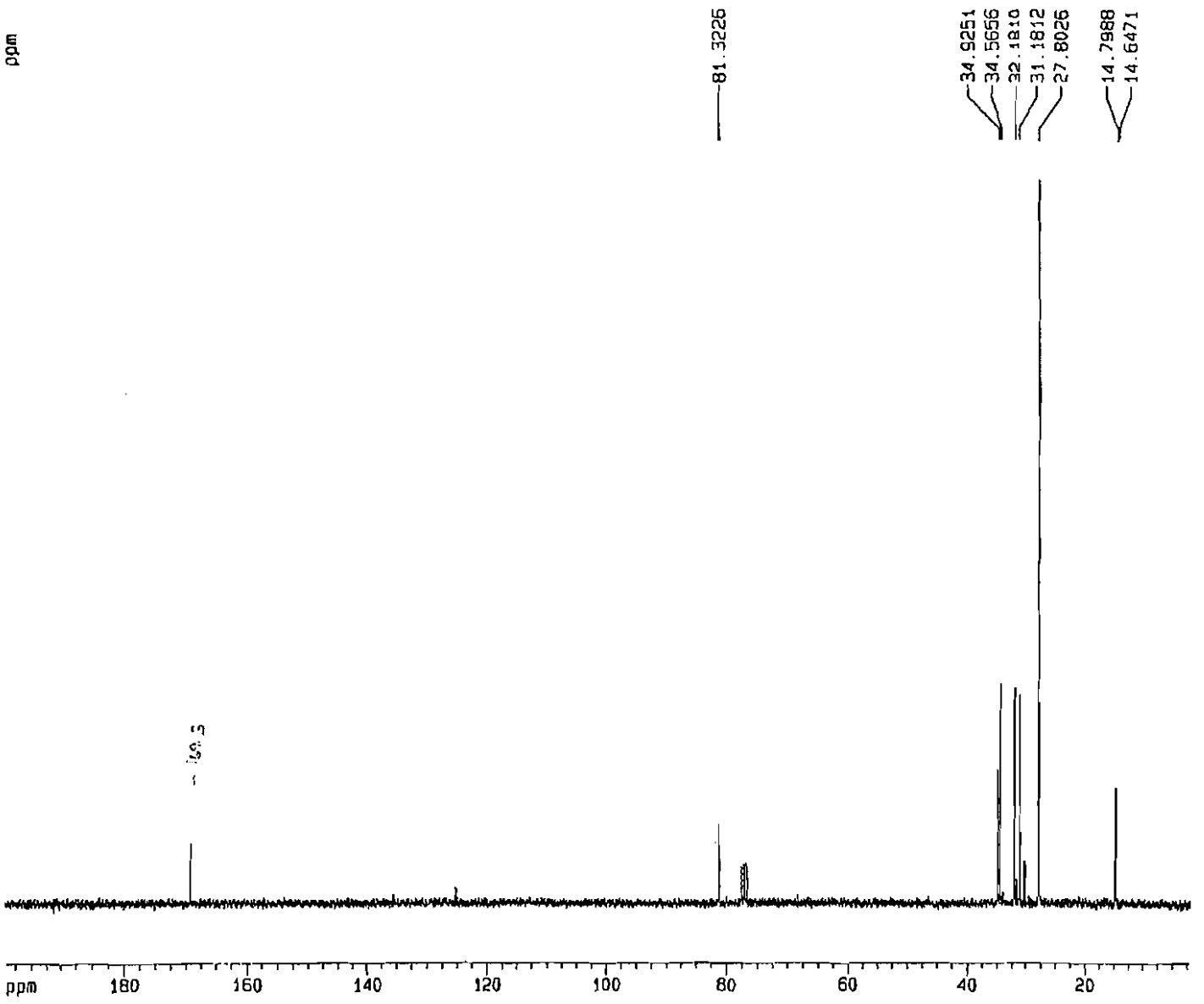
^{31}PNMR

D_2O, 121.5MHz

Integral
ppm
1.9087
1.0035
6.4889
0.9926
2.0482
9.6173
3.08880
3.00629
2.98135
2.78743
2.78192
2.77257
2.75711
2.72356
2.71074
2.70339
2.69676
2.67905
2.67380
2.65846
2.65313
2.63271
2.35714
2.33187
1.72564
1.70729
1.41075
1.36058
0.00027
^{1}H NMR
(CDCl$_3$, 300MHz)
PH_2
O^{t}Bu

