Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

1,5-(H, RO, RS) shift/6π-electrocyclic ring closure tandem processes on *N*-[(α-heterosubstituted)-2-tolyl]ketenimines: a case study of relative migratory aptitudes and activating effects

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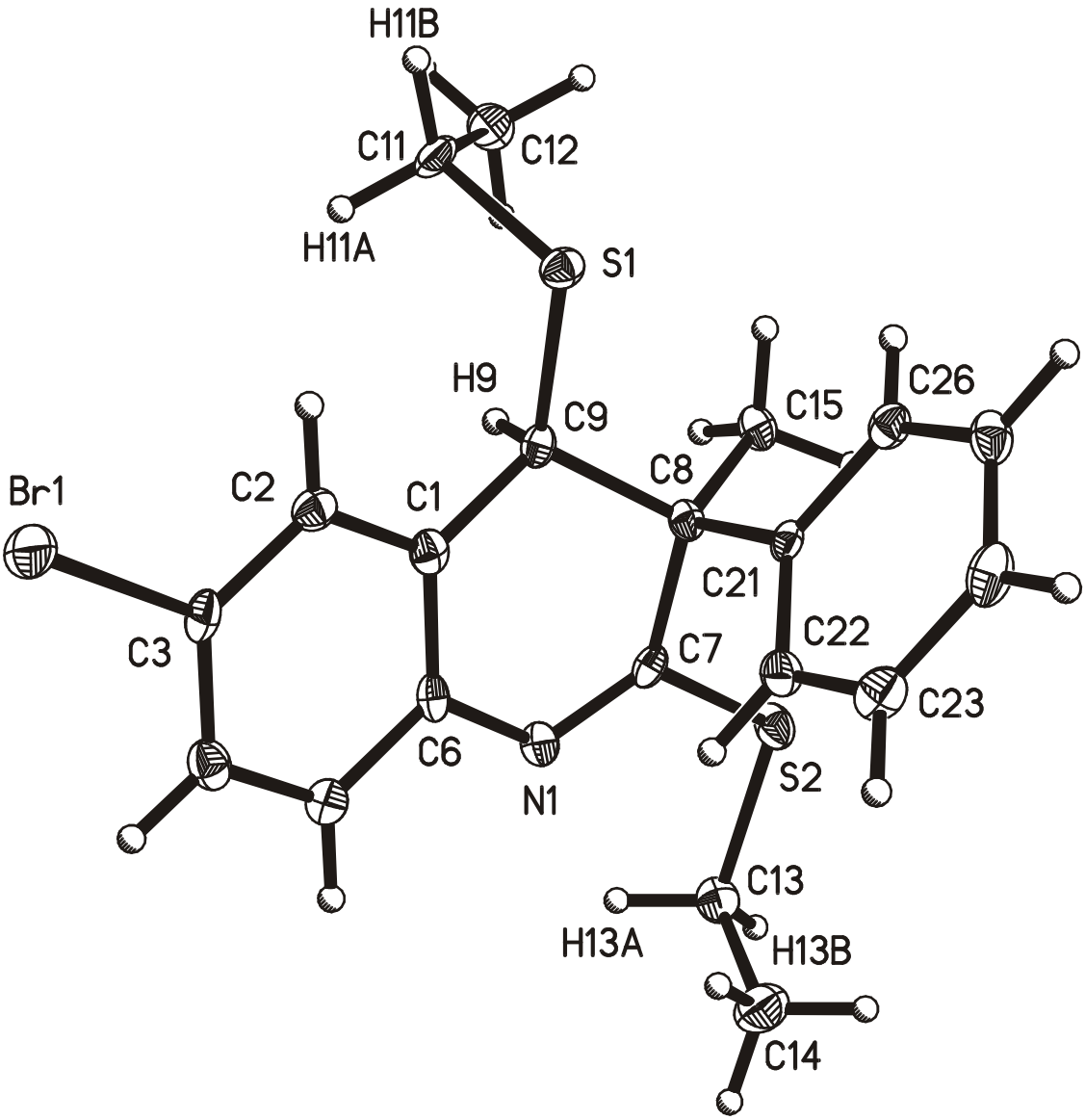
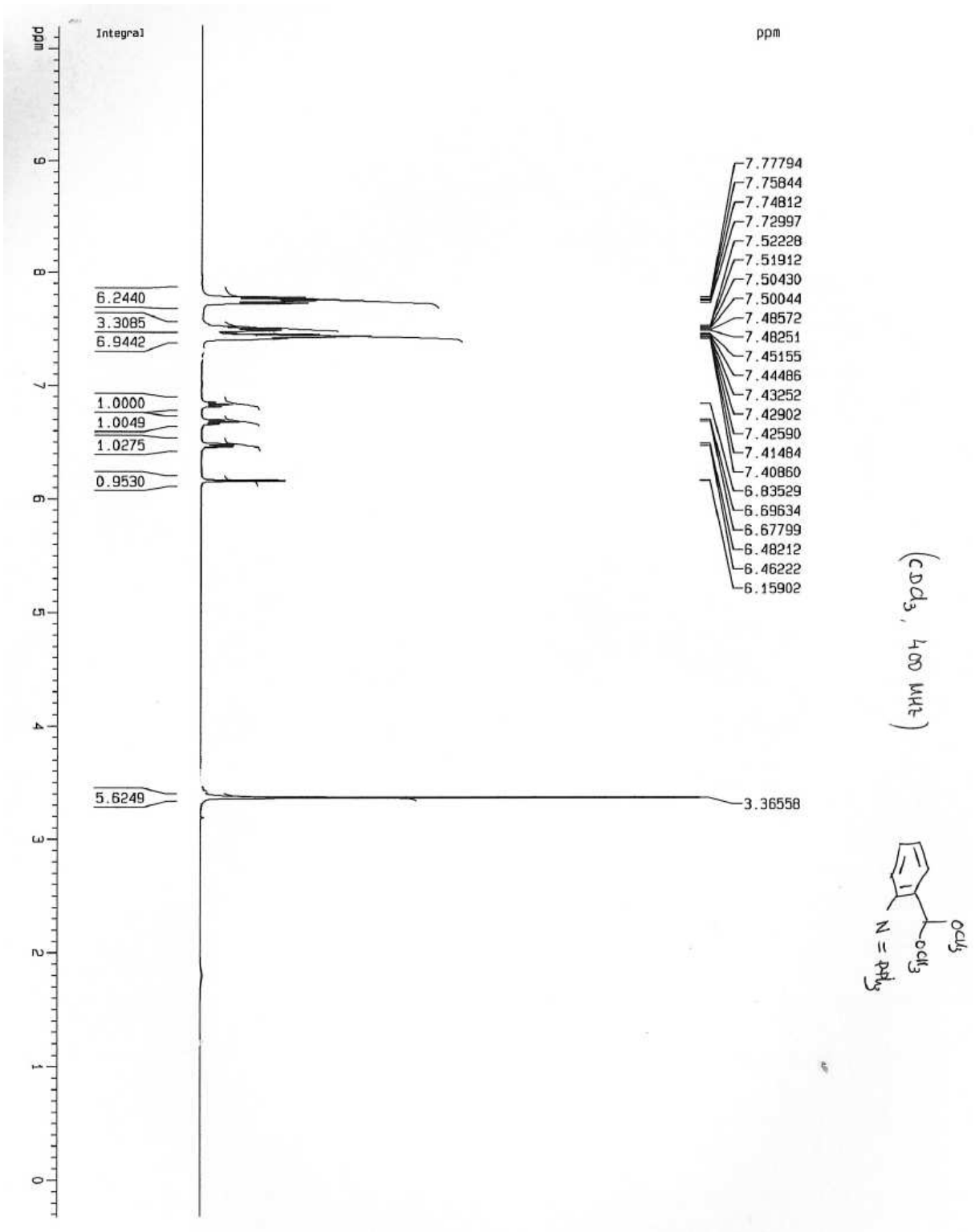
Figure S1: ORTEP representation of the crystal structure of ***cis*-20e**



^{1}H NMR of **10a**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7.52228
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7.50430
7.50044
7.48572
7.48251
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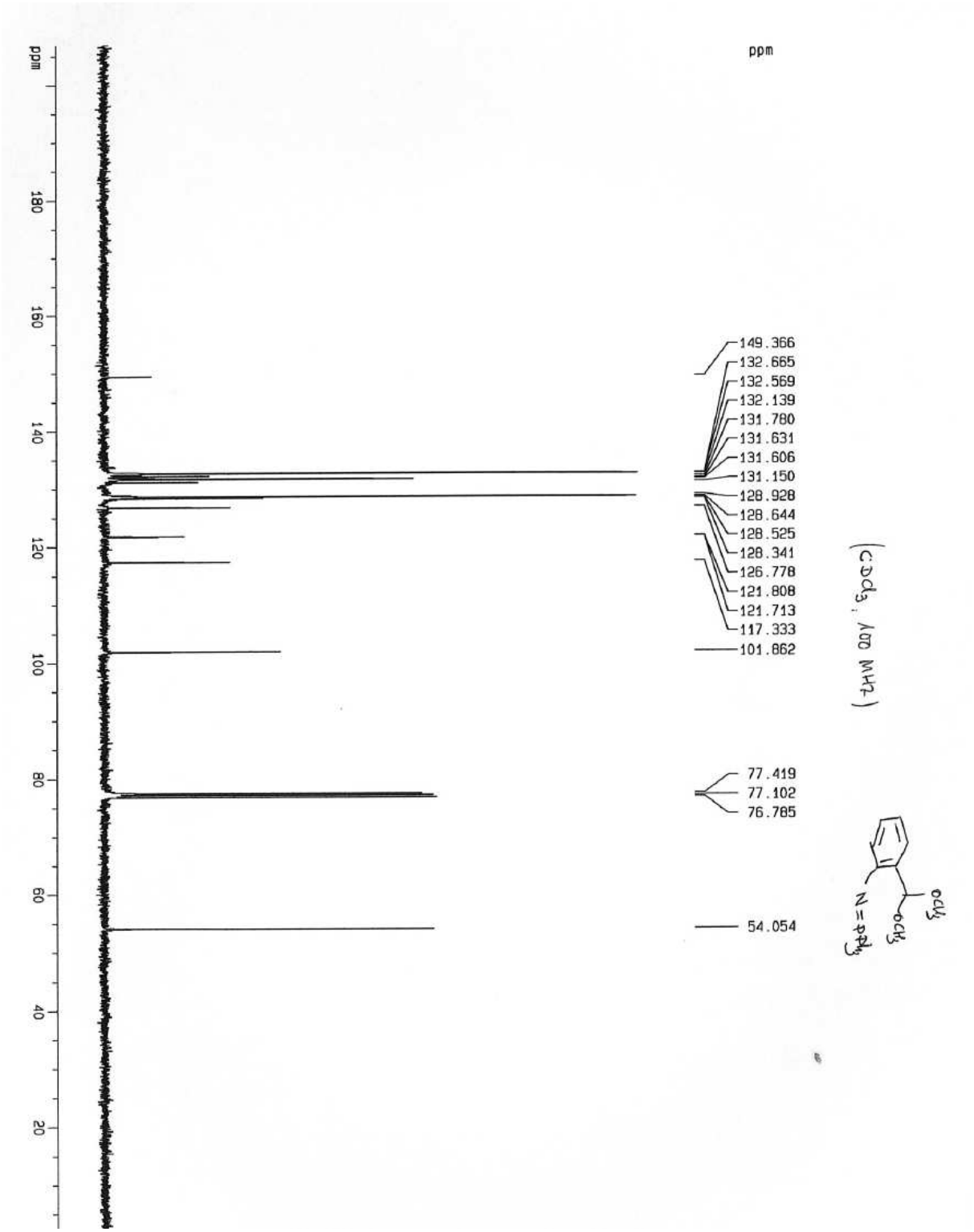
7.42902
7.42590
7.41484
7.40860
6.83529
6.69634
6.67799
6.48212
6.46222
6.15902
3.36558
(CDCl3, 400 MHz)
OCH3
OCH3
N = CHPh

^{13}C NMR of **10a**



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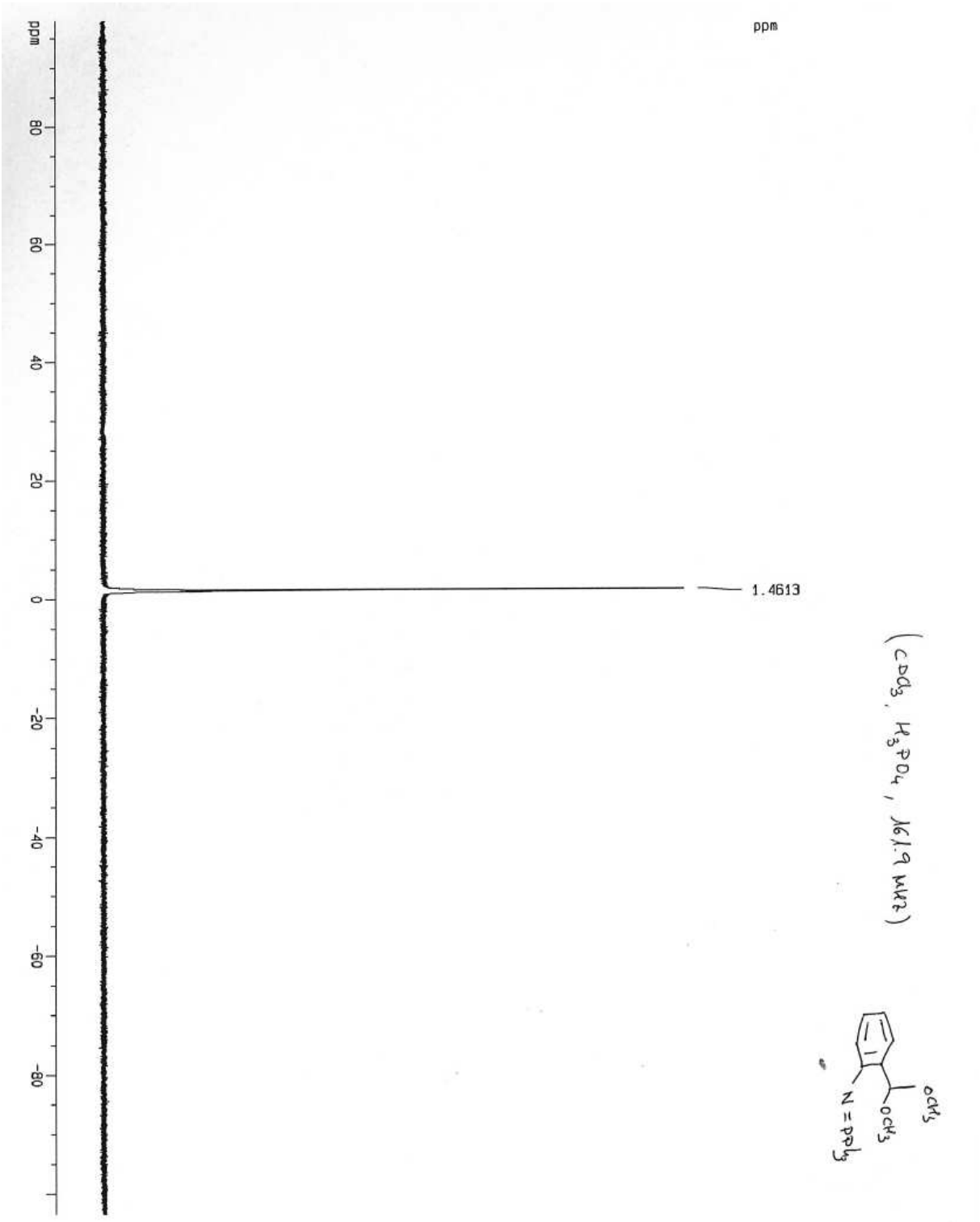
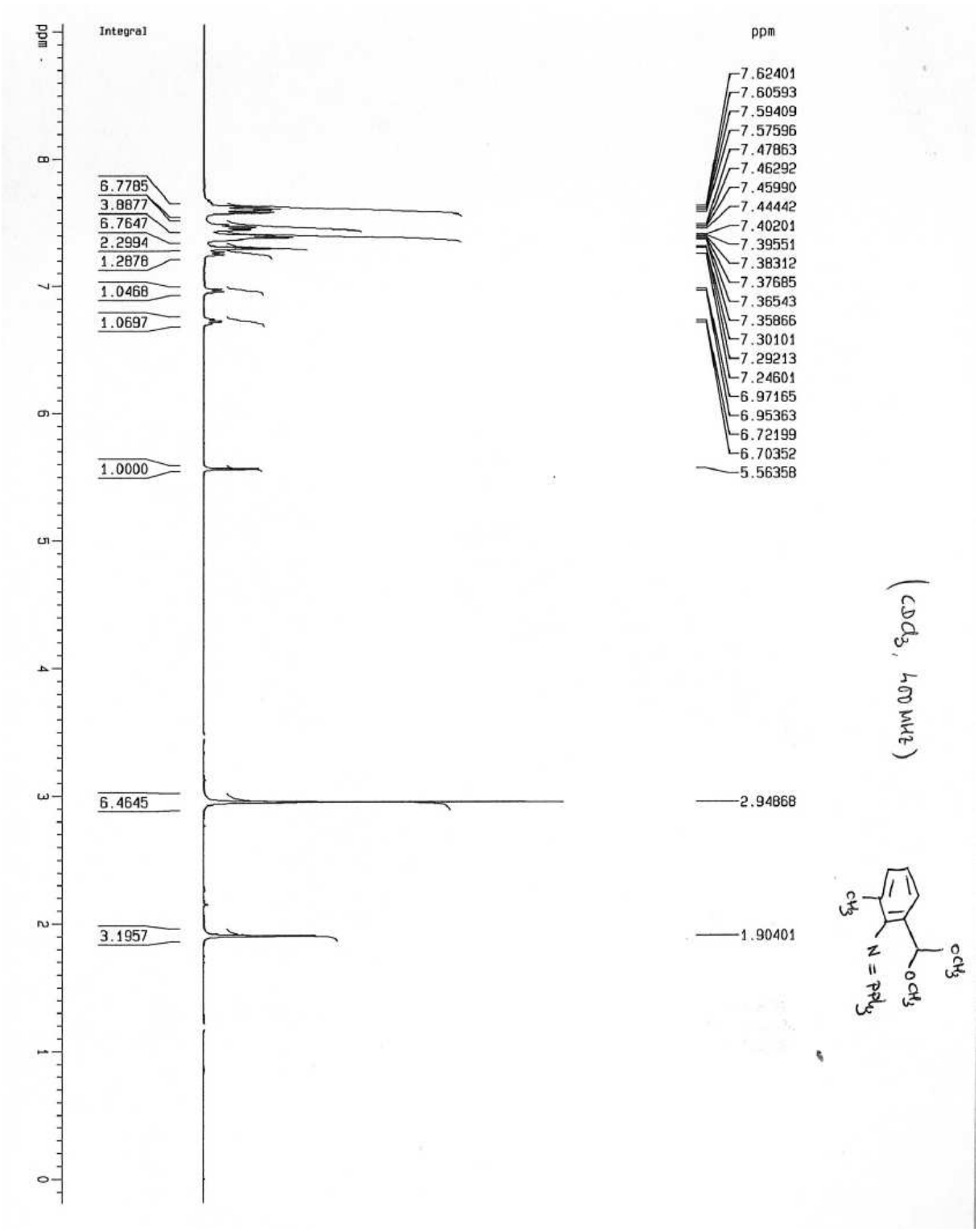


^{1}H NMR of **10b**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7.24601
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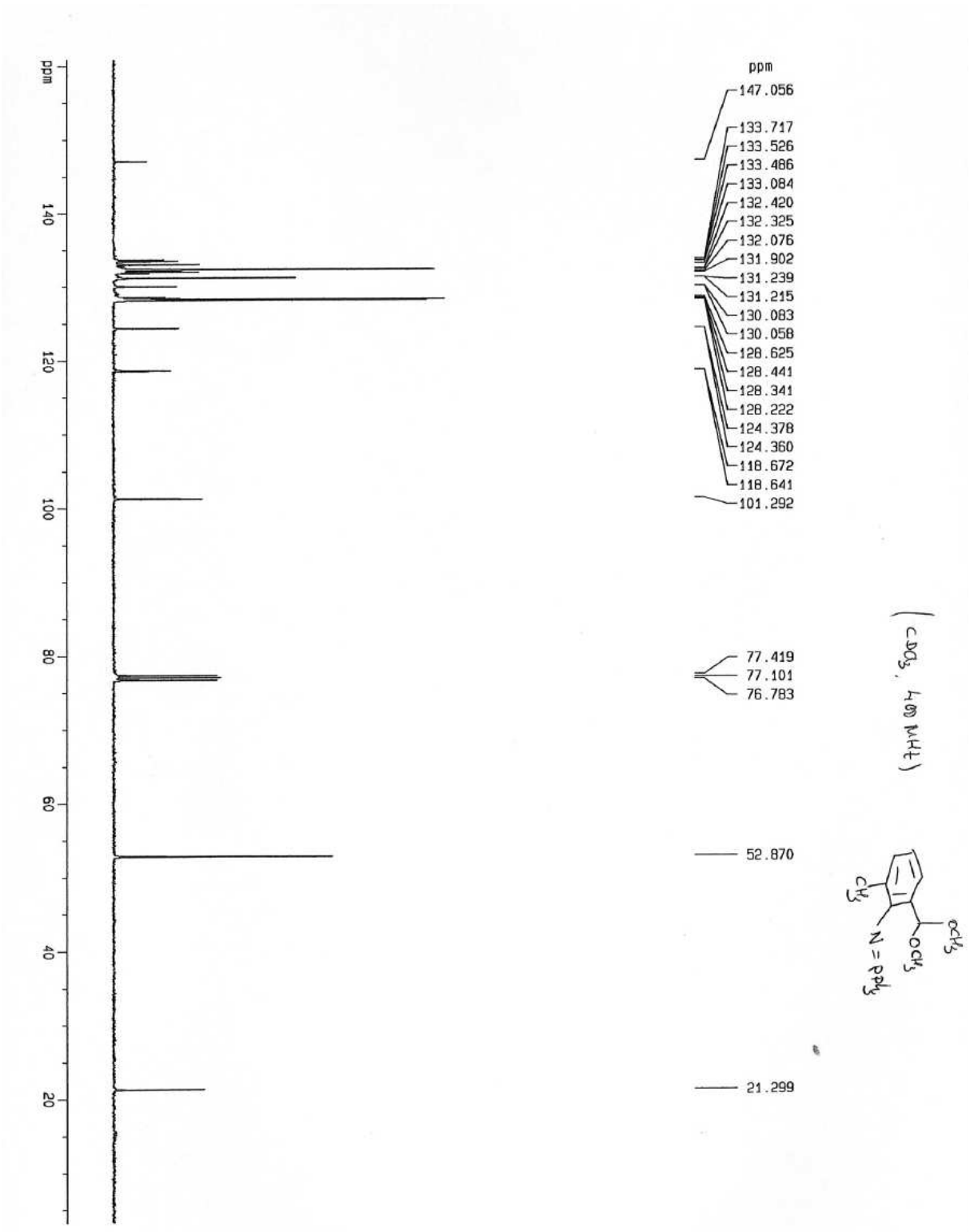
^{13}C NMR of **10b**



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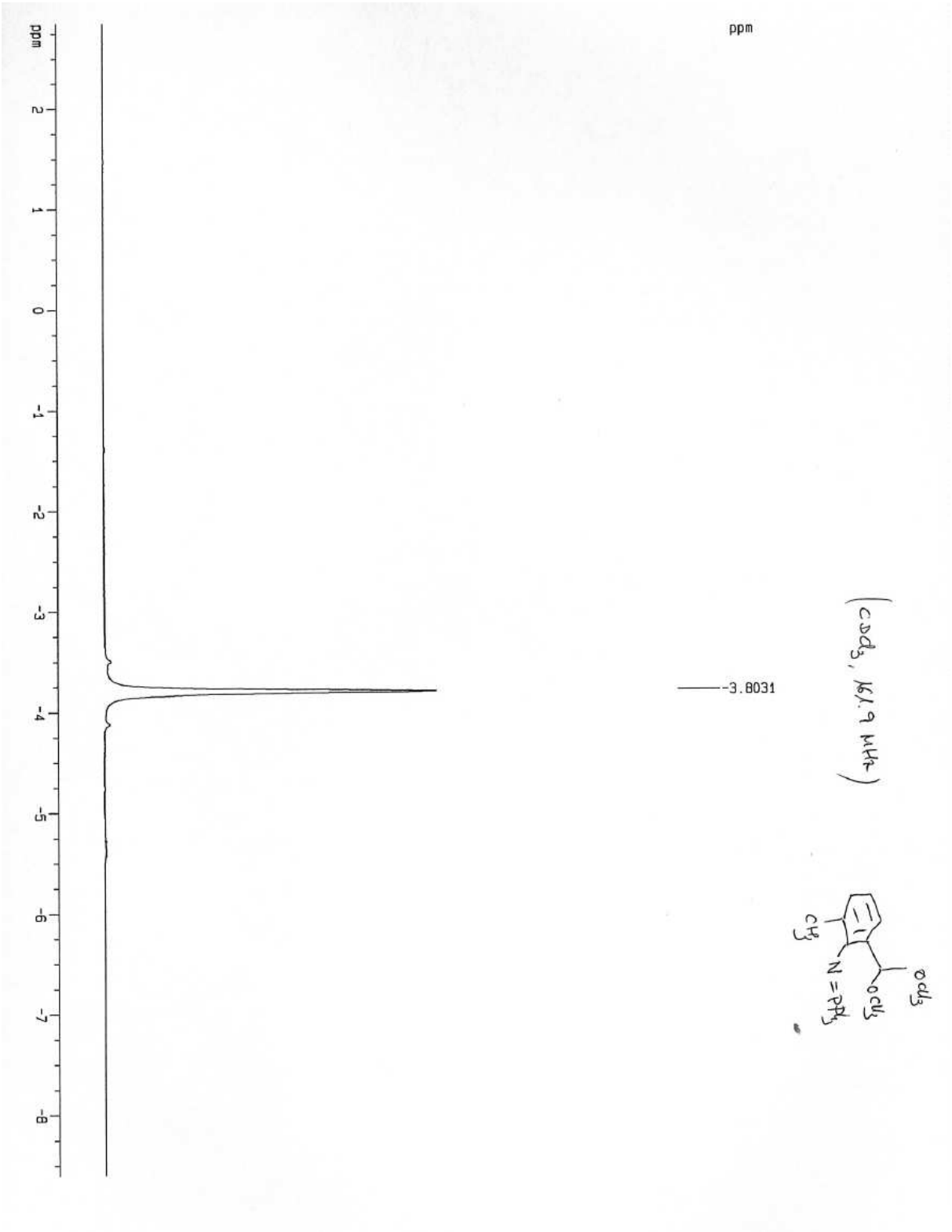

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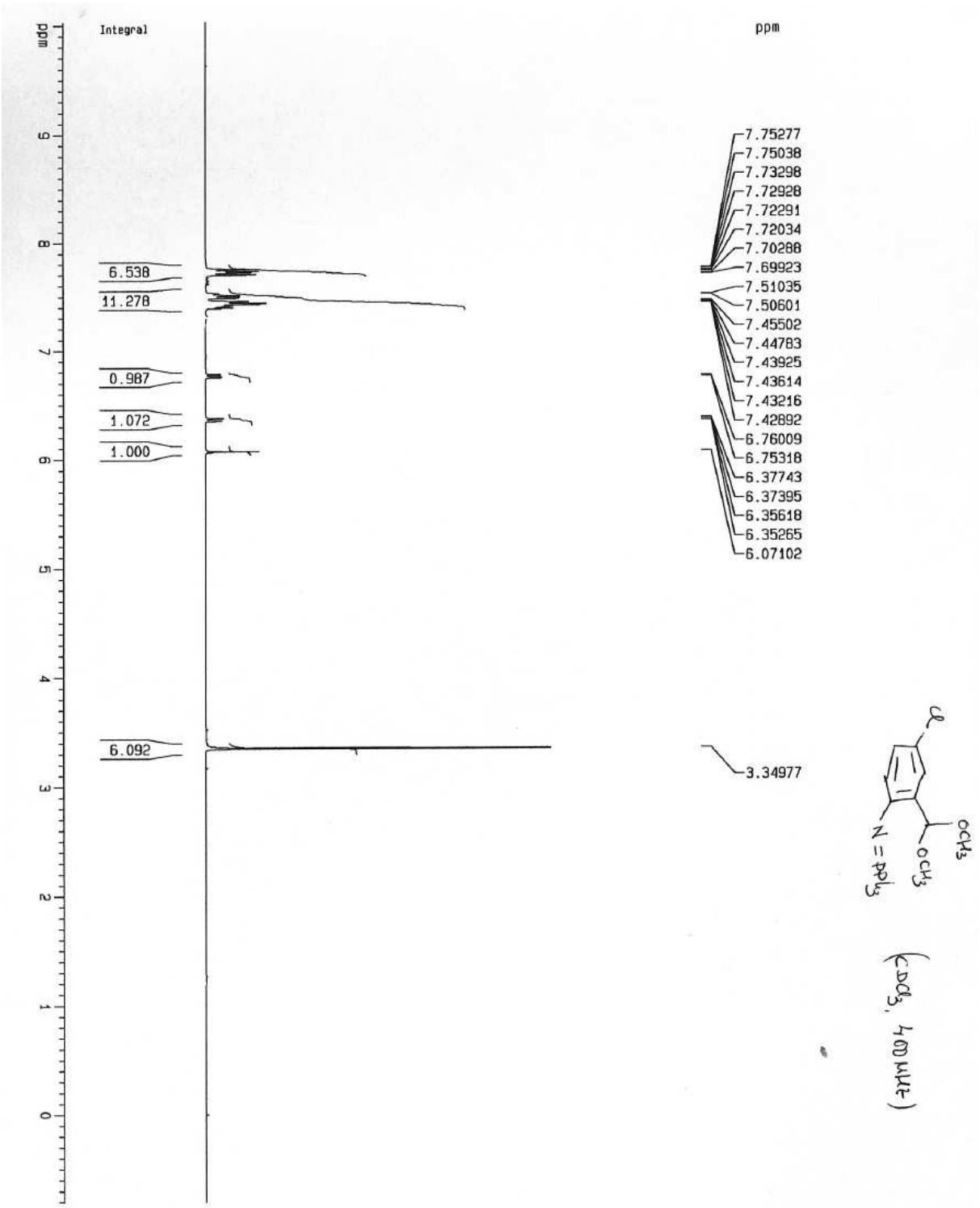
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7.42892
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6.35618
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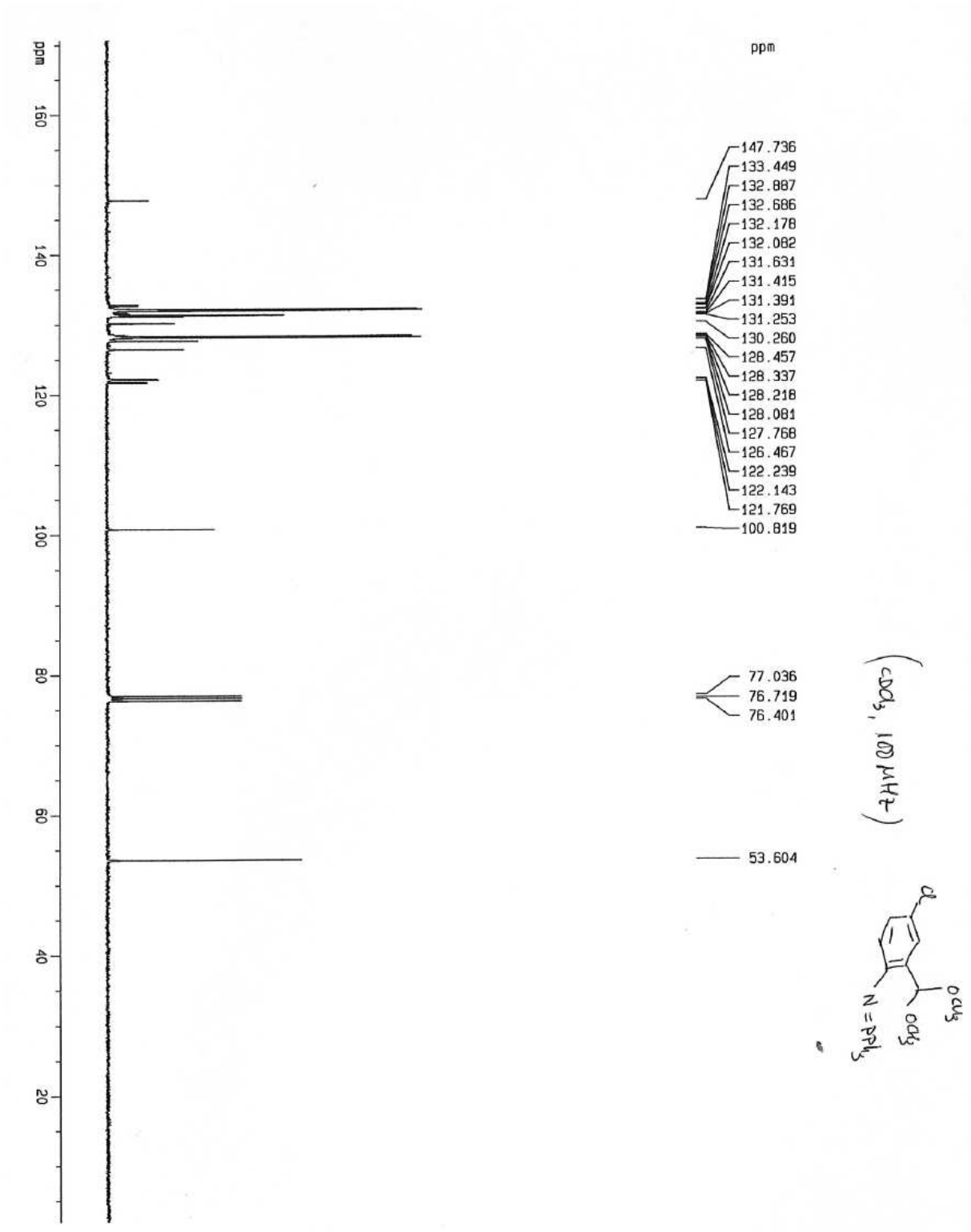
Cl
OCH3
OCH3
N = PPh3
(CDCl3, 400 MHz)

^{13}C NMR of **10c**



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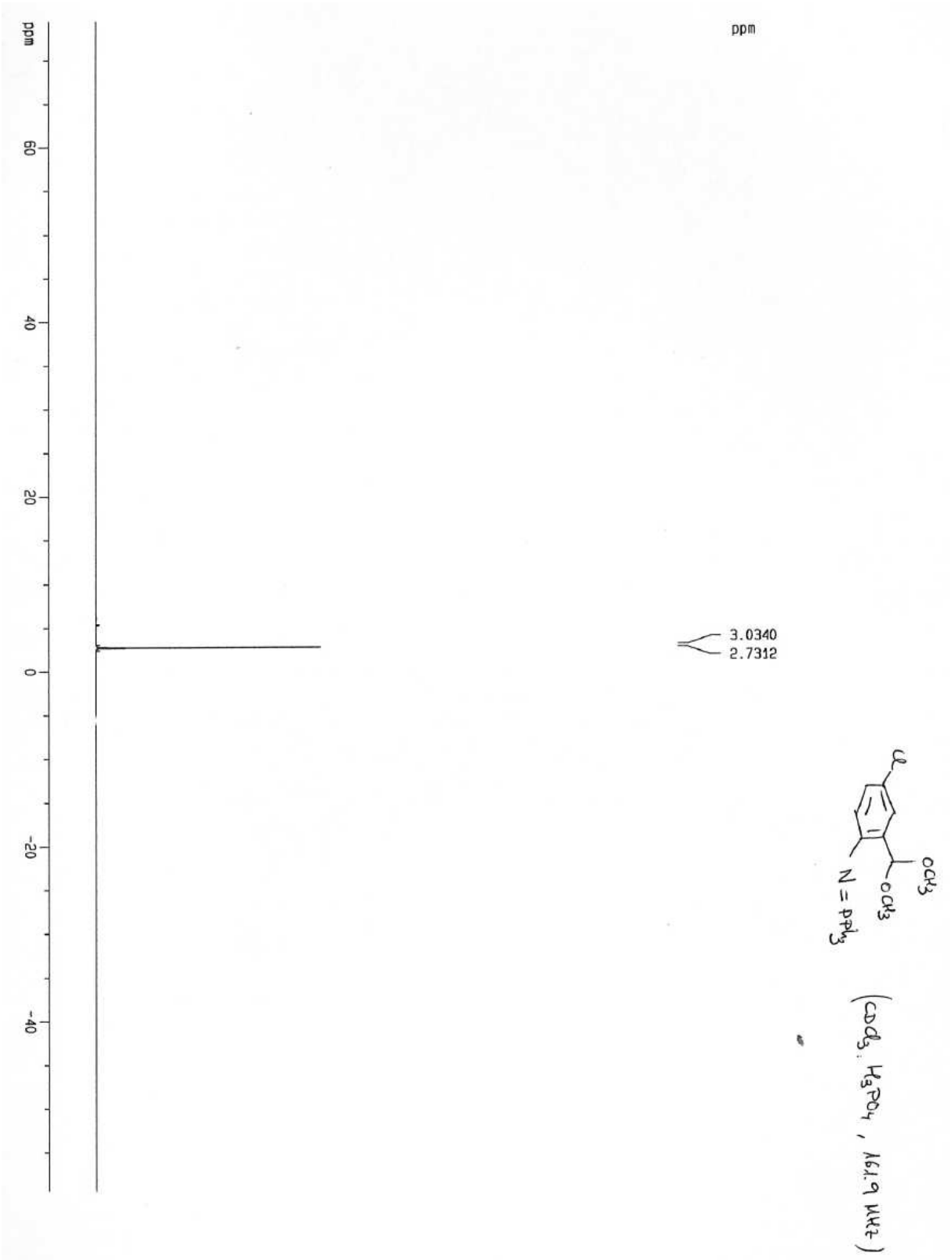
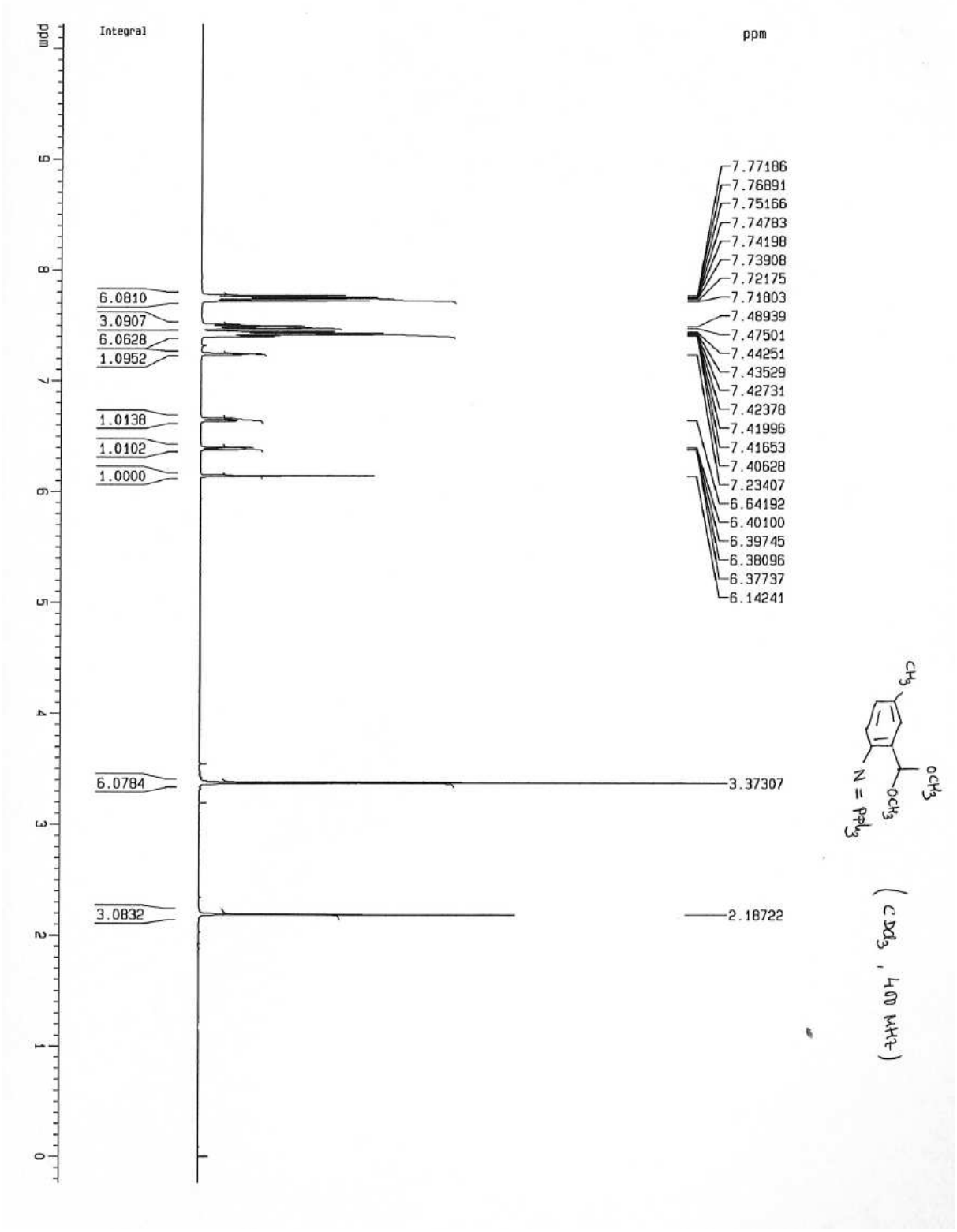


^{1}H NMR of **10d**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7.42378
7.41996
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7.40628
7.23407
6.64192
6.40100
6.39745
6.38096
6.37737
6.14241
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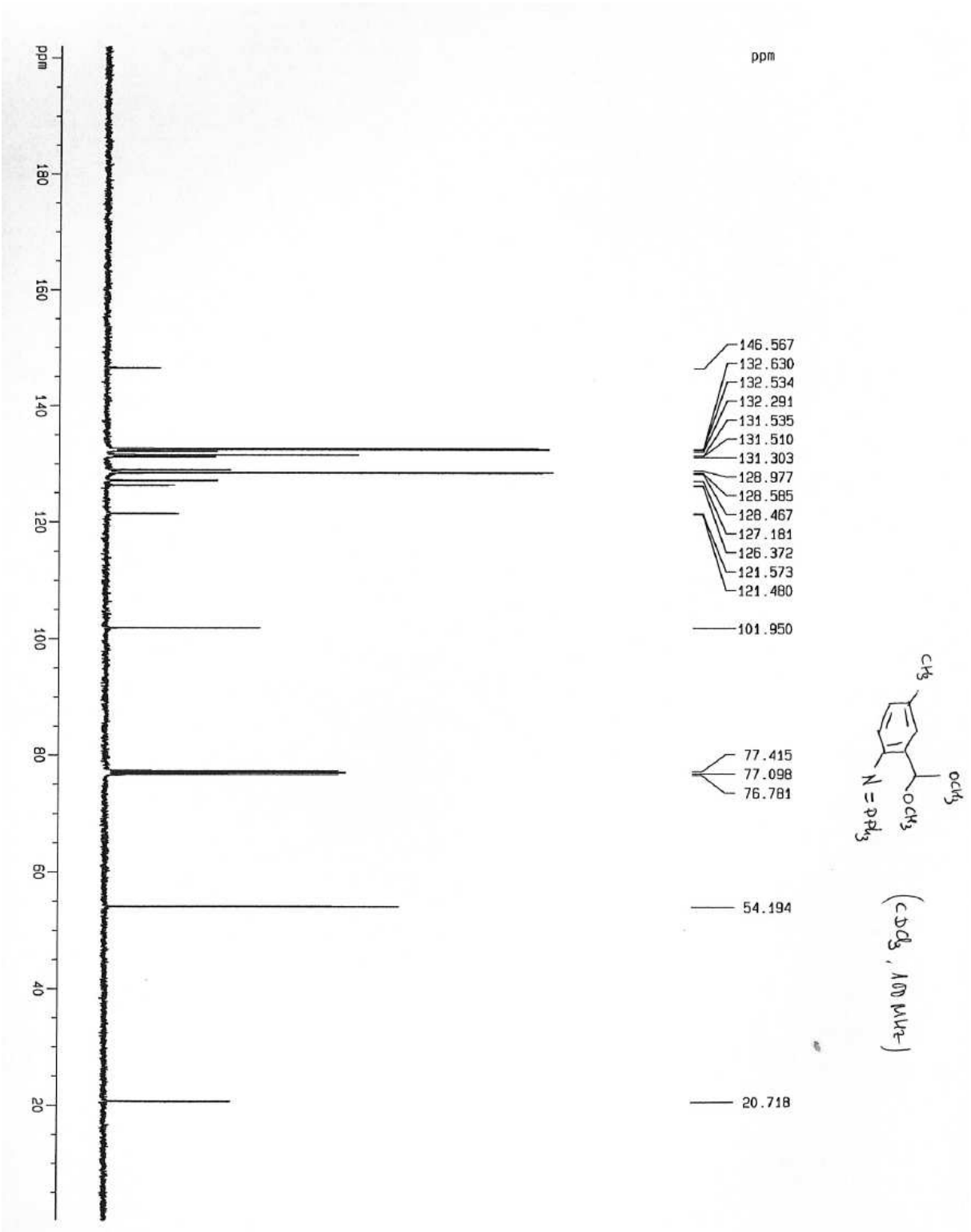
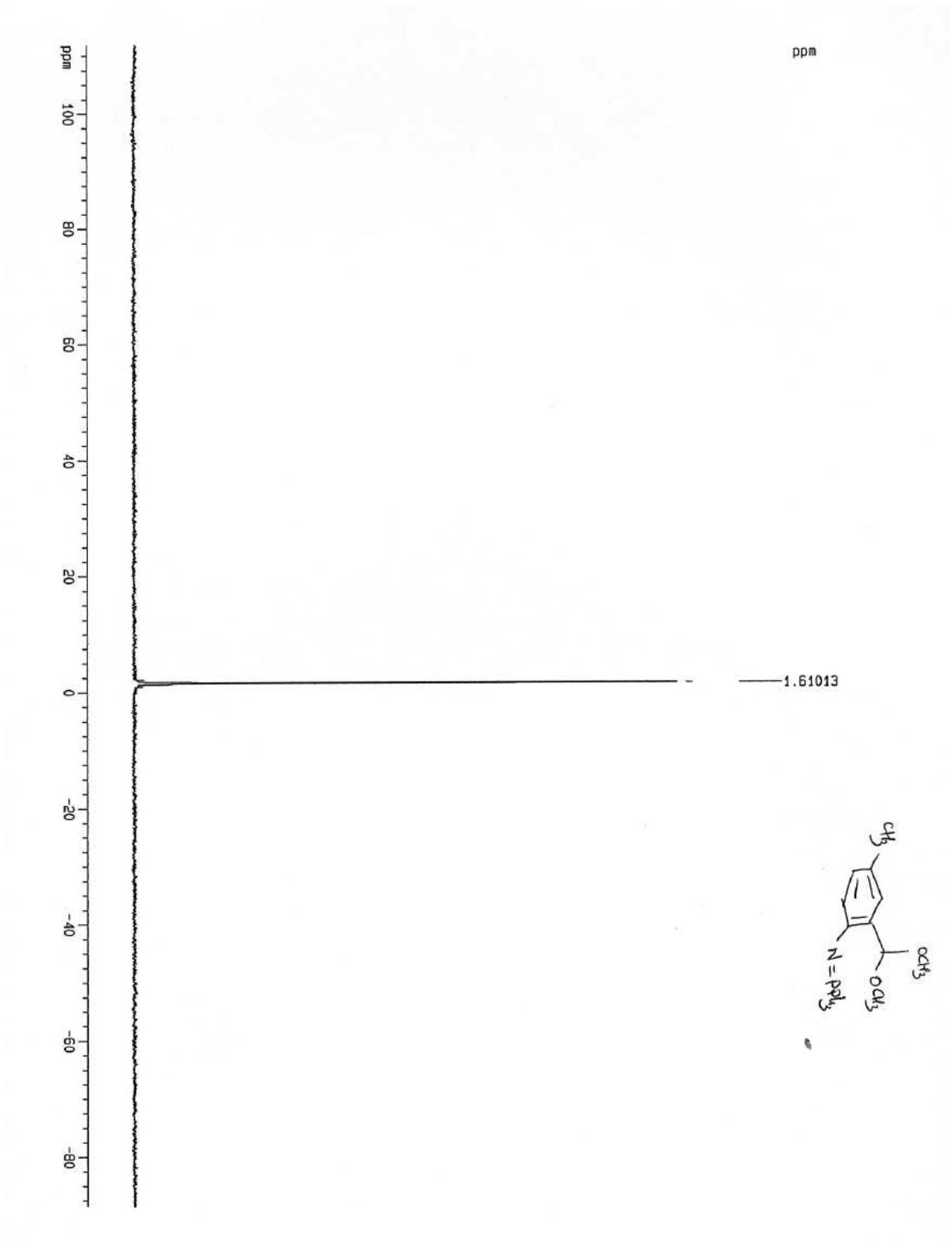
2.18722
CH3
OCH3
OCH3
N = PPh3
(CDCl3 , 400 MHz)

