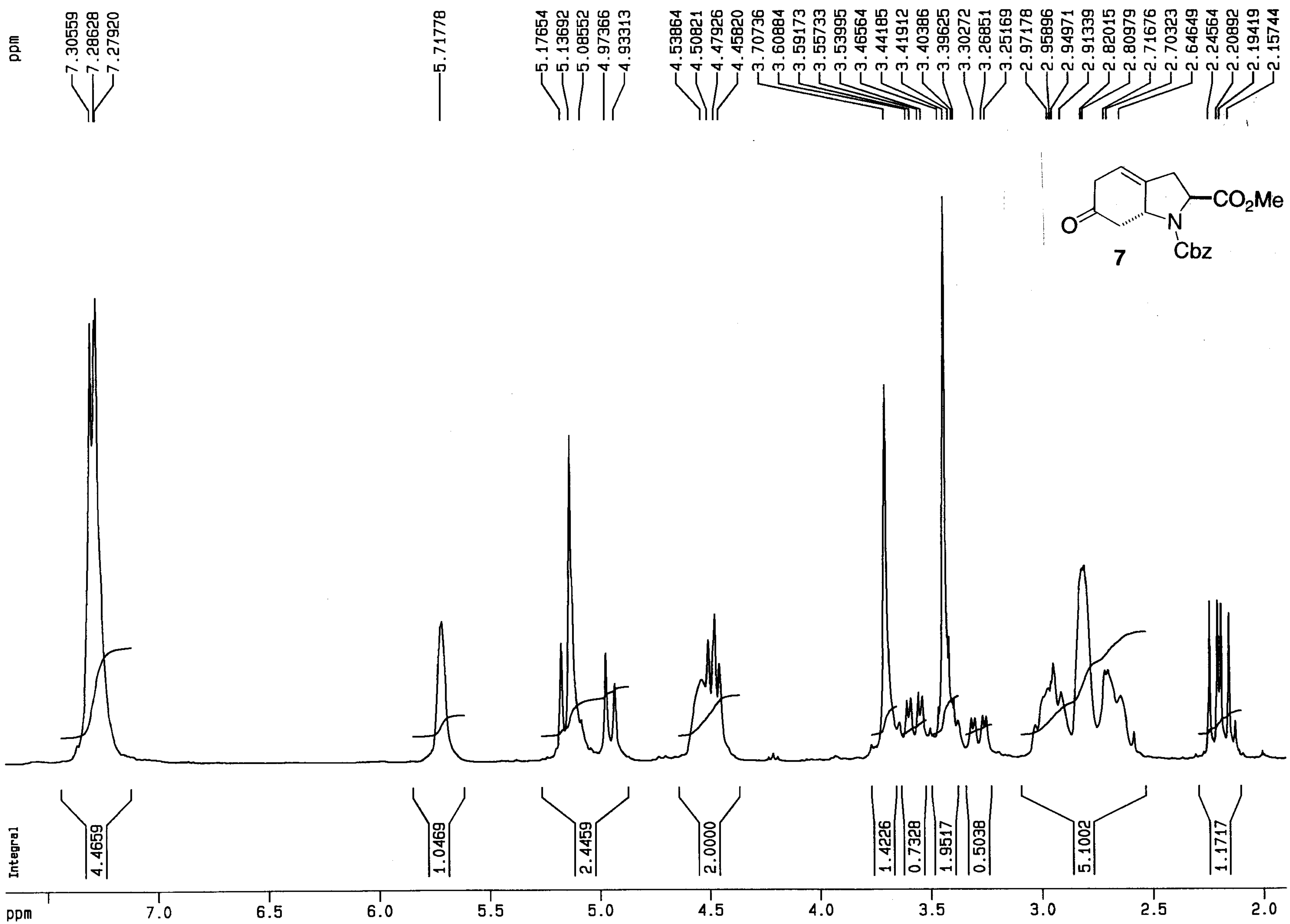