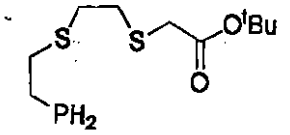
^{13}C NMR
($CDCl_3$, 75MHz)

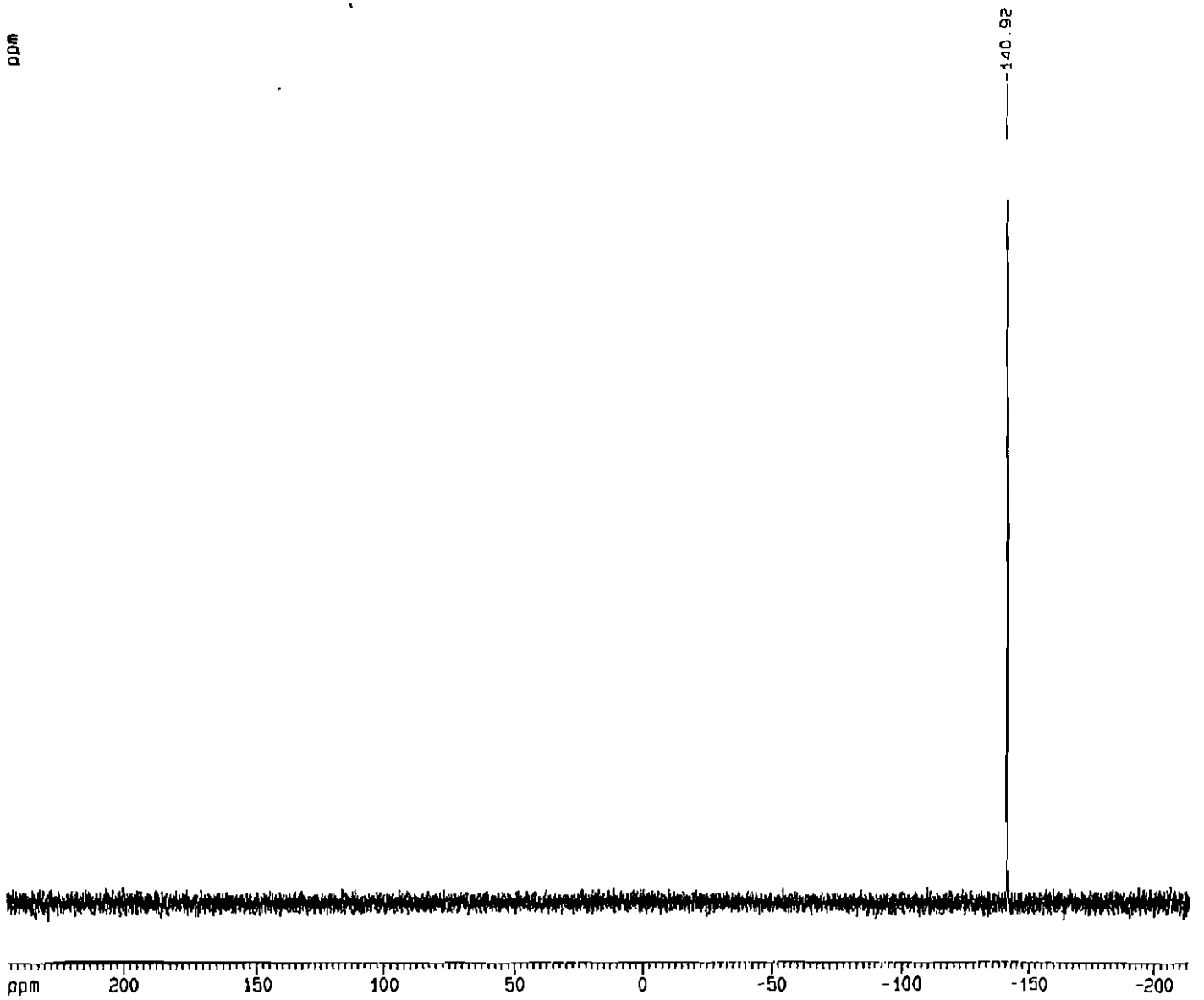