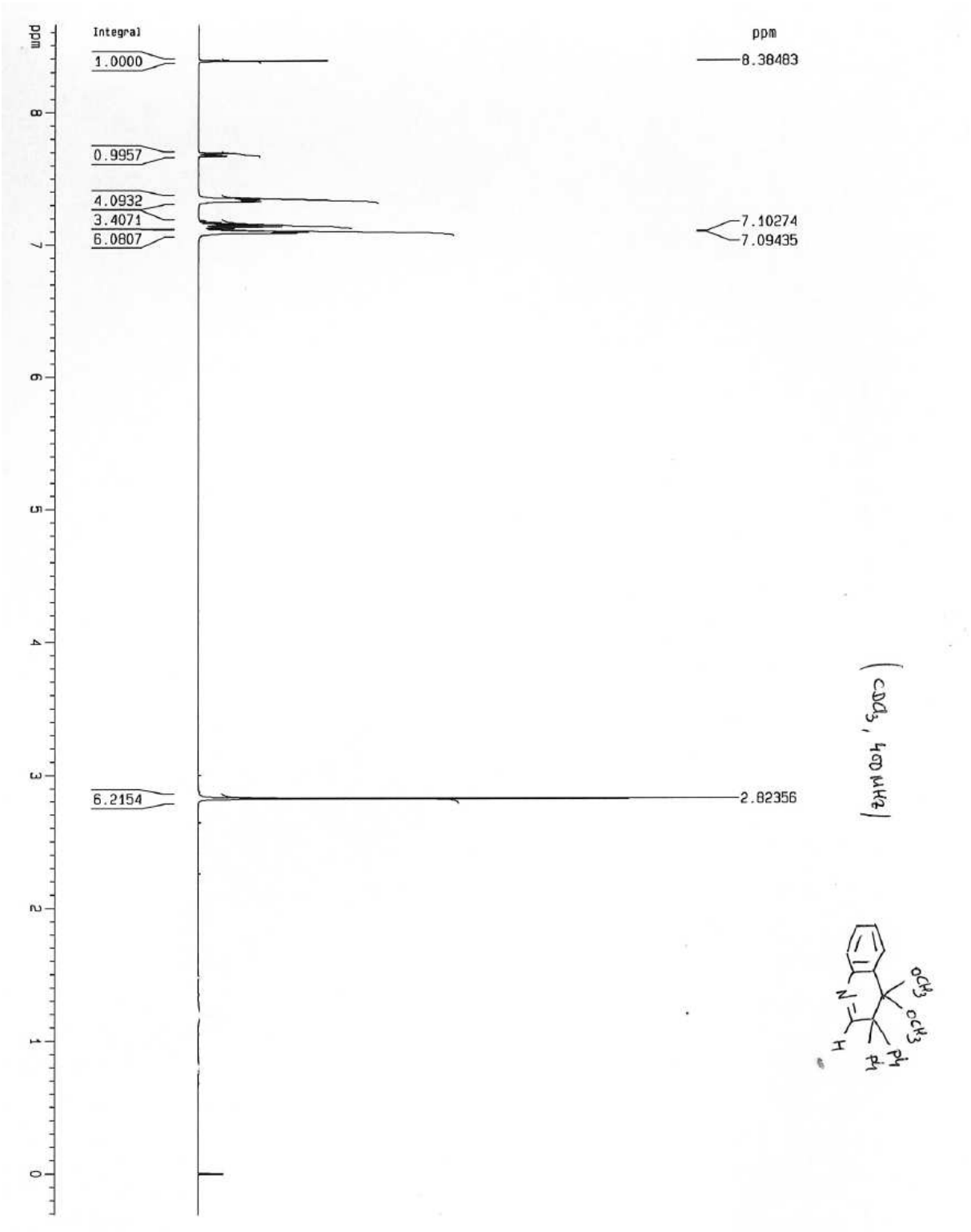
^{13}C NMR of **10d**



^{31}P NMR of **10d**



^{1}H NMR of **12a**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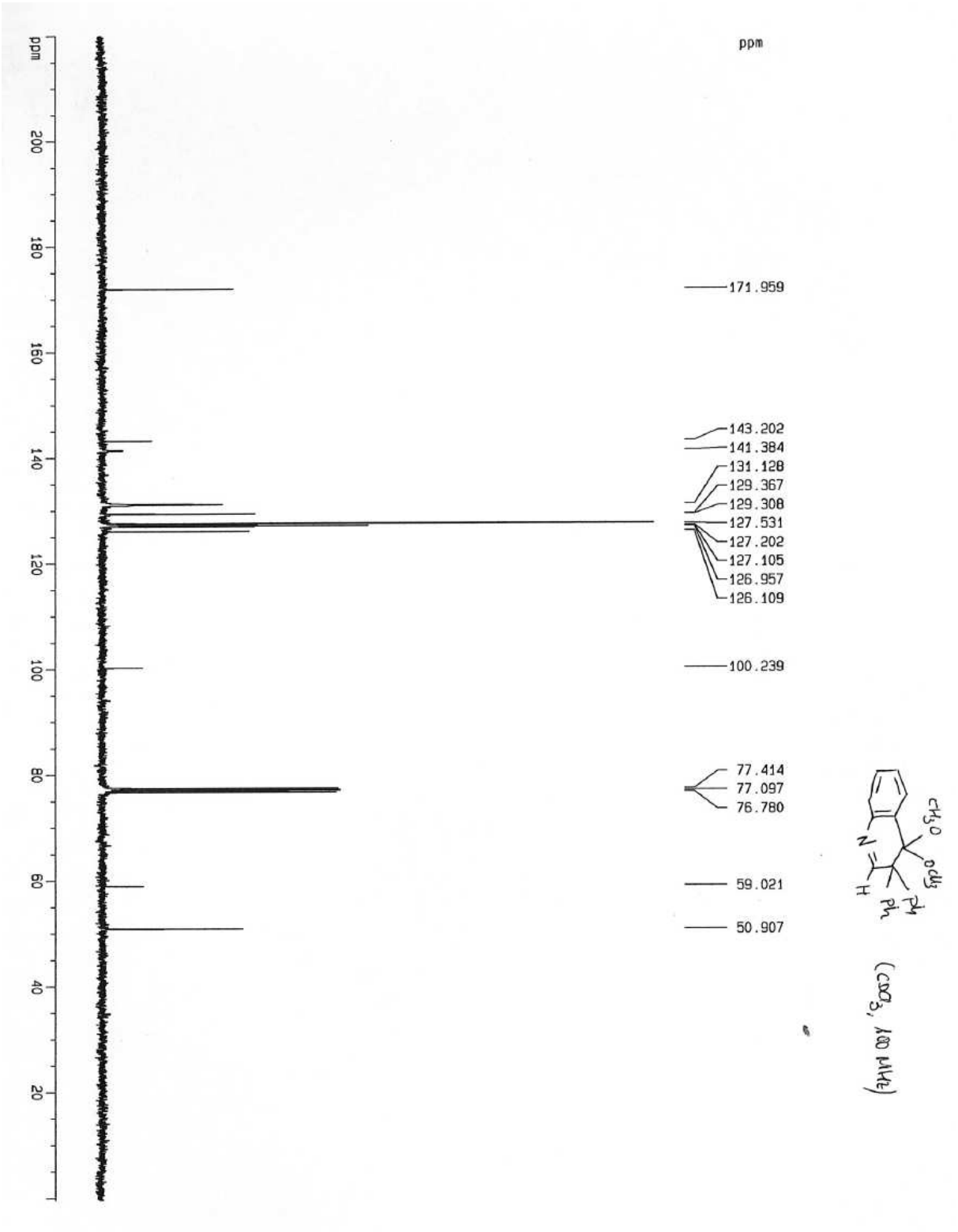
(CDCl3, 400 MHz)
OCH3
OCH3
N
H
Ph
Ph

^{13}C NMR of **12a**



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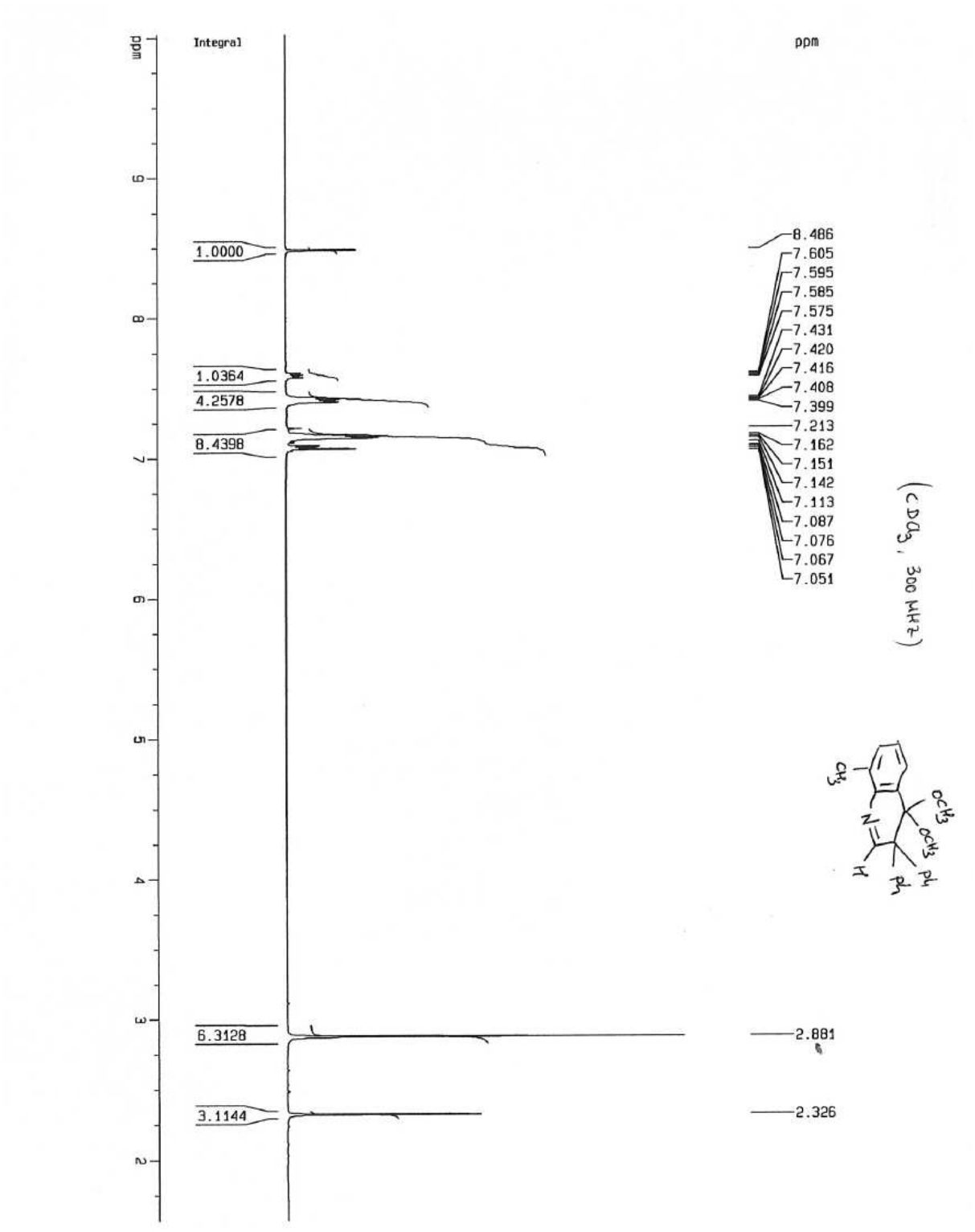
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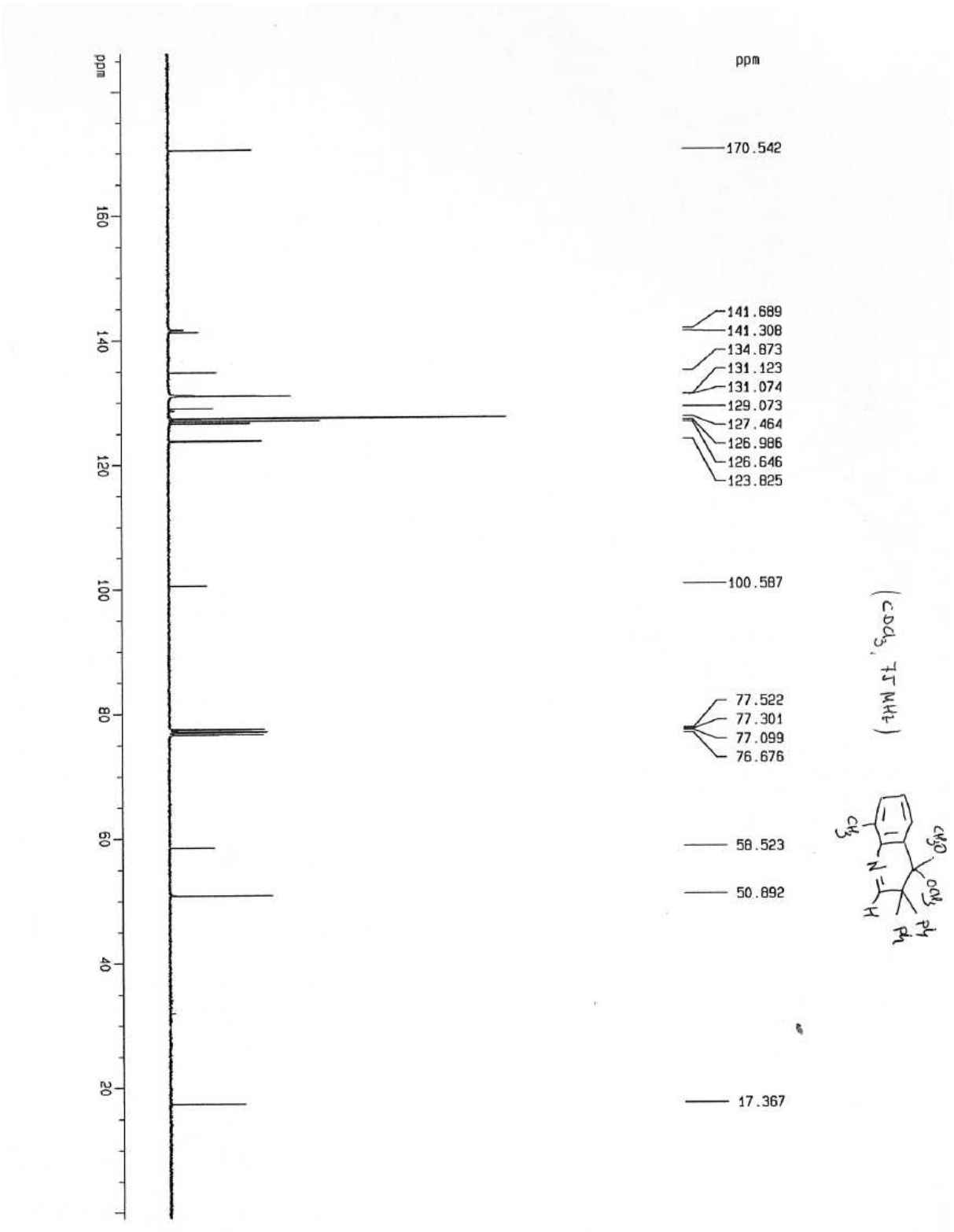
(CDCl3, 300 MHz)

^{13}C NMR of **12b**



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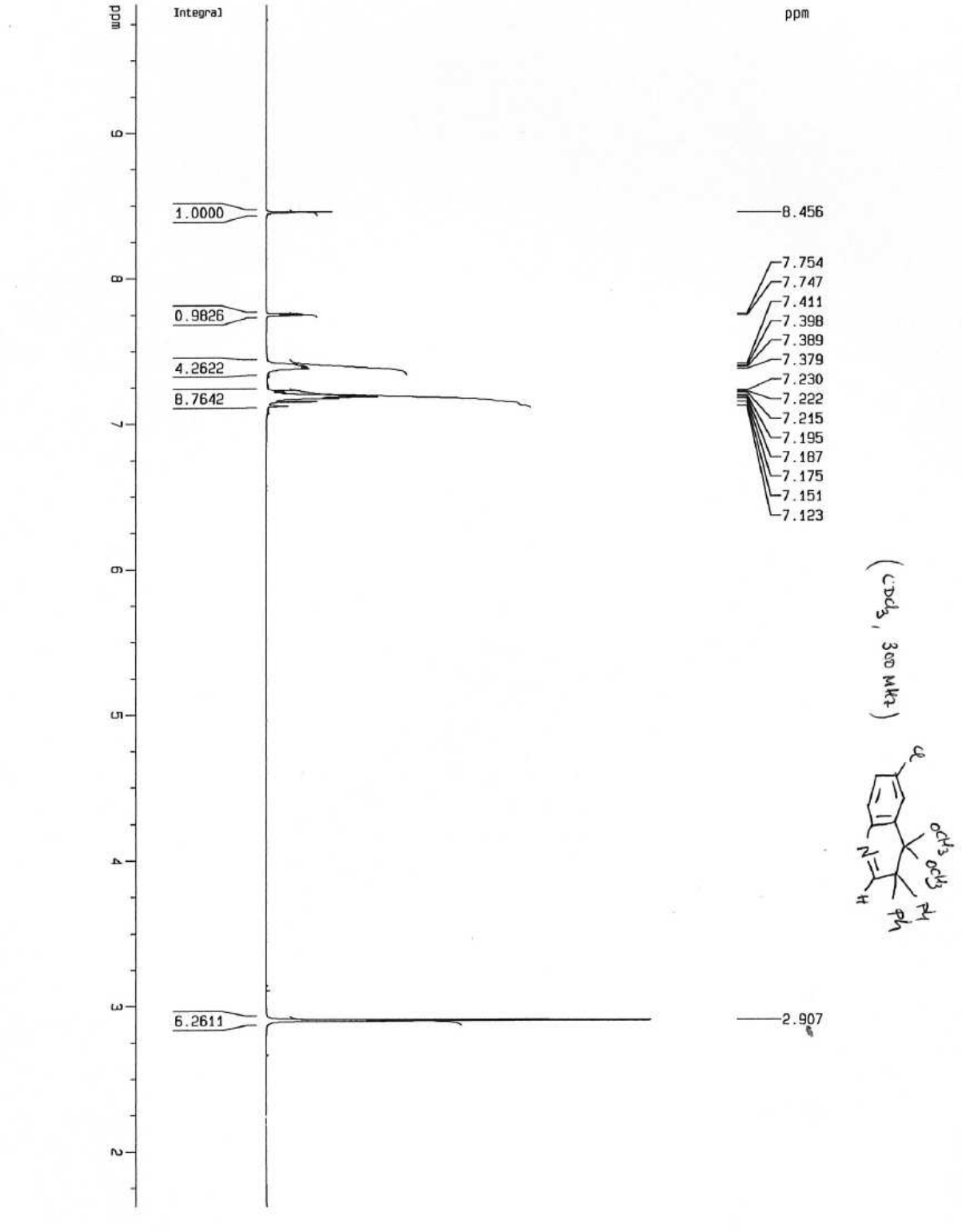
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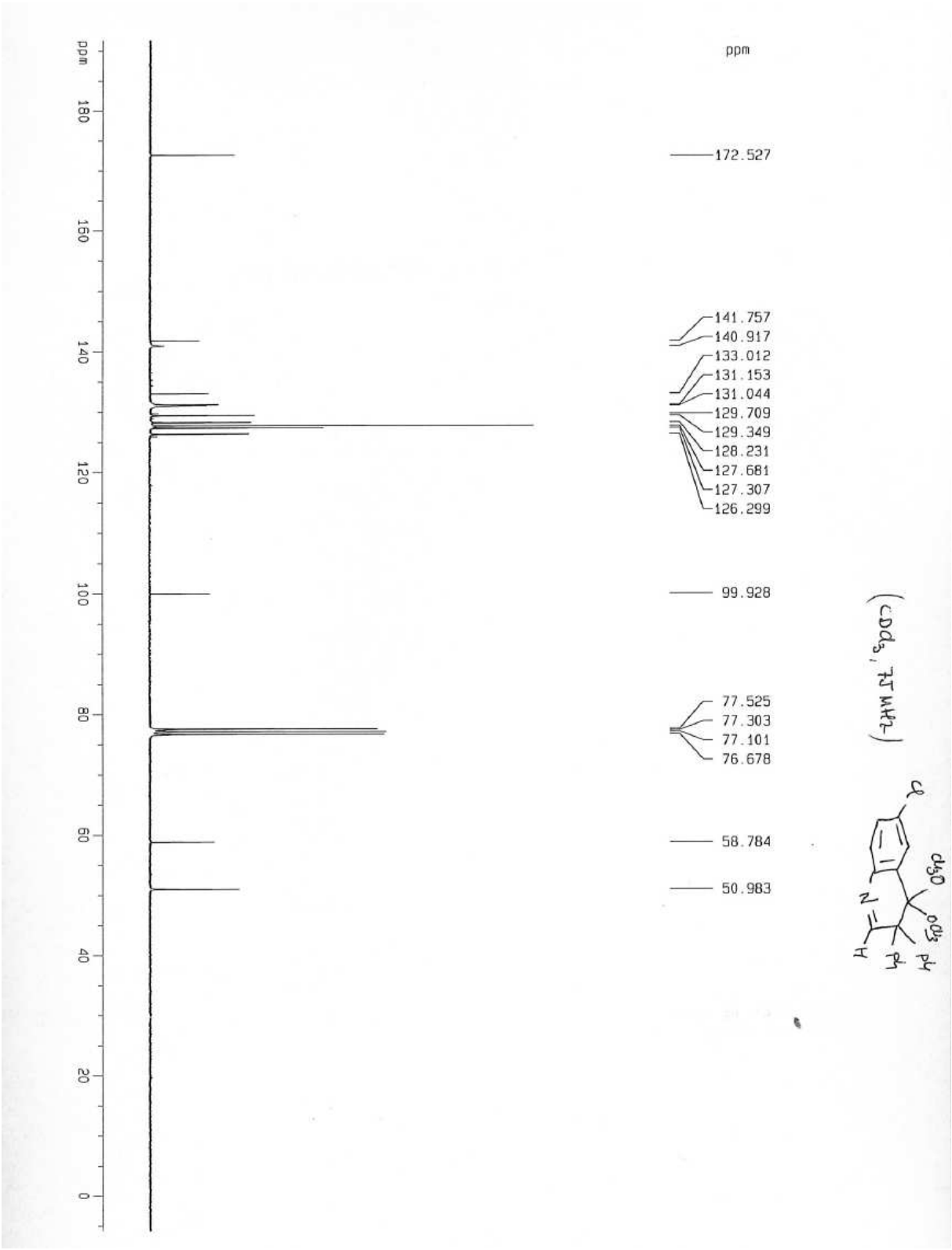
(CDCl3, 300 MHz)

^{13}C NMR of **12c**



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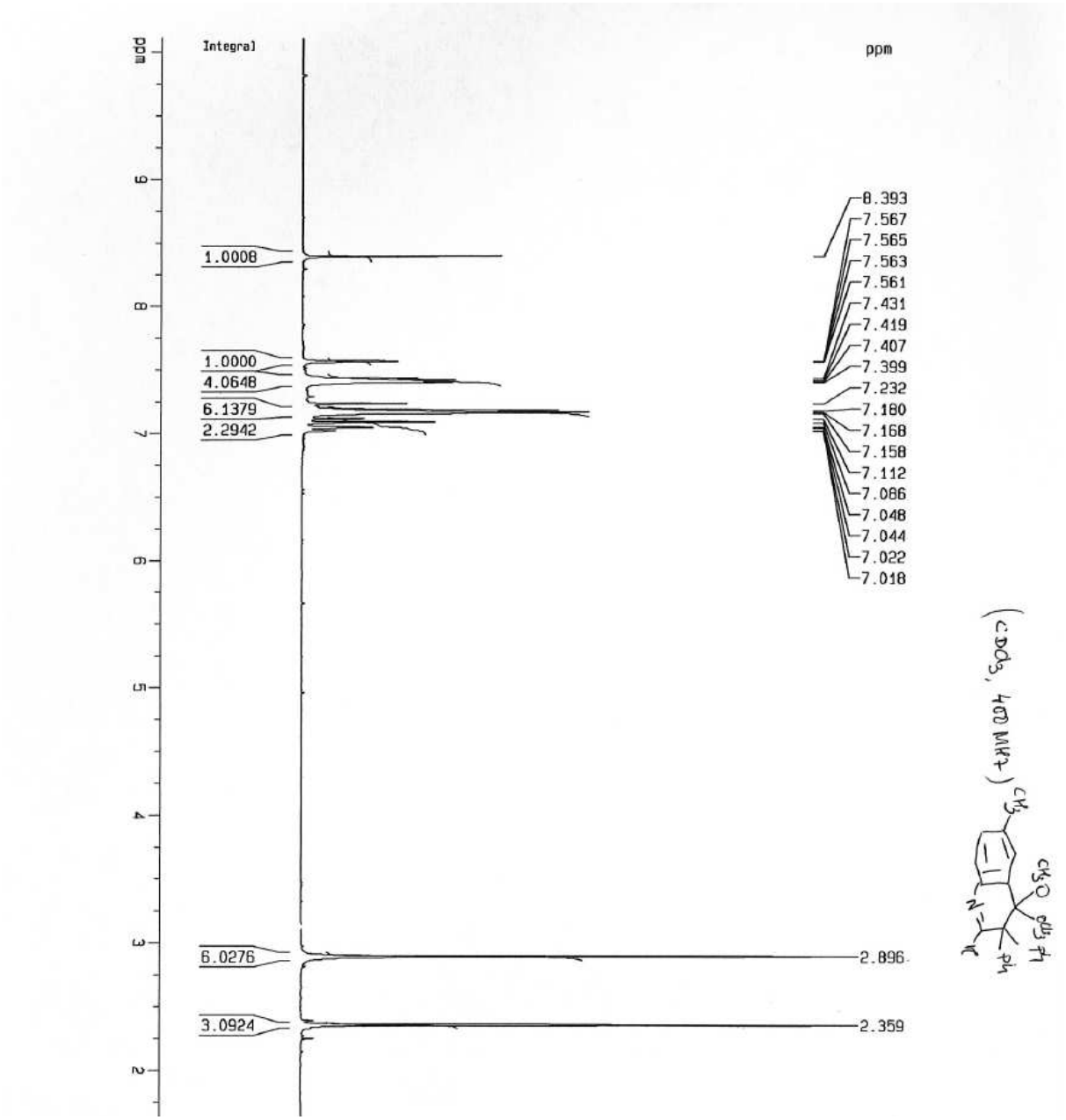
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7.407
7.399
7.232
7.180
7.168
7.158
7.112
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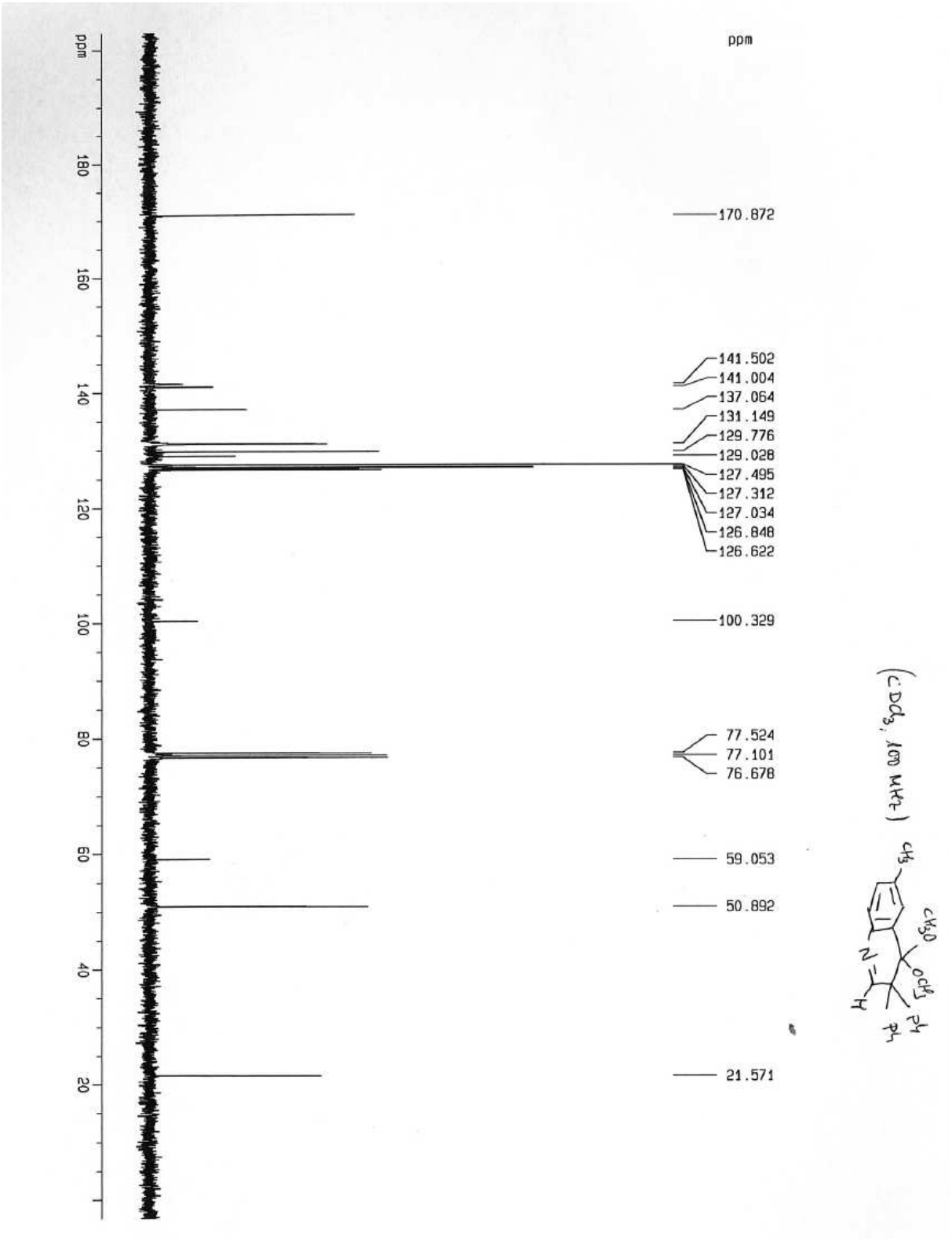
(CDCl3, 400 MHz)

^{13}C NMR of **12d**



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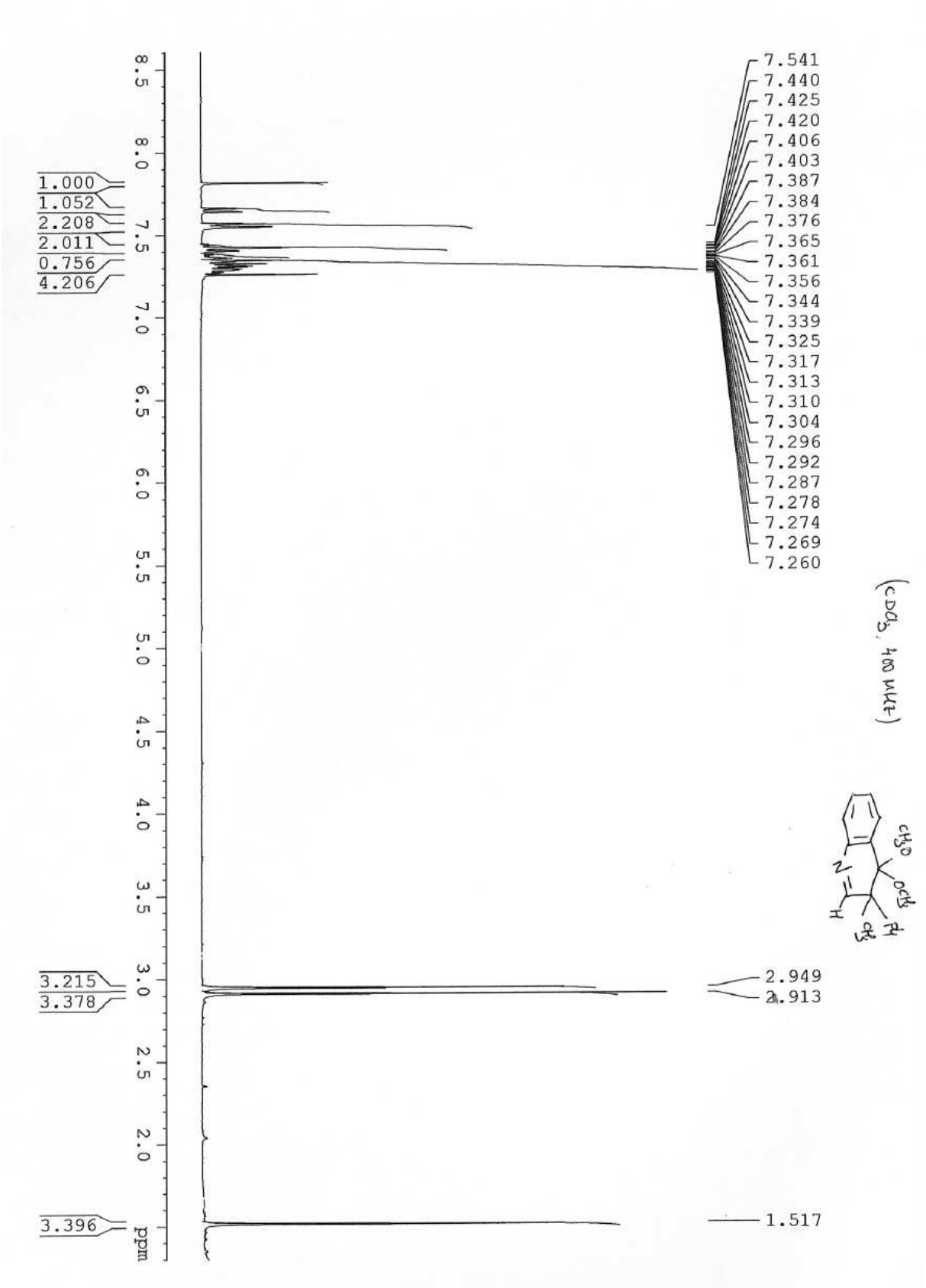

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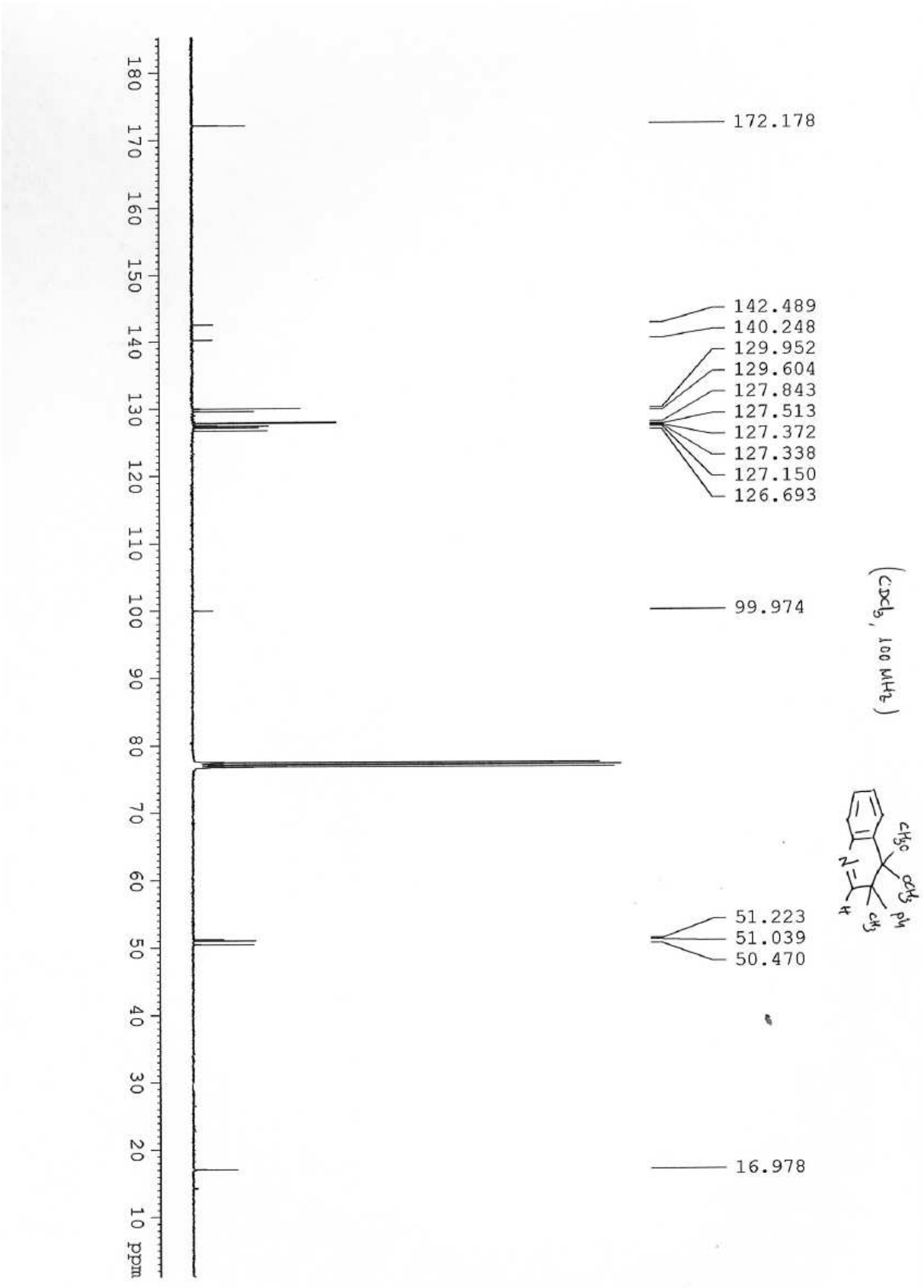

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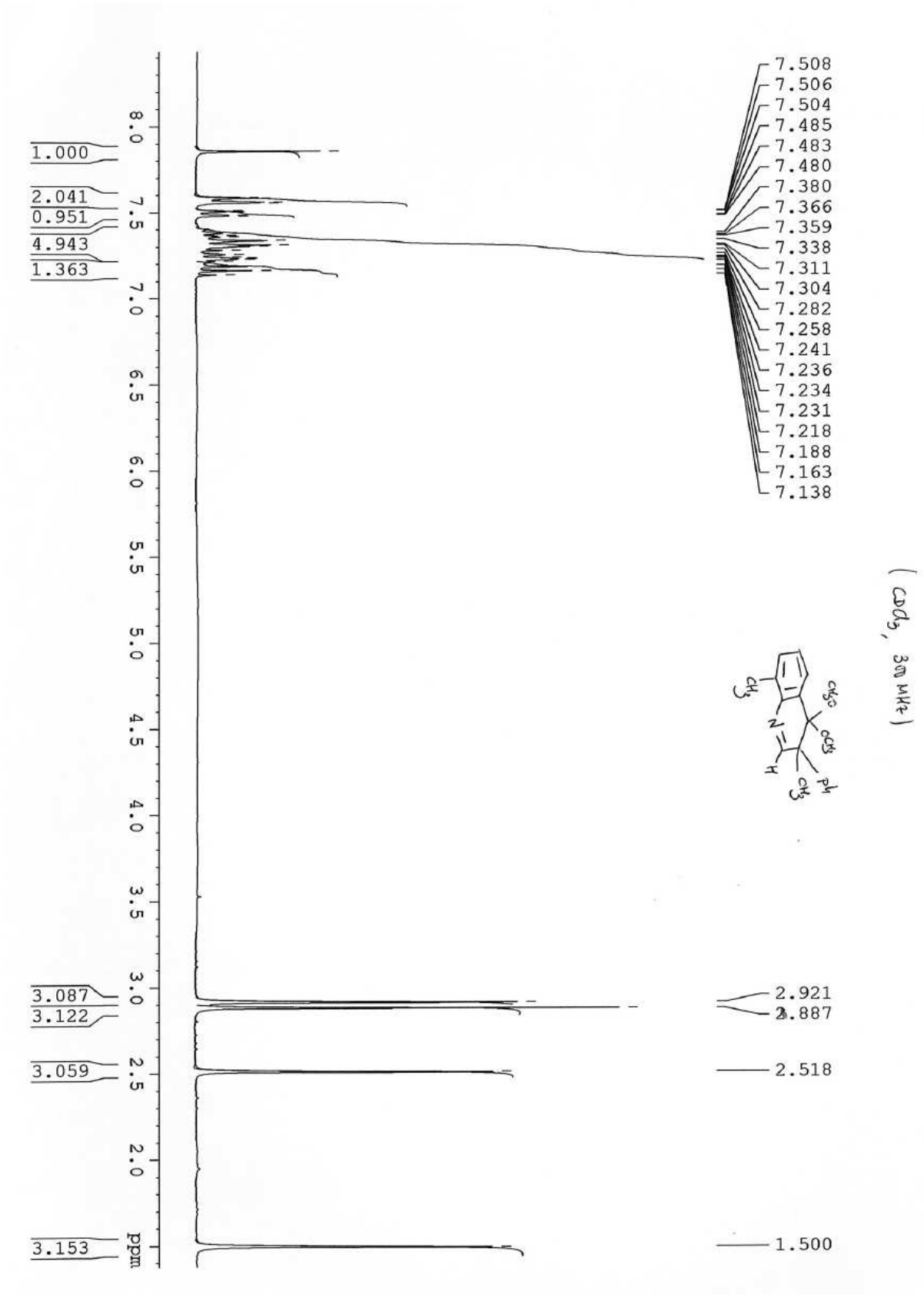

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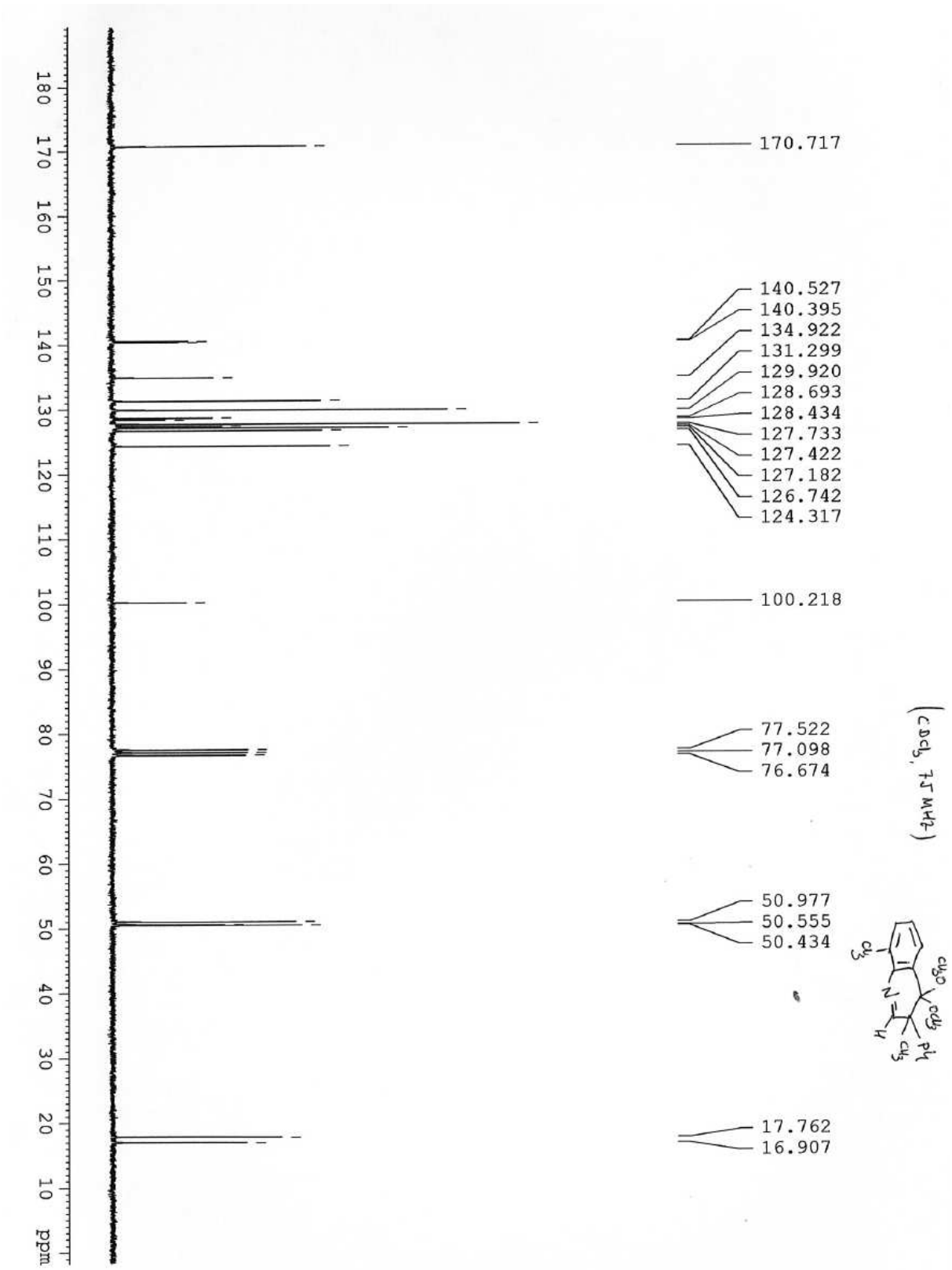

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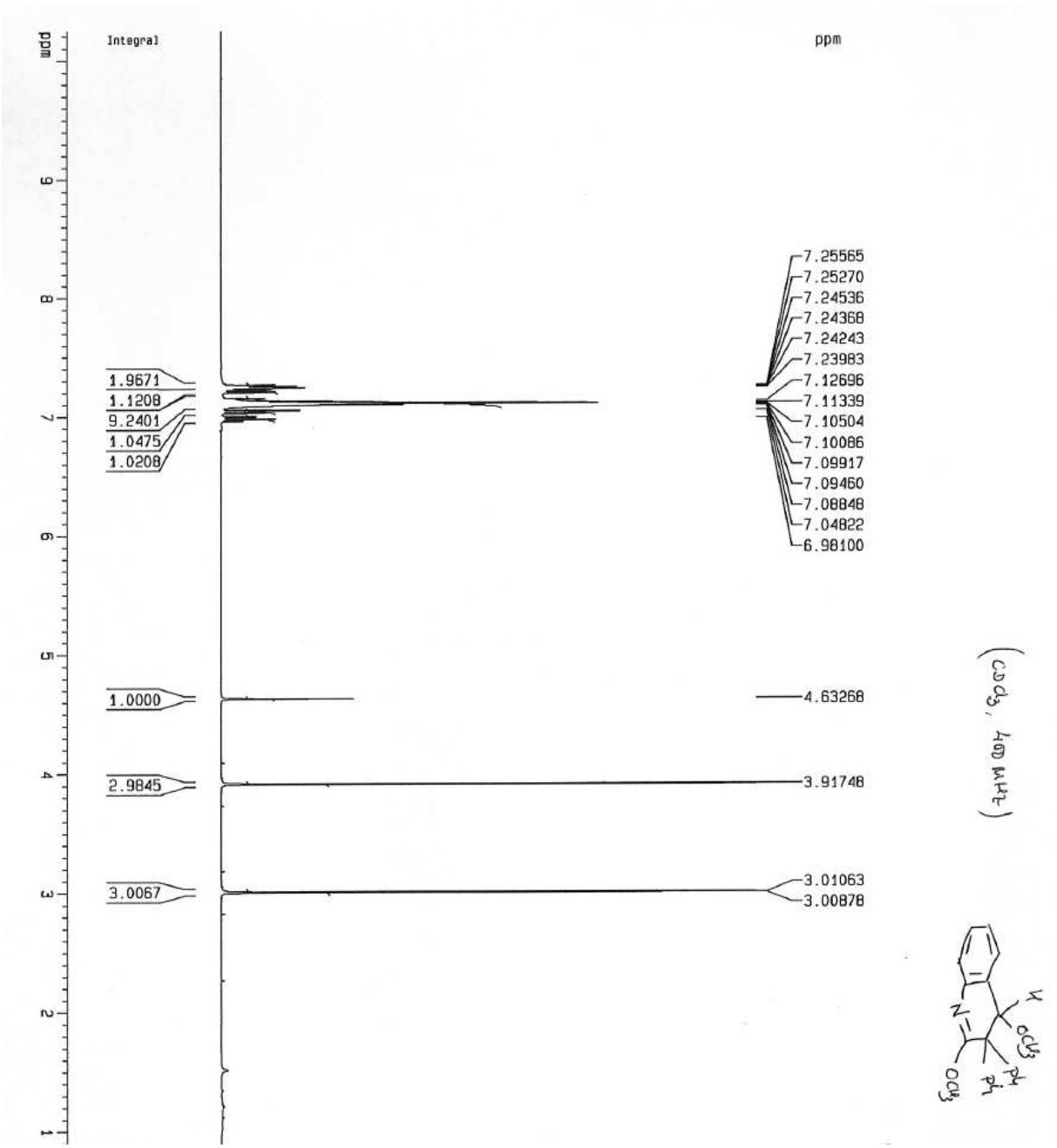

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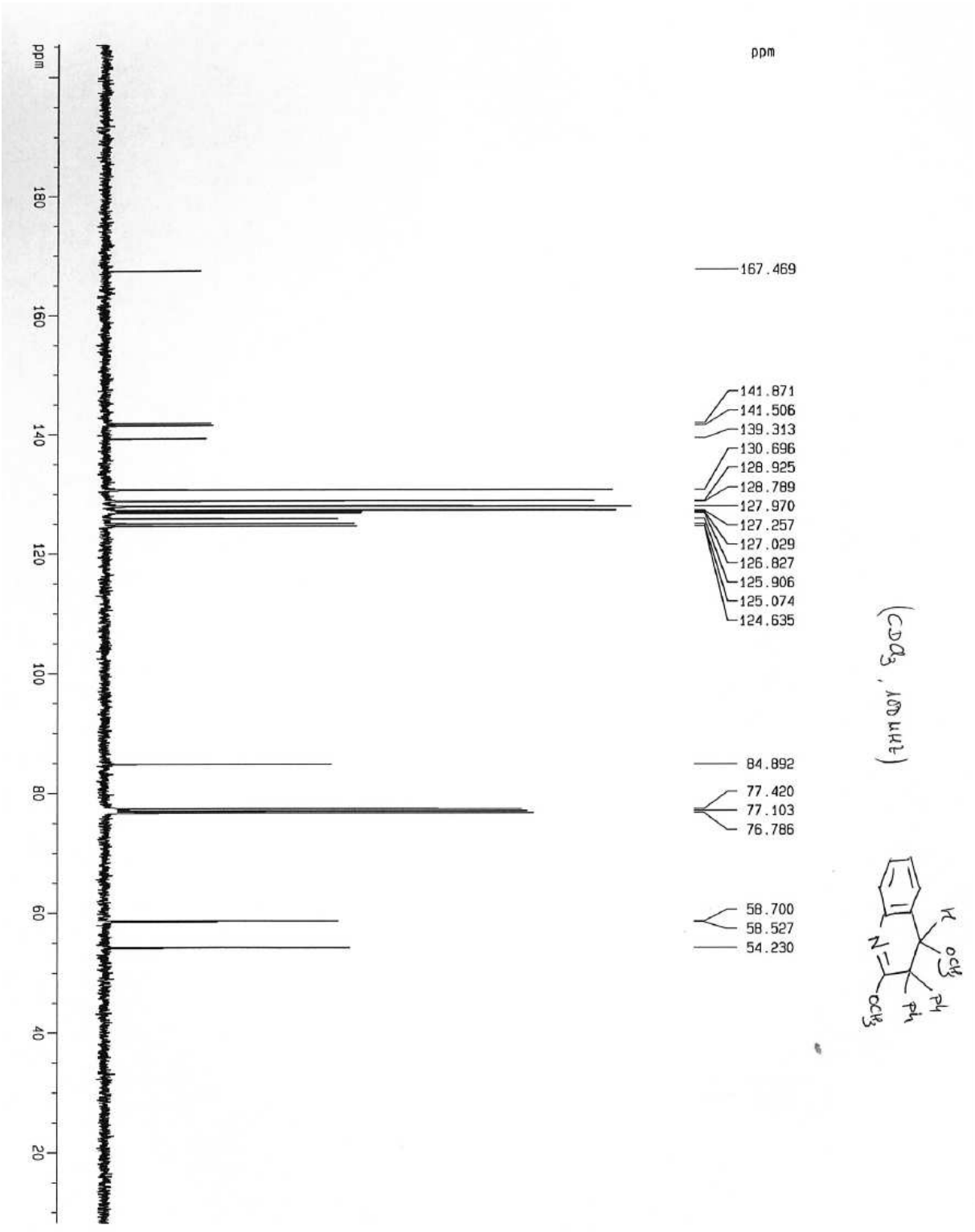

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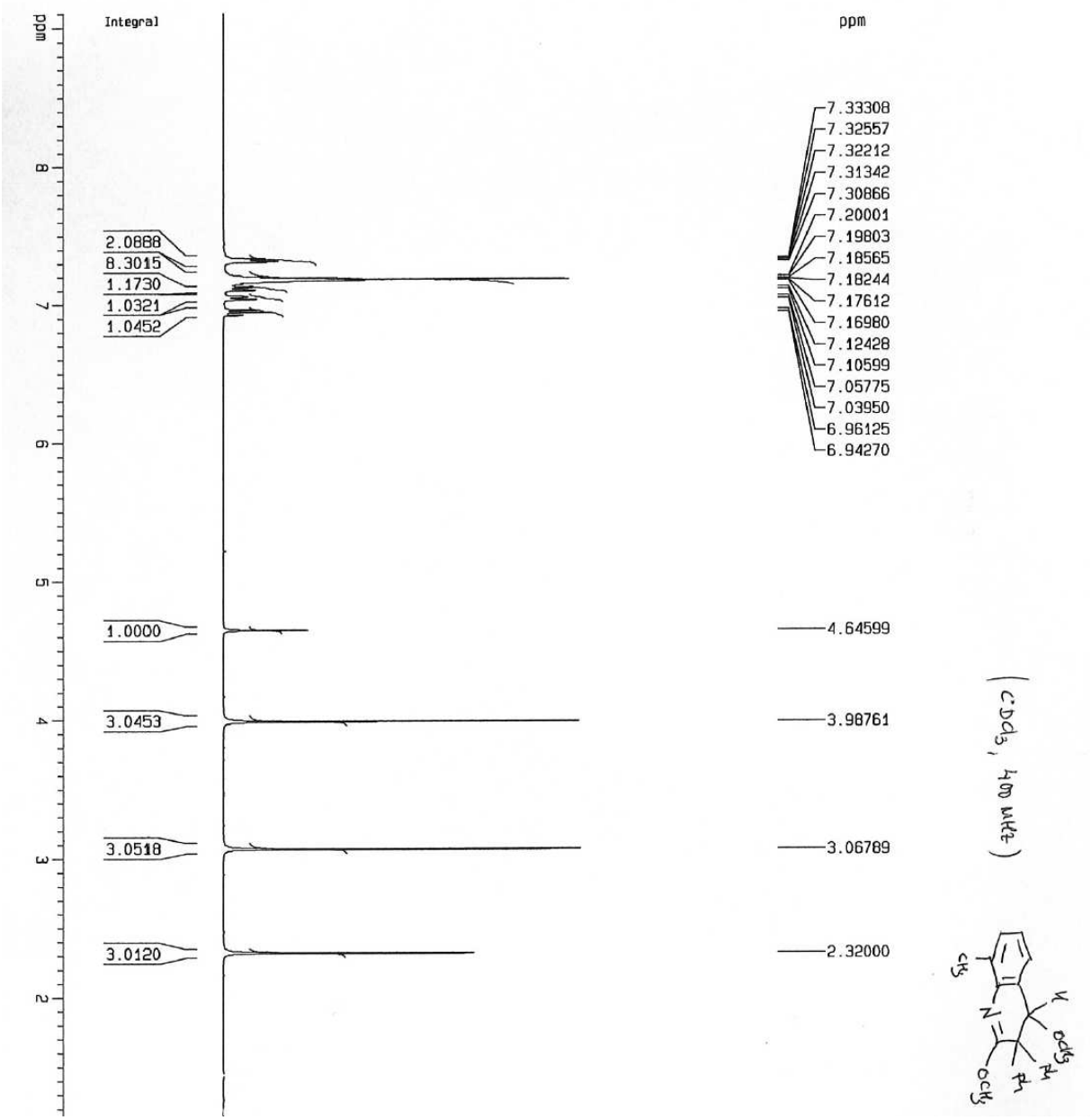
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7.12428
7.10599
7.05775
7.03950
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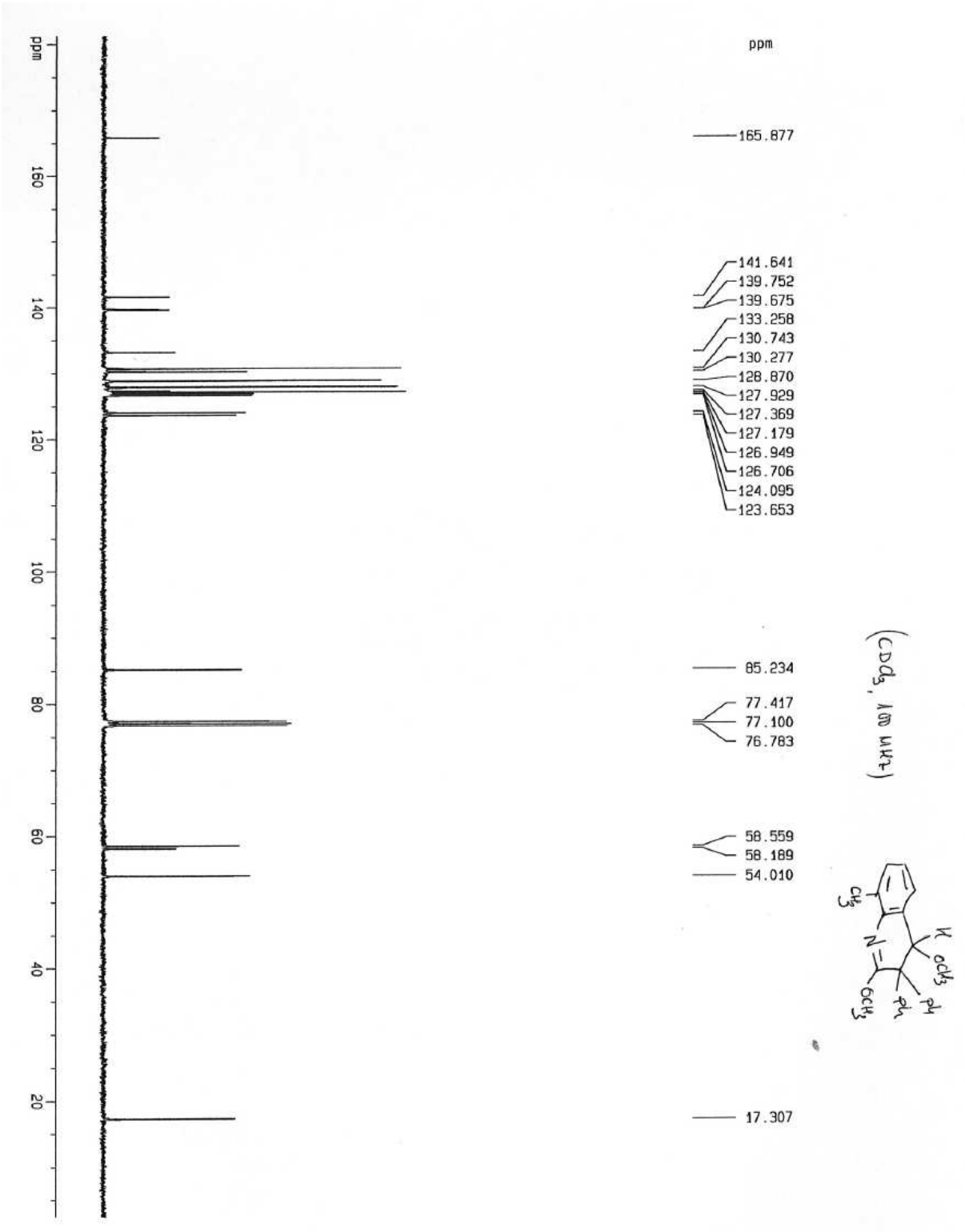
2.32000
(CDCl3, 400 MHz)

^{13}C NMR of **13b**



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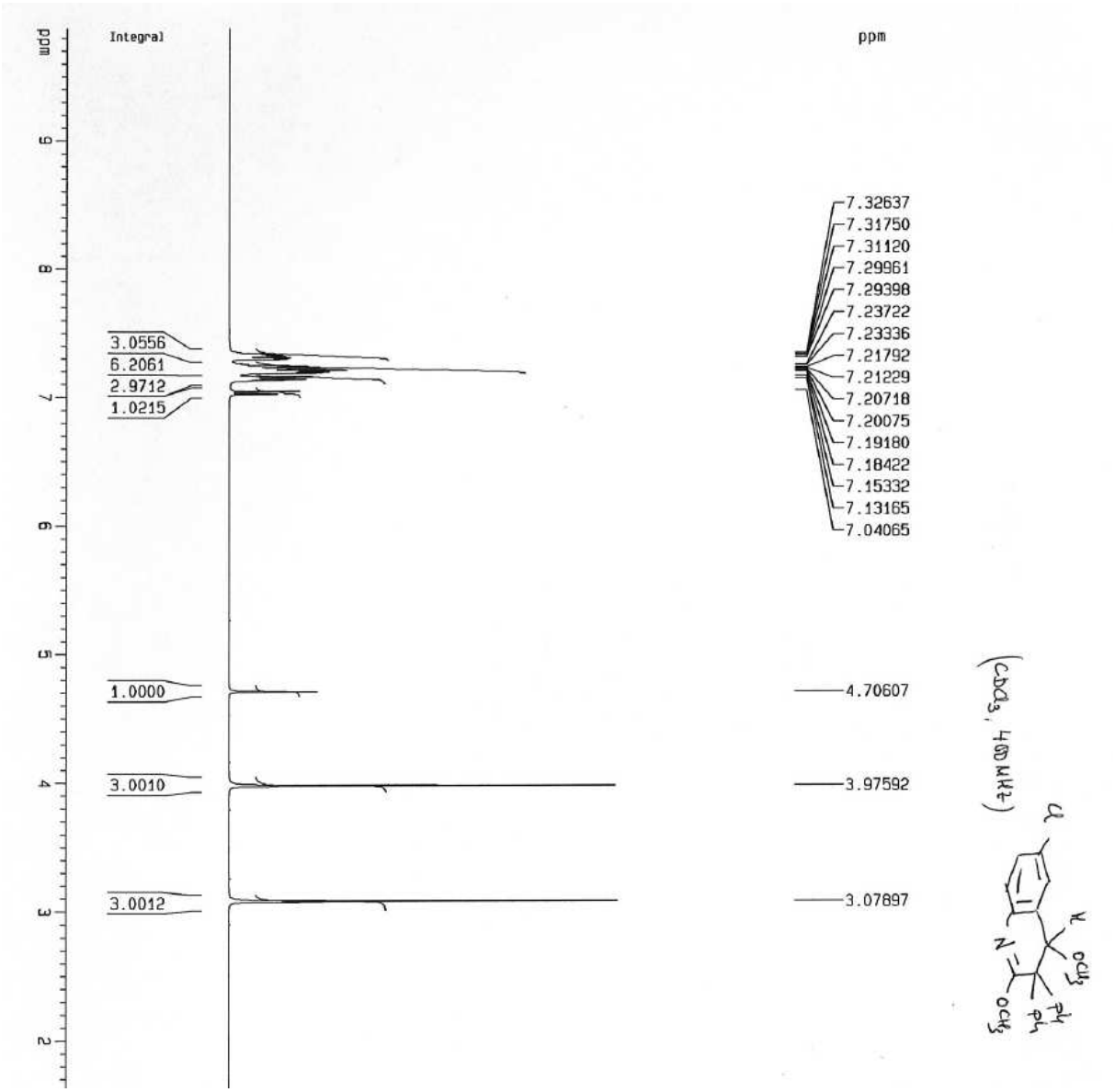

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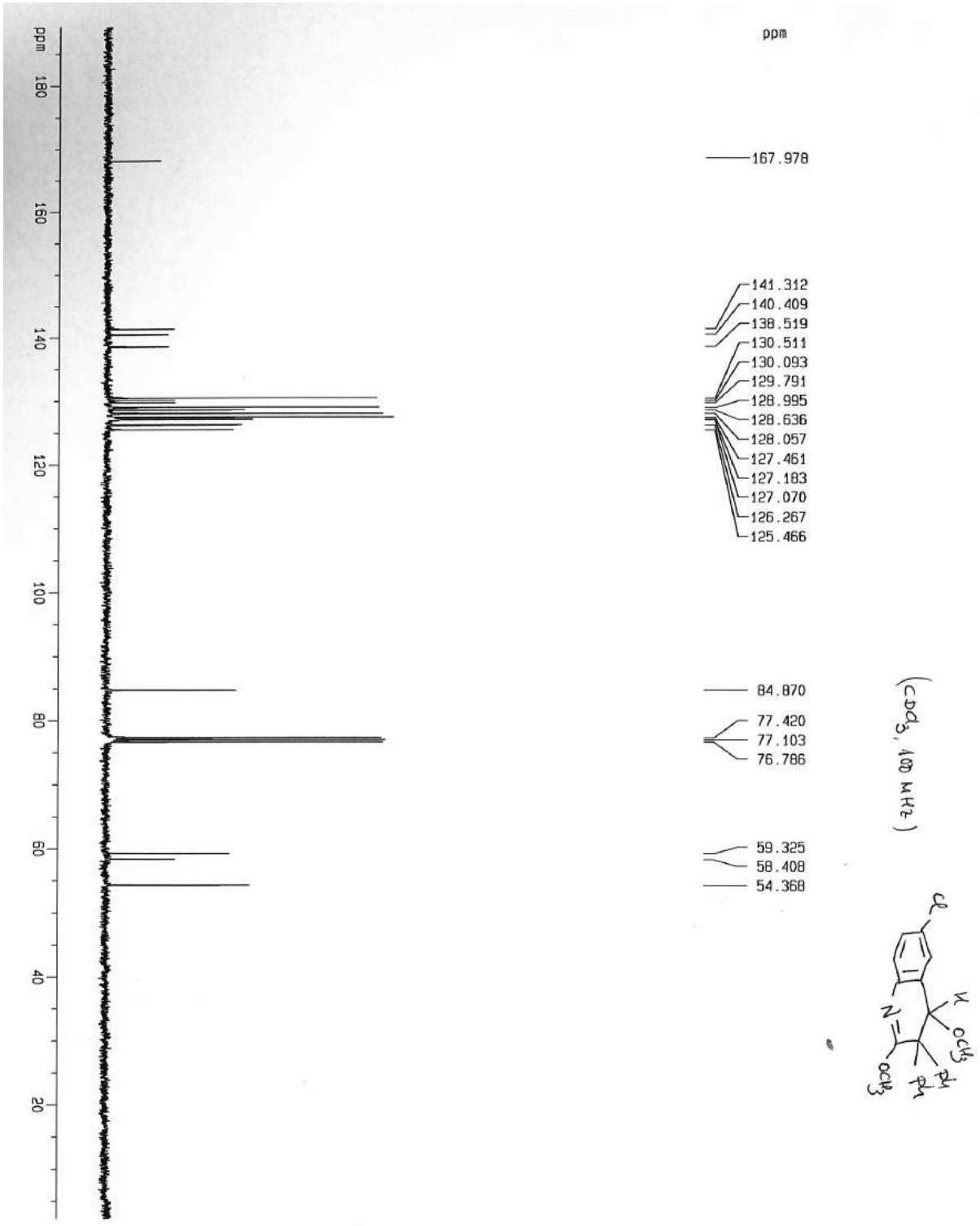

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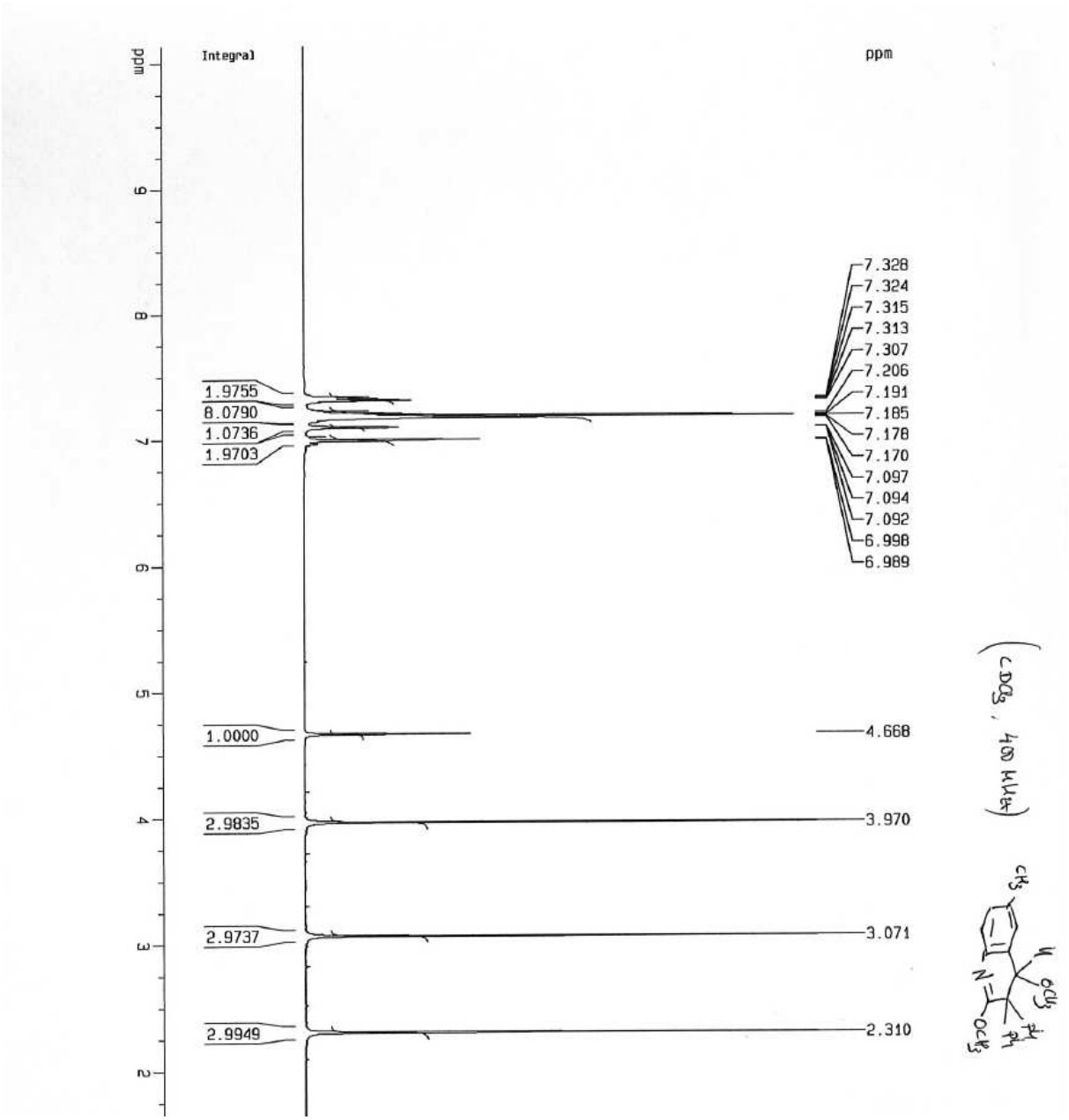

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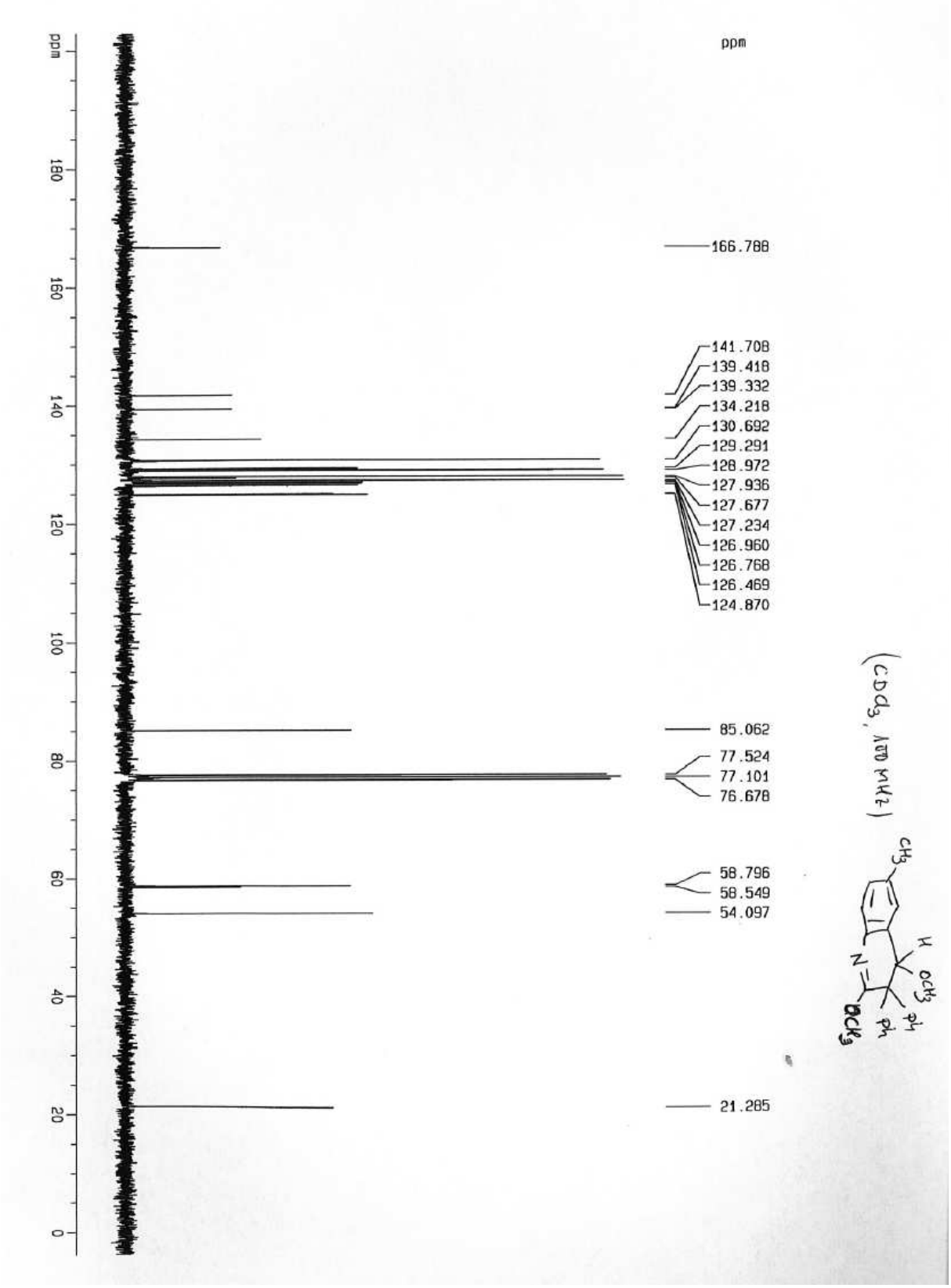

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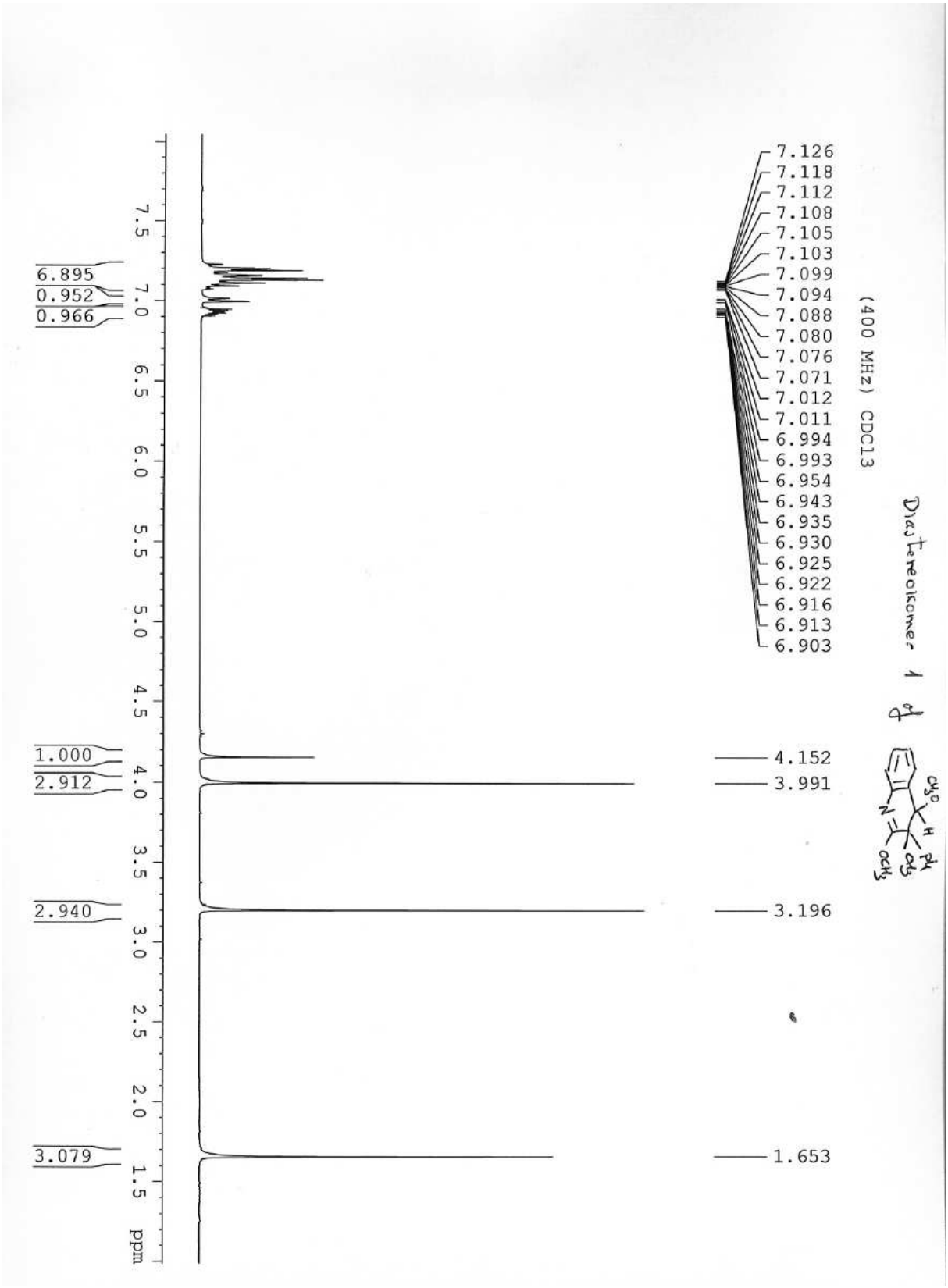
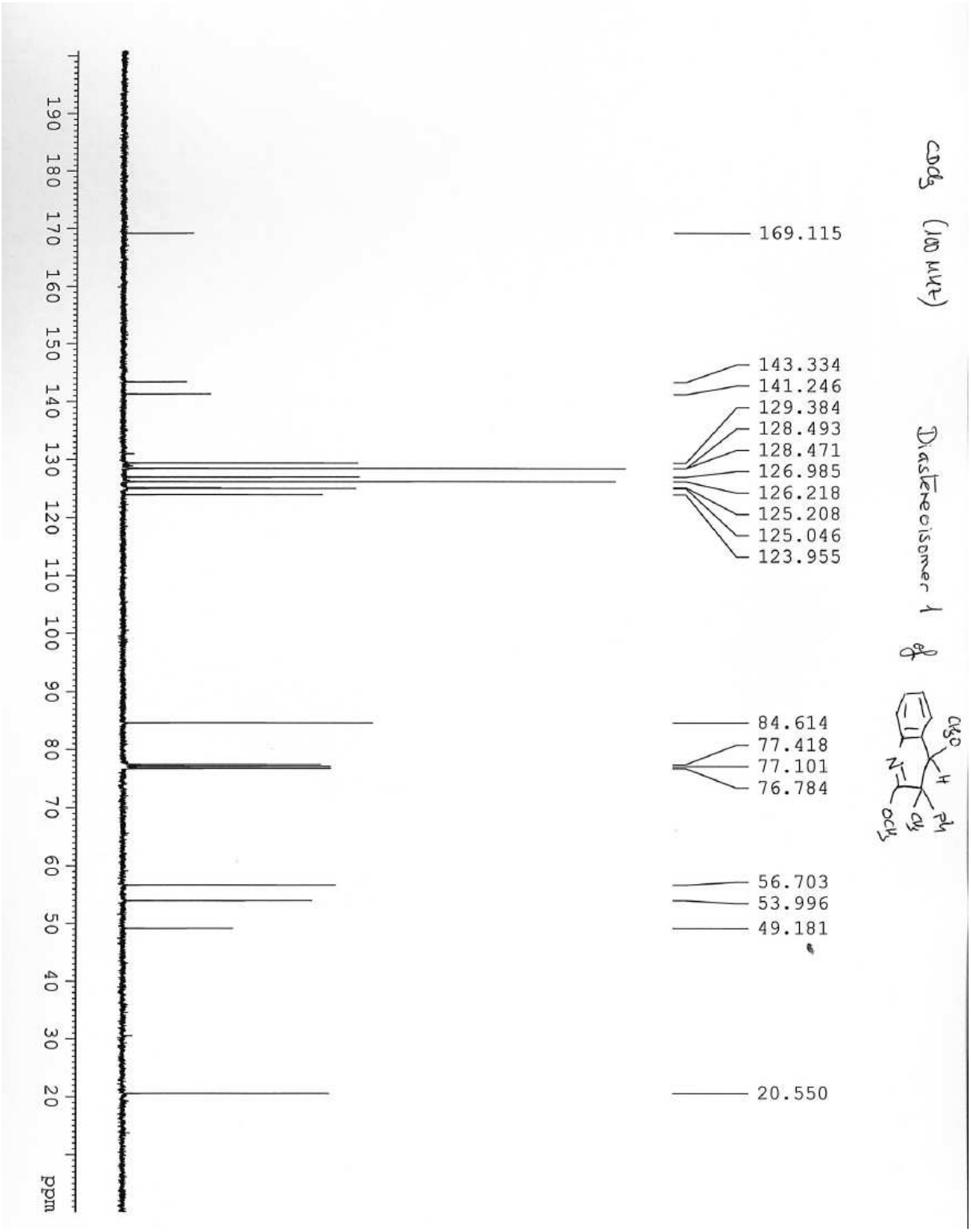


^{13}C NMR of **diastereoisomer 1 of 13e**



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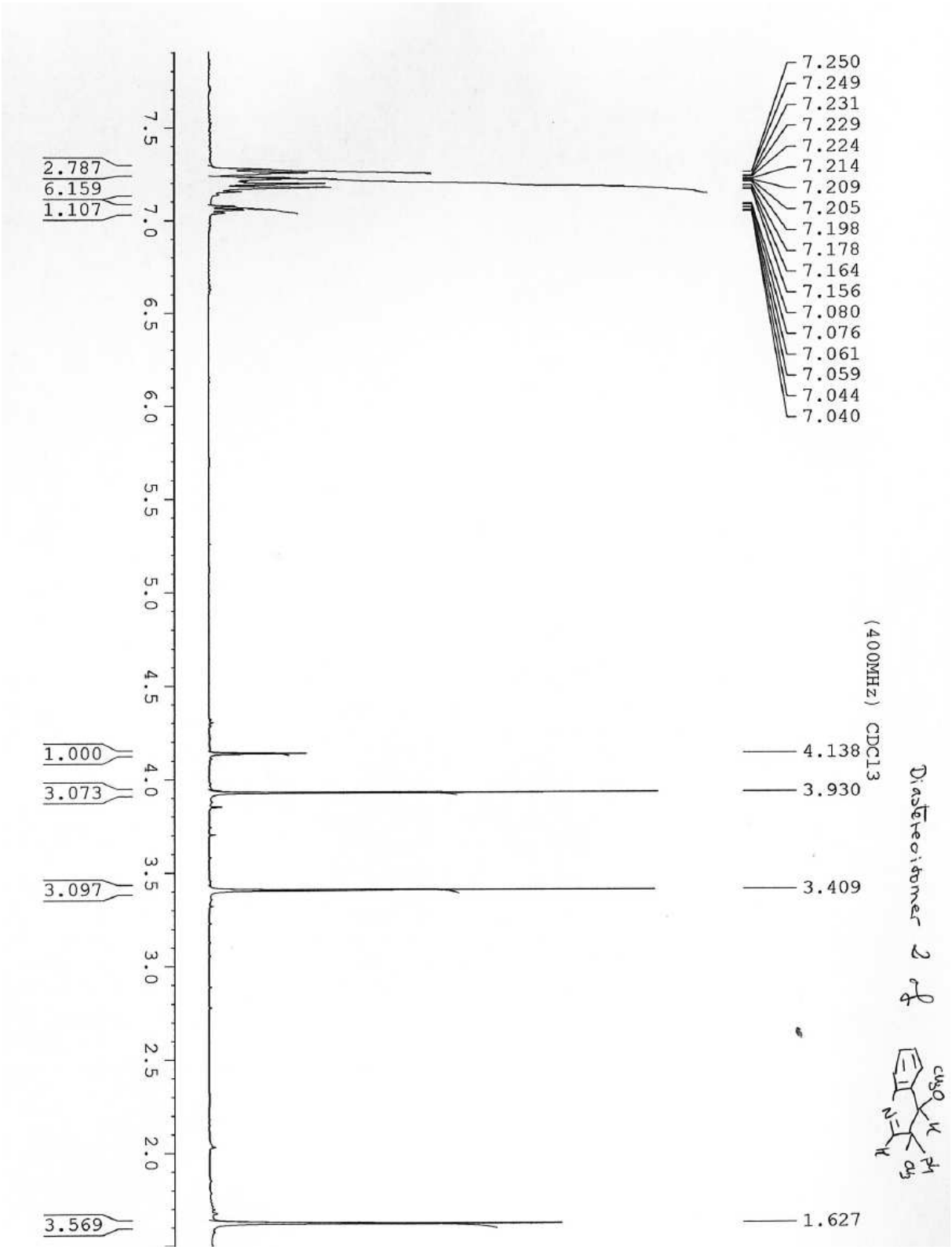

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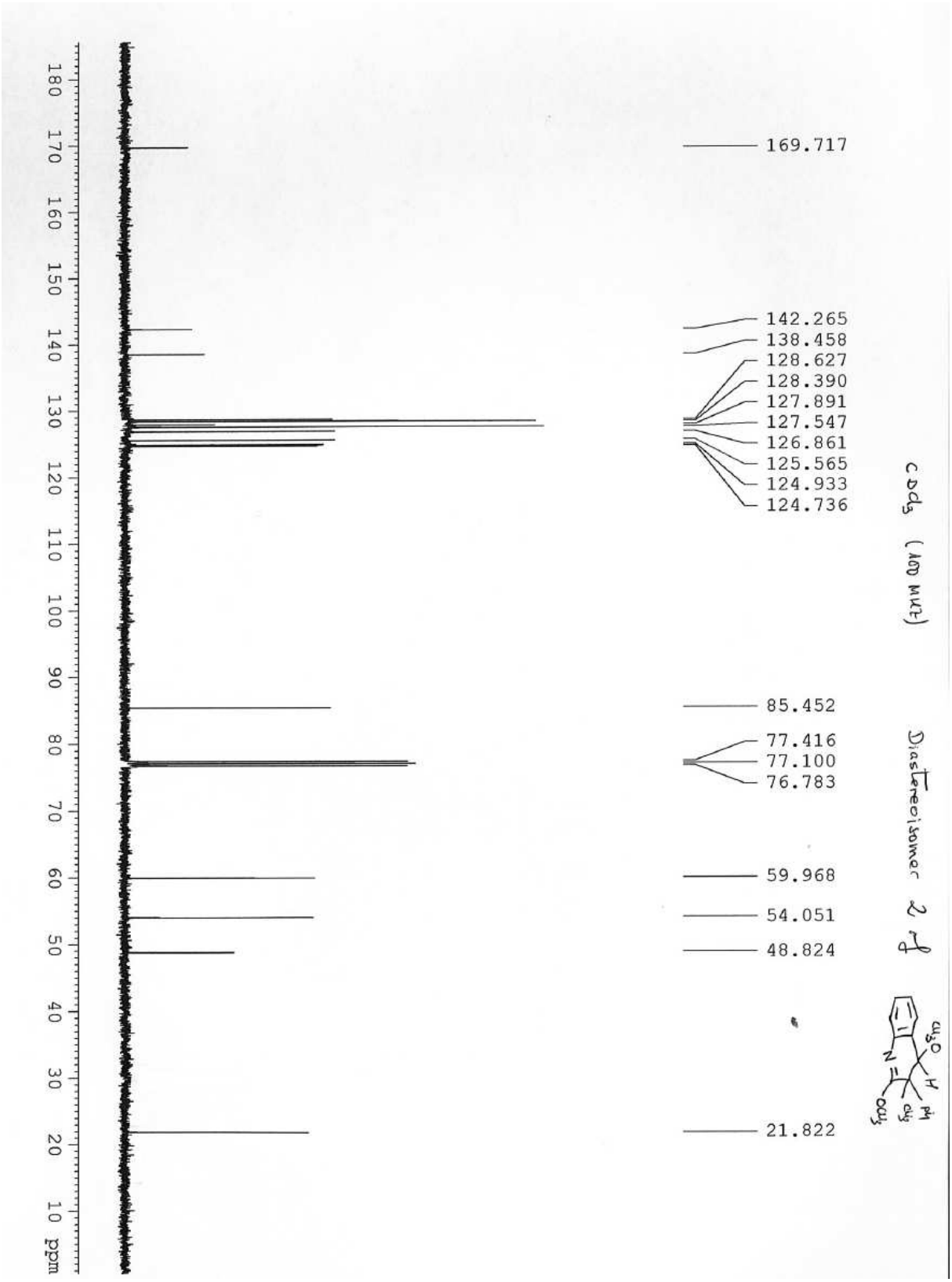

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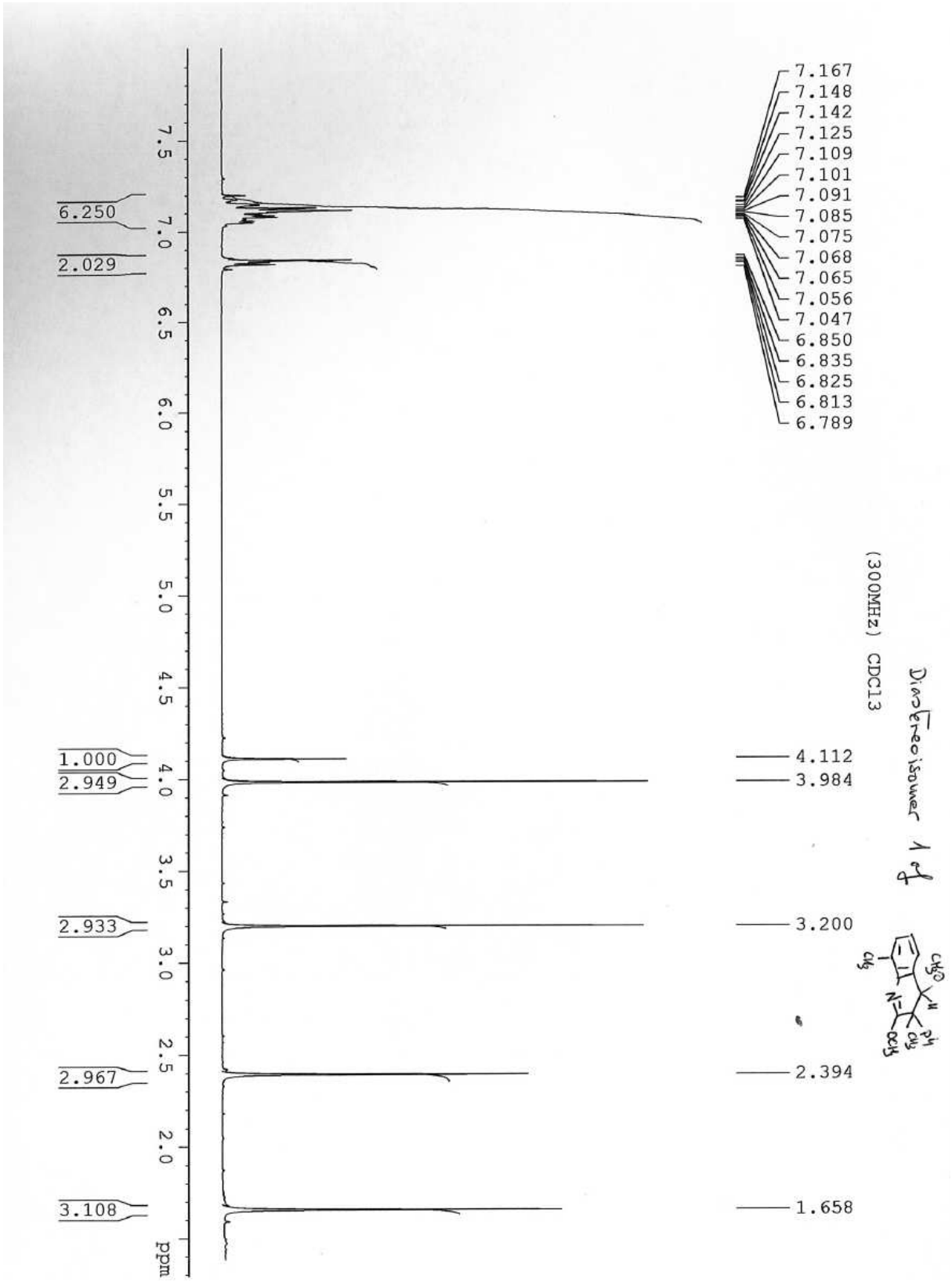