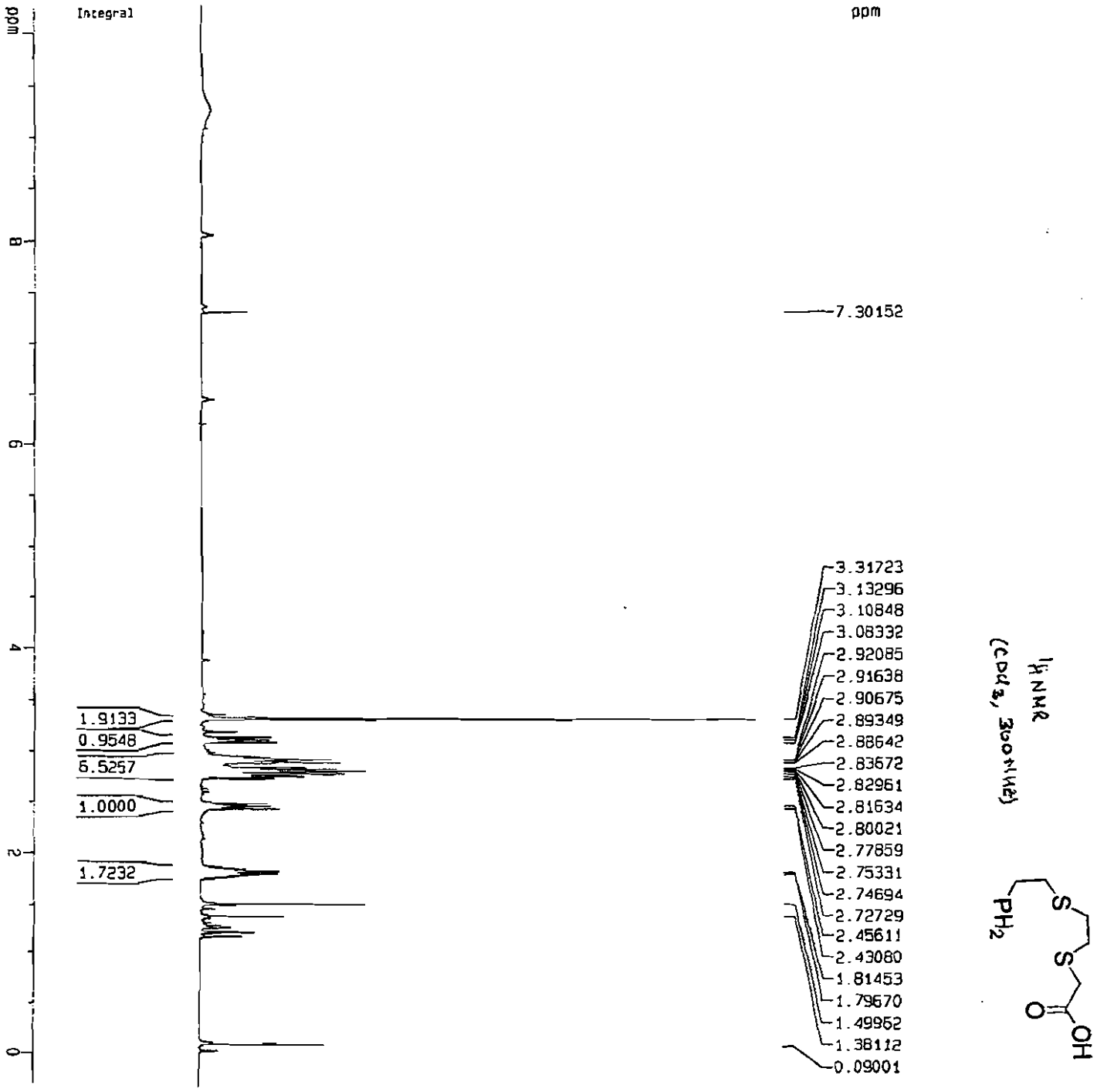


$^{31}P\{^{1}H\}$ NMR

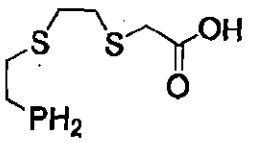
($CDCl_3$, 121 MHz)

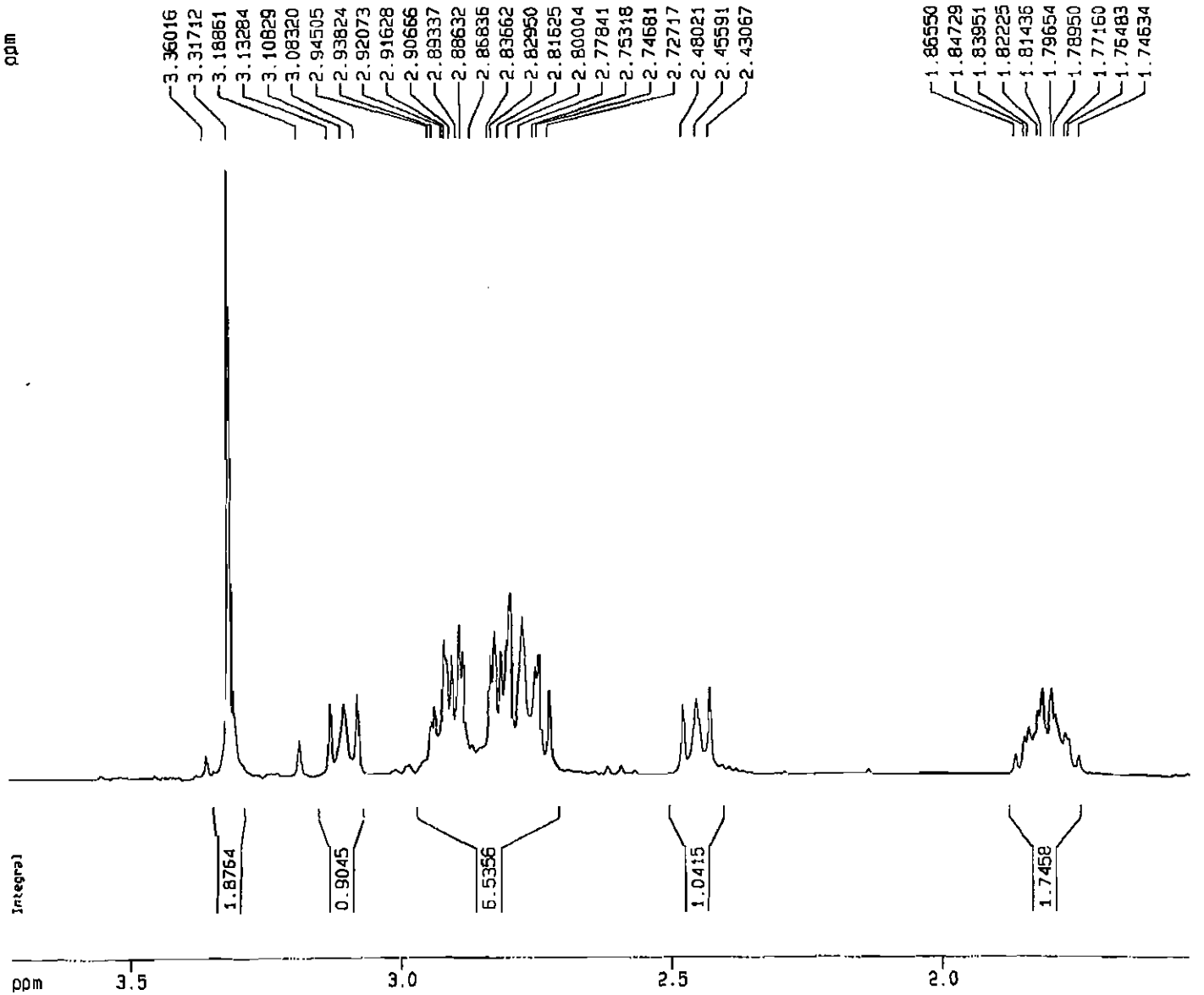





Integral
ppm
7.30152
3.31723
3.13296
3.10848
3.08332
2.92085
2.91638
2.90675
2.89349
2.88642
2.83672
2.82961
2.81634
2.80021
2.77859
2.75331
2.74694
2.72729
2.45611
2.43080
1.81453
1.79670
1.49952
1.38112
0.09001
1.9133
0.9548
6.5257
1.0000
1.7232
^{1}H NMR
($CDCl_3$, 300 MHz)
PH_2
S
S
O
OH