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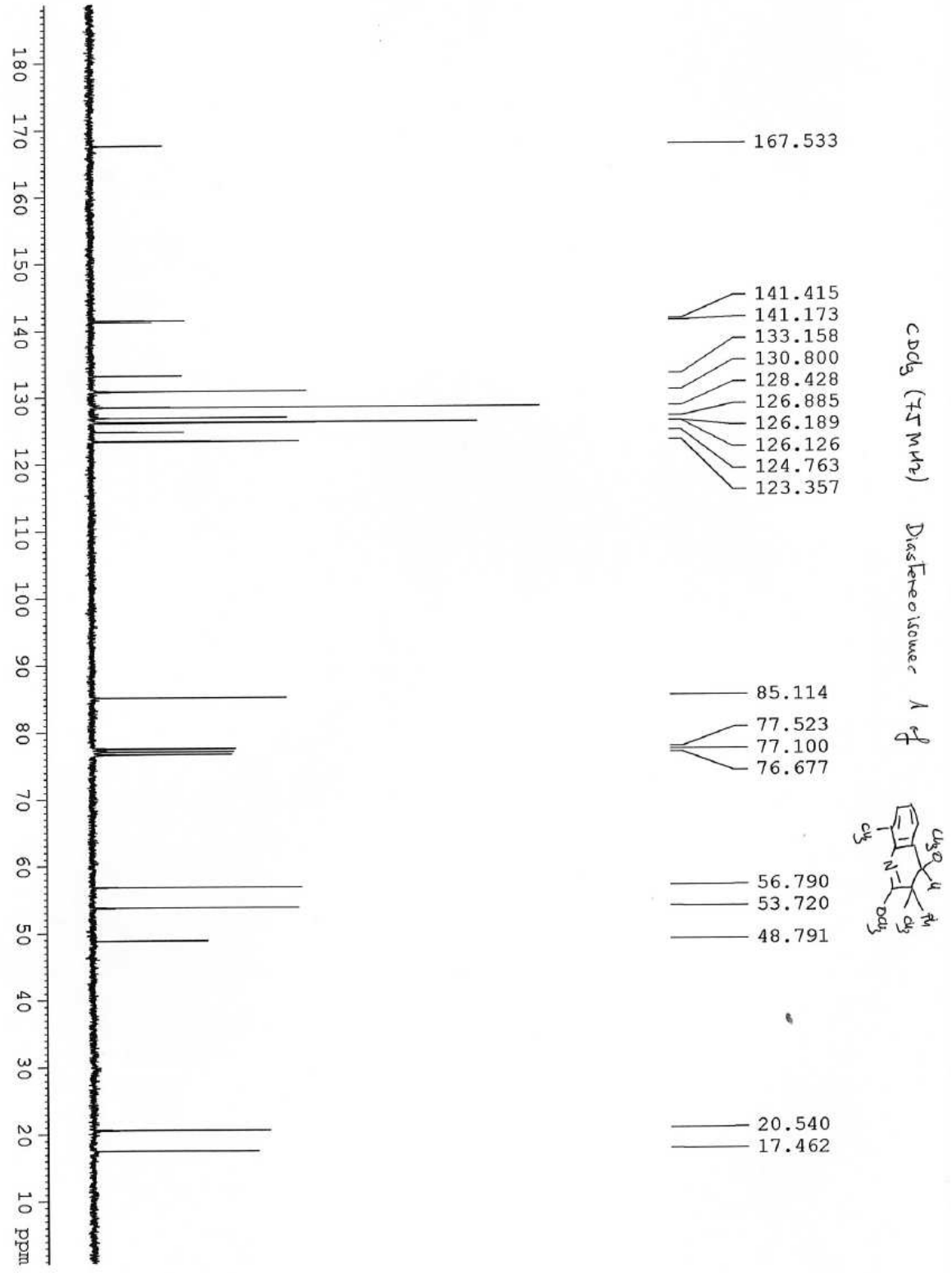

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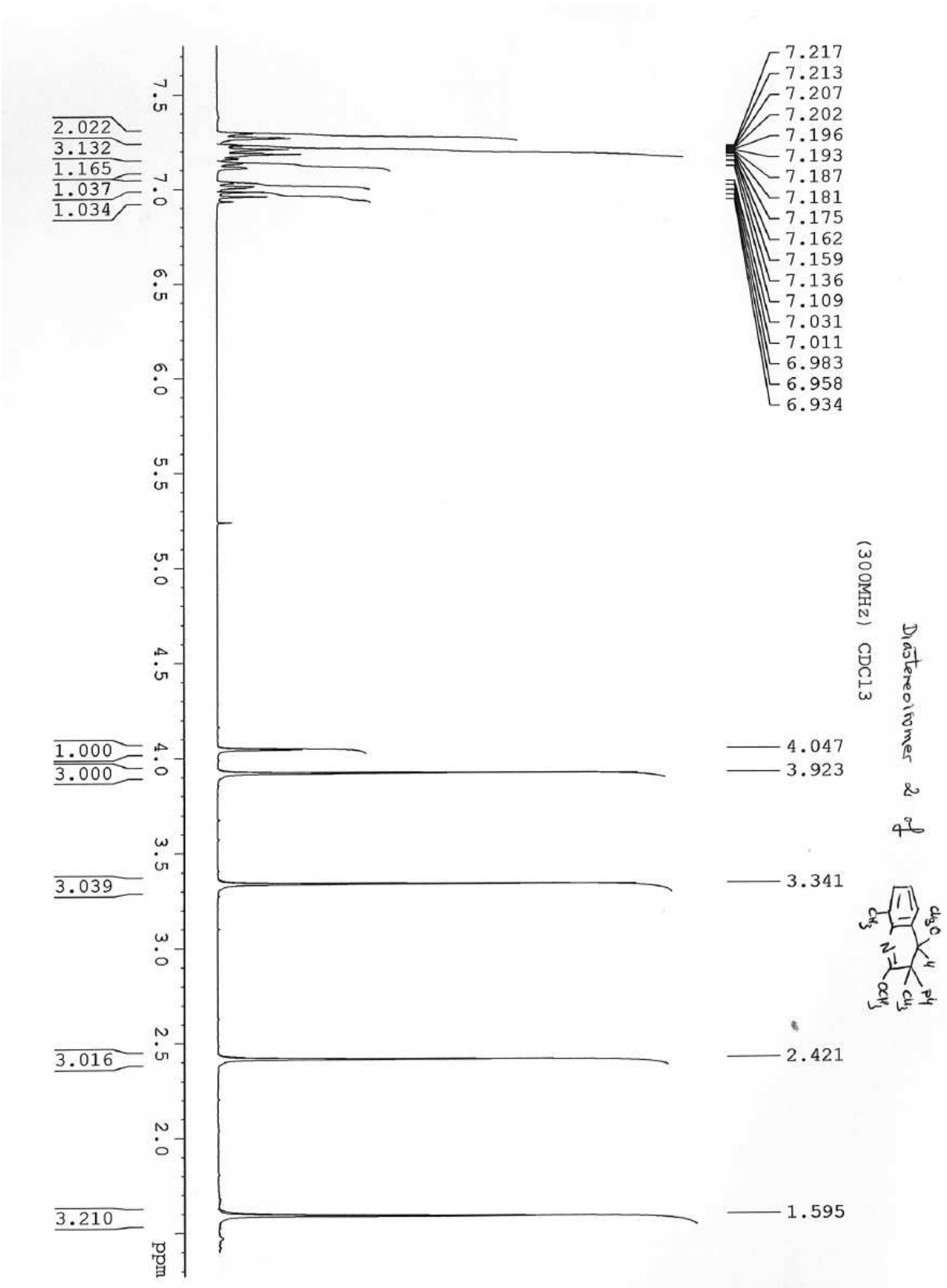

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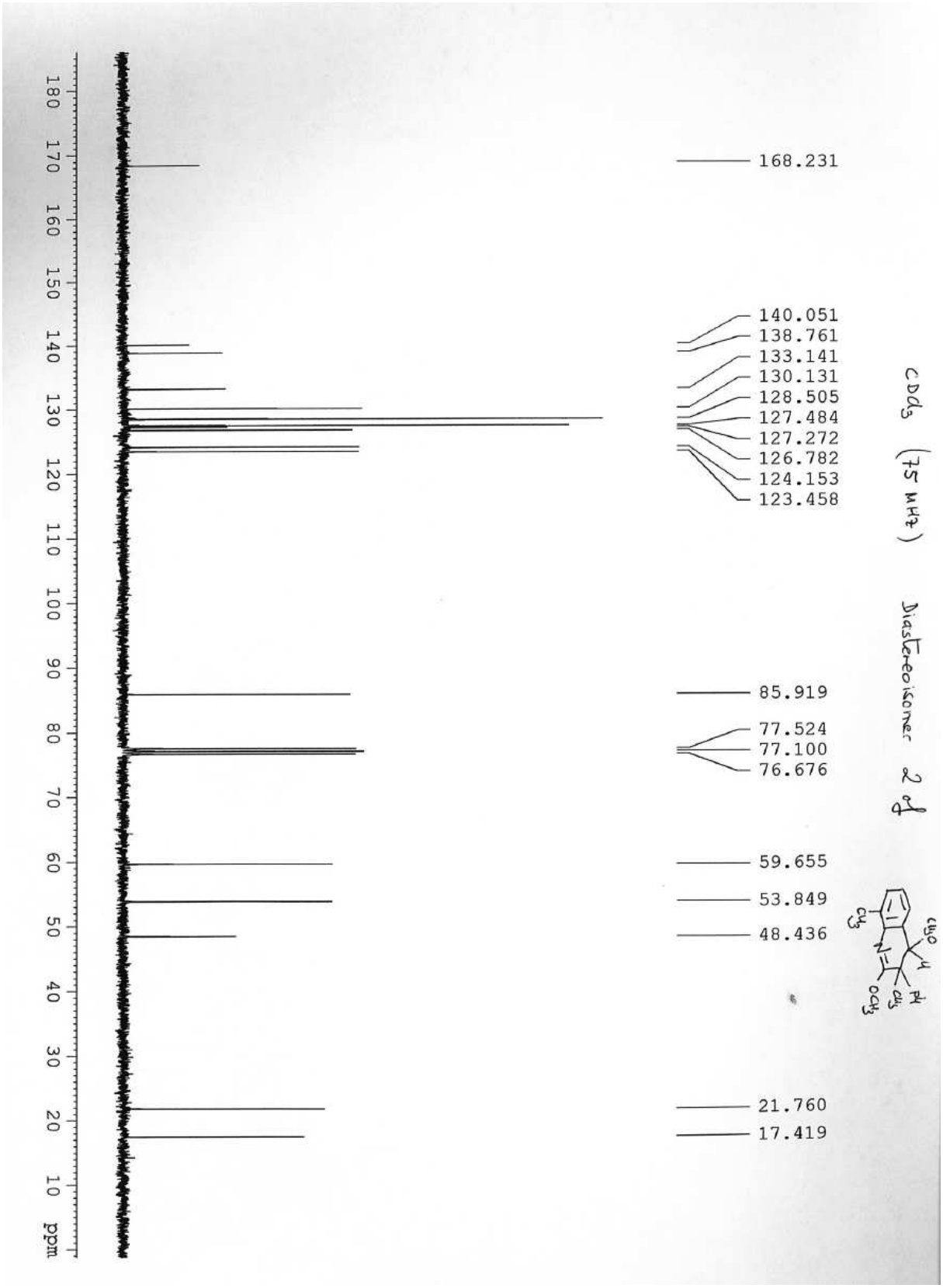

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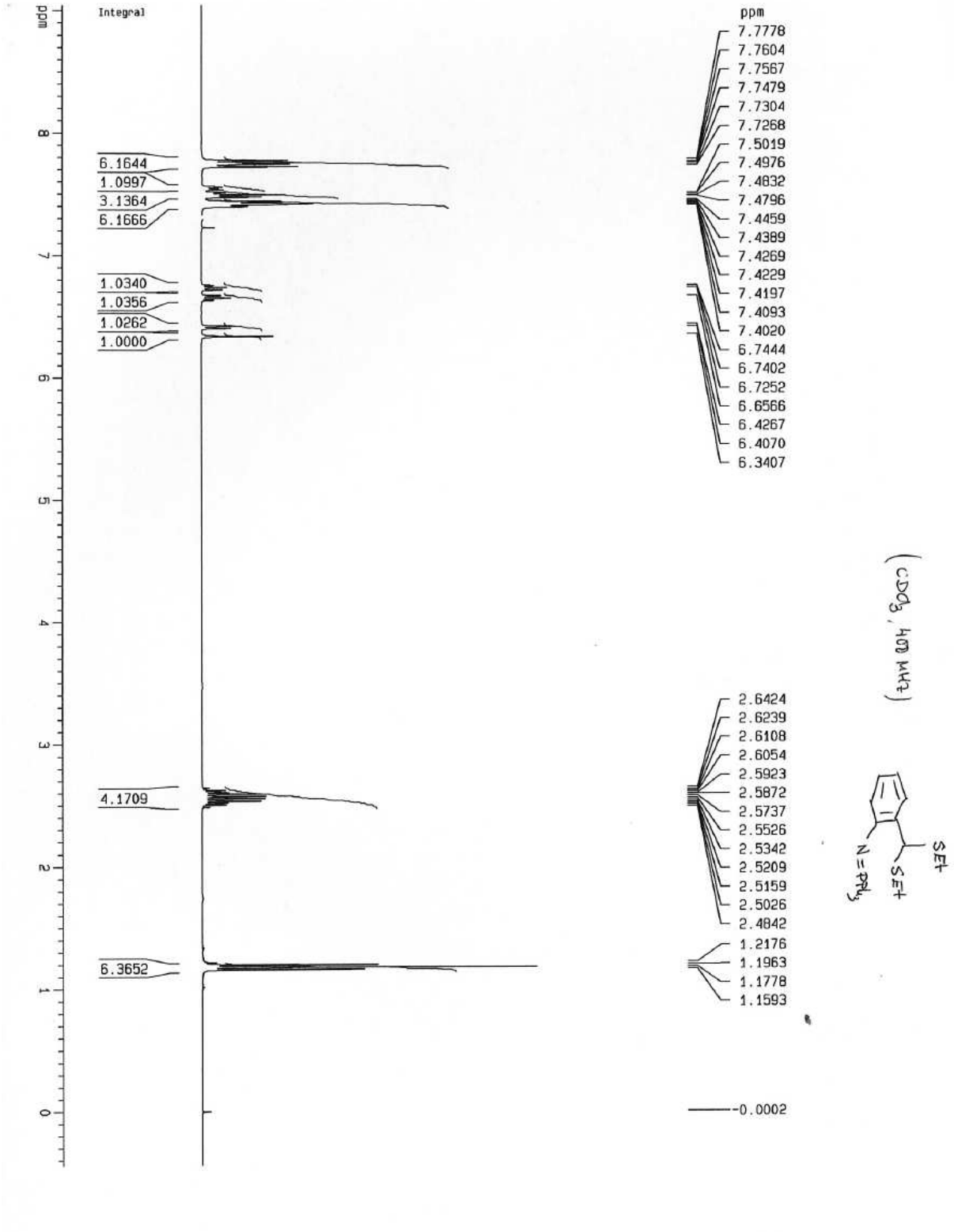
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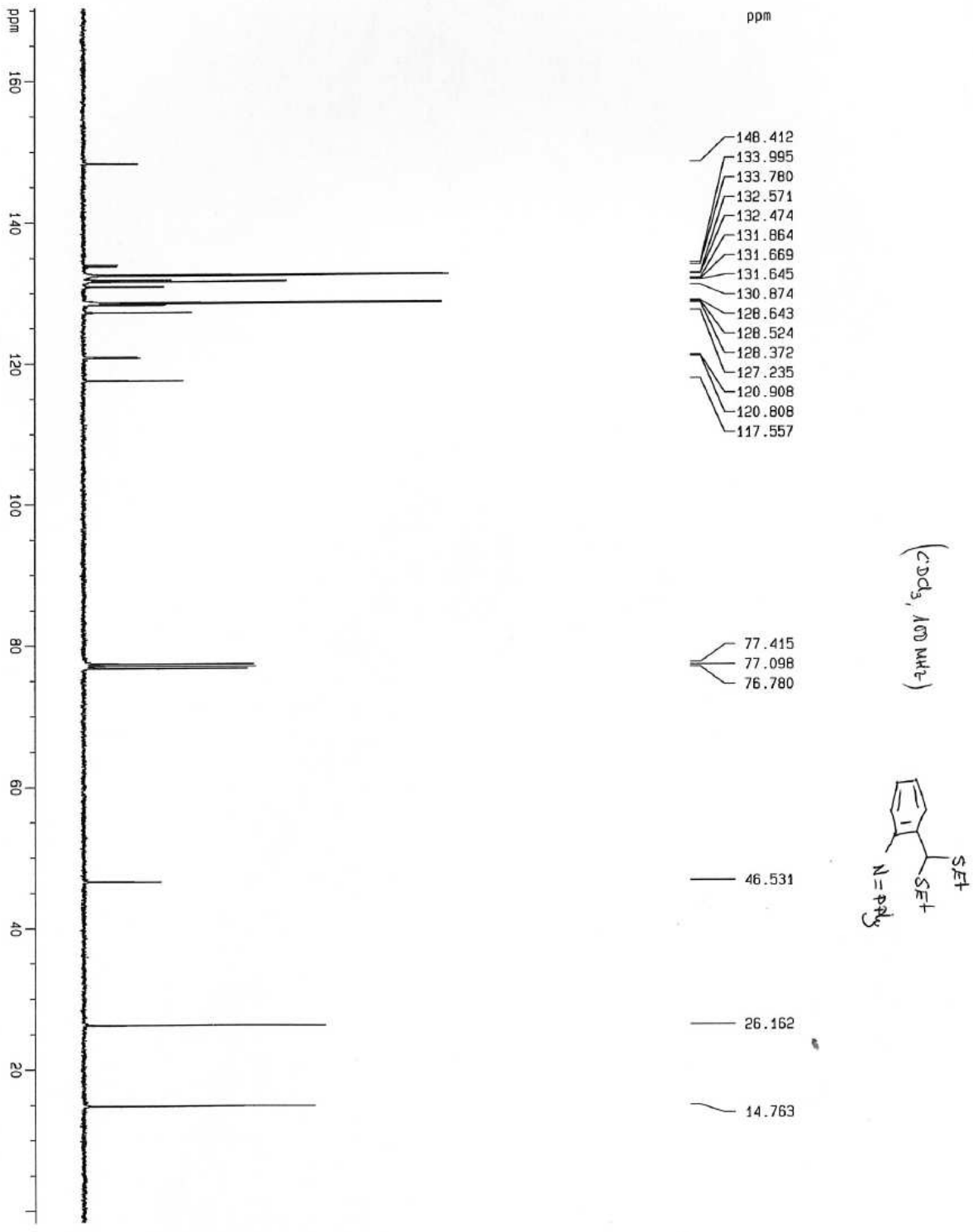
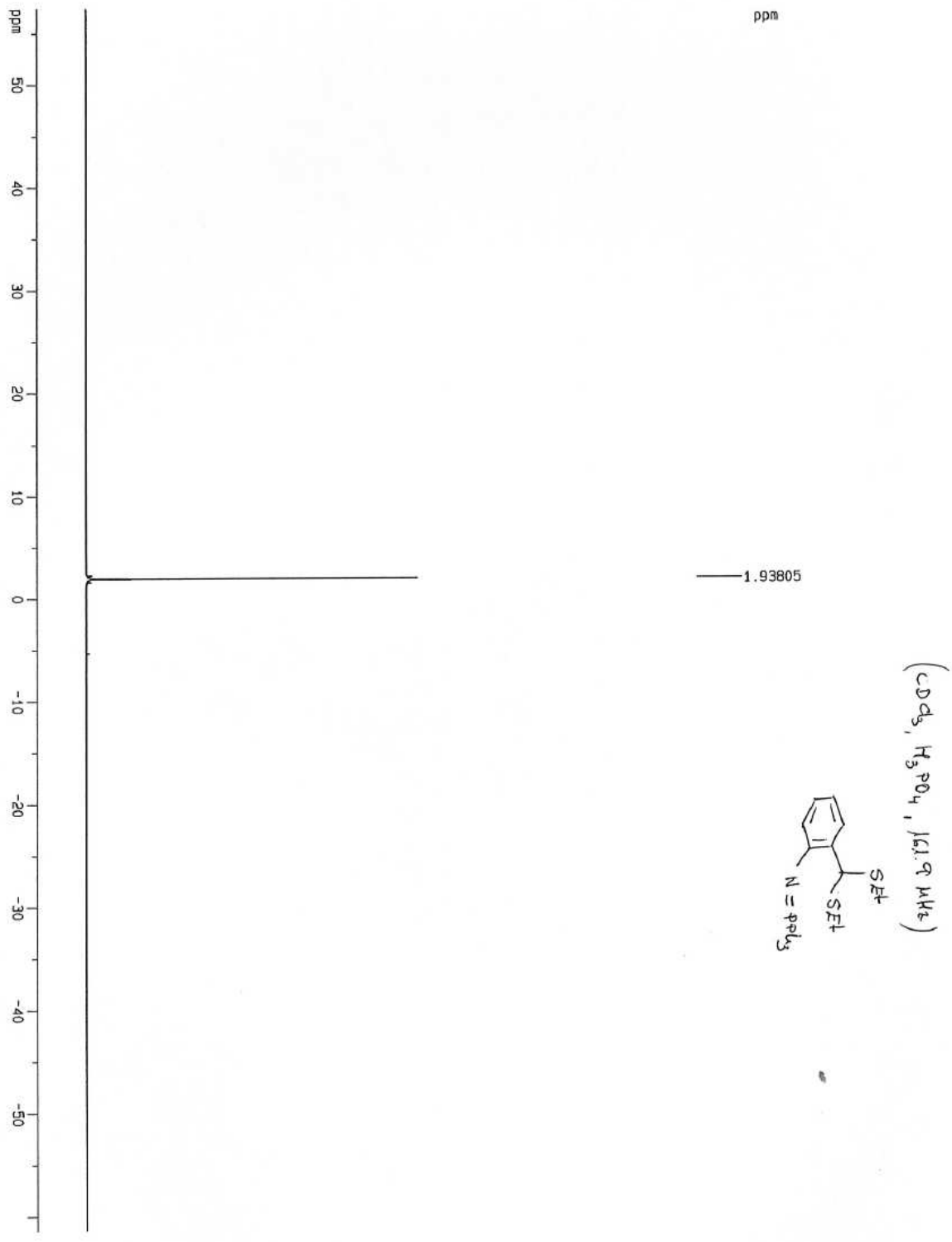
1.1593
-0.0002
(CDCl3, 400 MHz)
SEt
SEt
N=PPh3

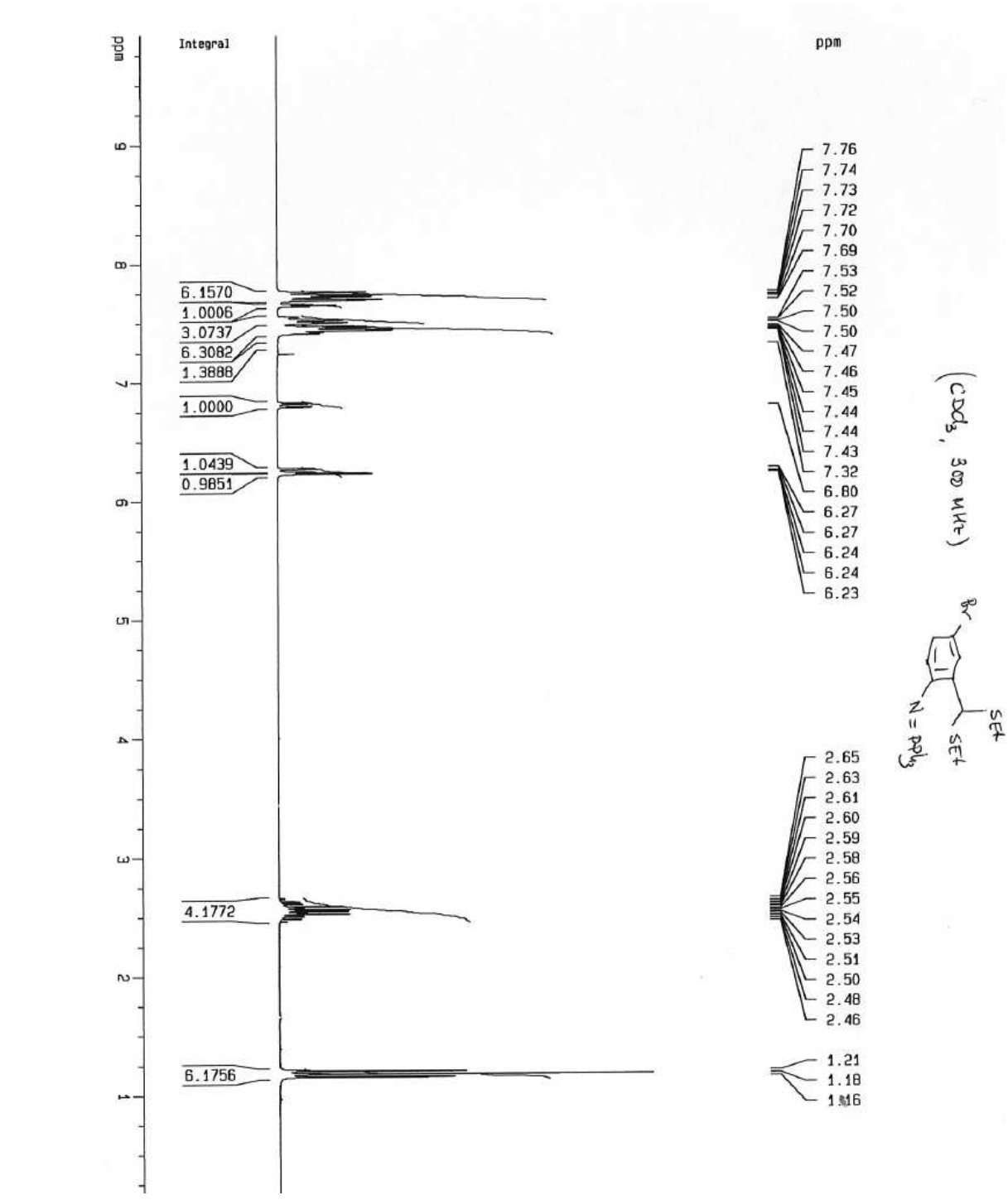
^{13}C NMR of **17a**



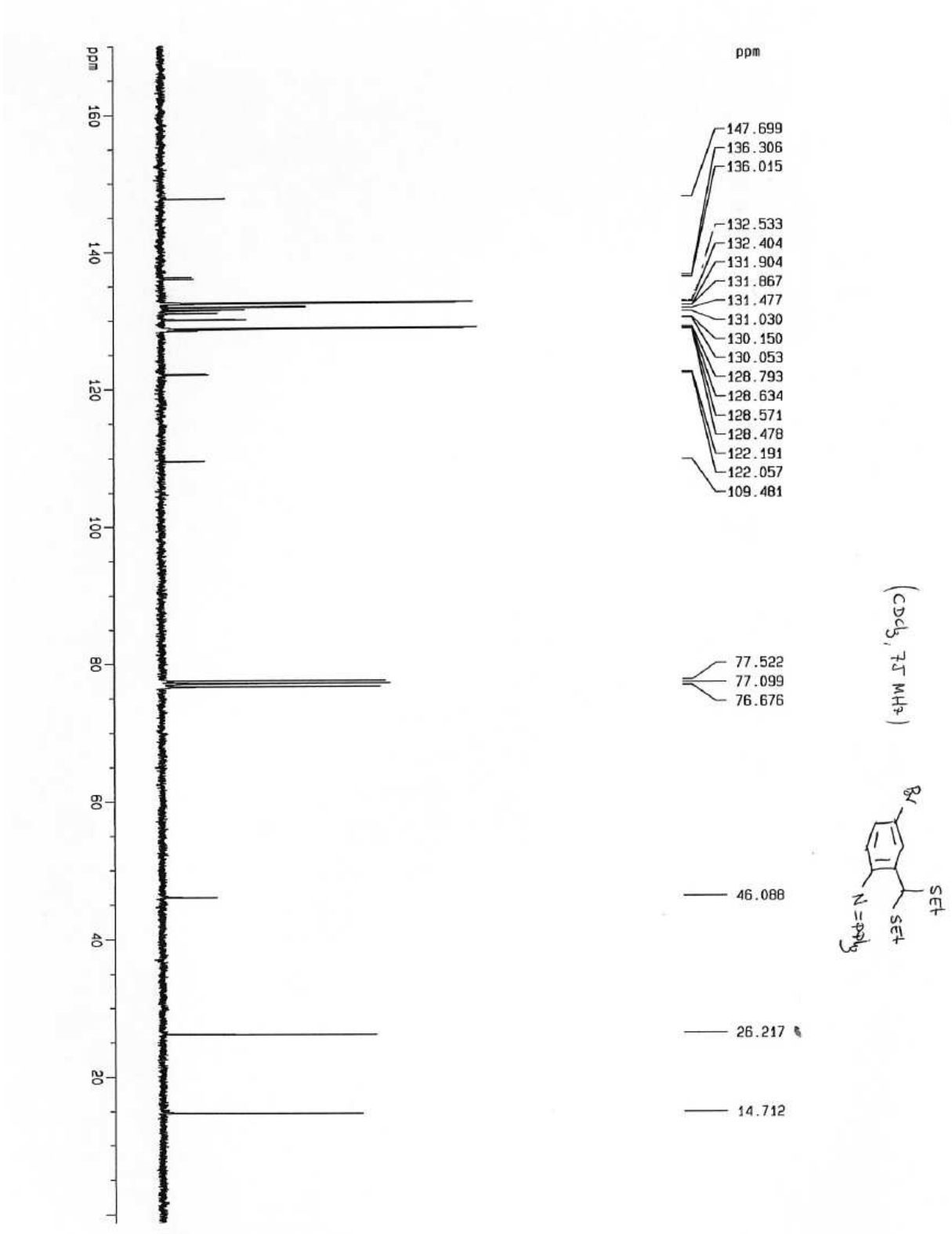
^{31}P NMR of **17a**



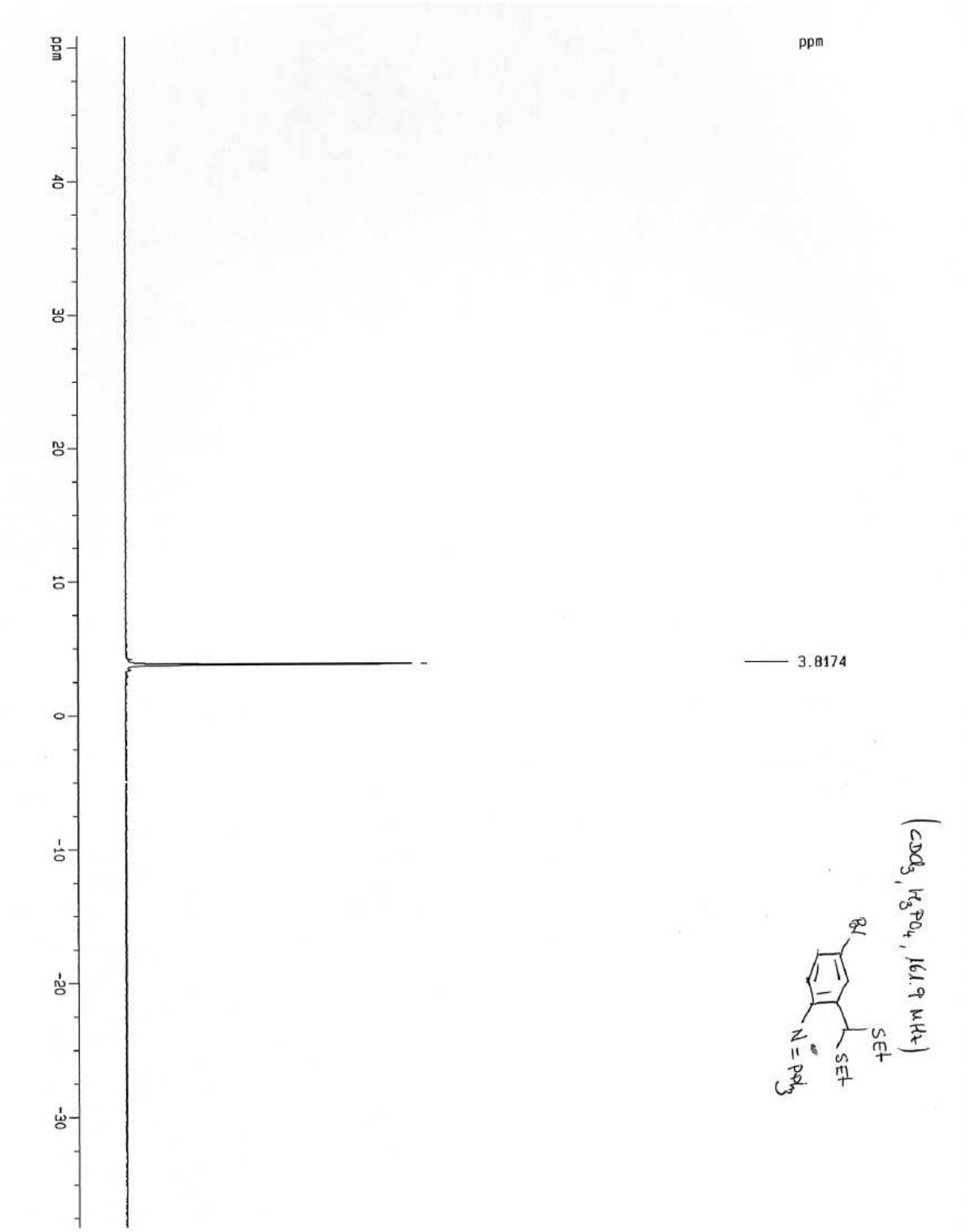
^{1}H NMR of **17b**


Integral
ppm
6.1570
1.0006
3.0737
6.3082
1.3888
1.0000
1.0439
0.9851
4.1772
6.1756
7.76
7.74
7.73
7.72
7.70
7.69
7.53
7.52
7.50
7.50
7.47
7.46
7.45
7.44
7.44
7.43
7.32
6.80
6.27
6.27
6.24
6.24
6.23
2.65
2.63
2.61
2.60
2.59
2.58
2.56
2.55
2.54
2.53
2.51
2.50
2.48
2.46
1.21
1.18
(CDCl3, 300 MHz)
SEt
SEt
N = PPh3