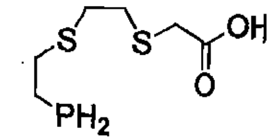
^{1}H NMR
($CDCl_3$, 300 MHz)

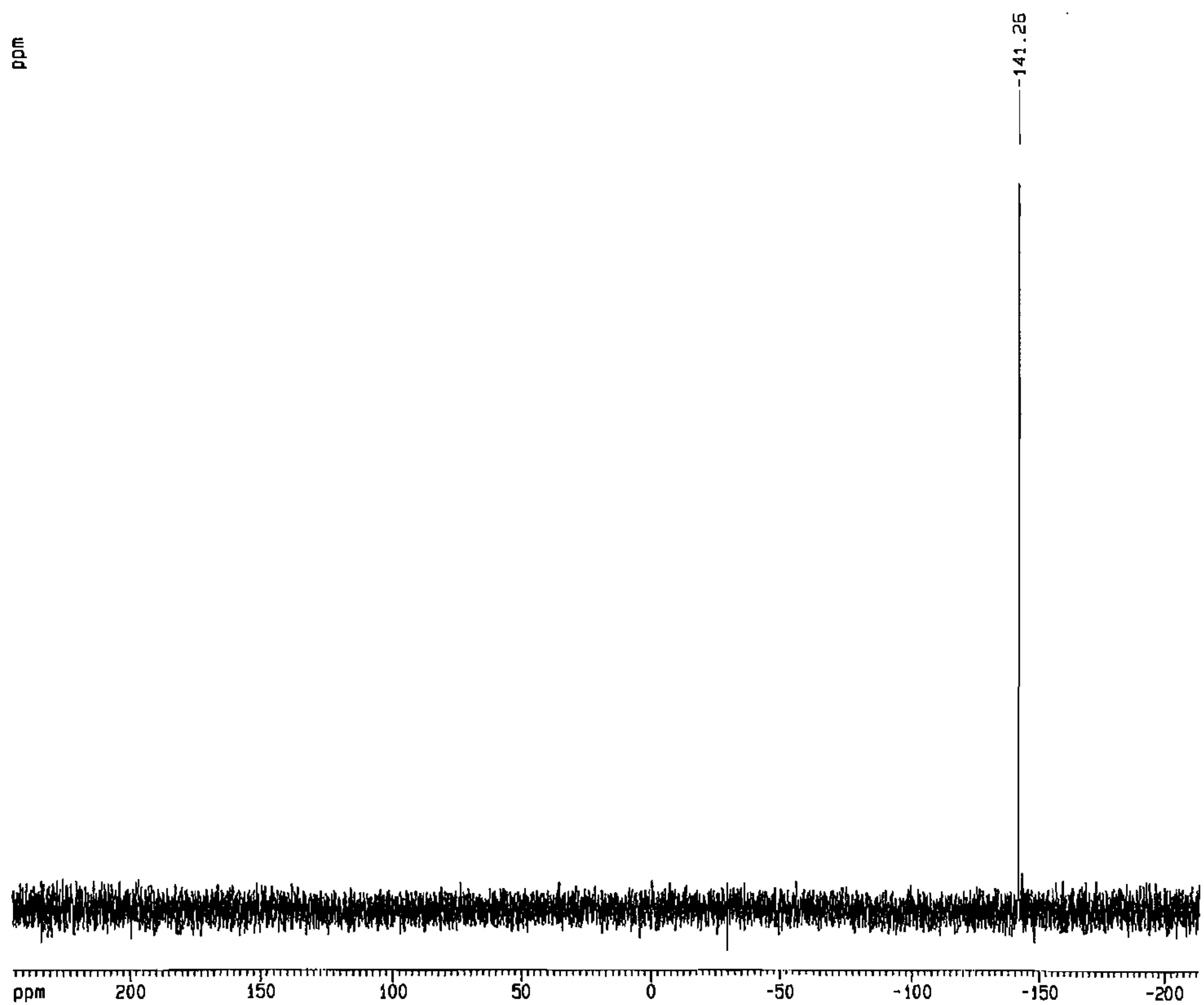




ppm
ppm
175.621
77.345
76.922
76.499
35.064
35.048
33.305
32.448
31.137
30.480
27.841
14.794
14.645
^{13}C NMR
($CDCl_3$, 75MHz)
PH_2
S
S
O
OH