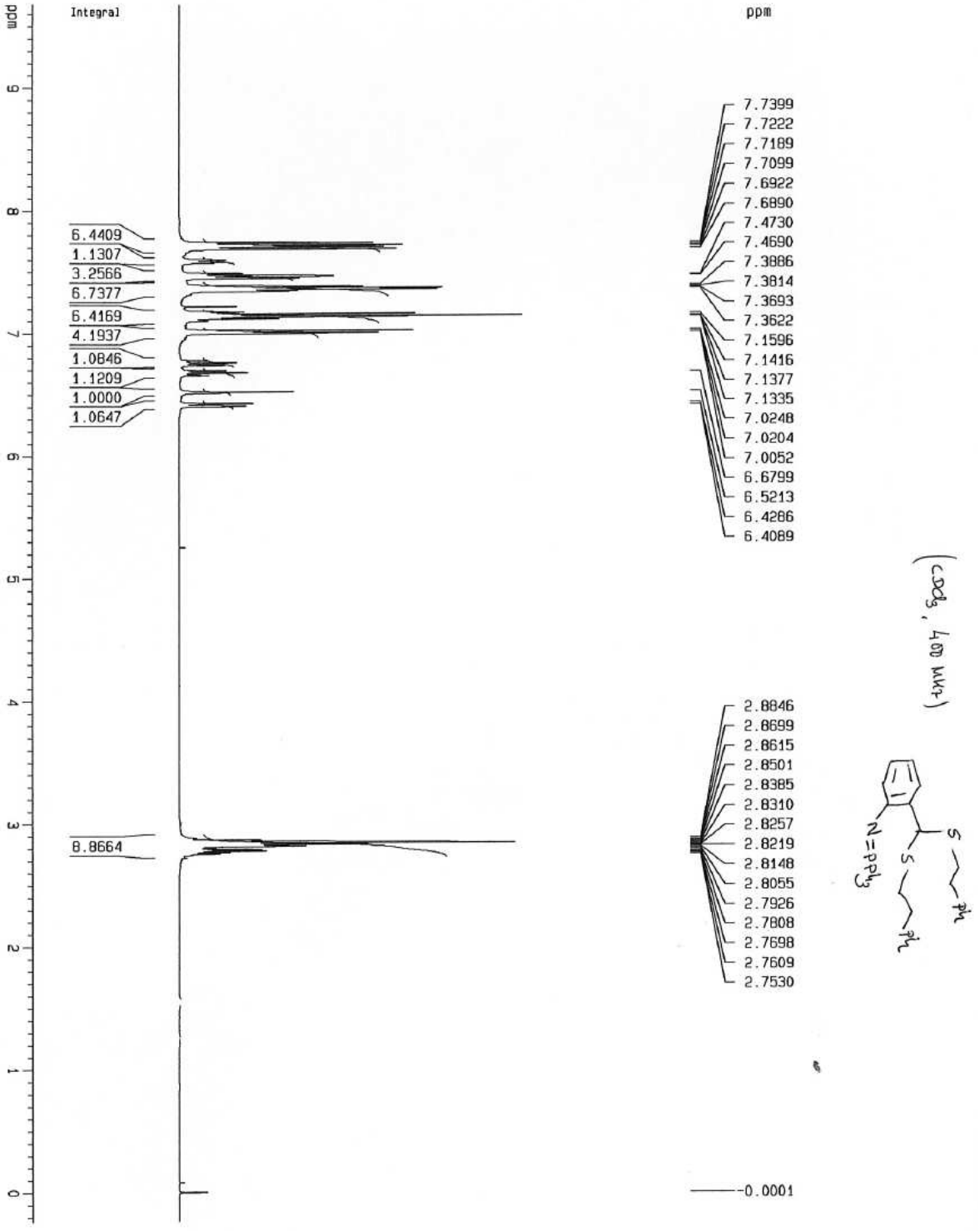
^{13}C NMR of **17b**



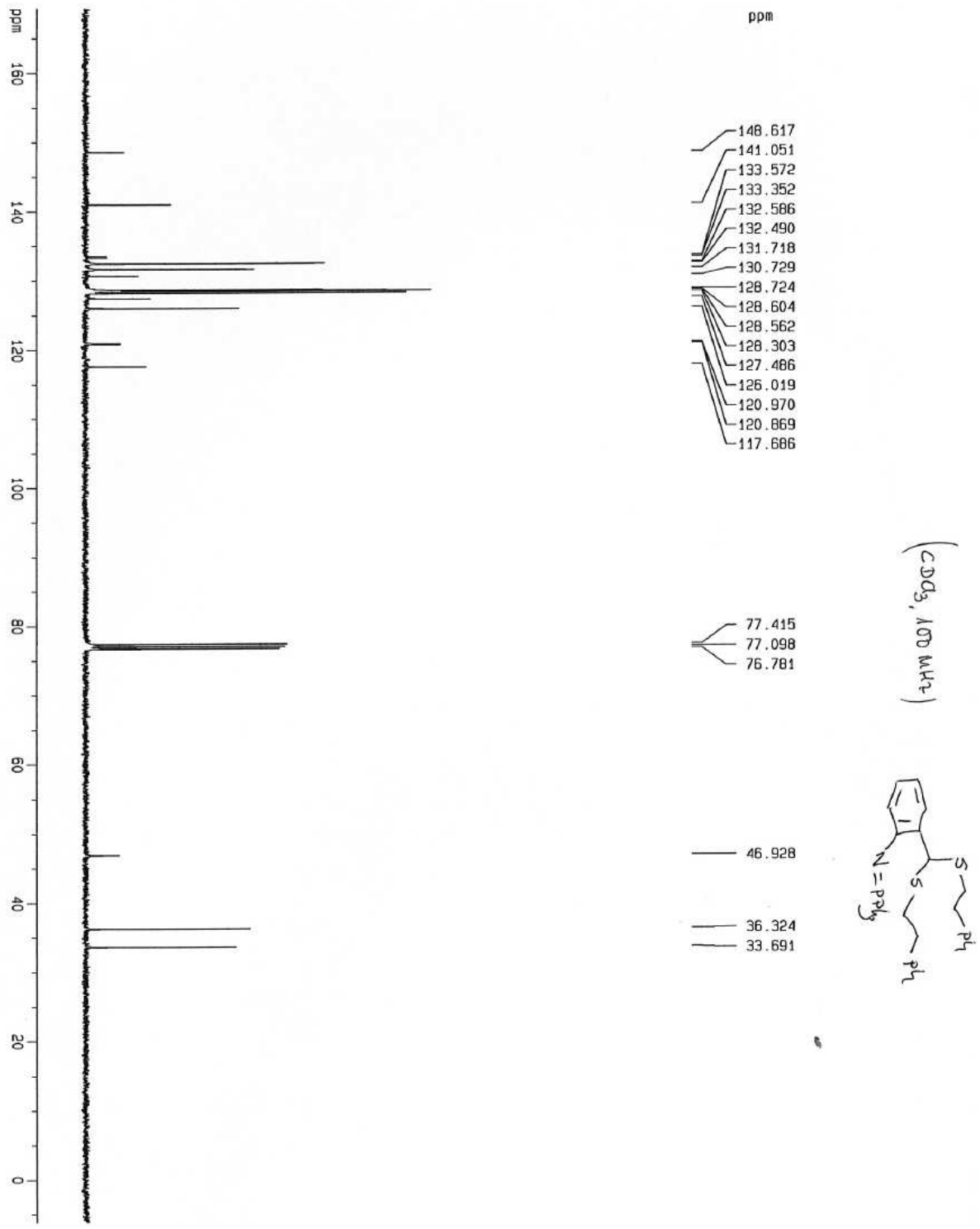
^{31}P NMR of **17b**



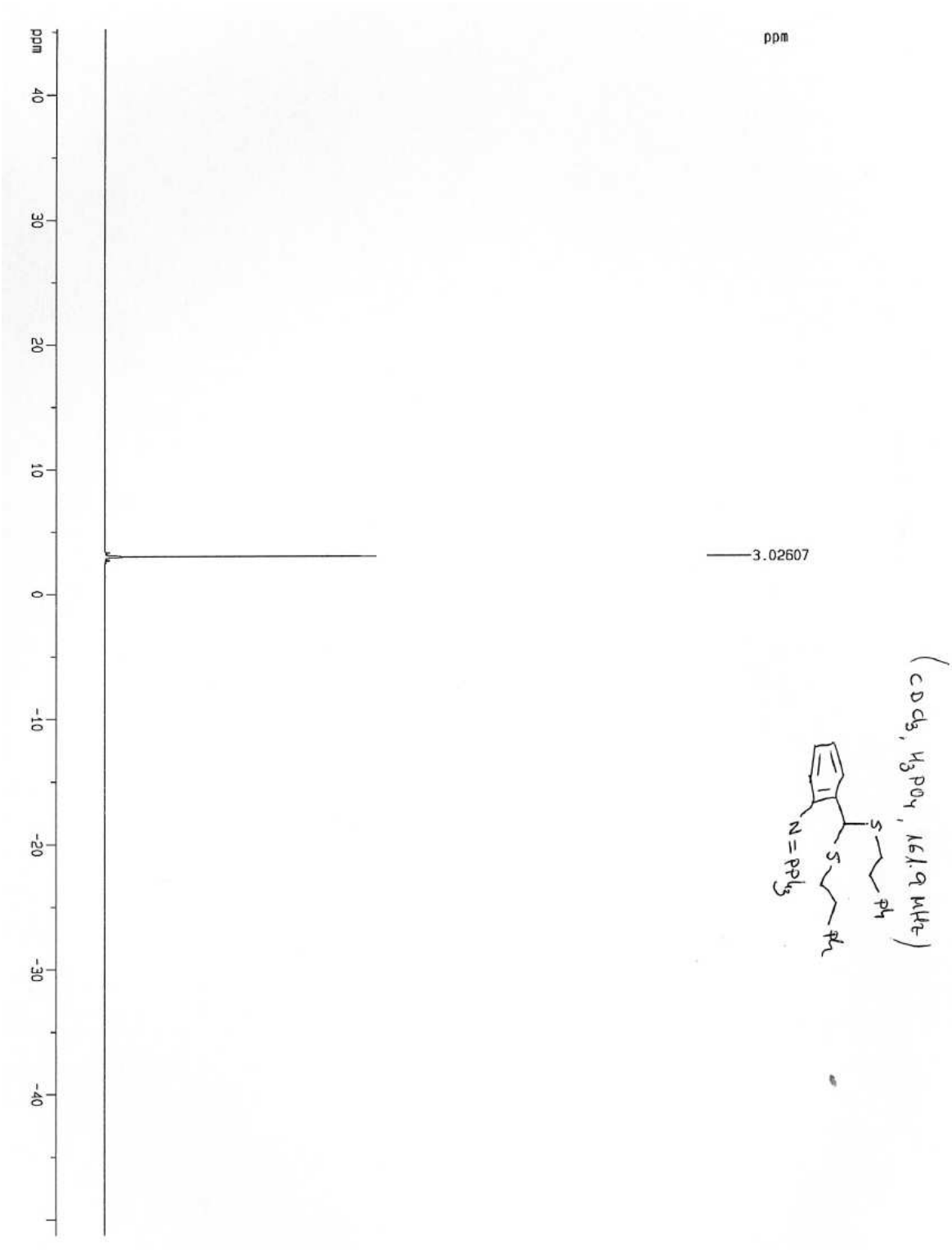
^{1}H NMR of **17c**



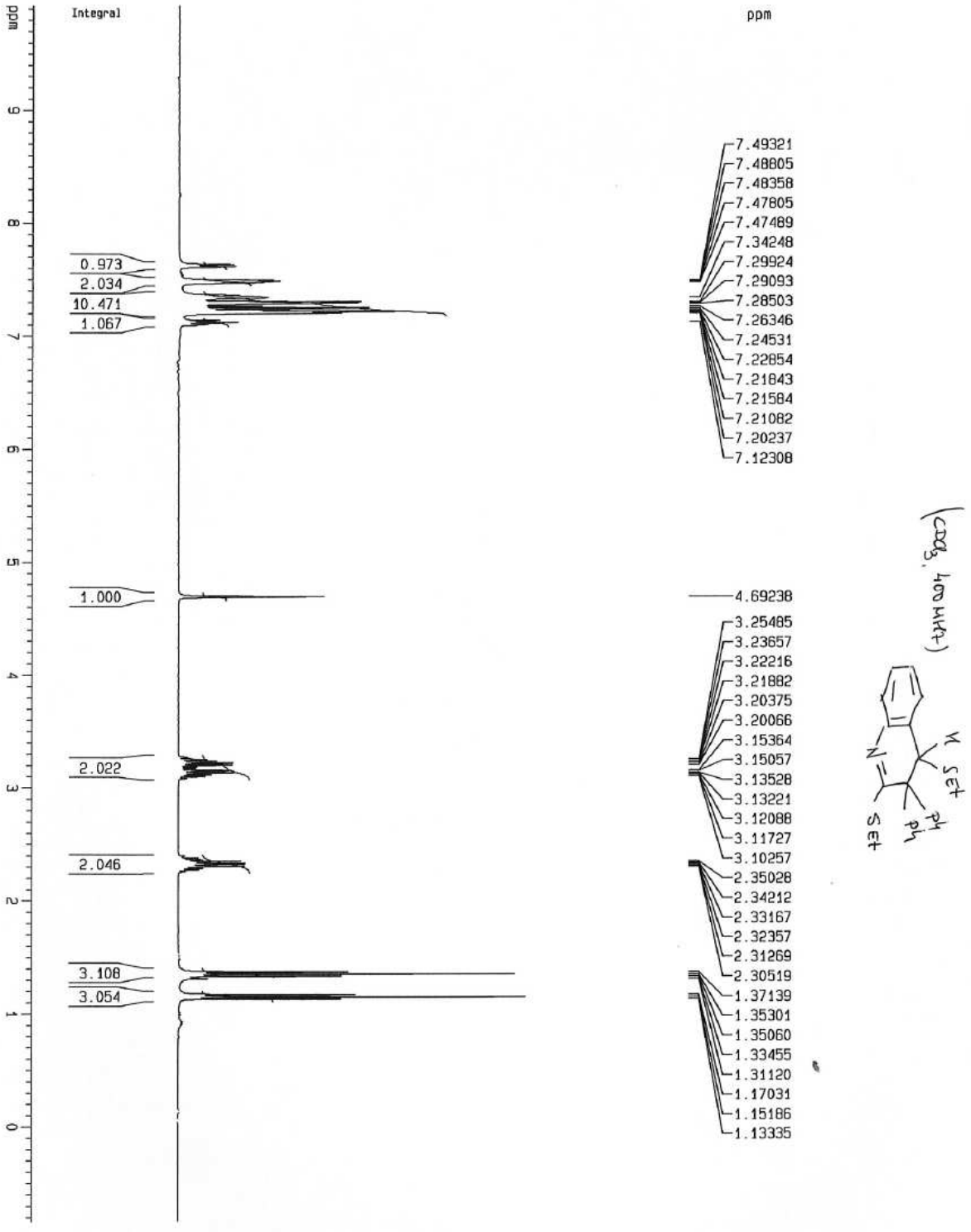
^{13}C NMR of **17c**



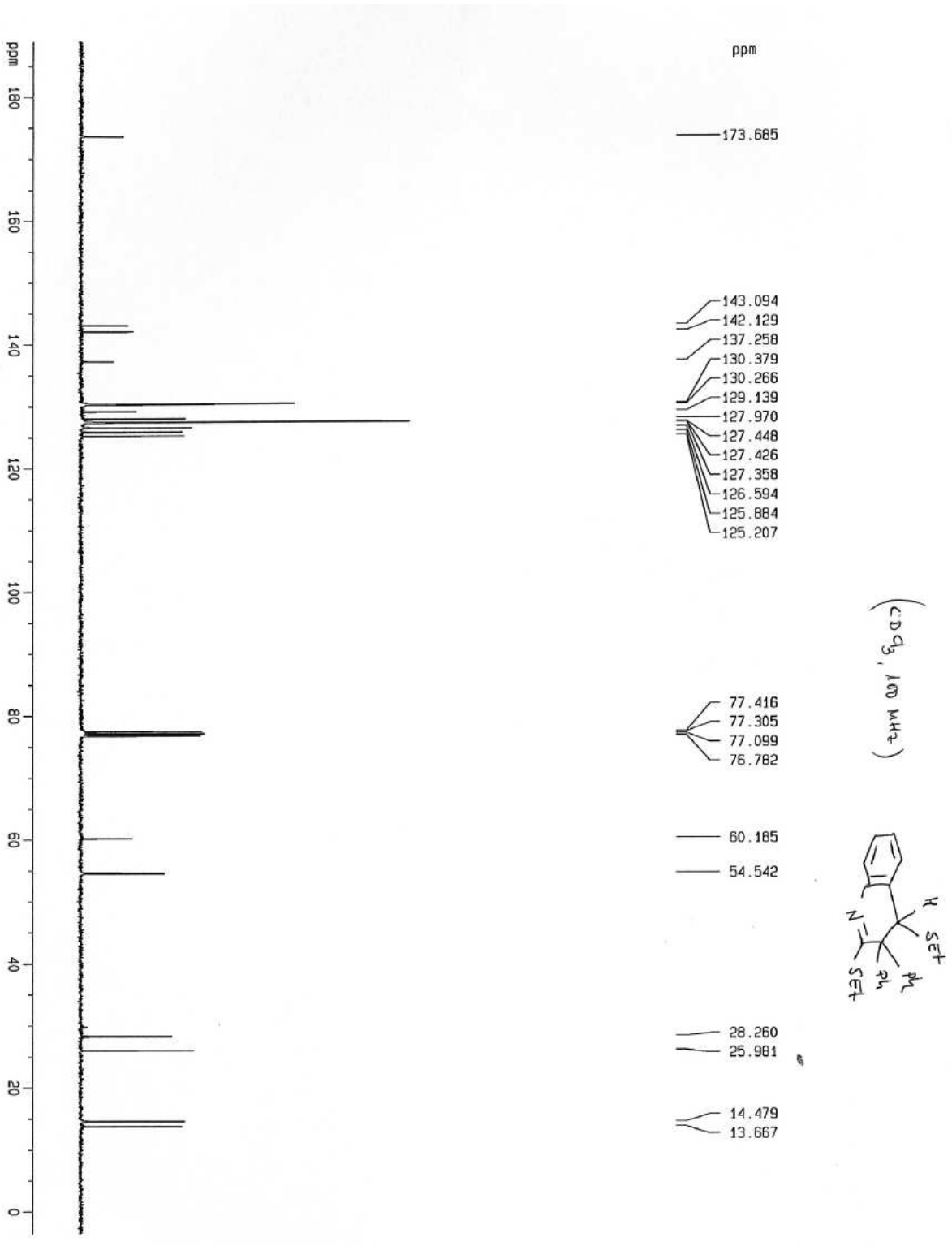
^{31}P NMR of **17c**



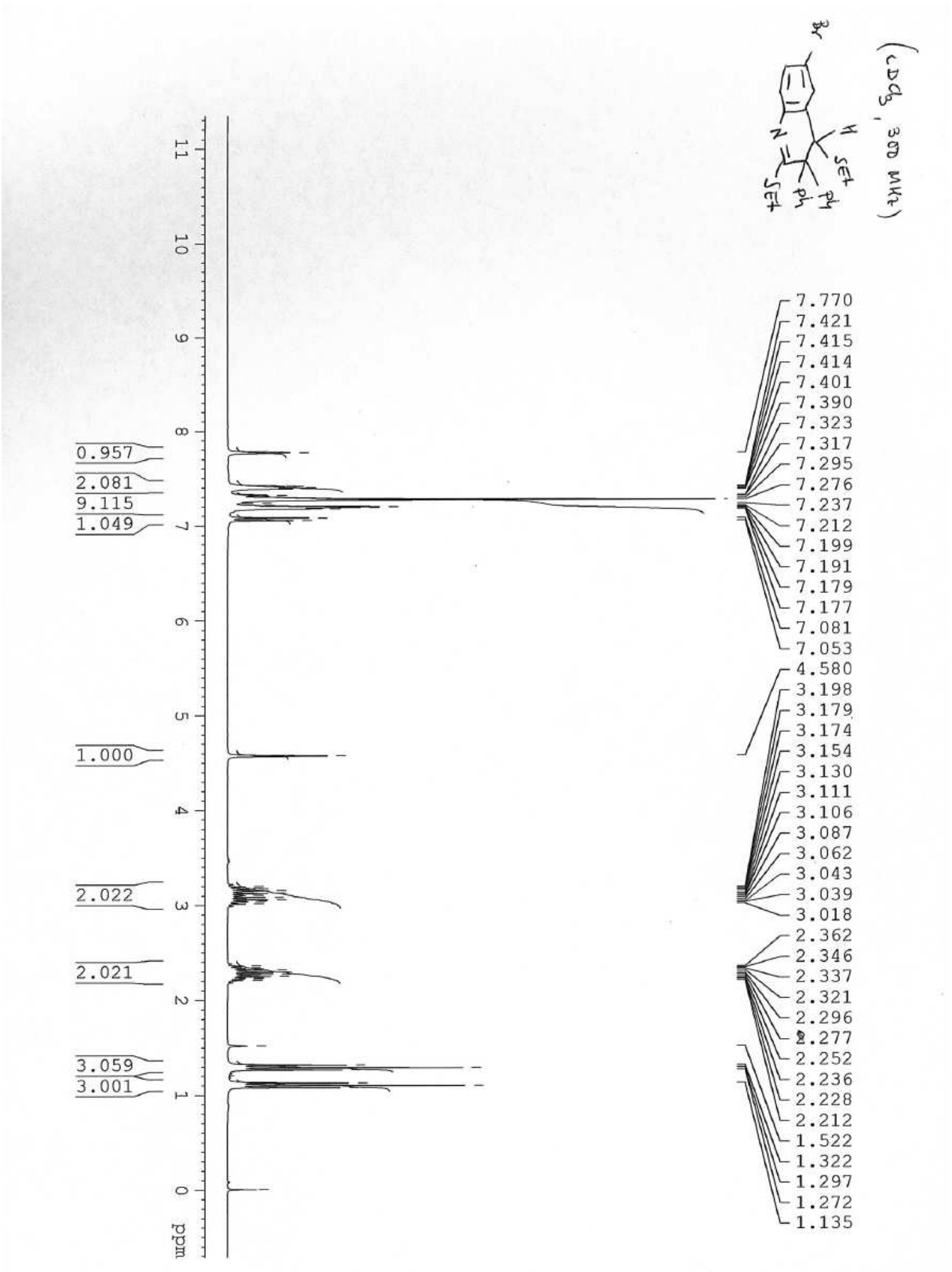
^{1}H NMR of **20a**



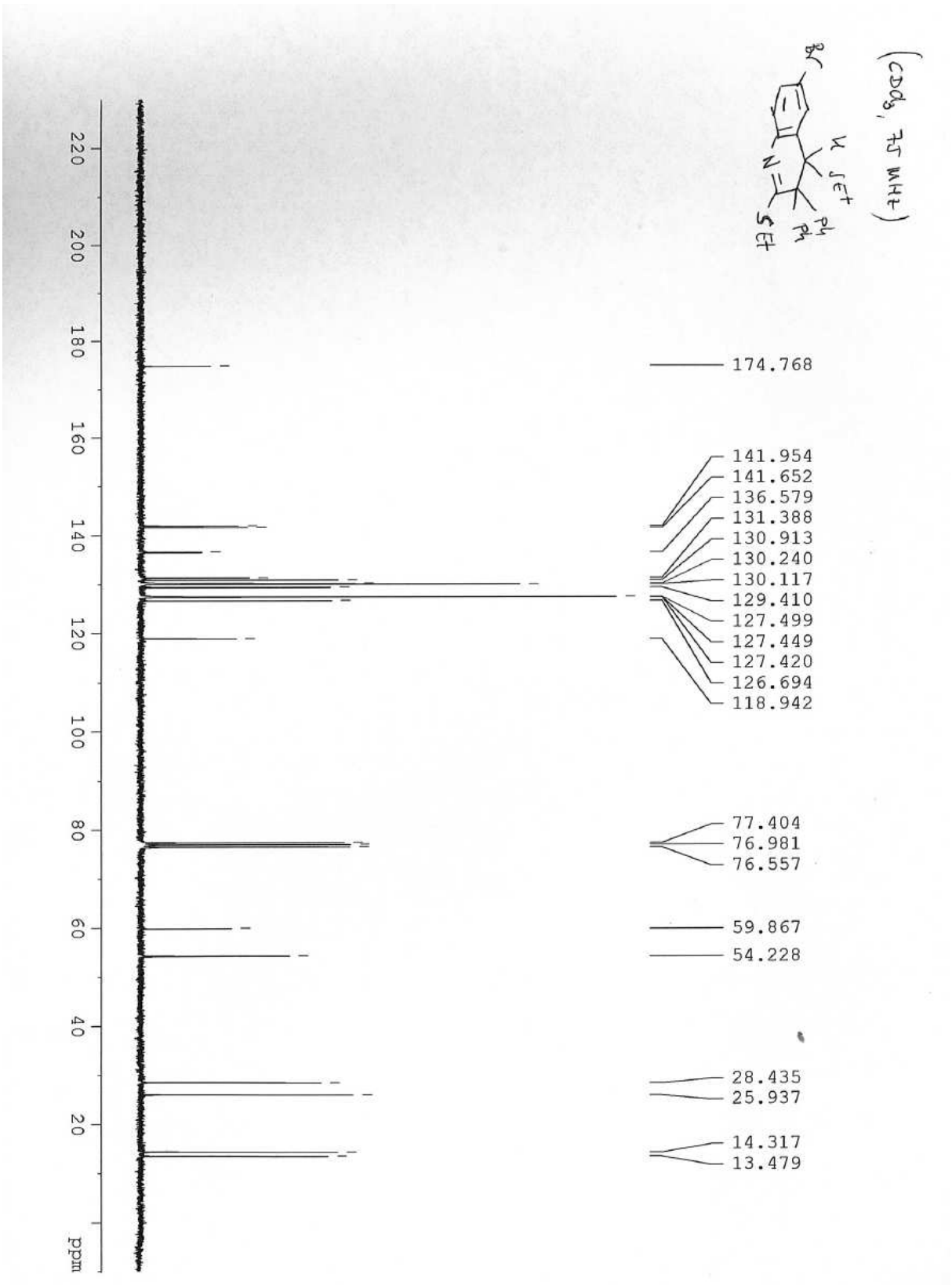
^{13}C NMR of **20a**



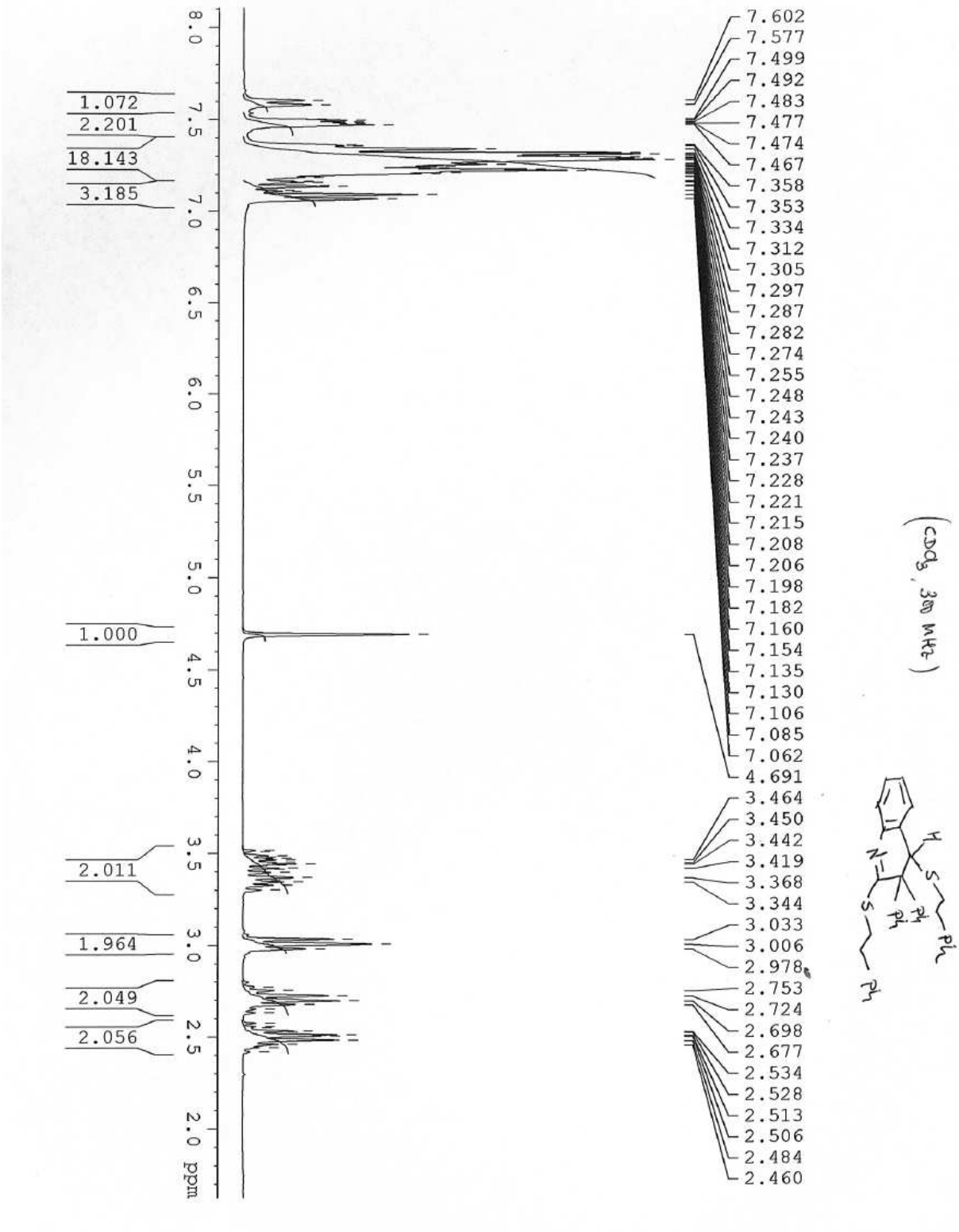
^{1}H NMR of **20b**


(CDCl3, 300 MHz)
7.770
7.421
7.415
7.414
7.401
7.390
7.323
7.317
7.295
7.276
7.237
7.212
7.199
7.191
7.179
7.177
7.081
7.053
4.580
3.198
3.179
3.174
3.154
3.130
3.111
3.106
3.087
3.062
3.043
3.039
3.018
2.362
2.346
2.337
2.321
2.296
2.277
2.252
2.236
2.228
2.212
1.522
1.322
1.297
1.272
1.135
0.957
2.081
9.115
1.049
1.000
2.022
2.021
3.059
3.001
ppm

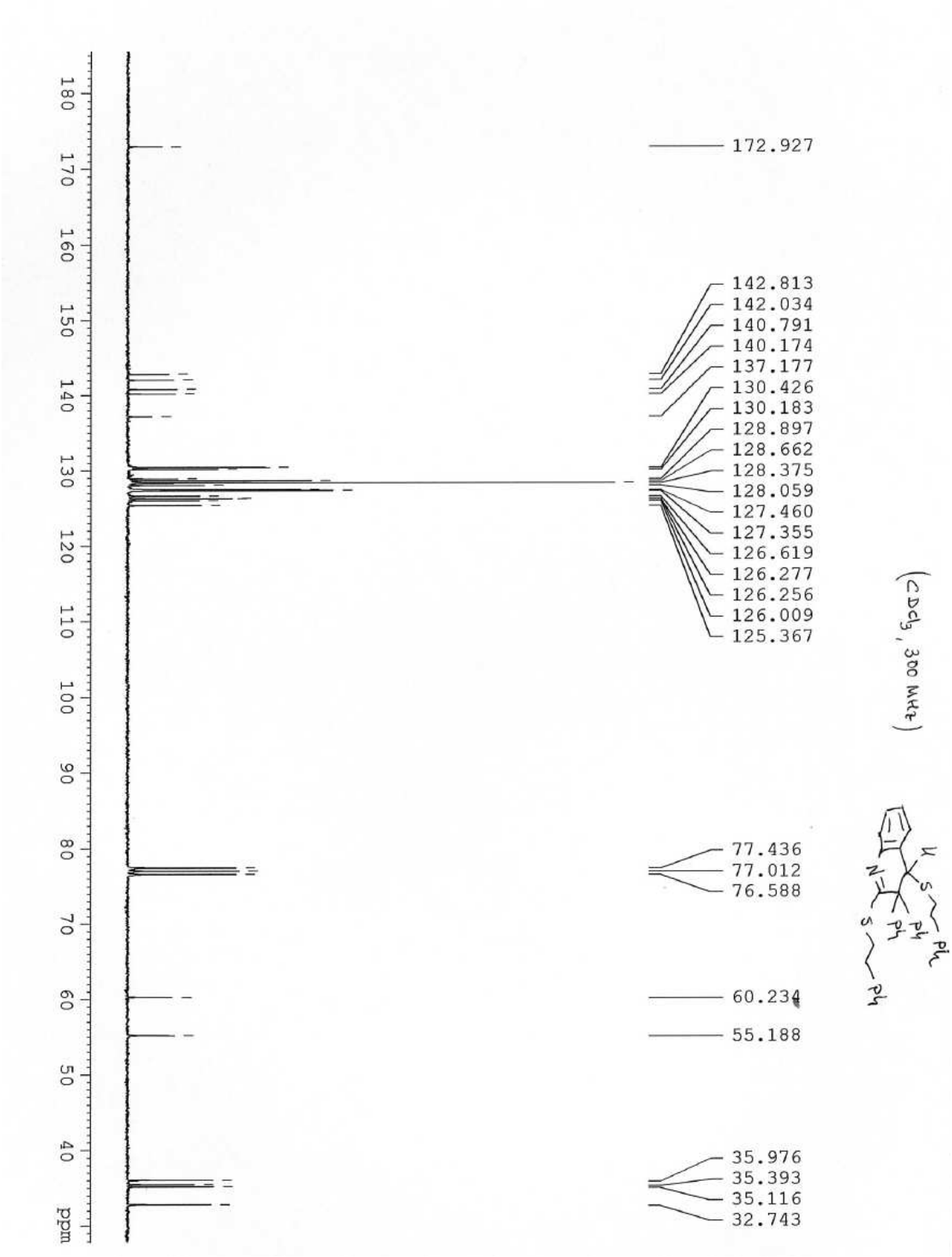
^{13}C NMR of **20b**



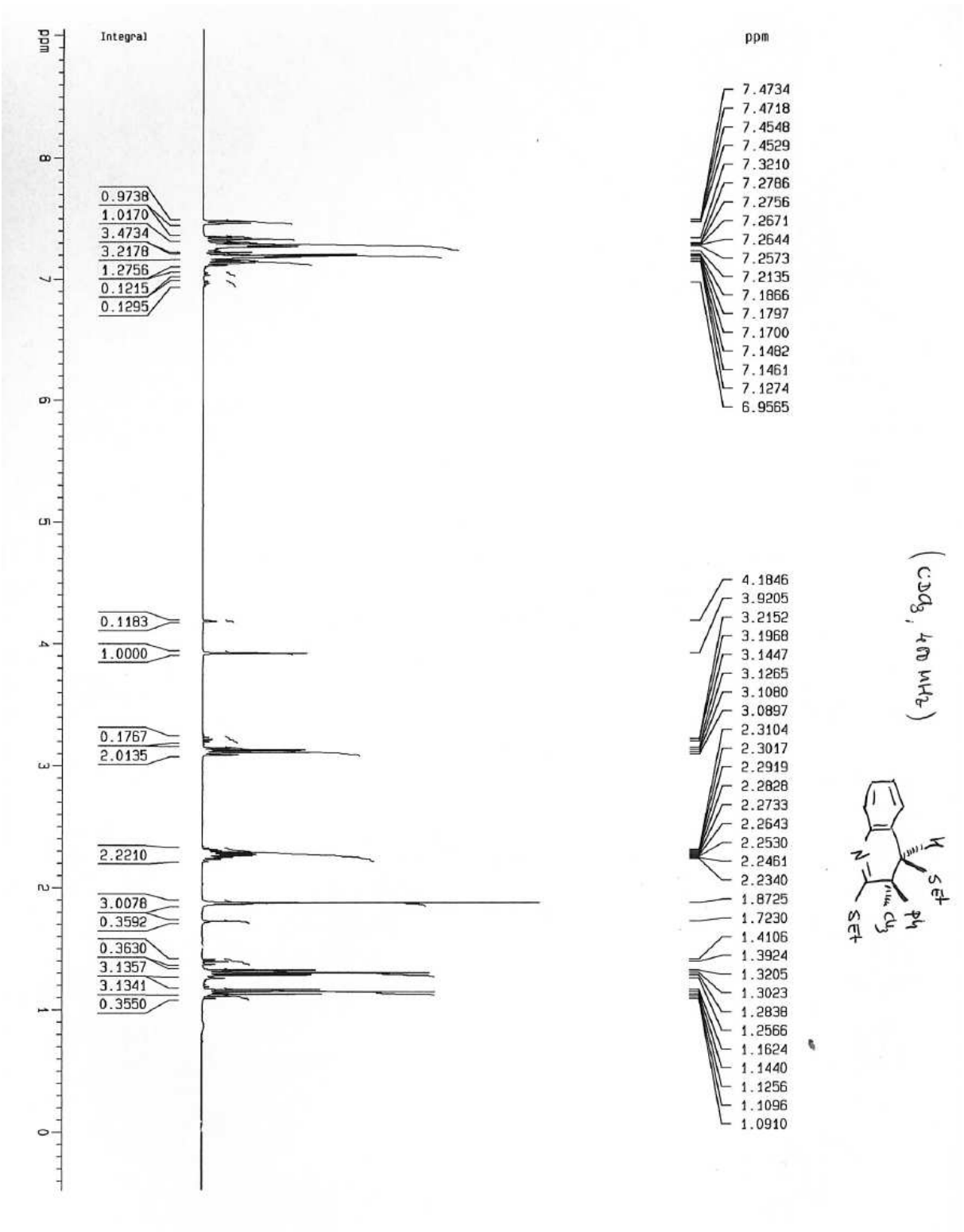
^{1}H NMR of **20c**



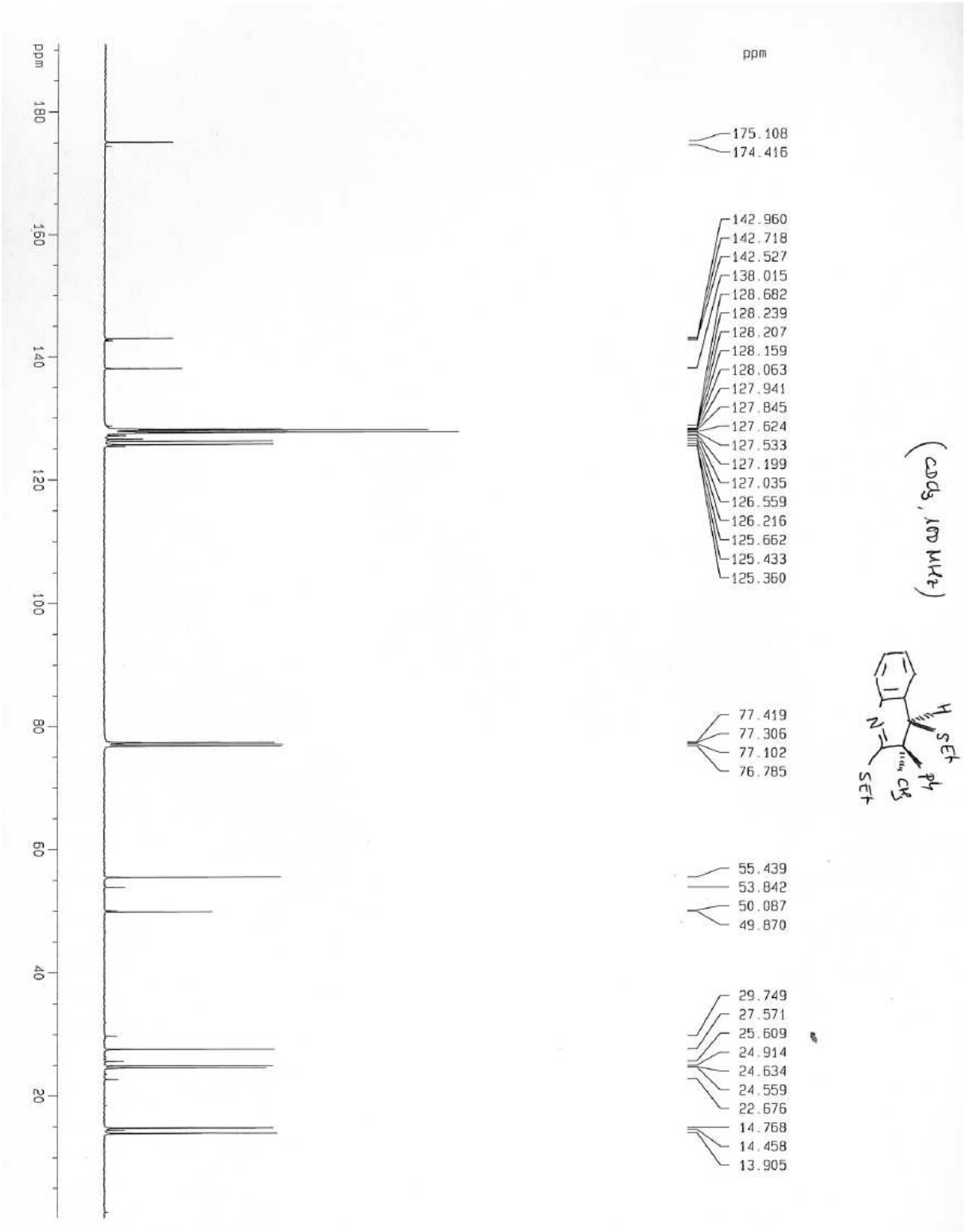
^{13}C NMR of **20c**



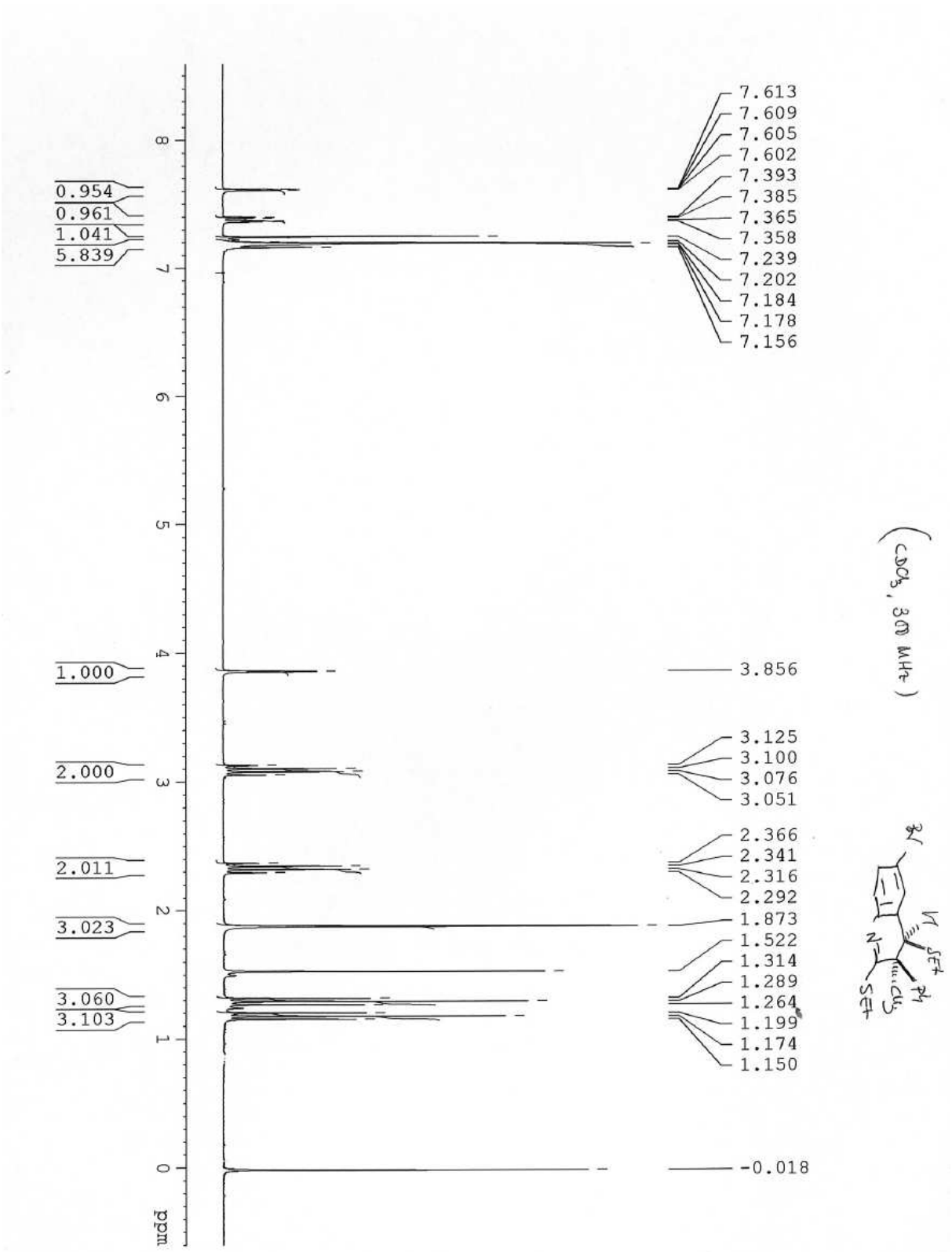
^{1}H NMR of ***cis*-20d** (containing small amount of ***trans*-20d**)



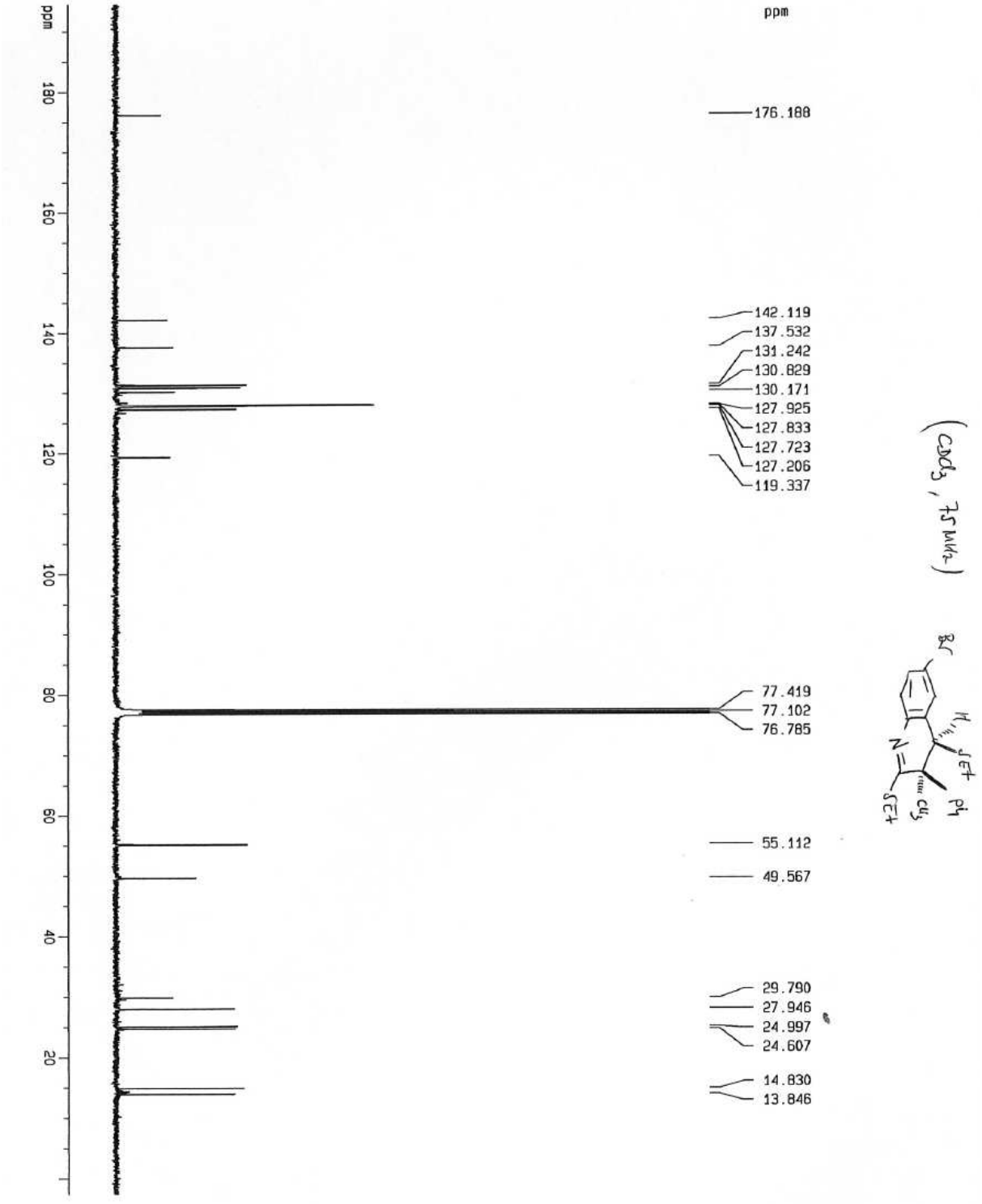
^{13}C NMR of ***cis*-20d** (containing small amount of ***trans*-20d**)



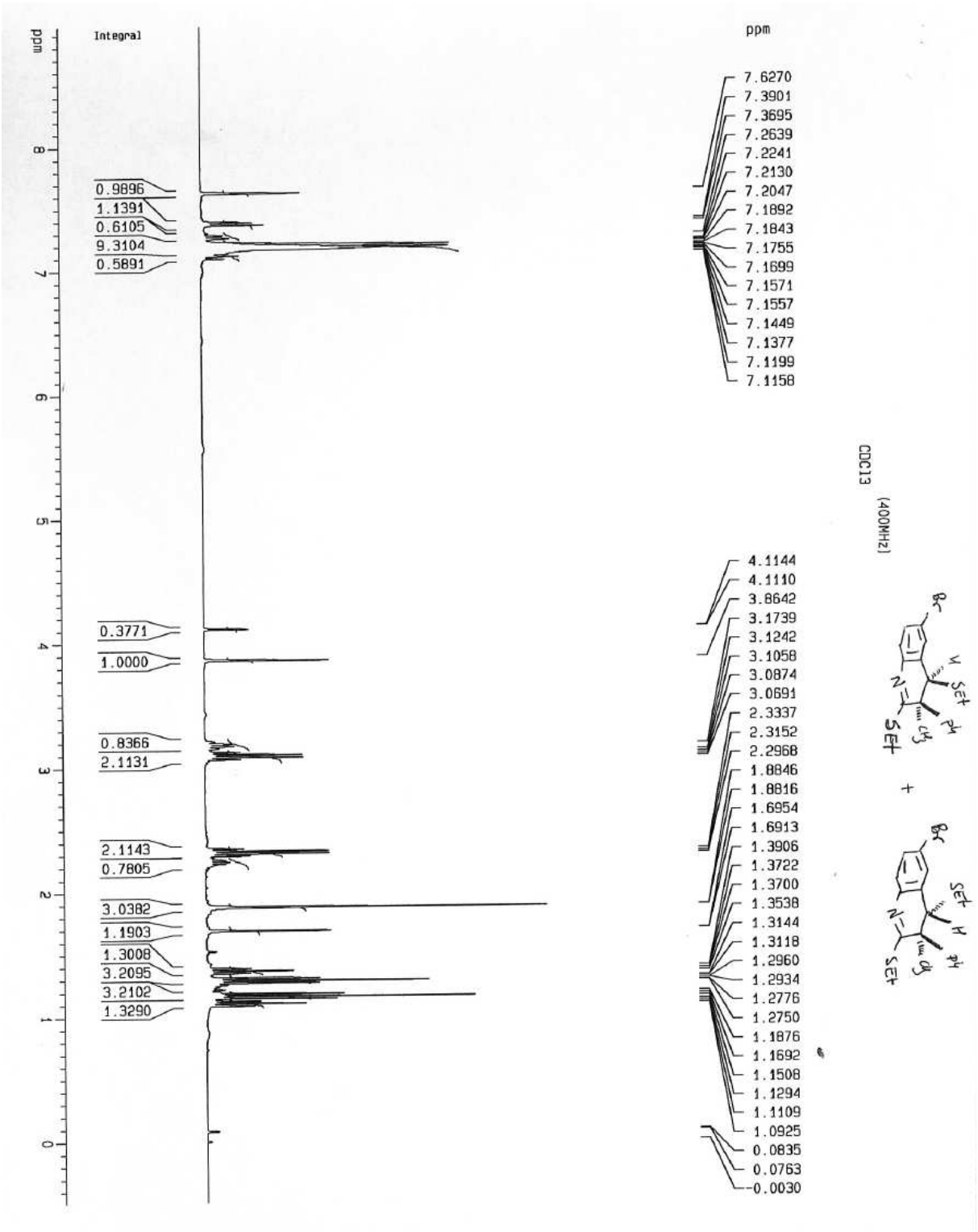
^{1}H NMR of ***cis*-20e**



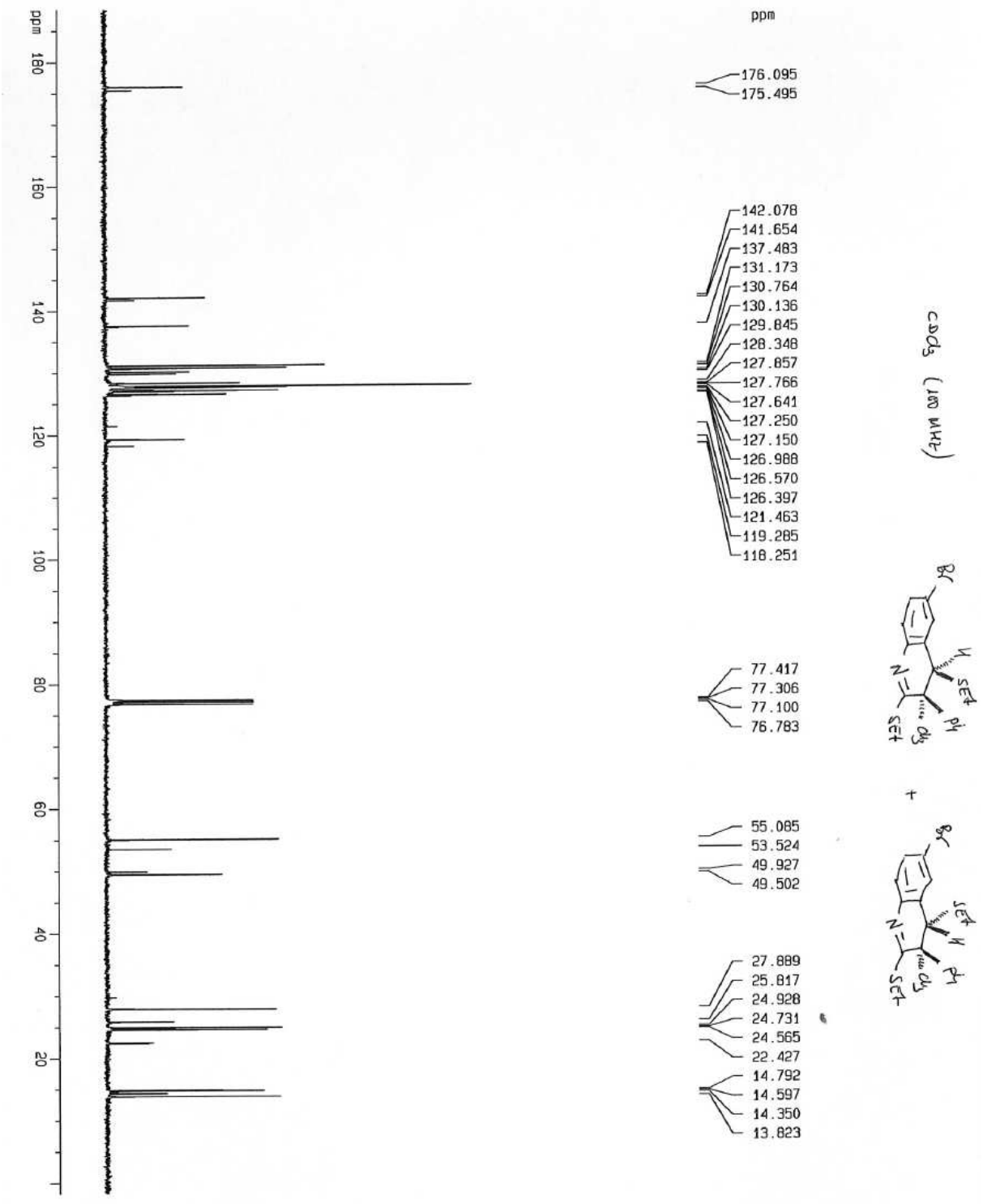
^{13}C NMR of ***cis*-20e**



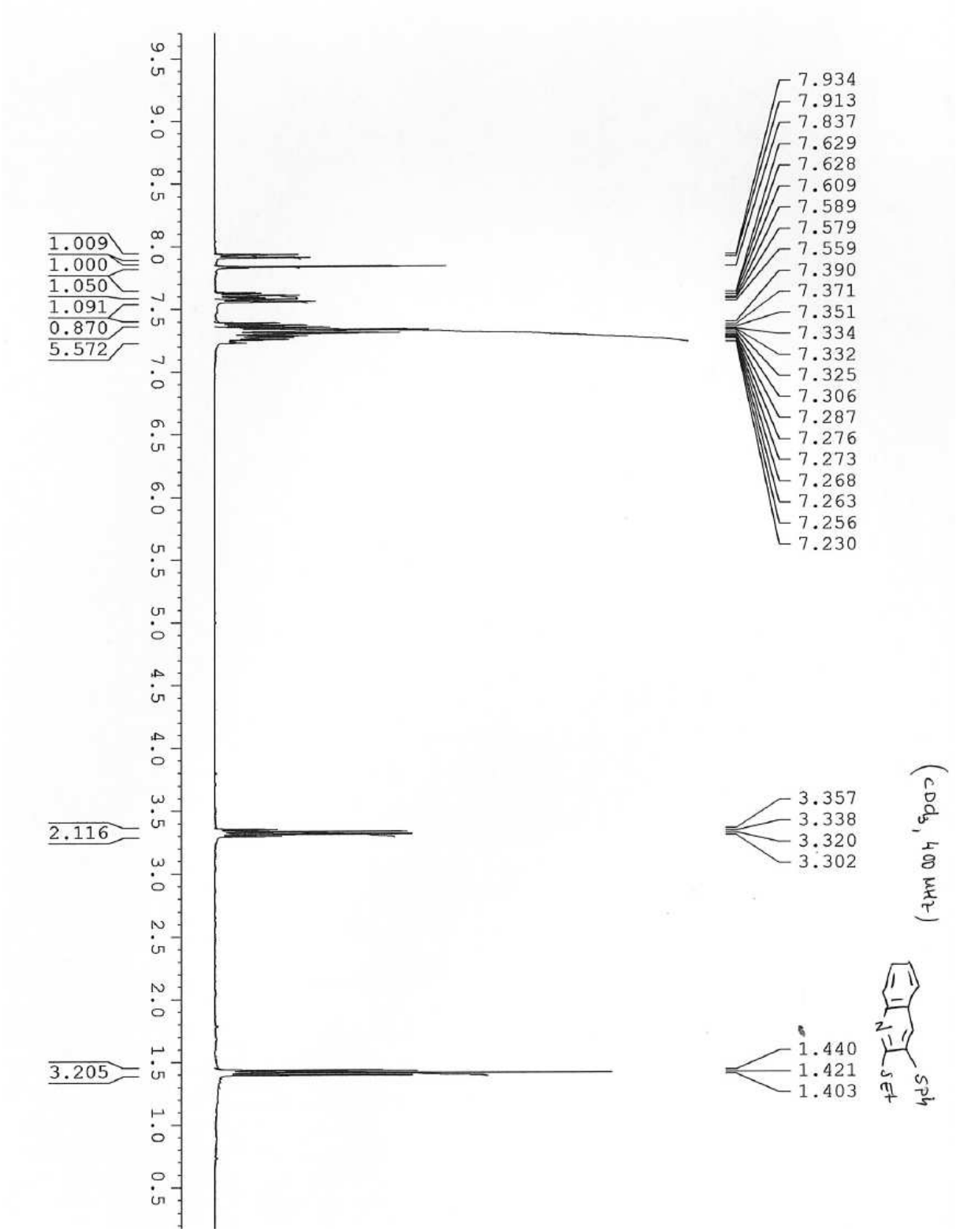
^{1}H NMR of ***cis*-20e** + ***trans*-20e**



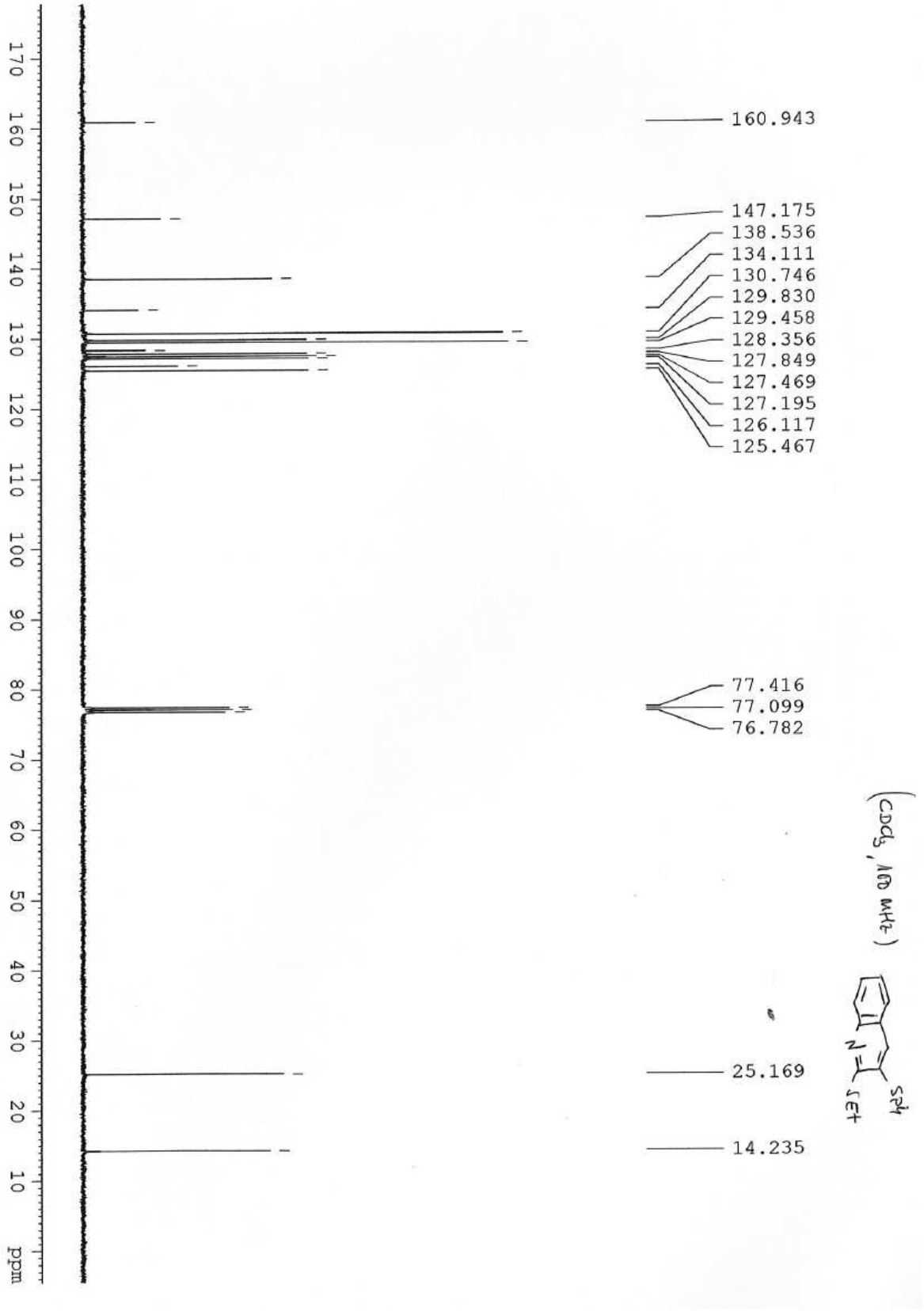
^{13}C NMR of ***cis*-20e** + ***trans*-20e**