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz)

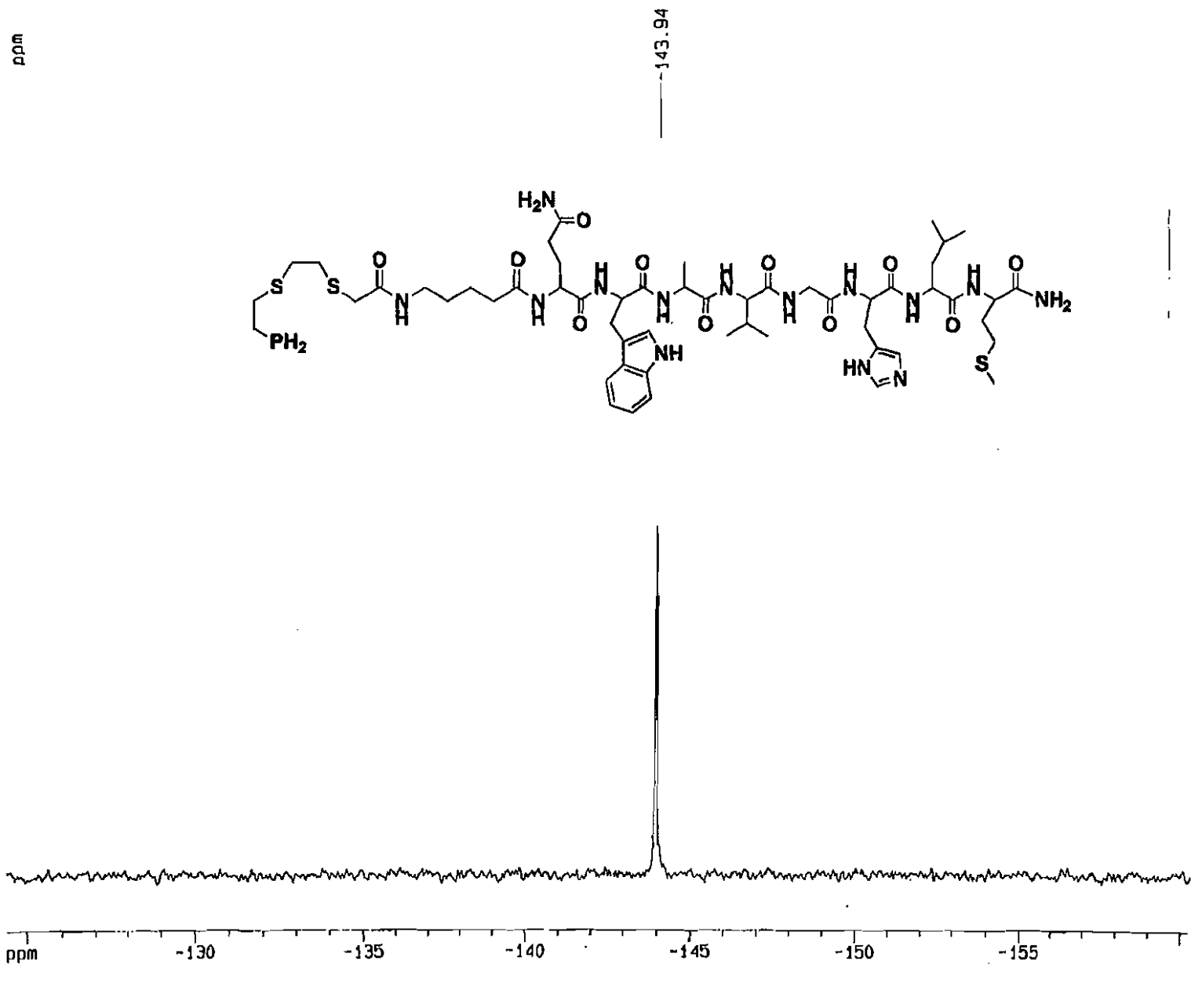




Purified (PH2) S2-5-Ava-BBN[7-14]NH2

$^{31}P\{^{1}H\}$ NMR

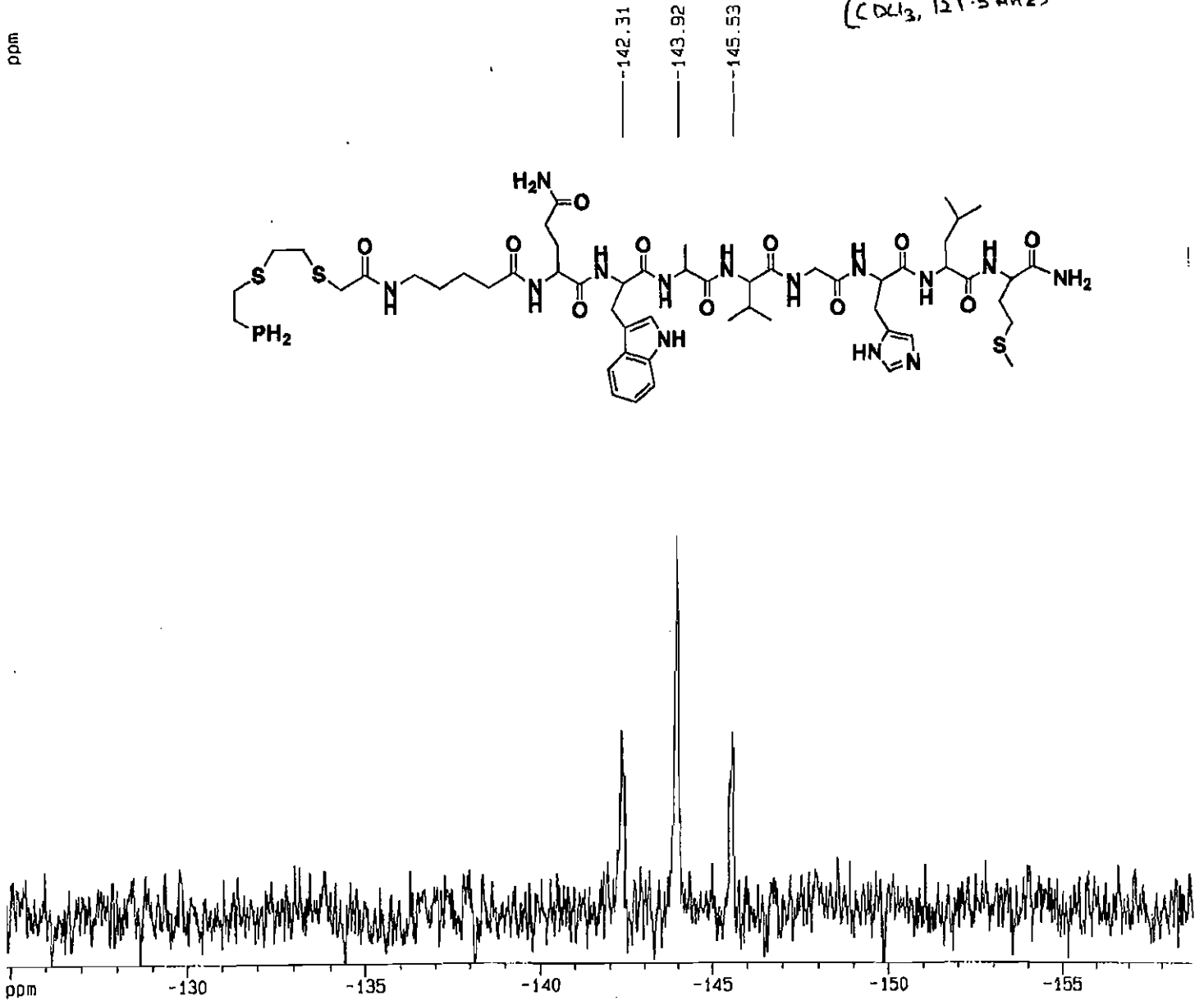
($CDCl_3$, 121.5 MHz)



Purified (PH2) S2-5-Ava-BBN[7-14]NH2

^{31}P NMR

($CDCl_3$, 121.5 MHz)



Purified PS2-5-Ava-BBN[7-14]NH2 phosphonium salt

$^{31}P\{^1H\}$ NMR,

($CDCl_3$, 121.5 MHz)

ppm

24.1764