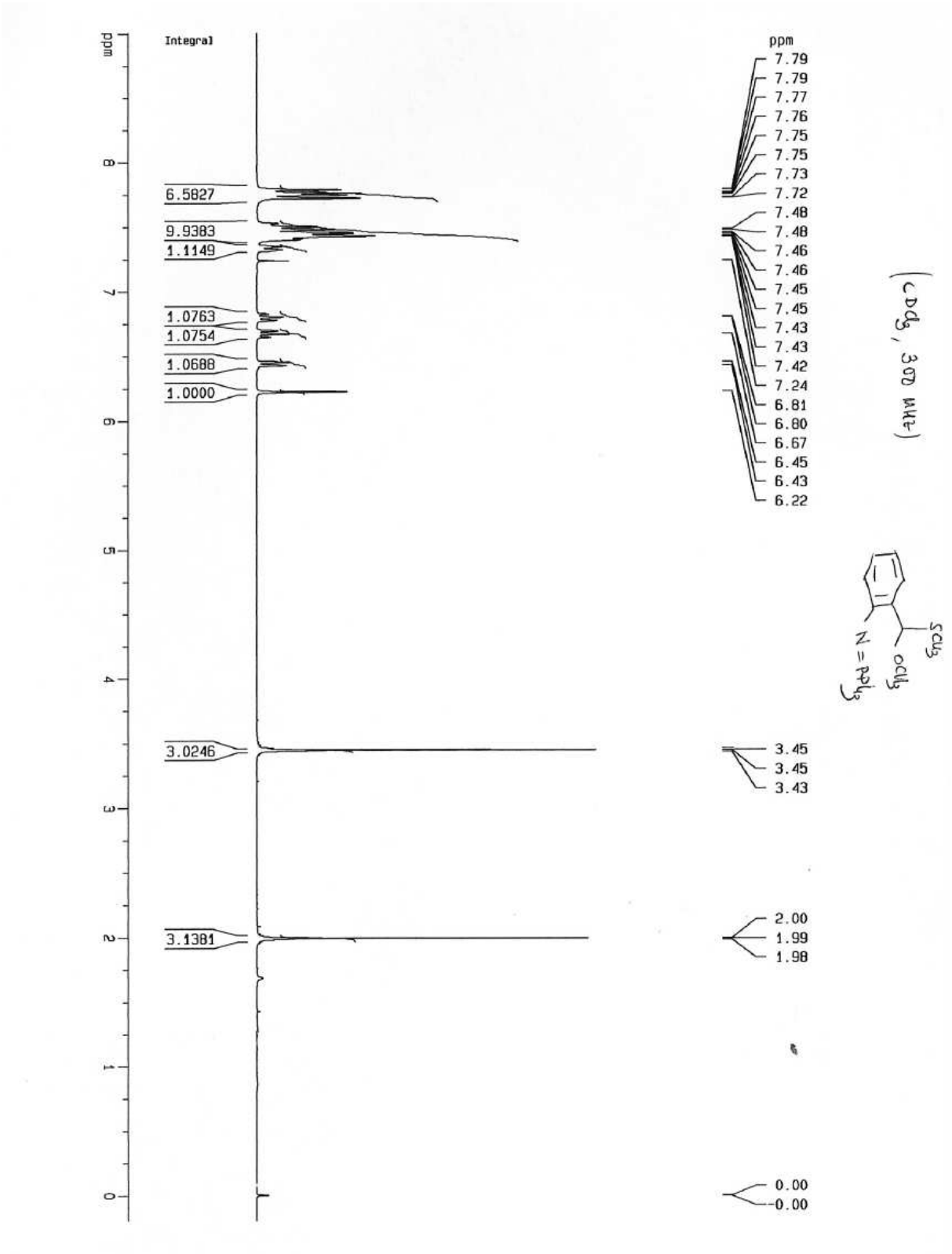
^{1}H NMR of **21**



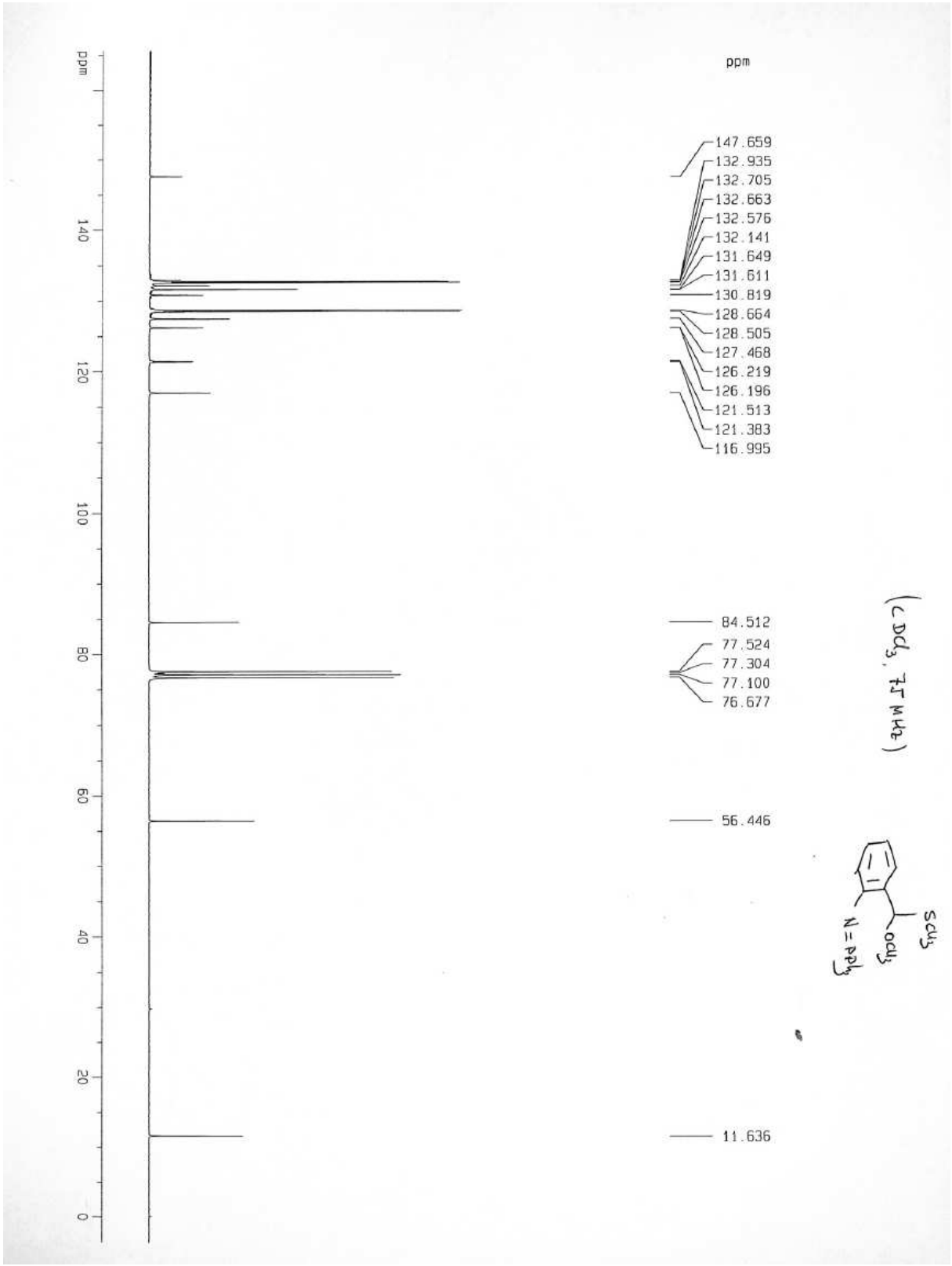
^{13}C NMR of **21**


160.943
147.175
138.536
134.111
130.746
129.830
129.458
128.356
127.849
127.469
127.195
126.117
125.467
77.416
77.099
76.782
25.169
14.235
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm
(CDCl3, 100 MHz)
Et
SPh
N

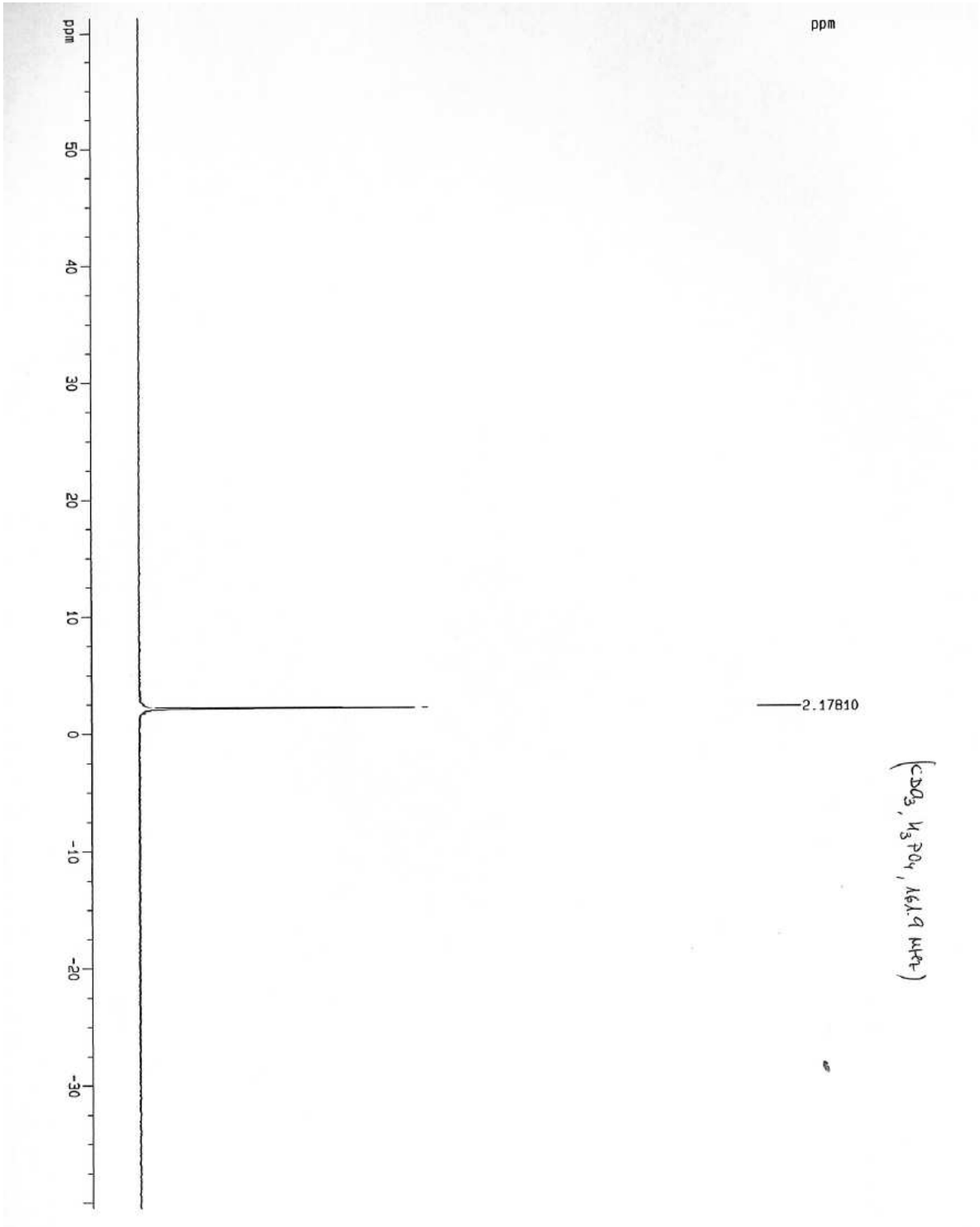
^{1}H NMR of **26**



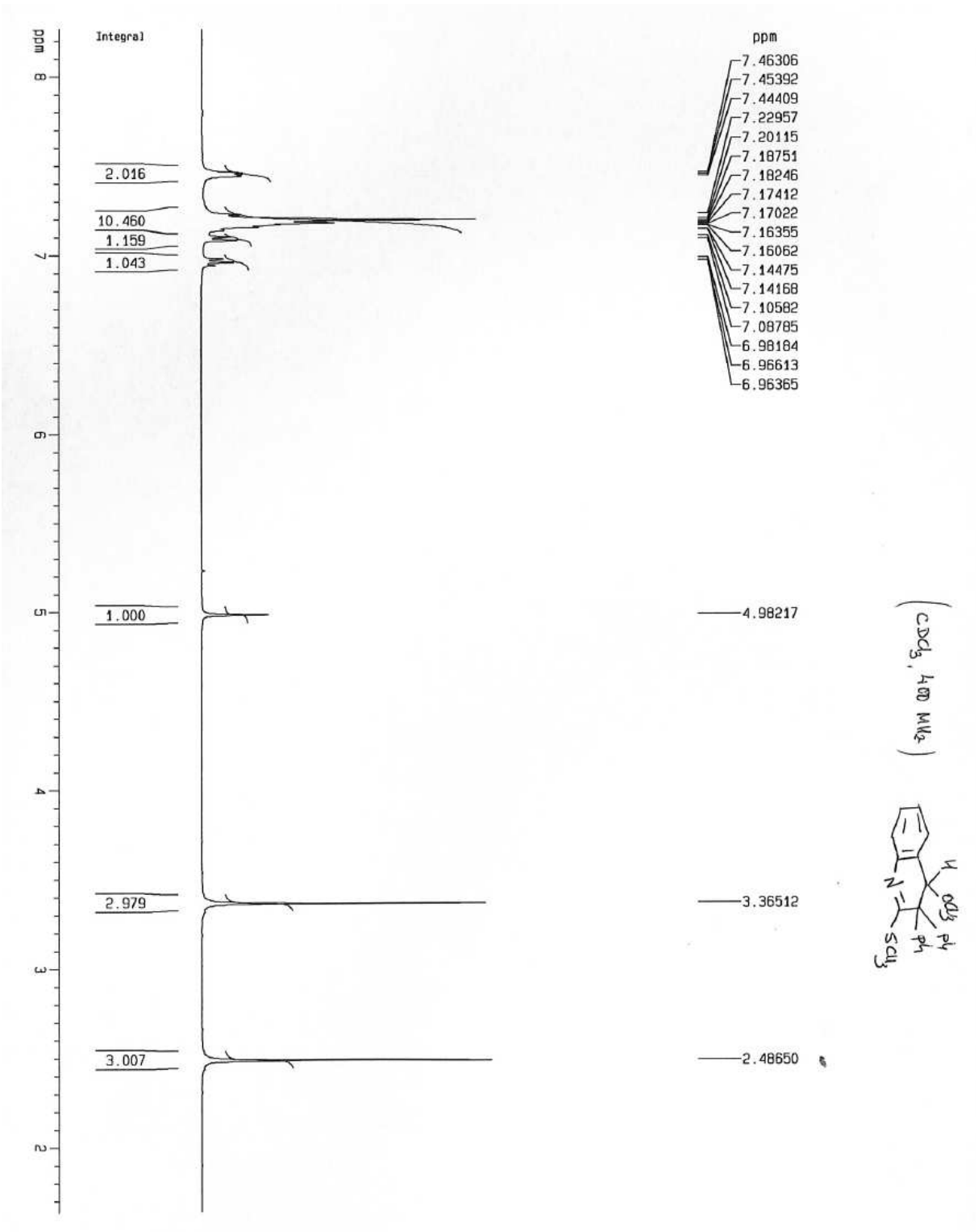
^{13}C NMR of **26**



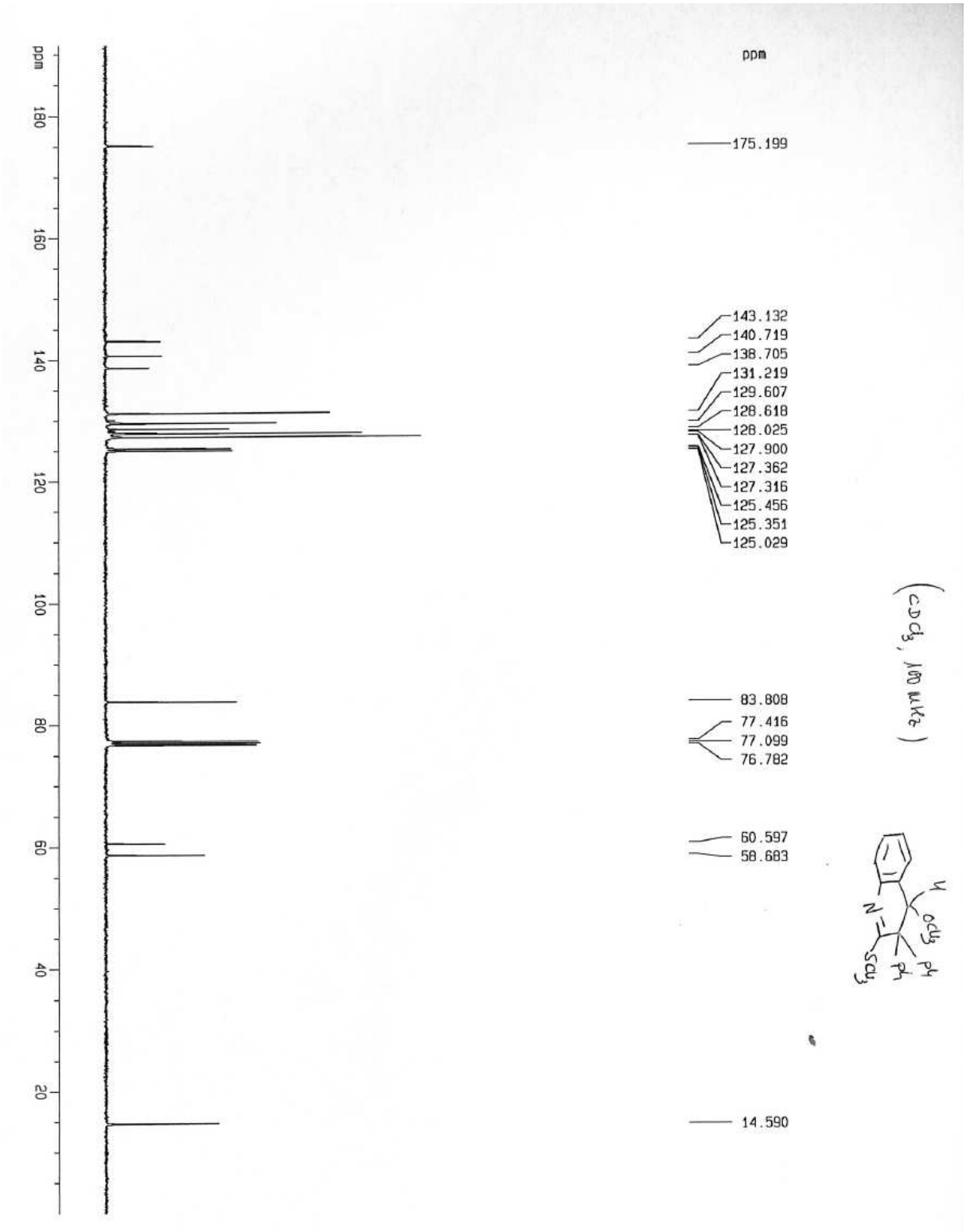
^{31}P NMR of **26**



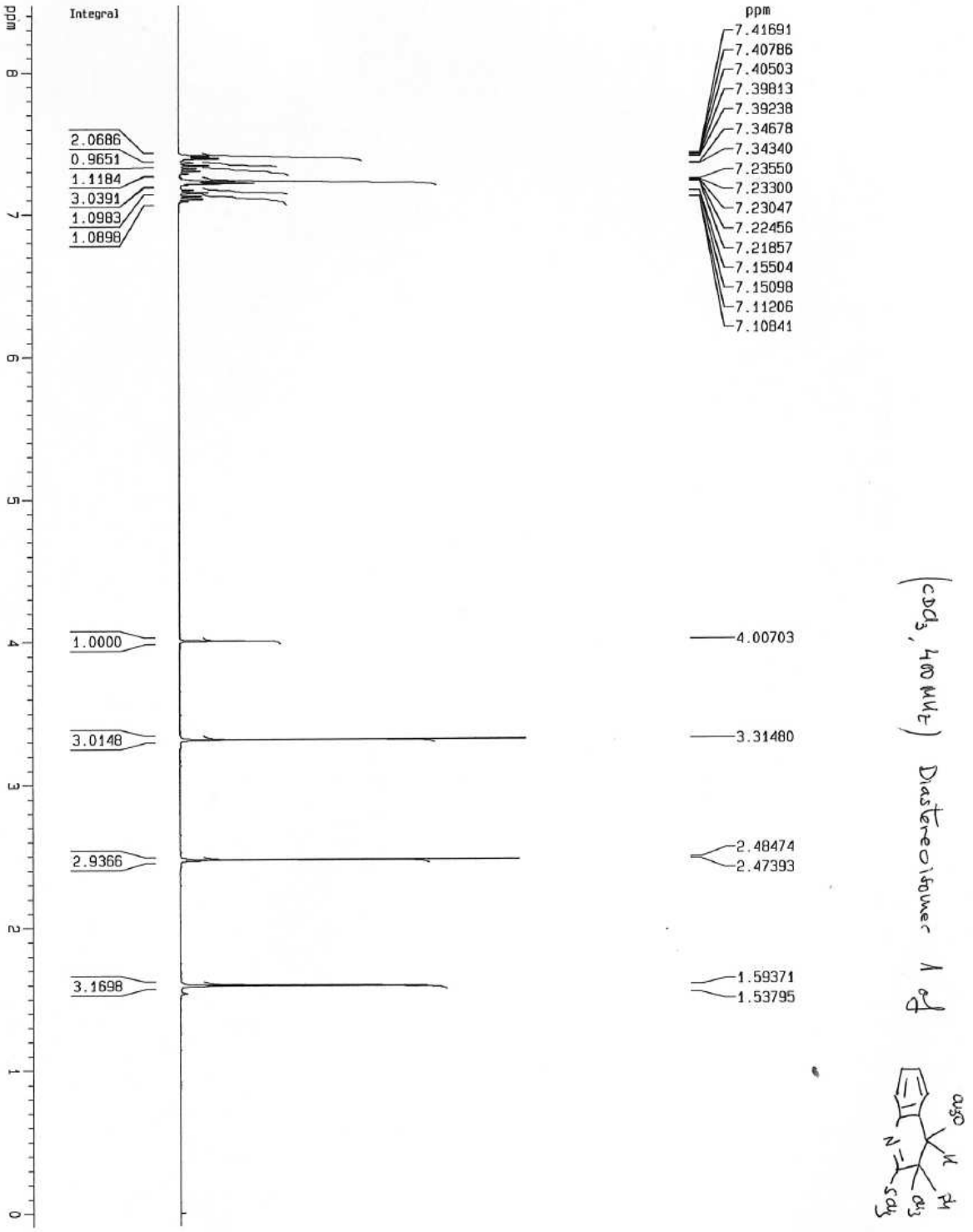
^{1}H NMR of **28a**



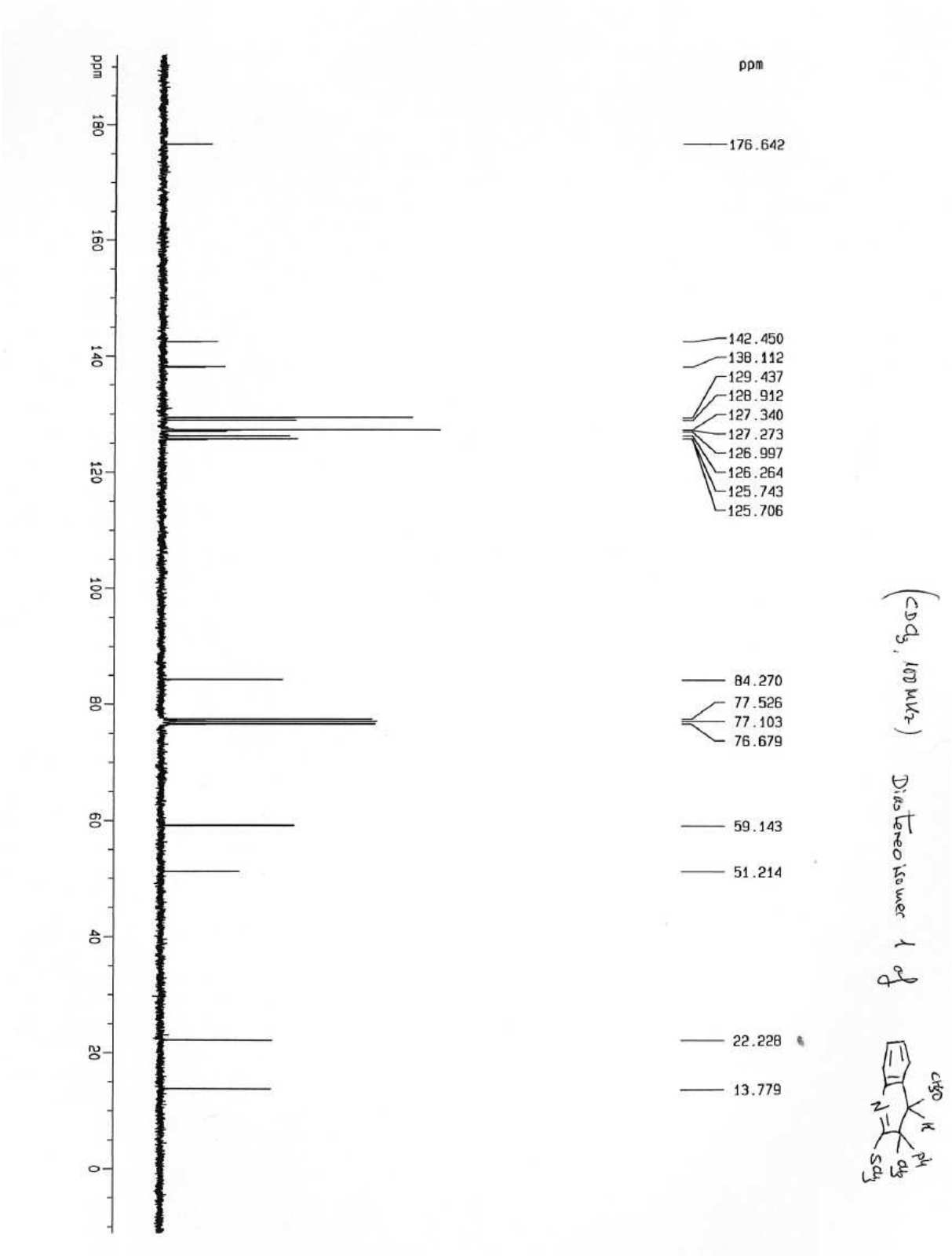
^{13}C NMR of **28a**



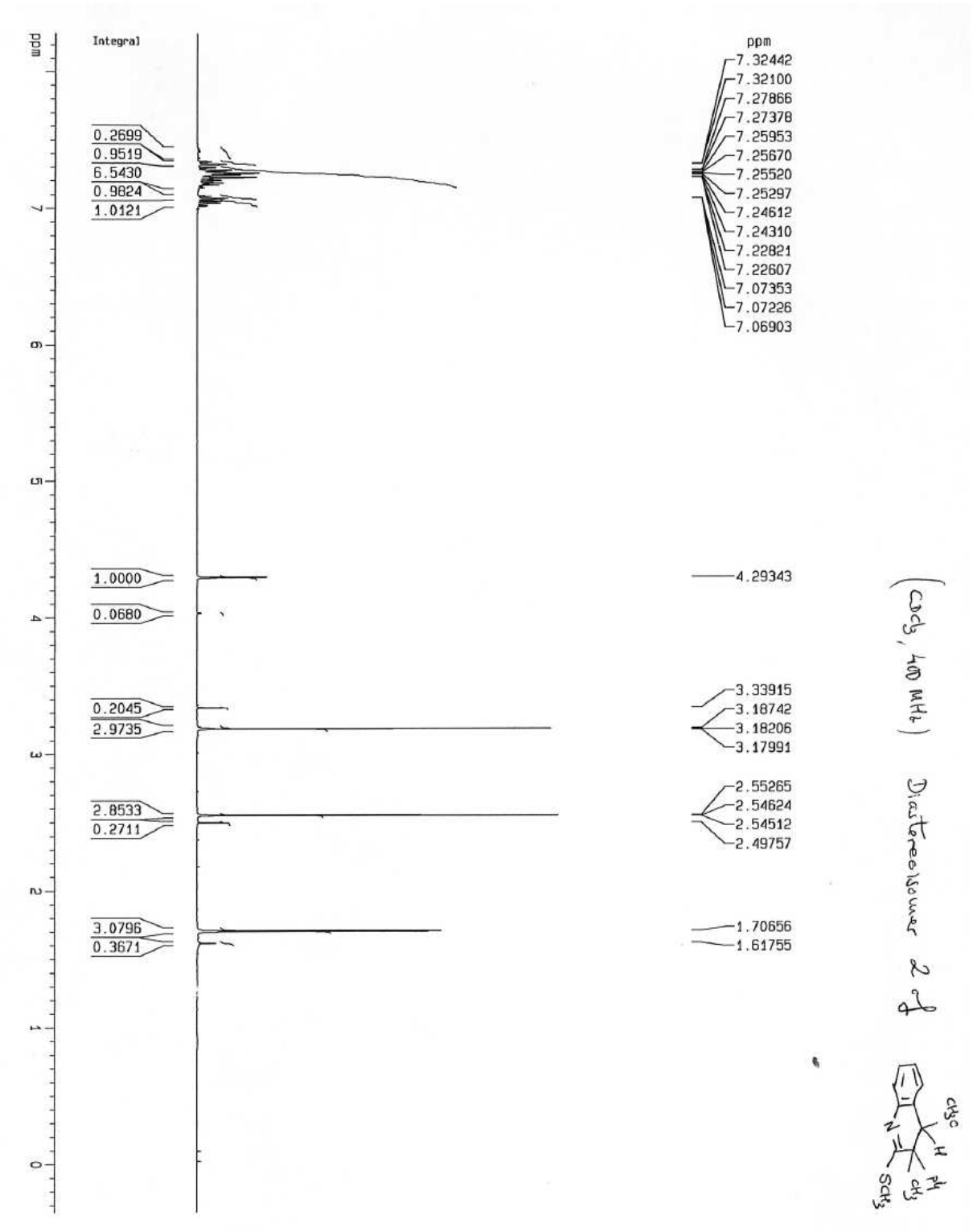
^{1}H NMR of **diastereoisomer 1 of 28b**



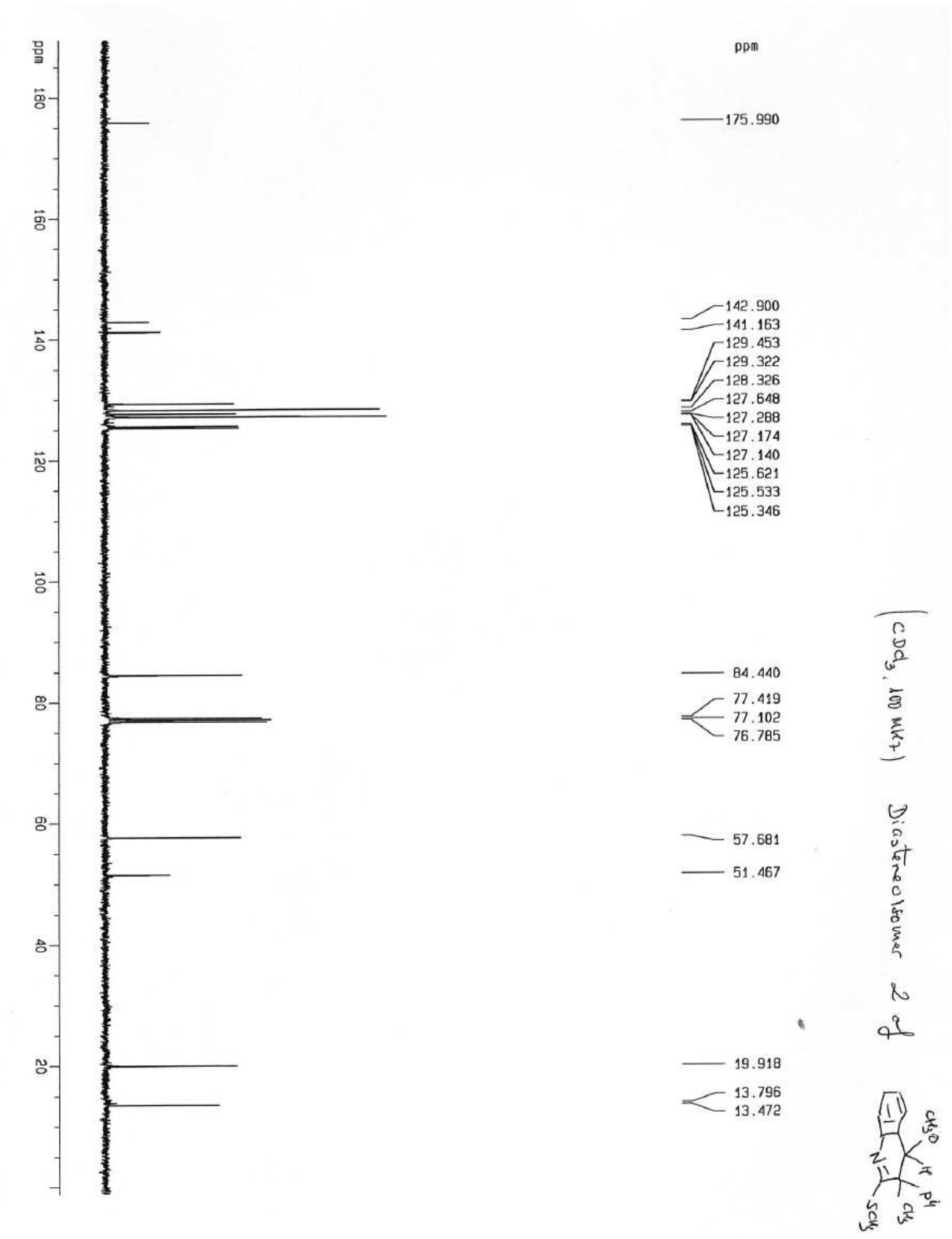
^{13}C NMR of **diastereoisomer 1 of 28b**



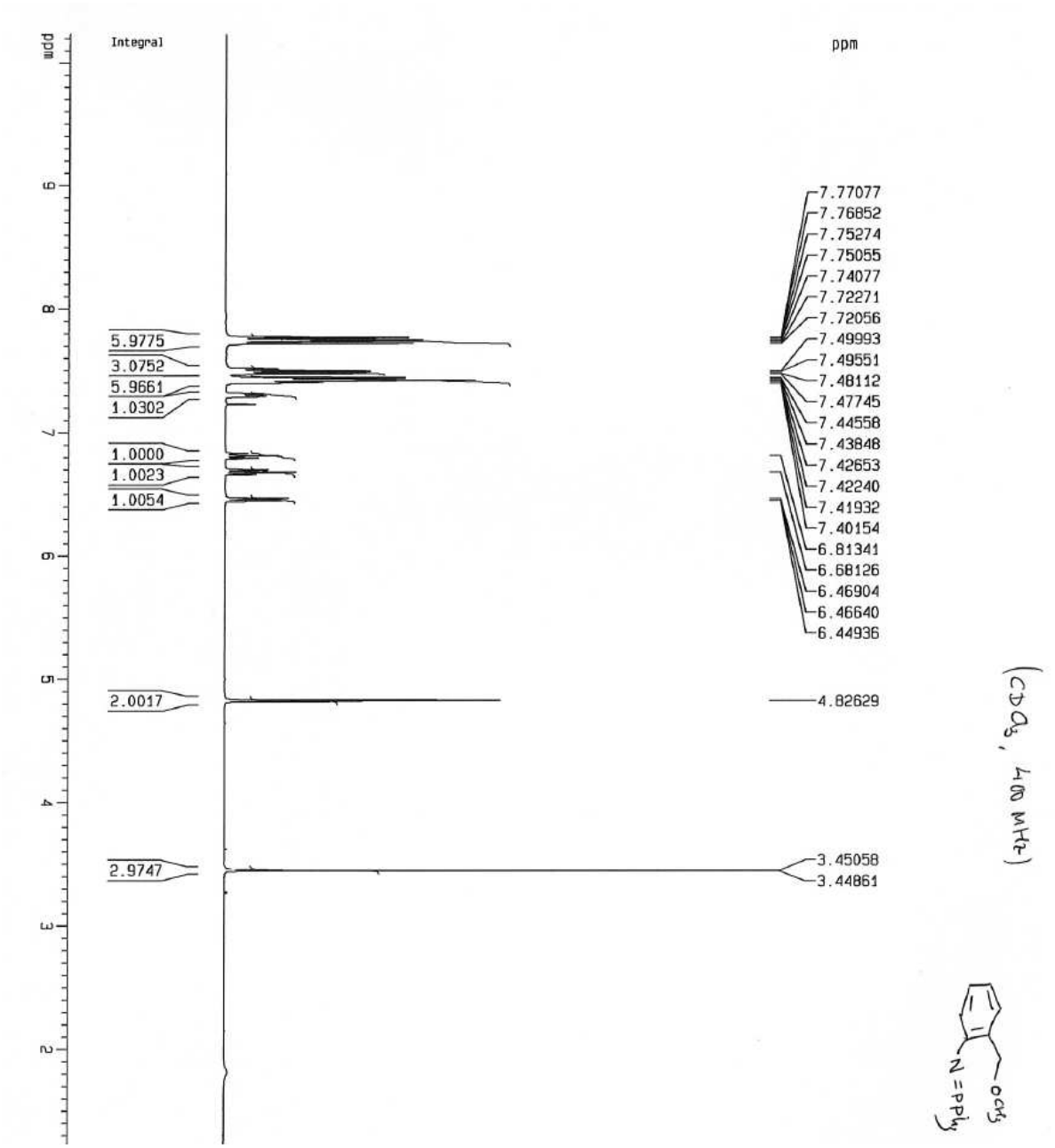
^{1}H NMR of **diastereoisomer 2 of 28b** (containing small amount of **diastereoisomer 1** of **28b**)



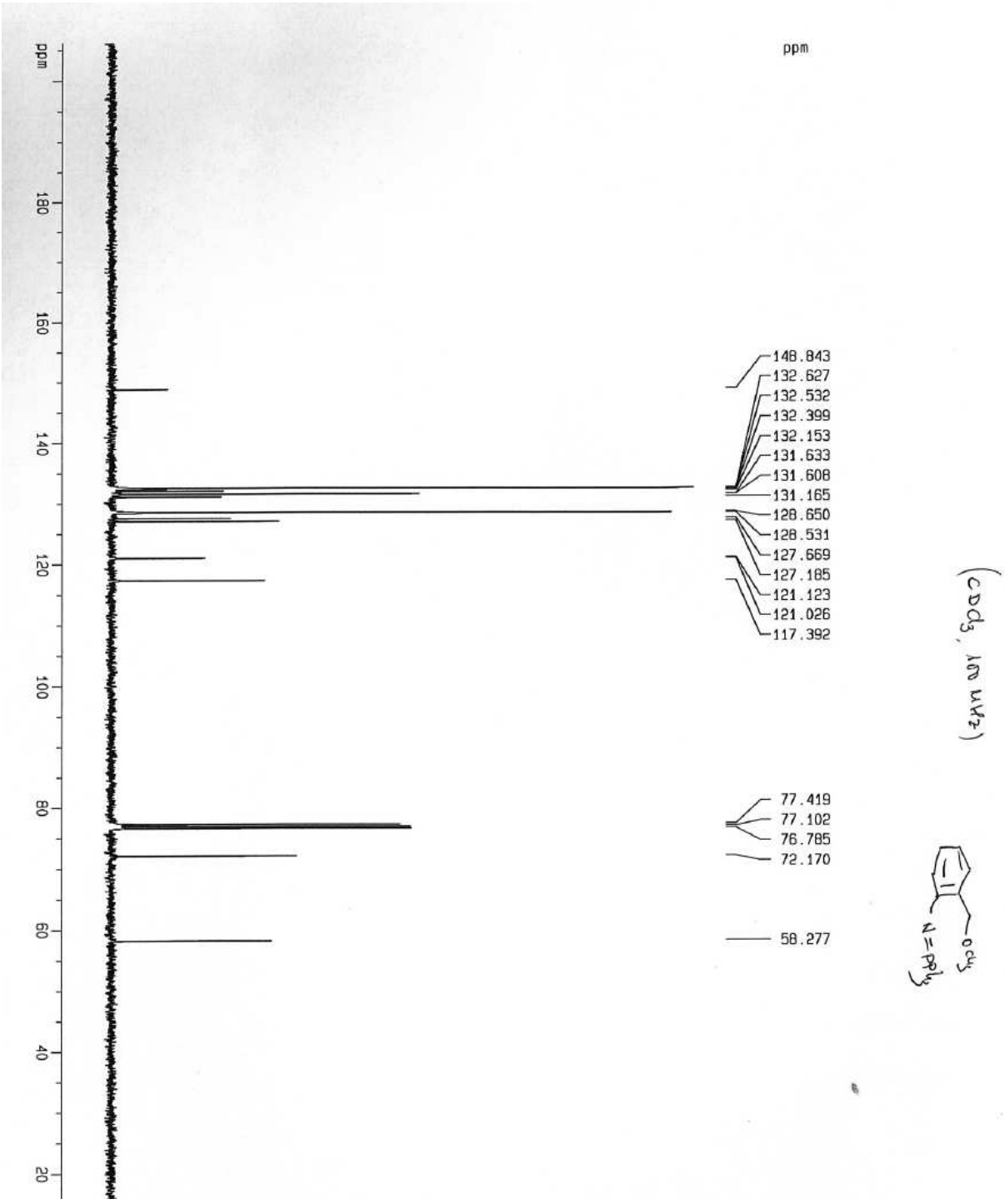
^{13}C NMR of **diastereoisomer 2 of 28b** (containing small amount of **diastereoisomer 1** of **28b**)



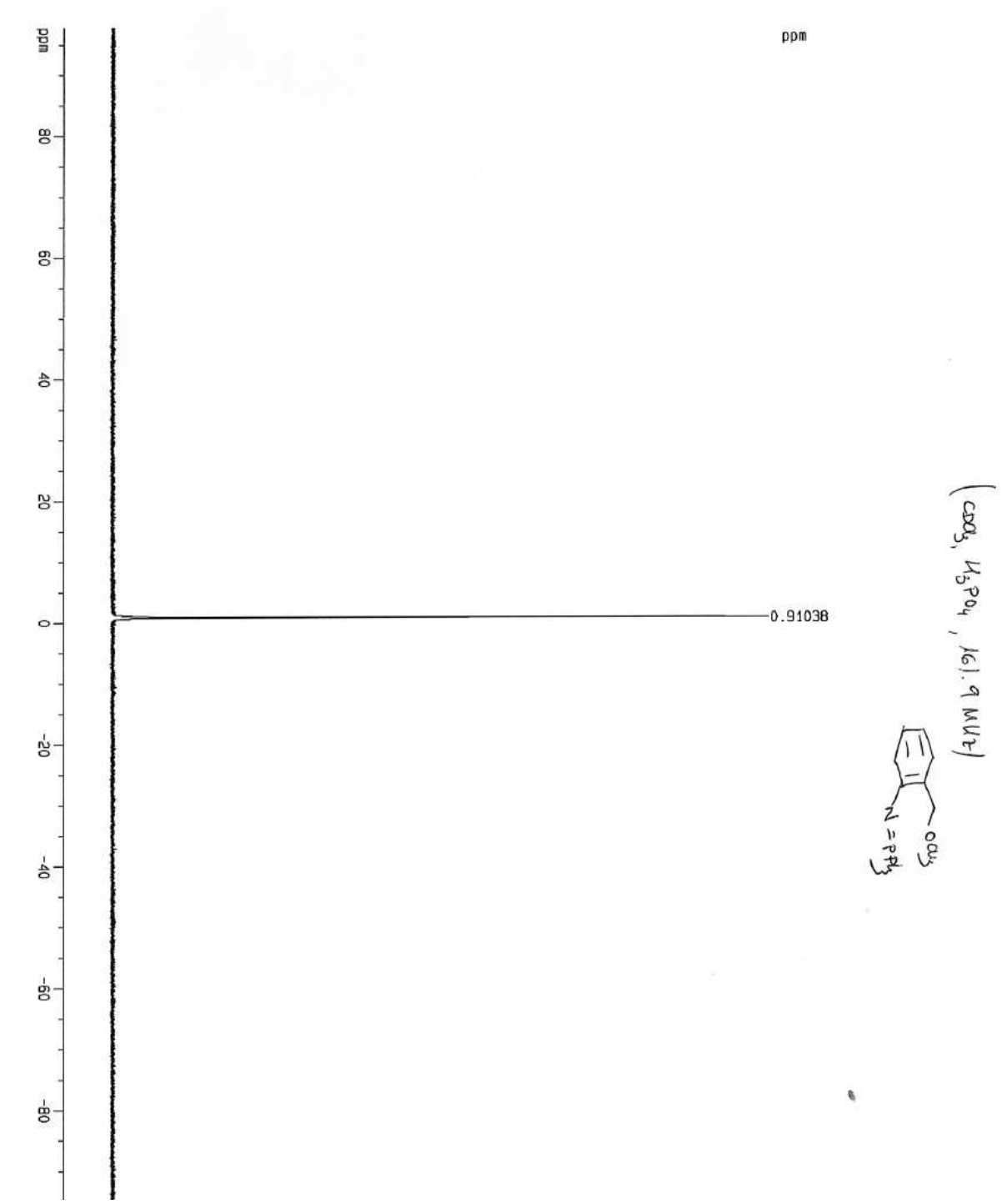
^{1}H NMR **31a**



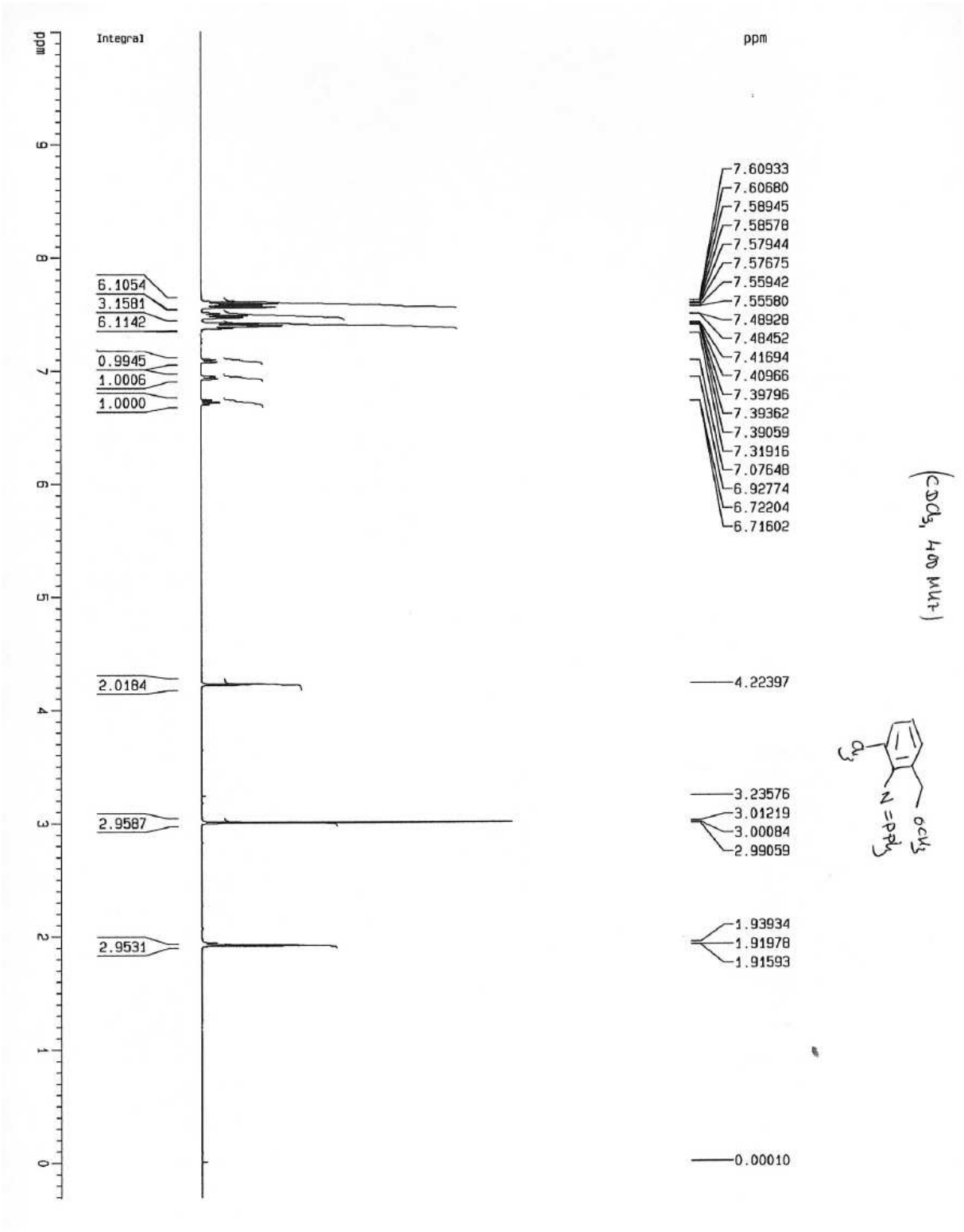
^{13}C NMR **31a**



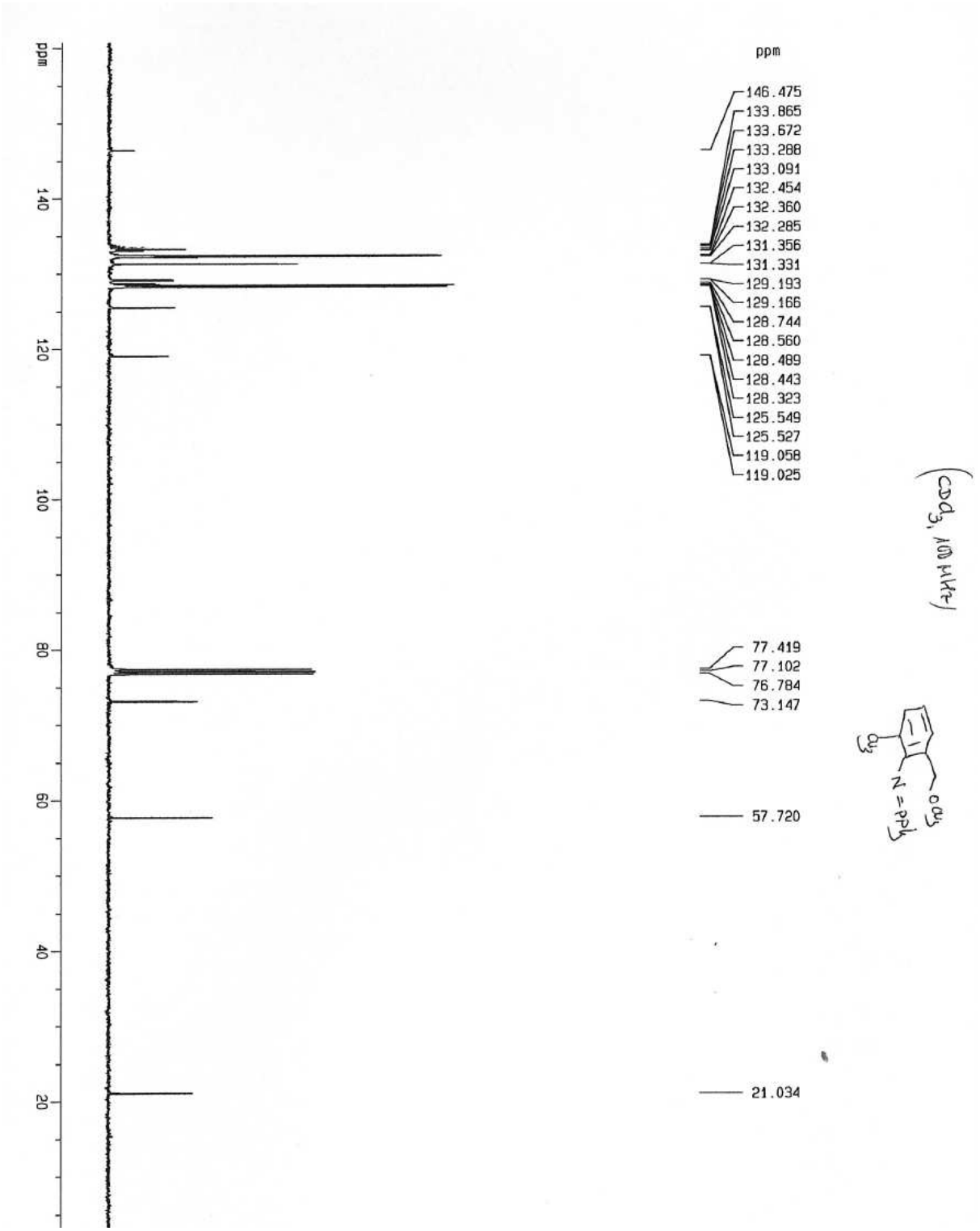
^{31}P NMR **31a**



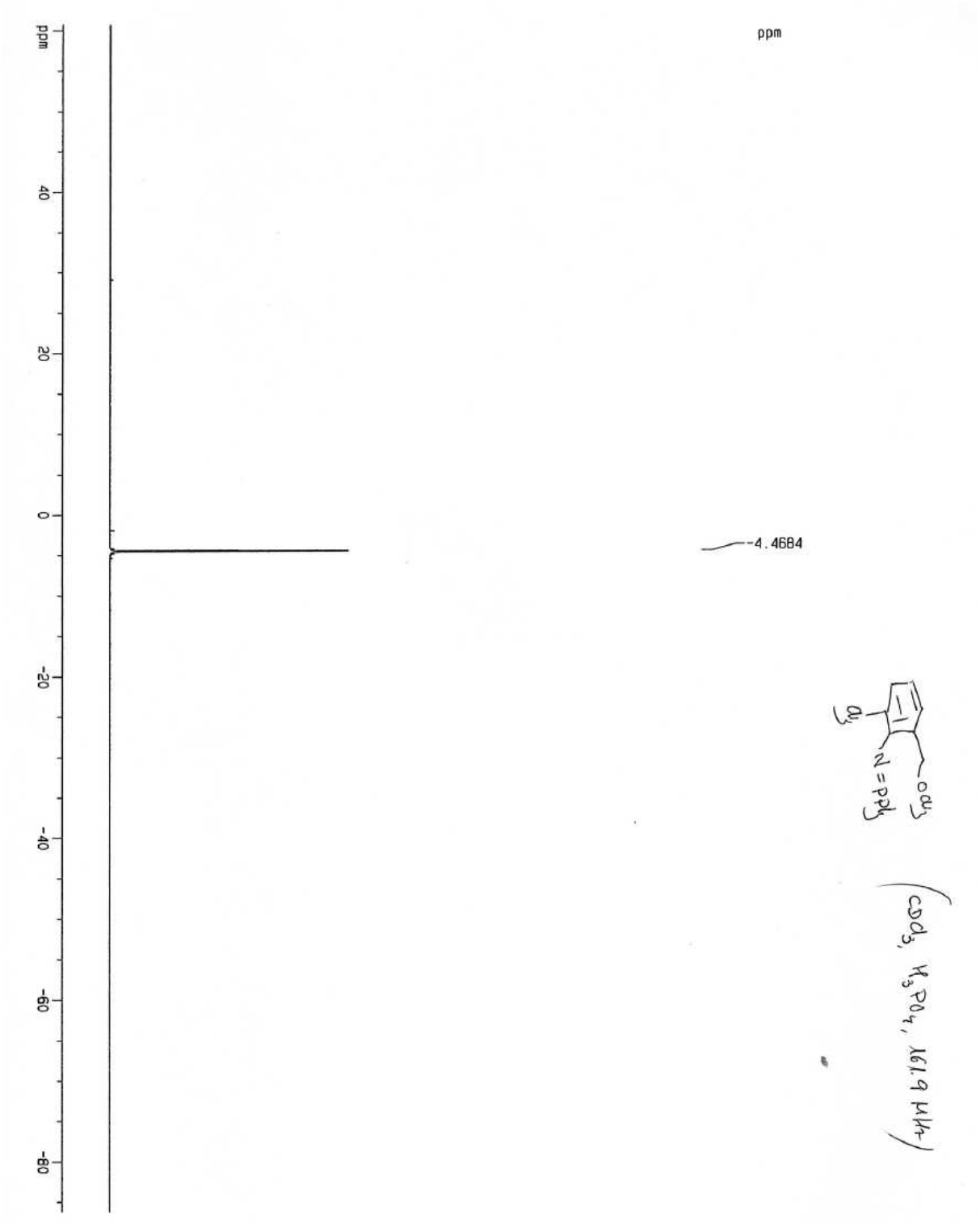
^{1}H NMR **31b**


ppm
Integral
6.1054
3.1581
6.1142
0.9945
1.0006
1.0000
2.0184
2.9587
2.9531
7.60933
7.60680
7.58945
7.58578
7.57944
7.57675
7.55942
7.55580
7.48928
7.48452
7.41694
7.40966
7.39796
7.39362
7.39059
7.31916
7.07648
6.92774
6.72204
6.71602
4.22397
3.23576
3.01219
3.00084
2.99059
1.93934
1.91978
1.91593
0.00010
(CDCl3, 400 MHz)
N=Py
OCH3

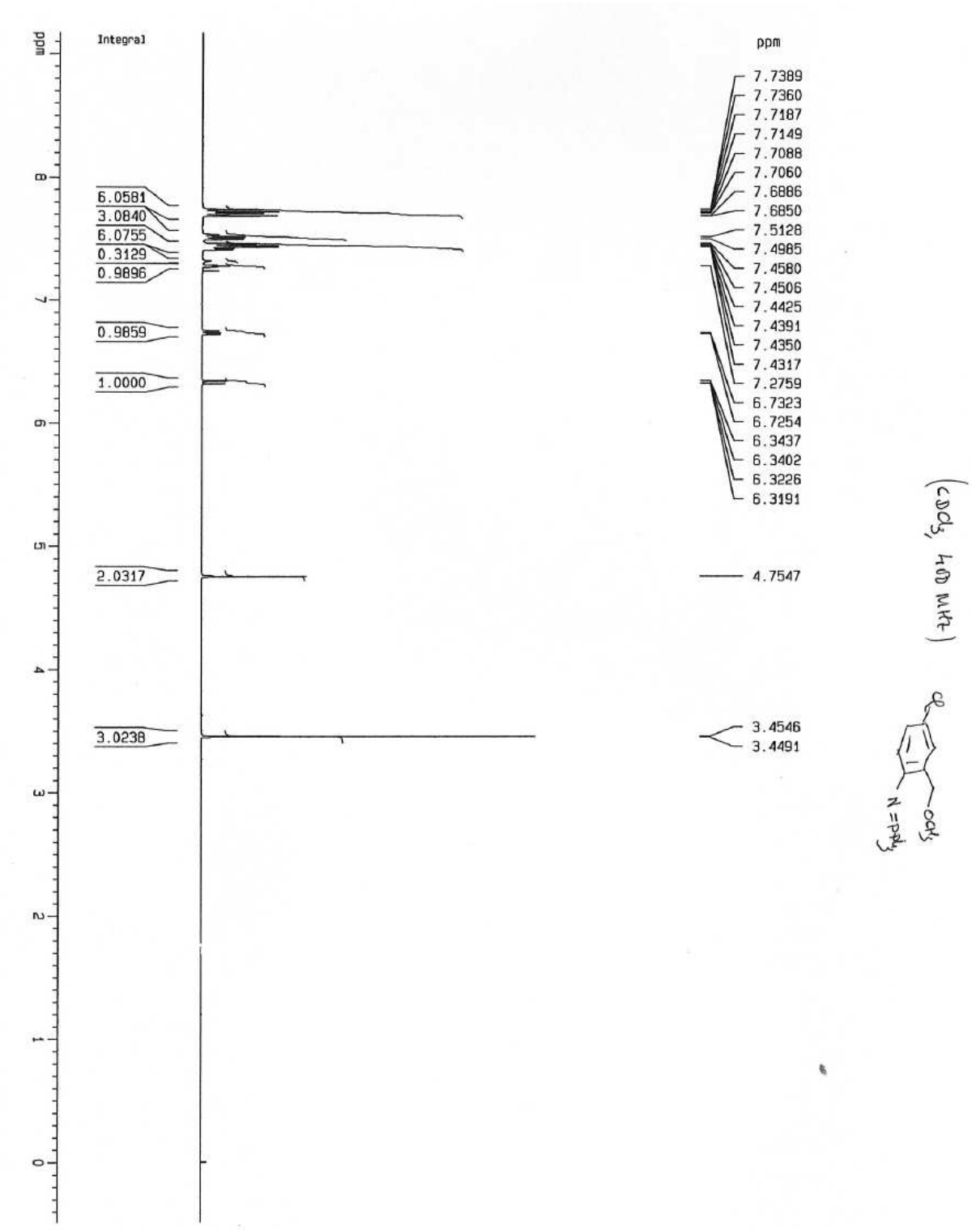
^{13}C NMR **31b**



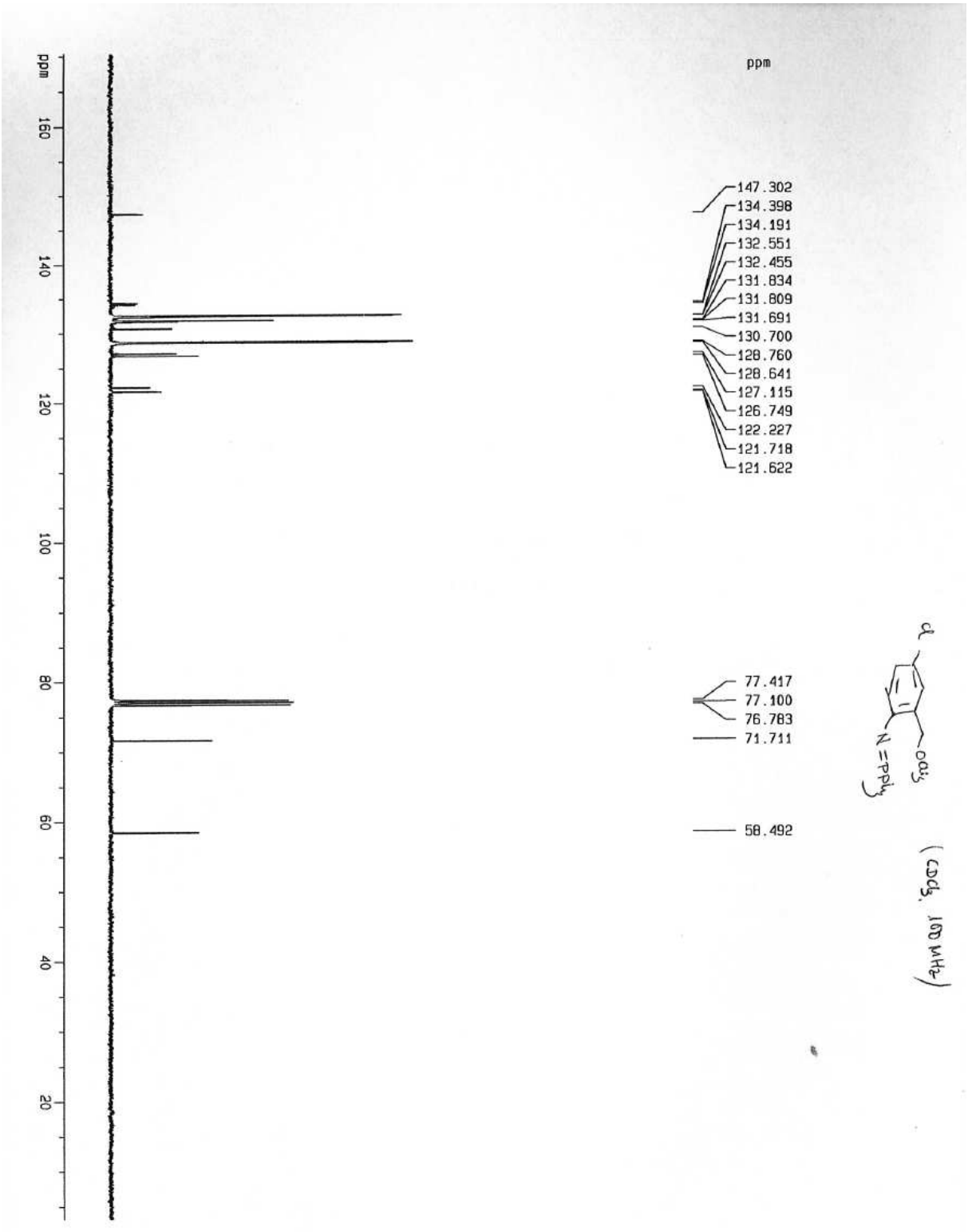
^{31}P NMR **31b**



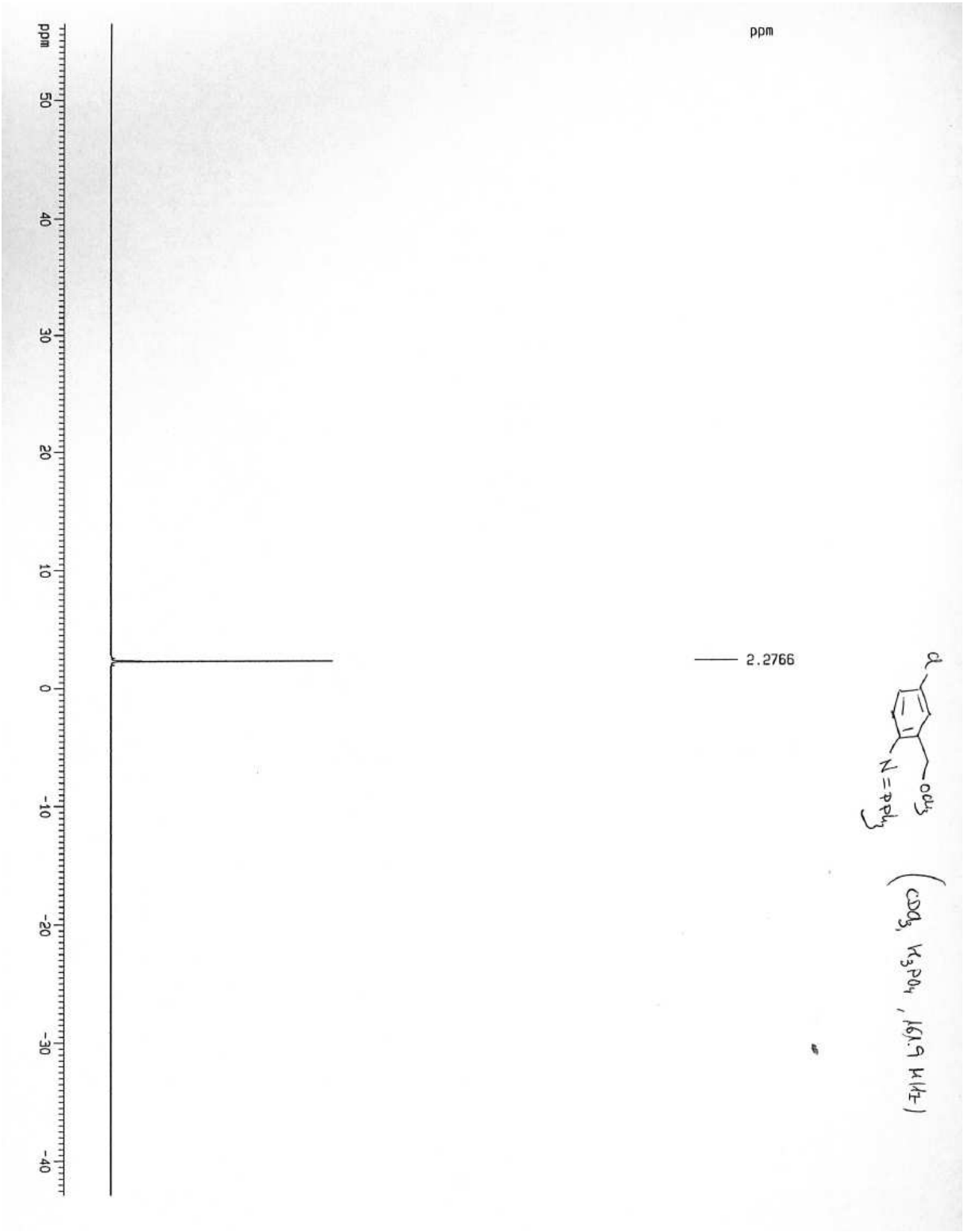
^{1}H NMR **31c**



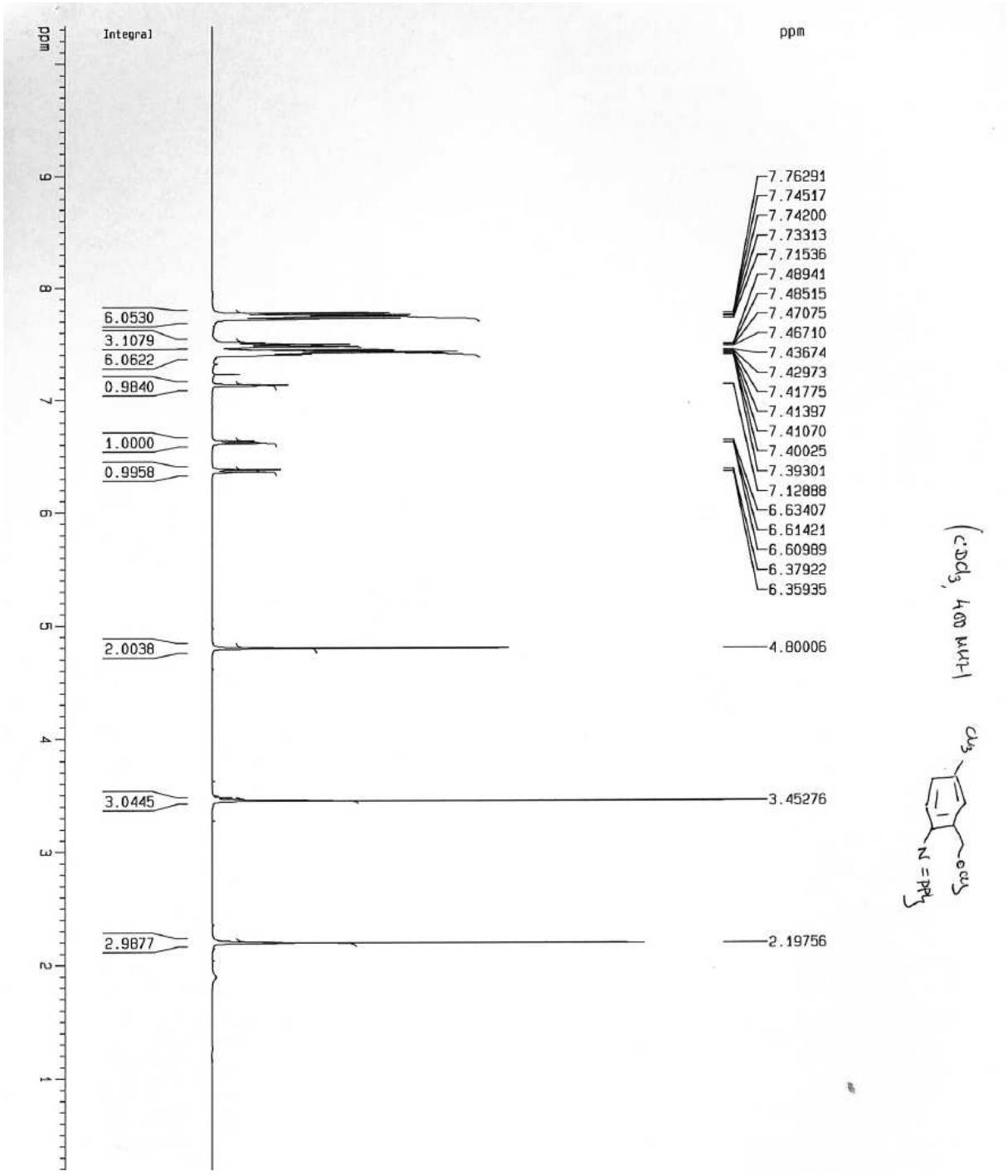
^{13}C NMR **31c**



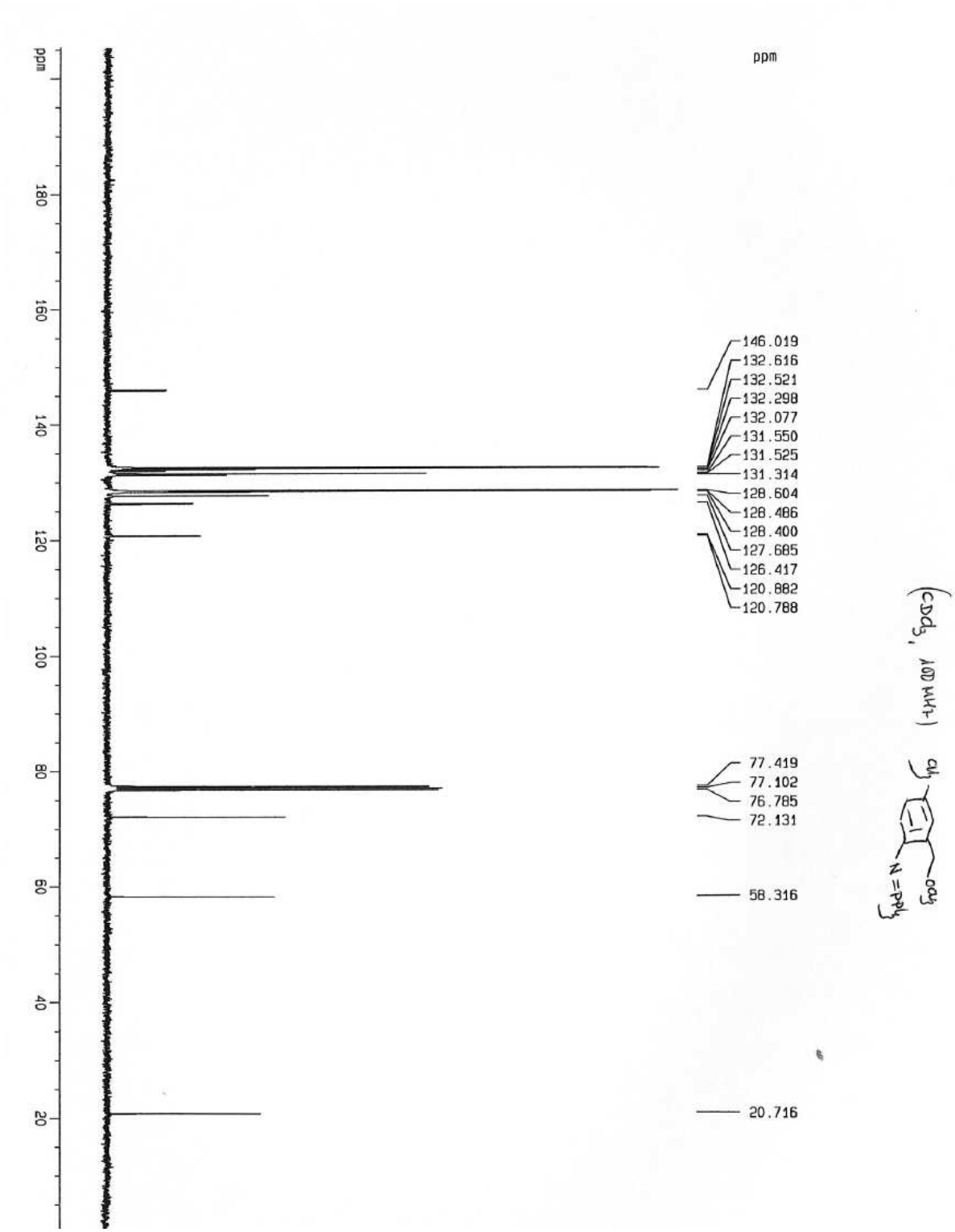
^{31}P NMR **31c**



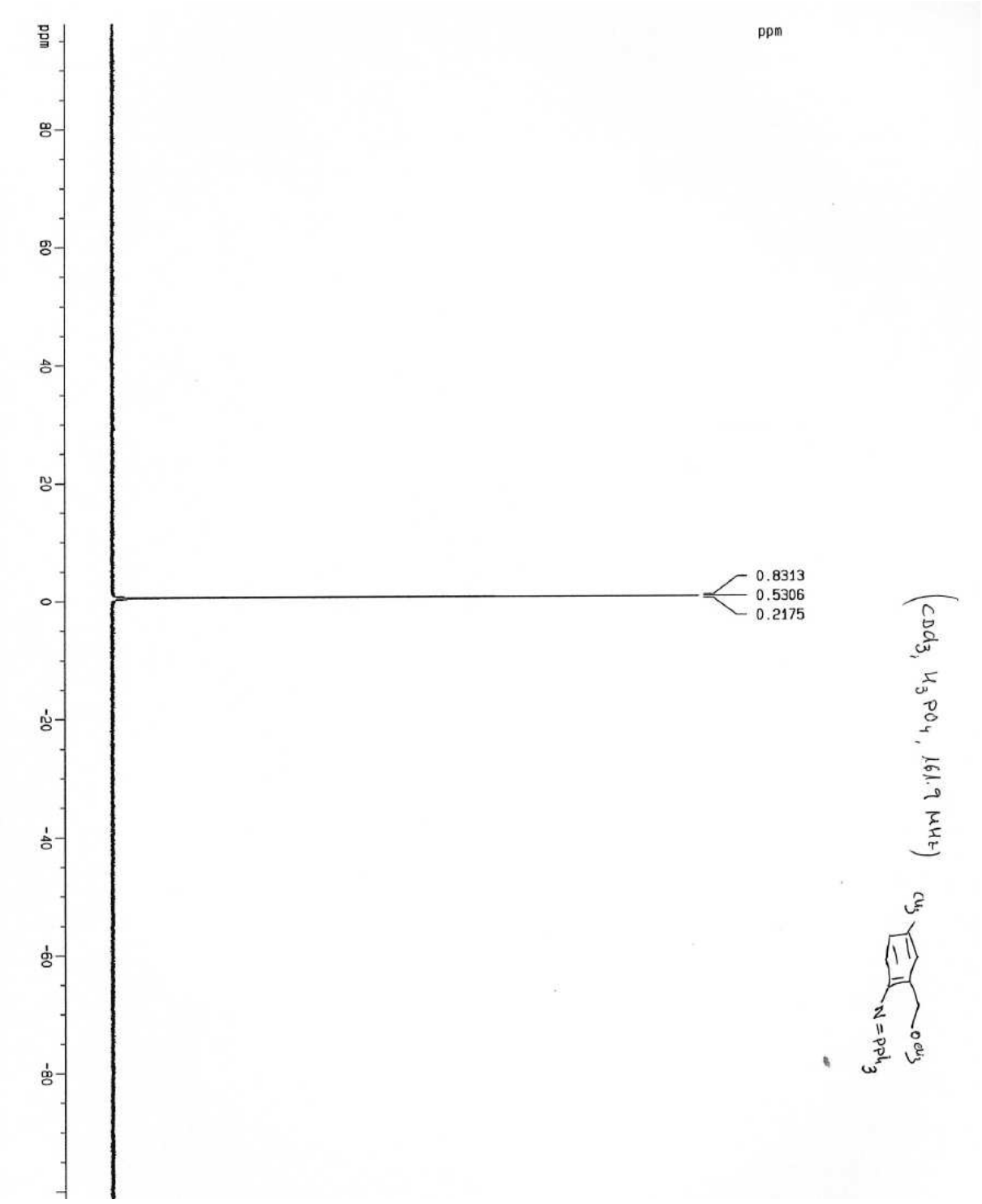
^{1}H NMR **31d**


ppm
Integral
ppm
6.0530
3.1079
6.0622
0.9840
1.0000
0.9958
2.0038
3.0445
2.9877
7.76291
7.74517
7.74200
7.73313
7.71536
7.48941
7.48515
7.47075
7.46710
7.43674
7.42973
7.41775
7.41397
7.41070
7.40025
7.39301
7.12888
6.63407
6.61421
6.60989
6.37922
6.35935
4.80006
3.45276
2.19756
(CDCl3, 400 MHz)
CH3
OCH3
N = PPh3

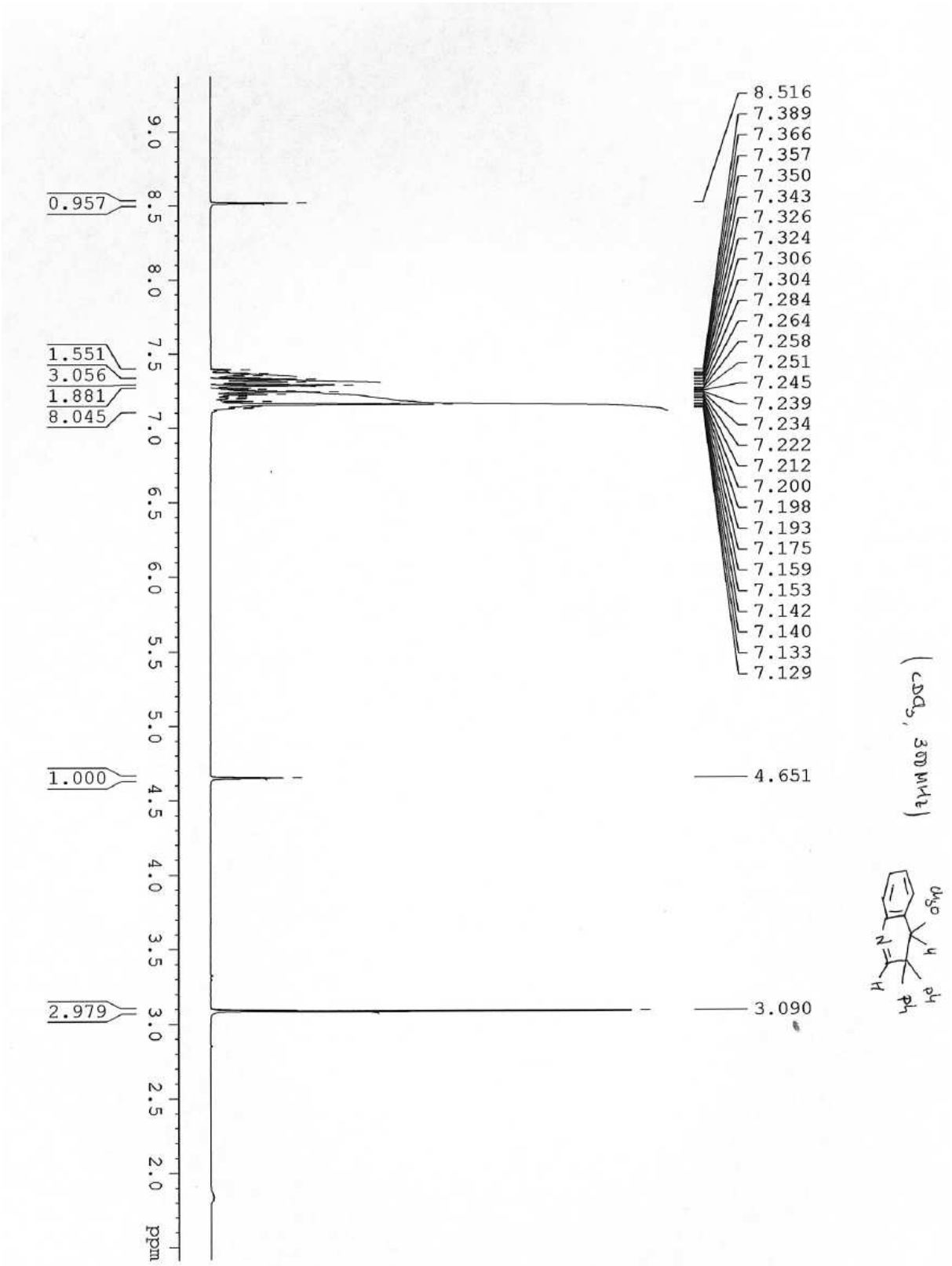
^{13}C NMR **31d**



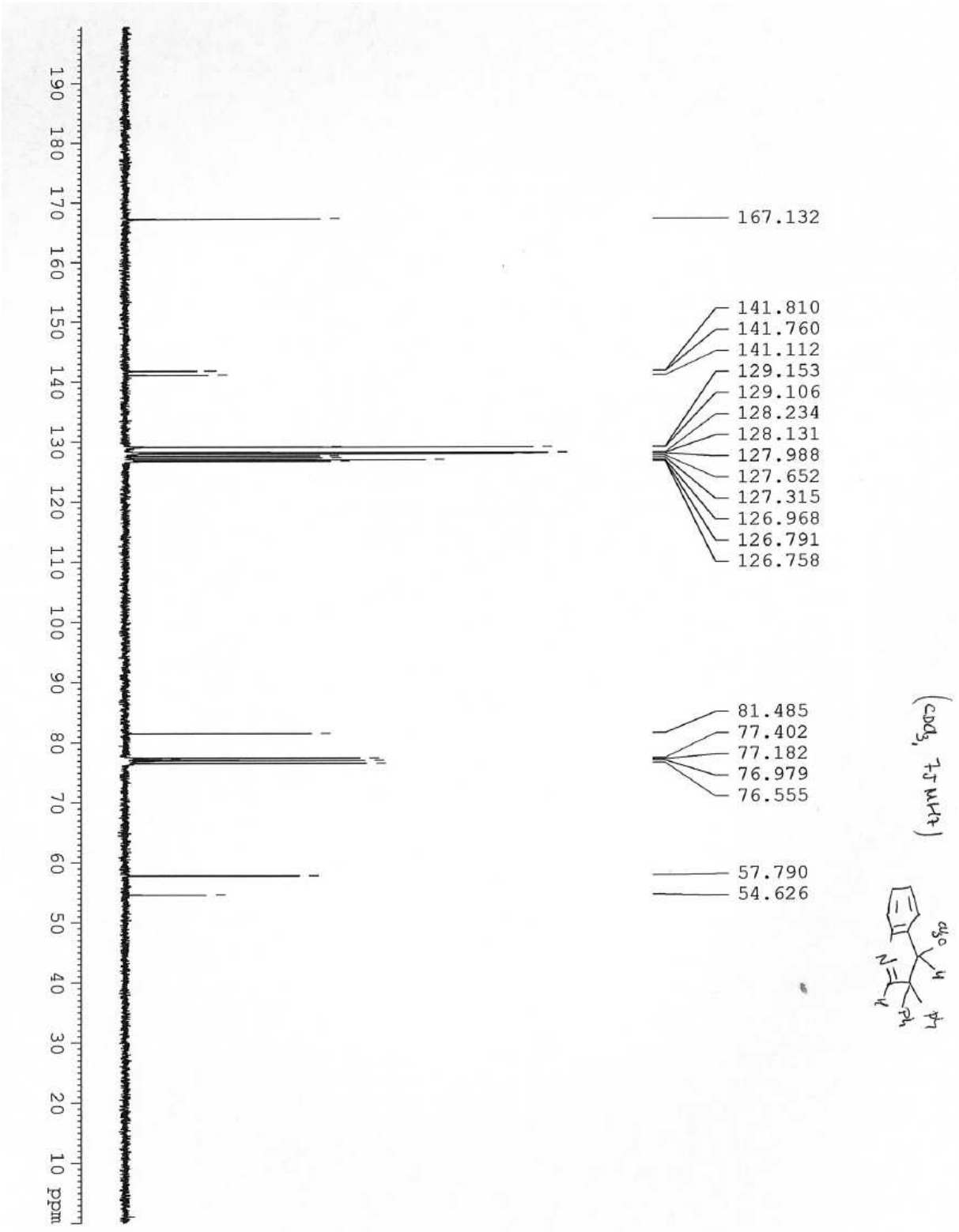
^{31}P NMR **31d**


ppm
ppm
80
60
40
20
0
-20
-40
-60
-80
0.8313
0.5306
0.2175
(CDCl3, H3PO4, 161.9 MHz)
Cy
OEt
N=PPh3

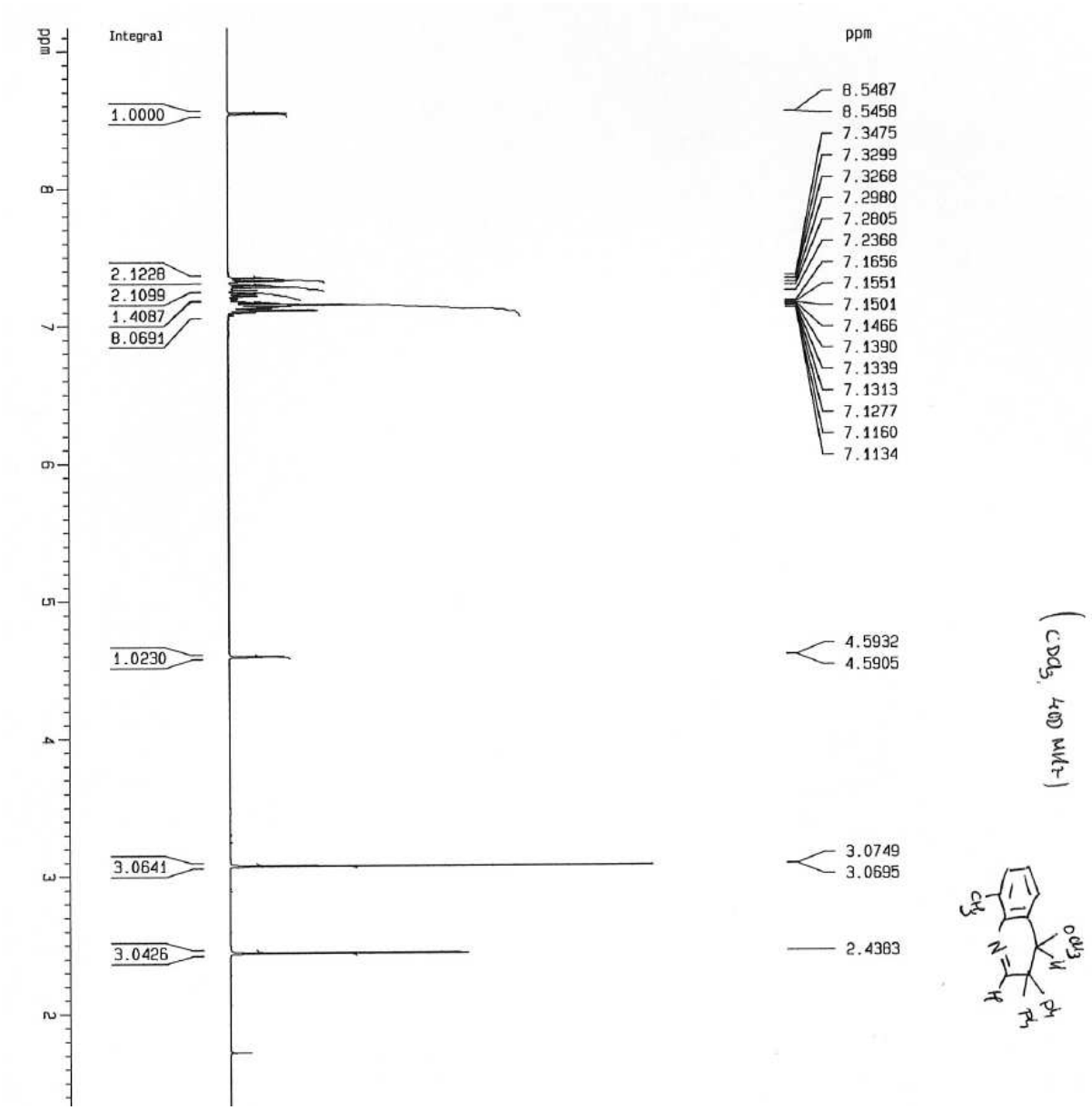
^{1}H NMR **34a**


8.516
7.389
7.366
7.357
7.350
7.343
7.326
7.324
7.306
7.304
7.284
7.264
7.258
7.251
7.245
7.239
7.234
7.222
7.212
7.200
7.198
7.193
7.175
7.159
7.153
7.142
7.140
7.133
7.129
4.651
3.090
0.957
1.551
3.056
1.881
8.045
1.000
2.979
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
(CDCl3, 300 MHz)

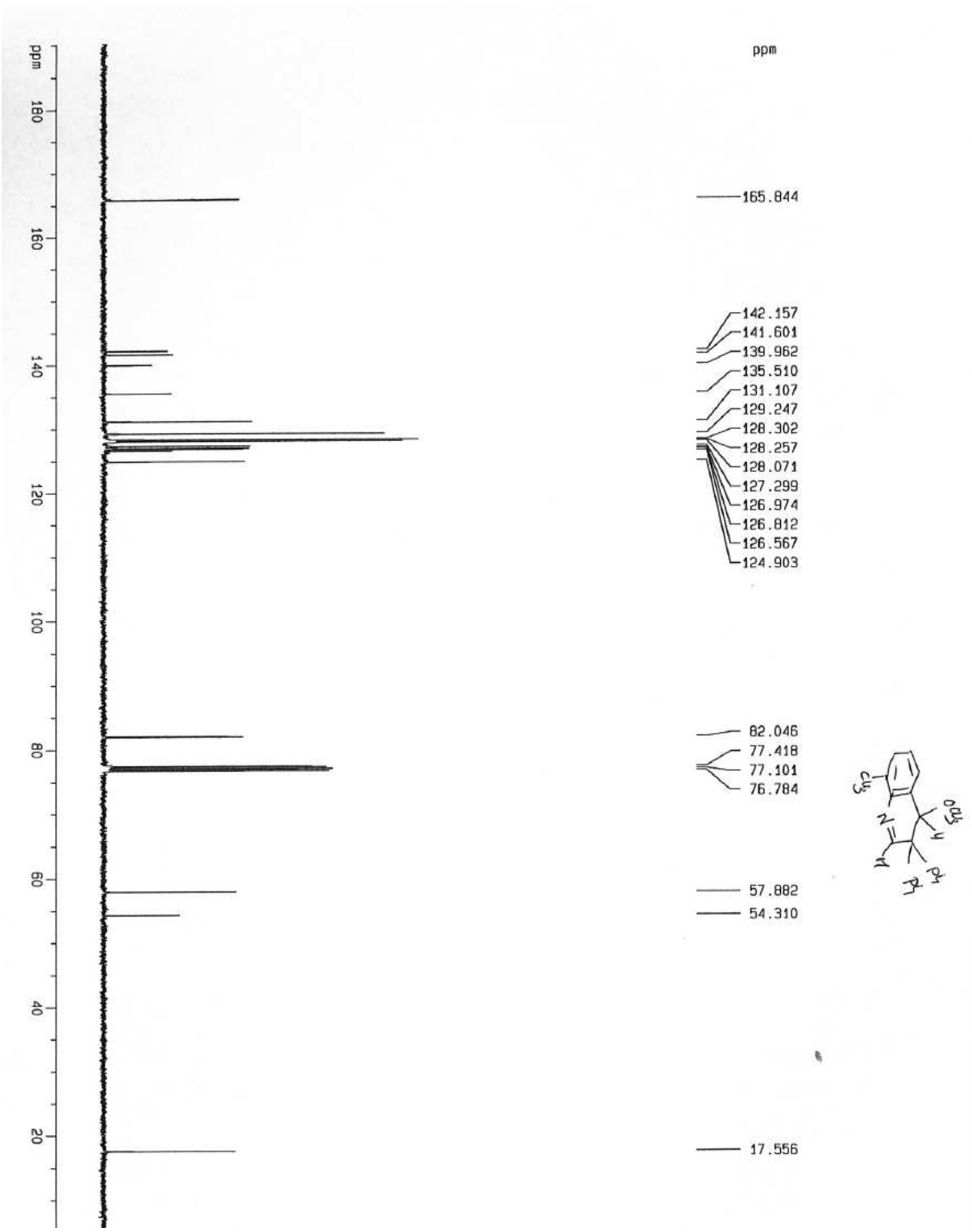
^{13}C NMR **34a**



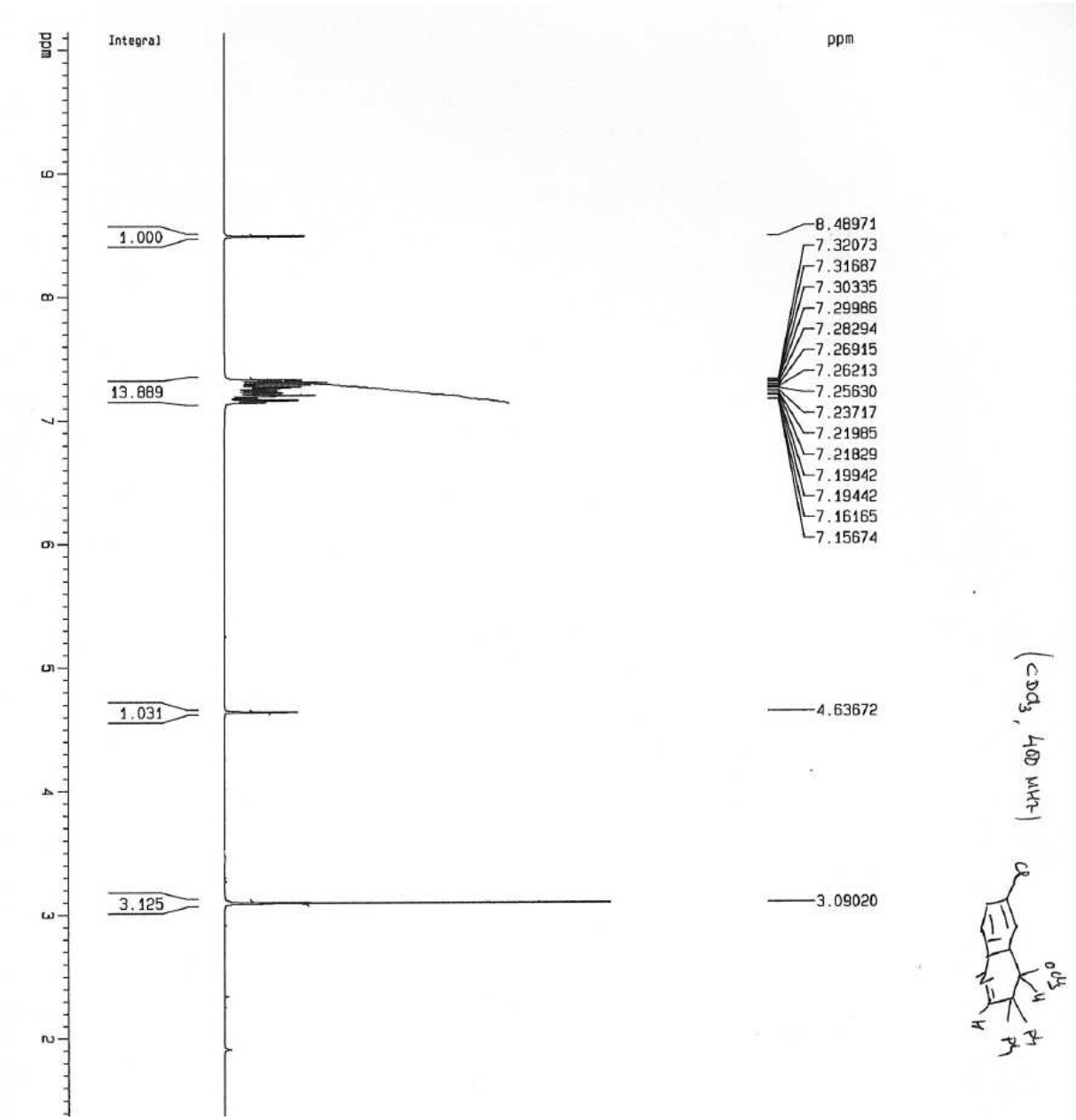
^{1}H NMR **34b**


Integral
ppm
1.0000
2.1228
2.1099
1.4087
8.0691
1.0230
3.0641
3.0426
8.5487
8.5458
7.3475
7.3299
7.3268
7.2980
7.2805
7.2368
7.1656
7.1551
7.1501
7.1466
7.1390
7.1339
7.1313
7.1277
7.1160
7.1134
4.5932
4.5905
3.0749
3.0695
2.4383
CDCl3, 400 MHz

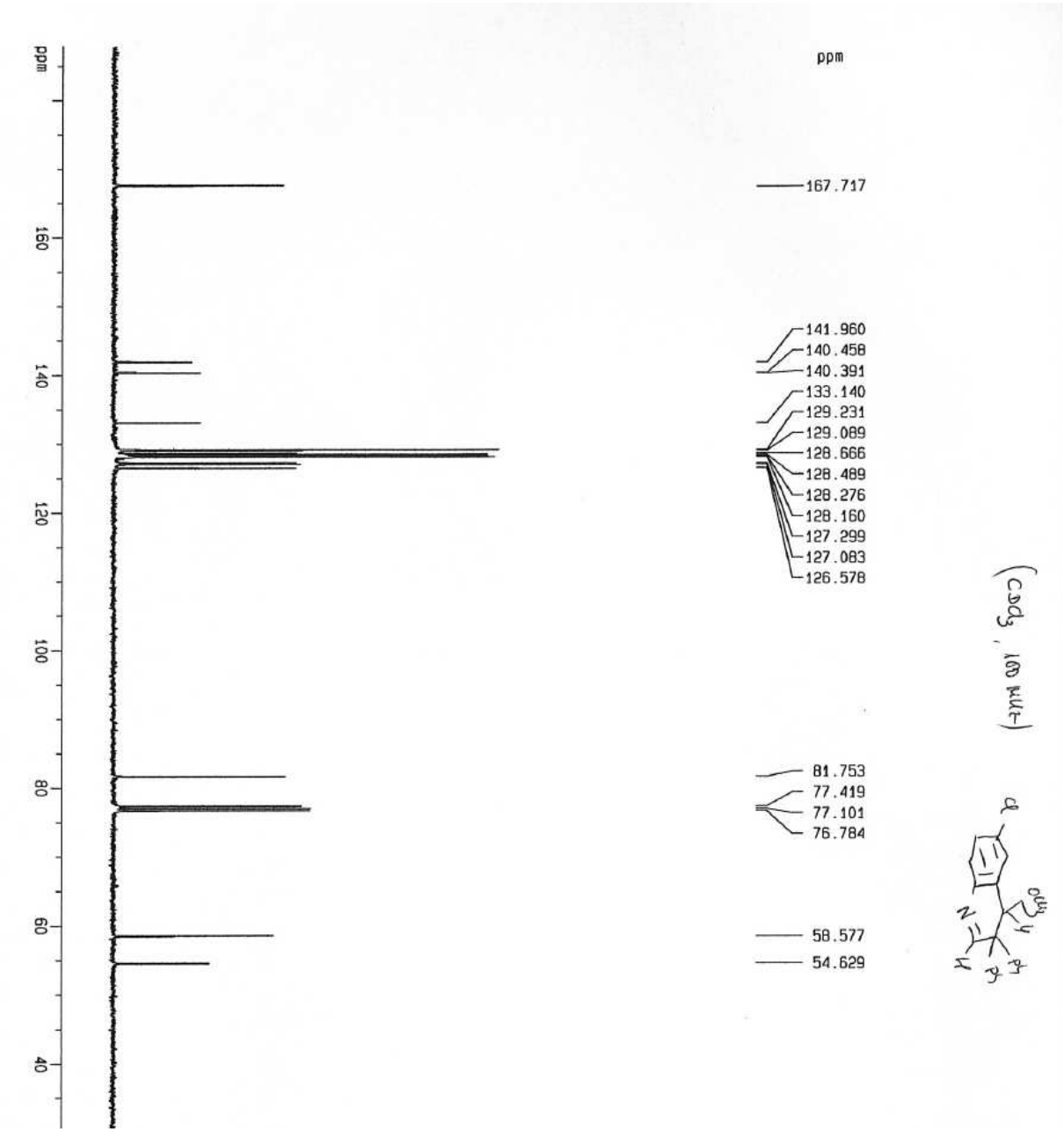
^{13}C NMR **34b**


ppm
180
160
140
120
100
80
60
40
20
ppm
165.844
142.157
141.601
139.962
135.510
131.107
129.247
128.302
128.257
128.071
127.299
126.974
126.812
126.567
124.903
82.046
77.418
77.101
76.784
57.882
54.310
17.556

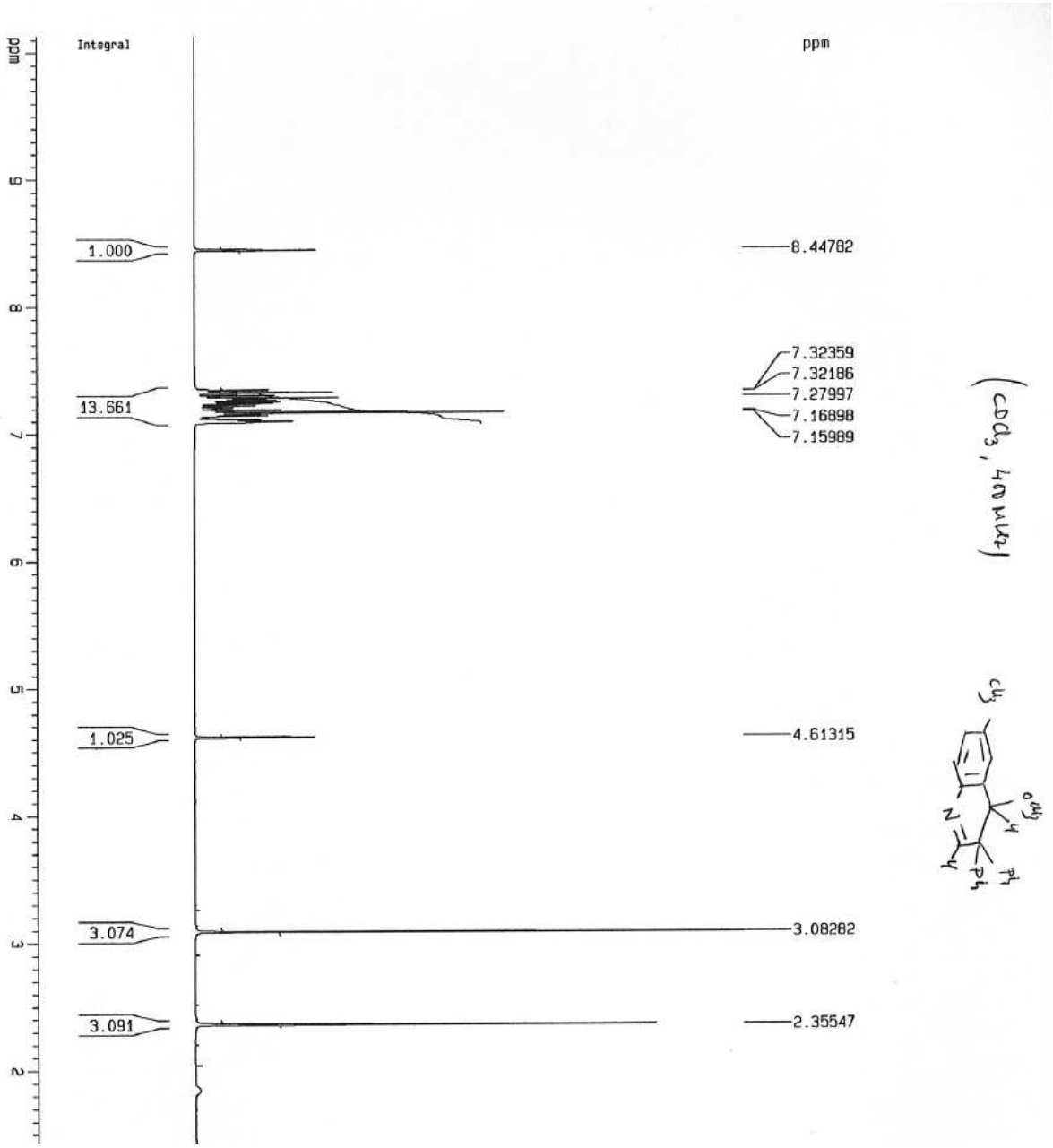
^{1}H NMR **34c**


Integral
ppm
1.000
13.889
1.031
3.125
8.48971
7.32073
7.31687
7.30335
7.29986
7.28294
7.26915
7.26213
7.25630
7.23717
7.21985
7.21829
7.19942
7.19442
7.16165
7.15674
4.63672
3.09020
(CDCl3, 400 MHz)

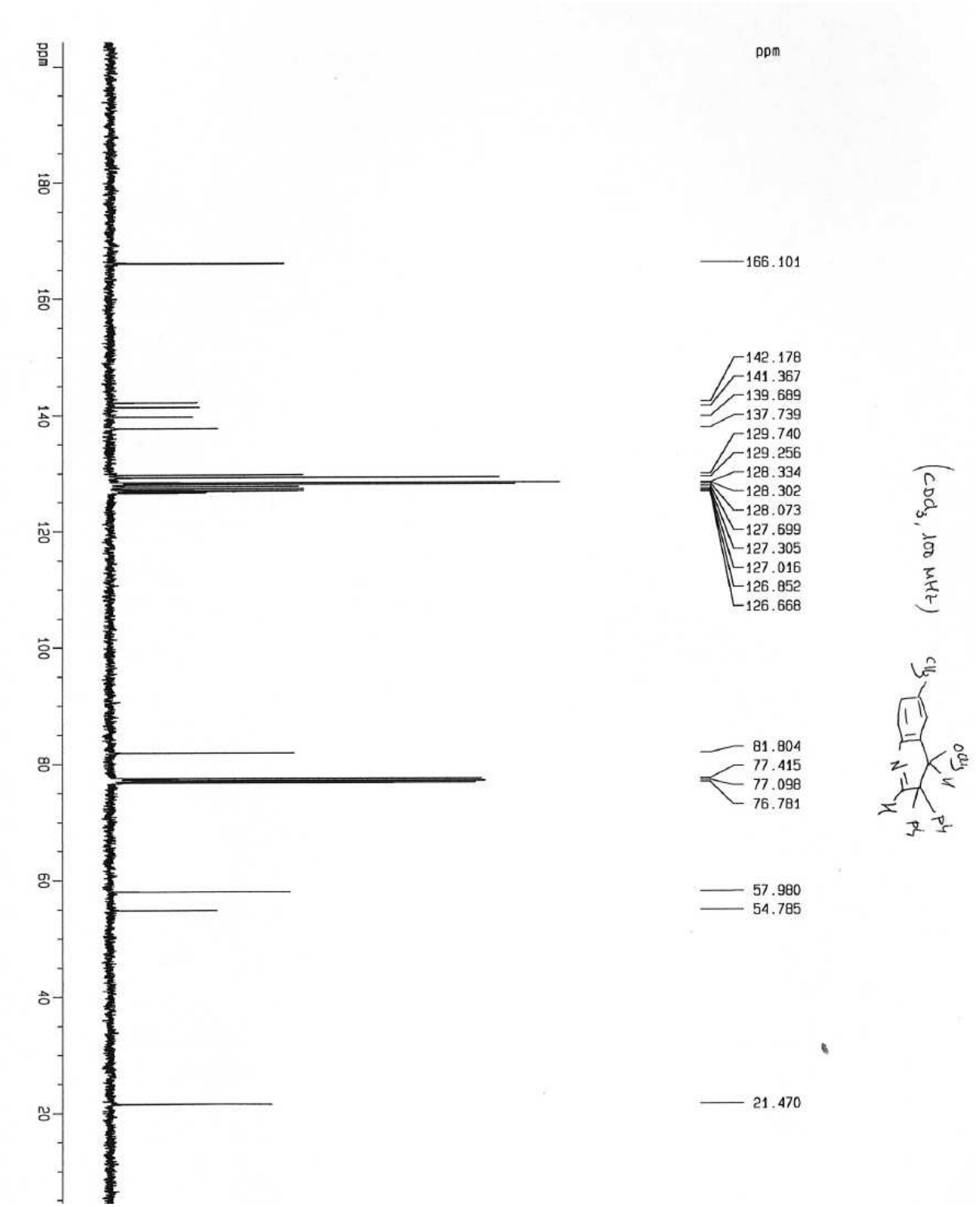
^{13}C NMR **34c**



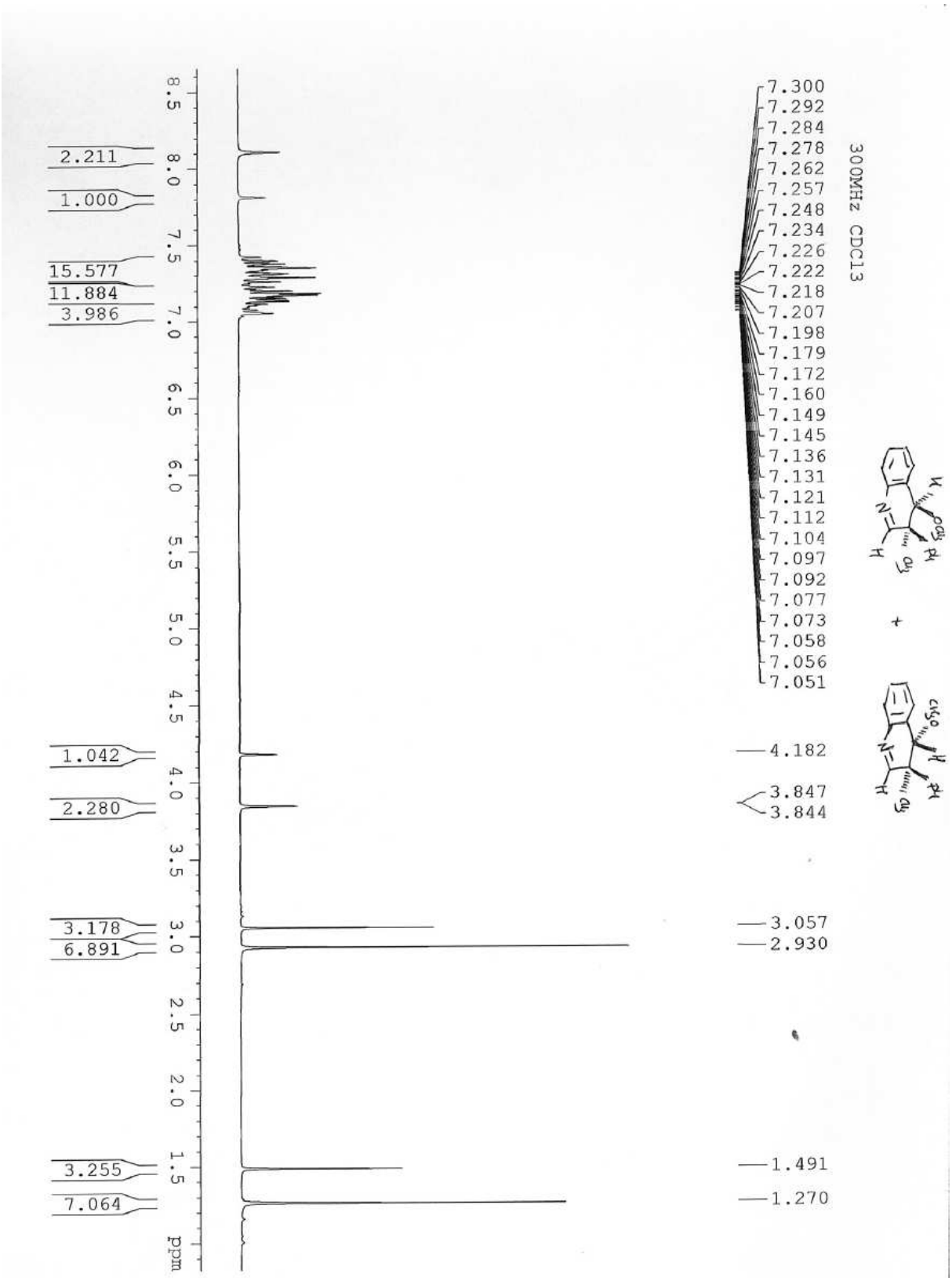
^{1}H NMR **34d**


Integral
ppm
1.000
13.661
1.025
3.074
3.091
8.44782
7.32359
7.32186
7.27997
7.16898
7.15989
4.61315
3.08282
2.35547
(CDCl3, 400 MHz)

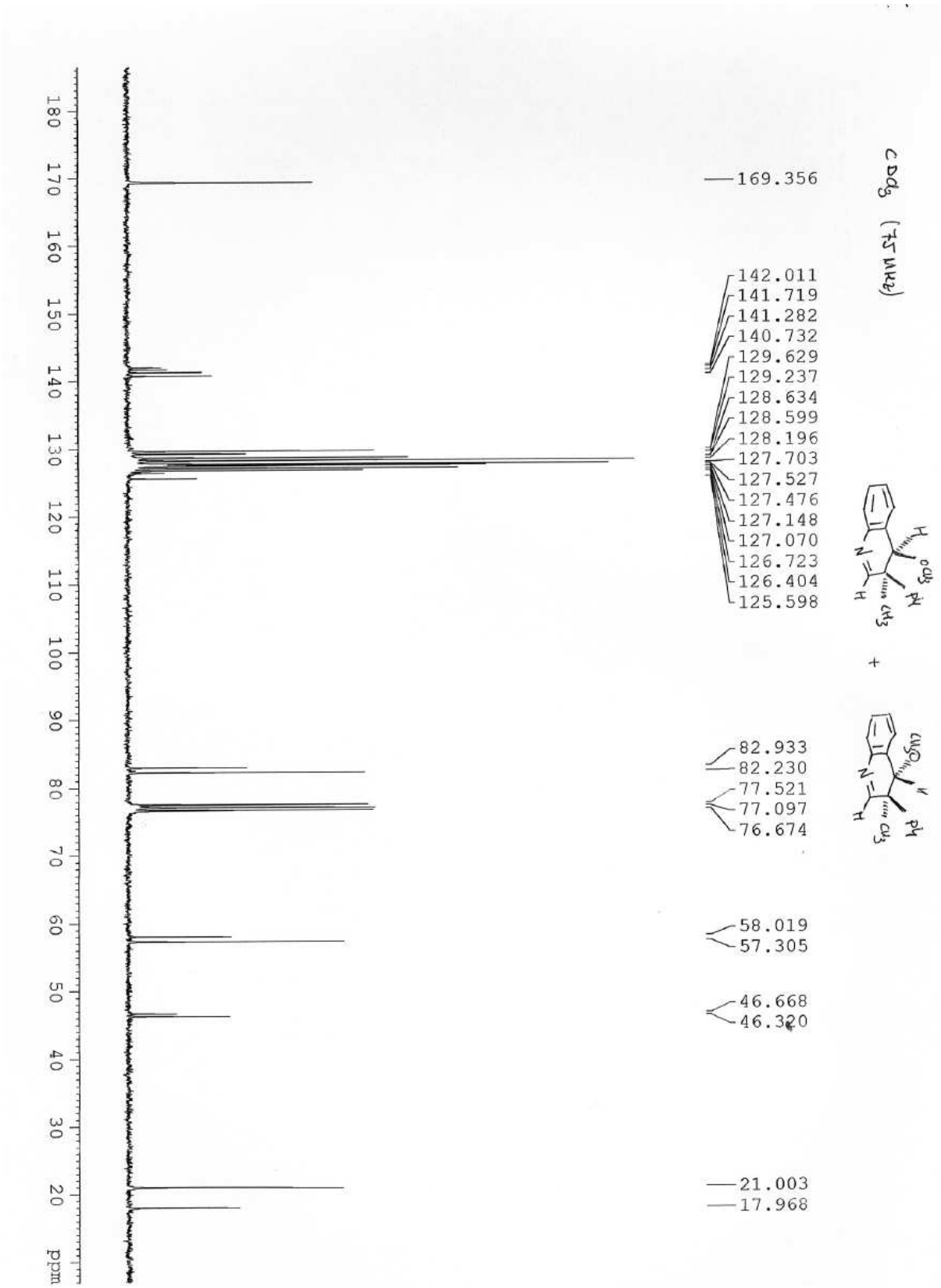
^{13}C NMR **34d**



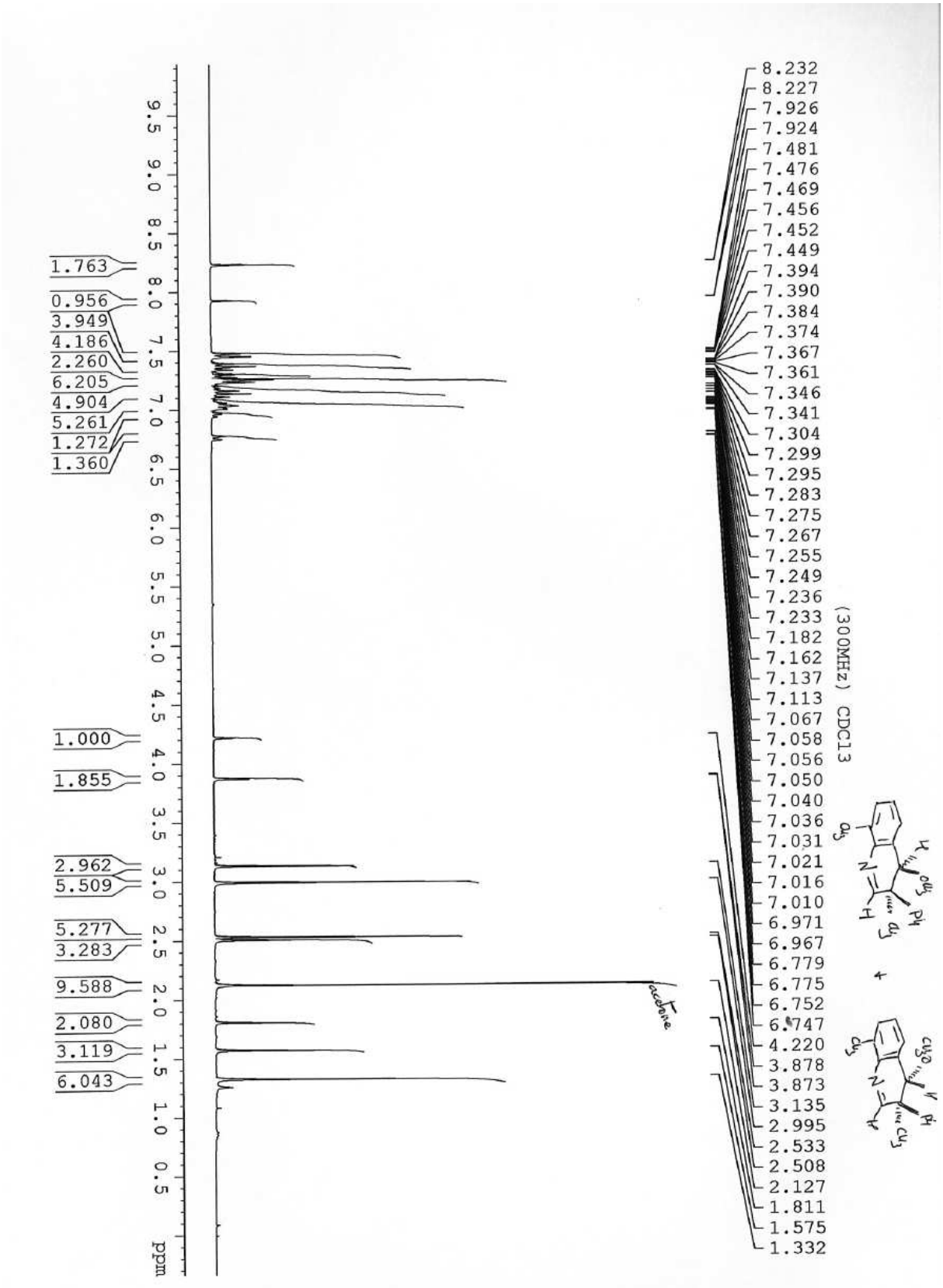
^{1}H NMR of ***cis*-34e + *trans*-34e**



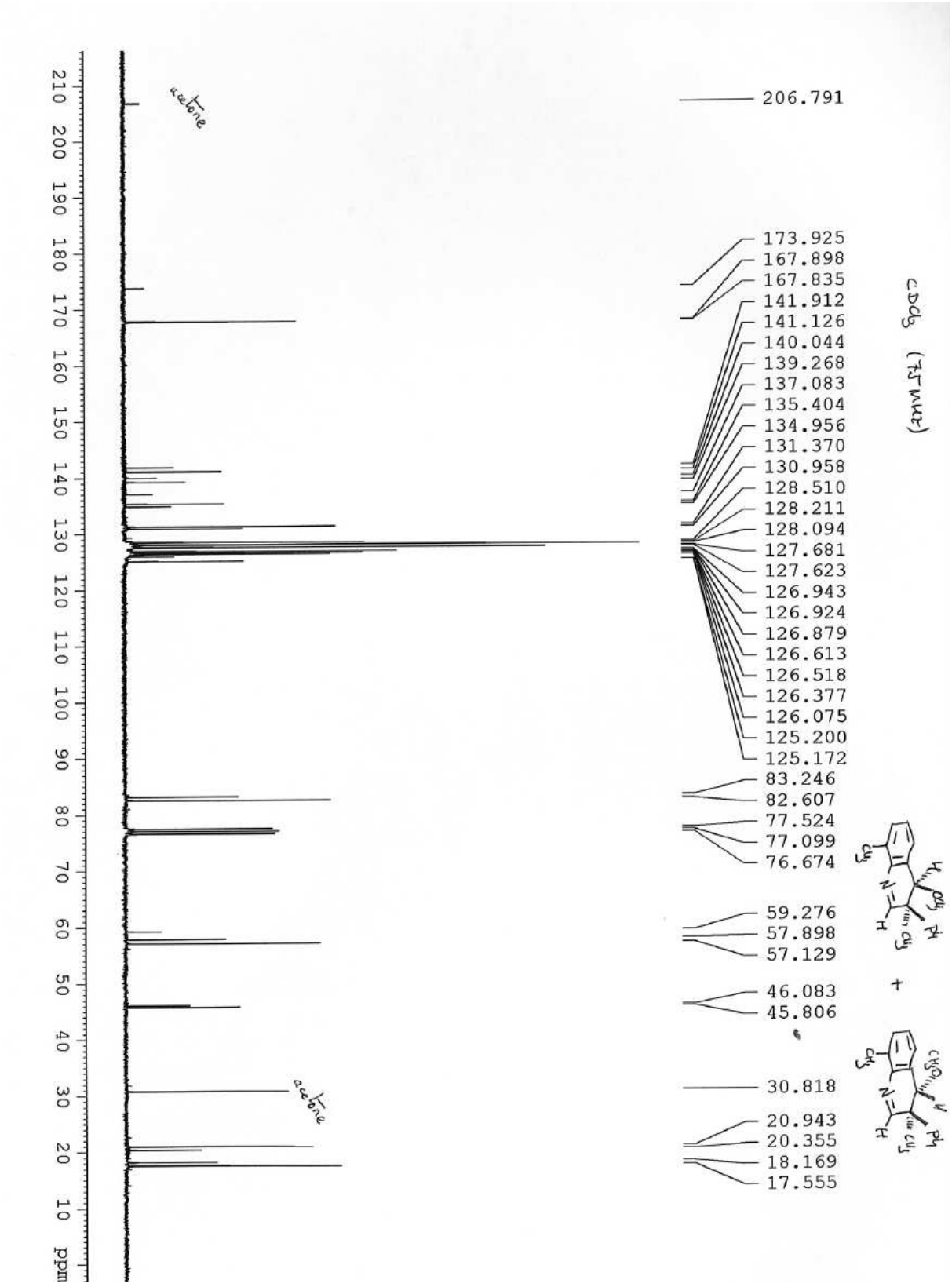
^{13}C NMR of ***cis*-34e + *trans*-34e**



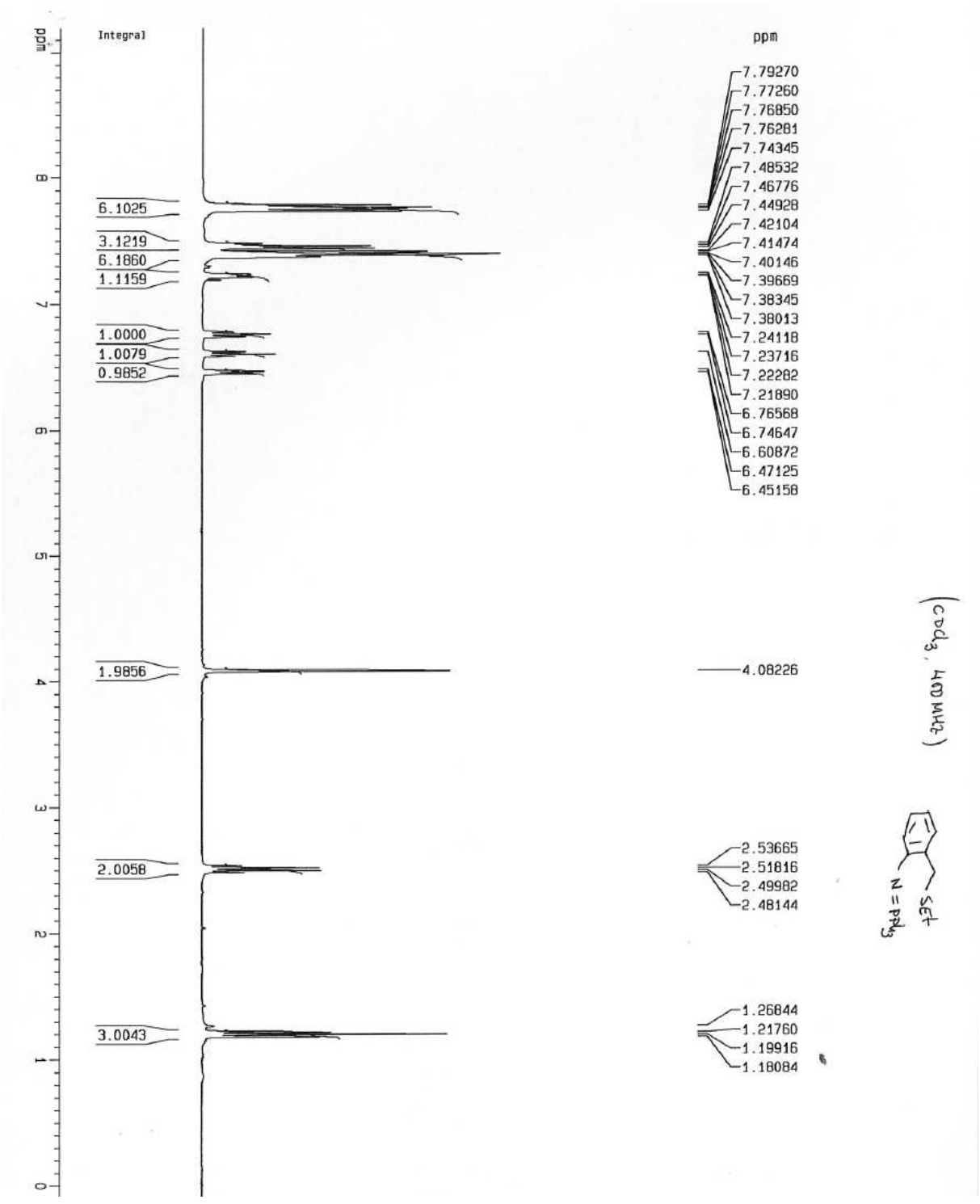
^{1}H NMR of ***cis*-34f + *trans*-34f**



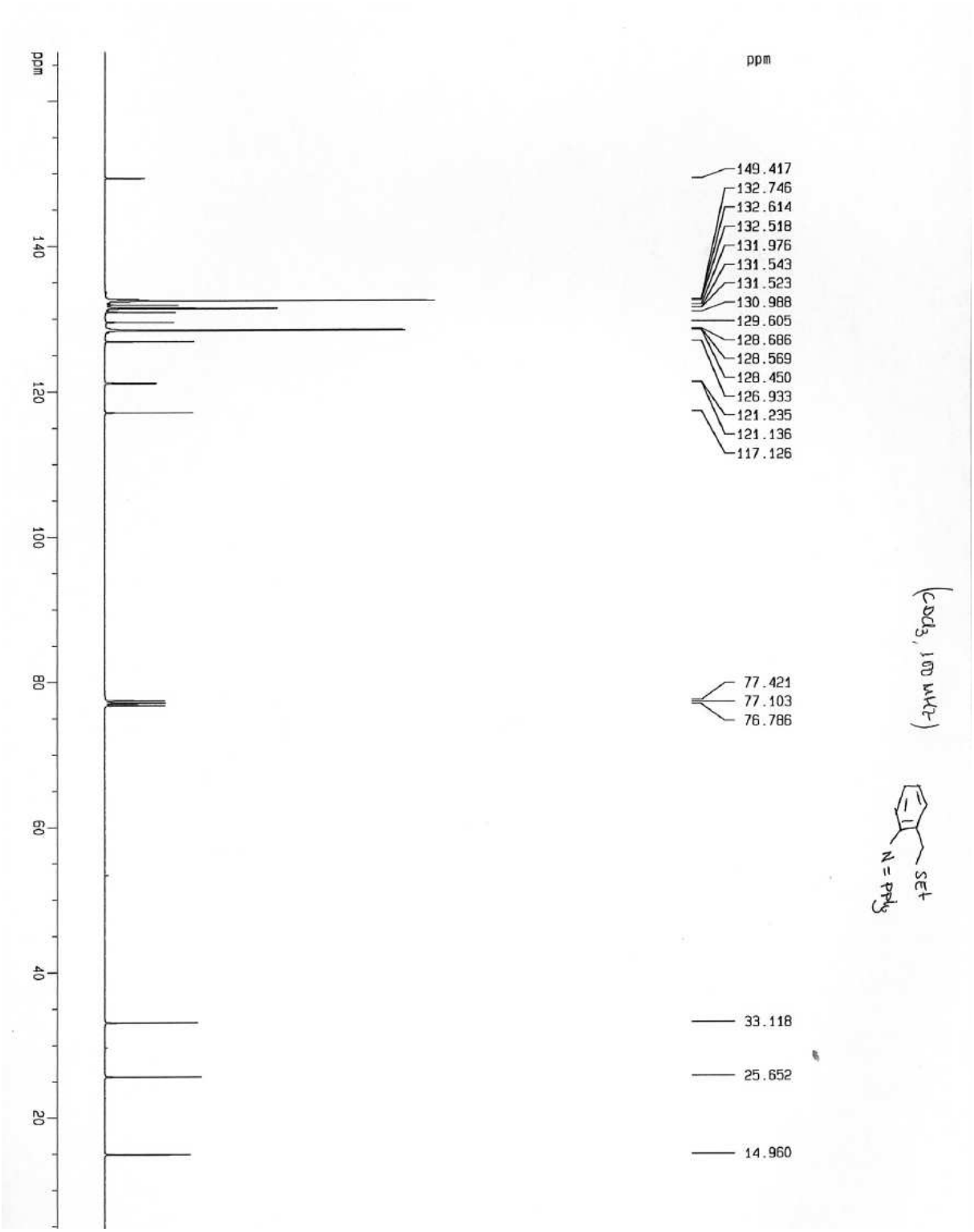
^{13}C NMR of ***cis*-34f + *trans*-34f**



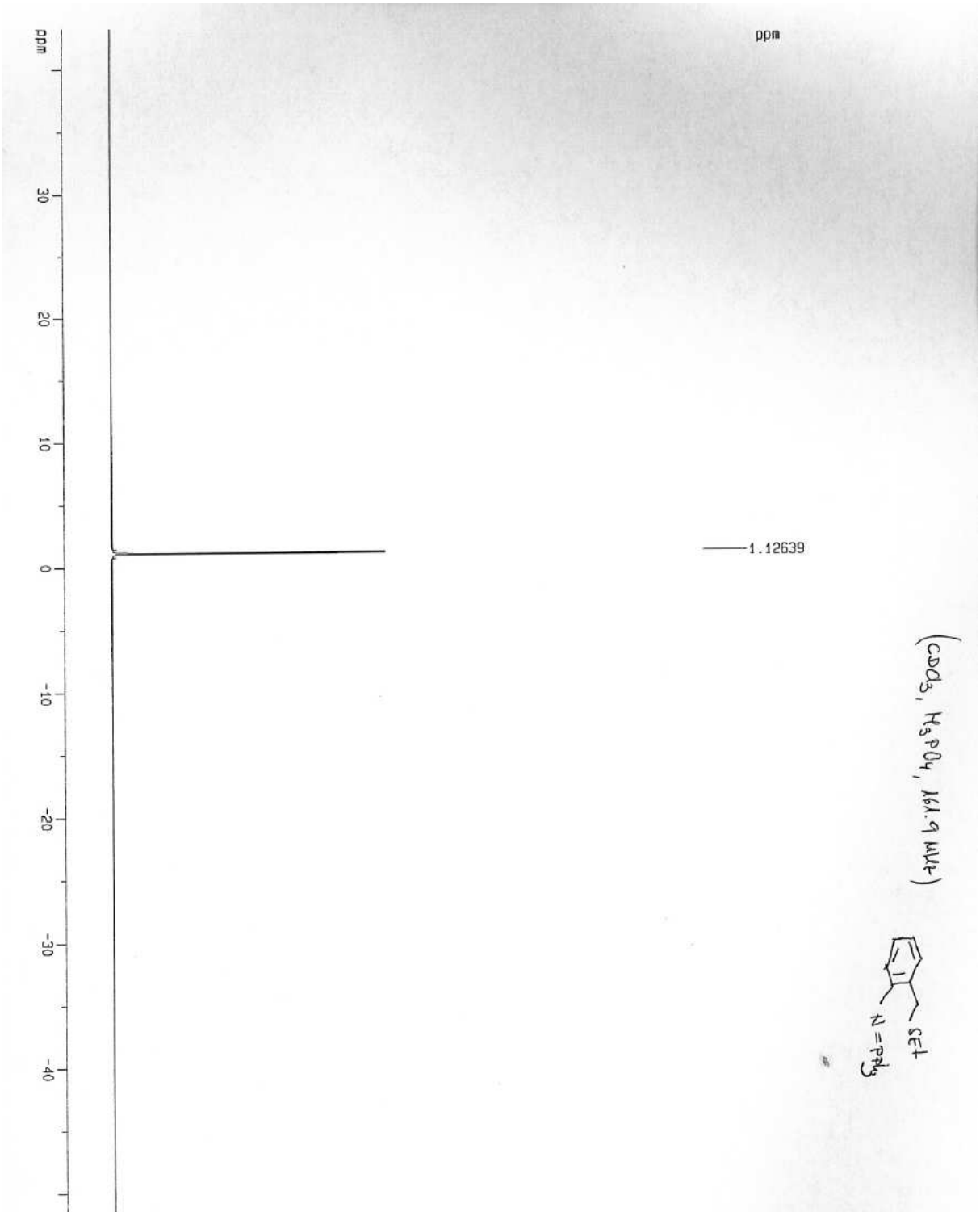
^{1}H NMR **37**


ppm
Integral
6.1025
3.1219
6.1860
1.1159
1.0000
1.0079
0.9852
1.9856
2.0058
3.0043
ppm
7.79270
7.77260
7.76850
7.76281
7.74345
7.48532
7.46776
7.44928
7.42104
7.41474
7.40146
7.39669
7.38345
7.38013
7.24118
7.23716
7.22282
7.21890
6.76568
6.74647
6.60872
6.47125
6.45158
4.08226
2.53665
2.51816
2.49982
2.48144
1.26844
1.21760
1.19916
1.18084
CDCl3, 400 MHz
SEt
N = PPh3

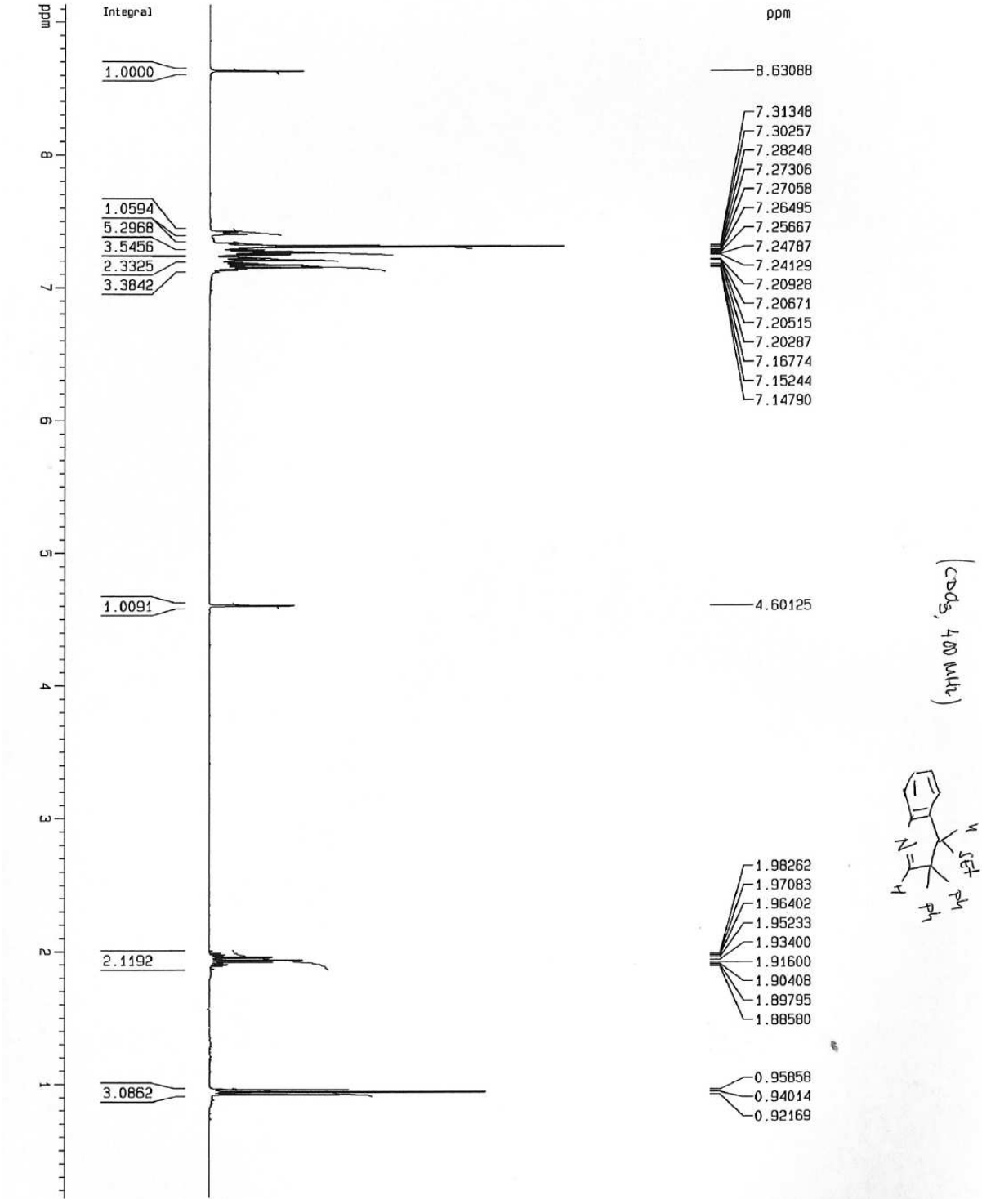
^{13}C NMR **37**



^{31}P NMR **37**


ppm
ppm
30
20
10
0
-10
-20
-30
-40
1.12639
(CDCl3, H3PO4, 161.9 MHz)
SET
N=PPh3

^{1}H NMR **39**


ppm
Integral
1.0000
1.0594
5.2968
3.5456
2.3325
3.3842
1.0091
2.1192
3.0862
8.63088
7.31348
7.30257
7.28248
7.27306
7.27058
7.26495
7.25667
7.24787
7.24129
7.20928
7.20671
7.20515
7.20287
7.16774
7.15244
7.14790
4.60125
1.98262
1.97083
1.96402
1.95233
1.93400
1.91600
1.90408
1.89795
1.88580
0.95858
0.94014
0.92169
(CDCl3, 400 MHz)

^{13}C NMR **39**