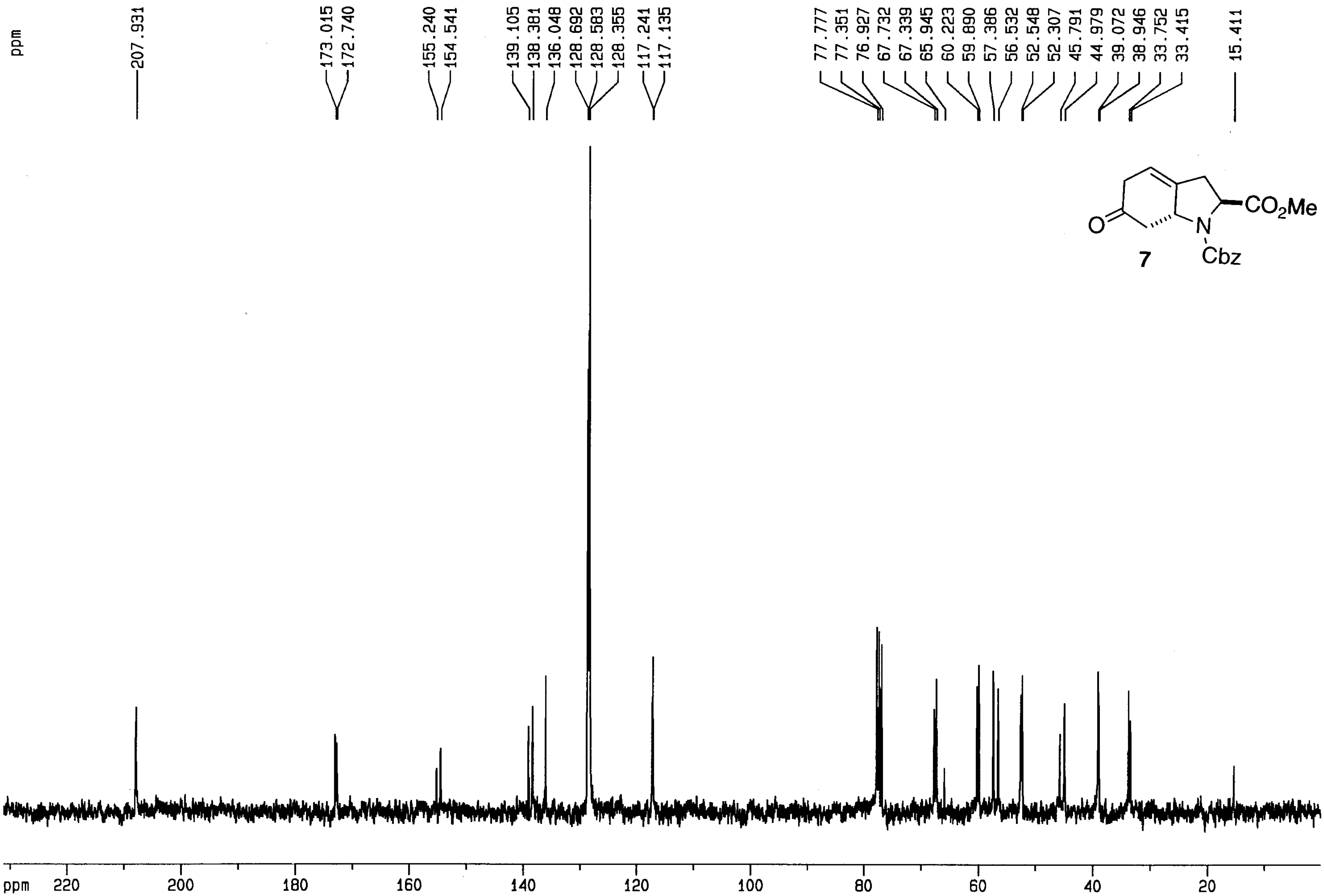
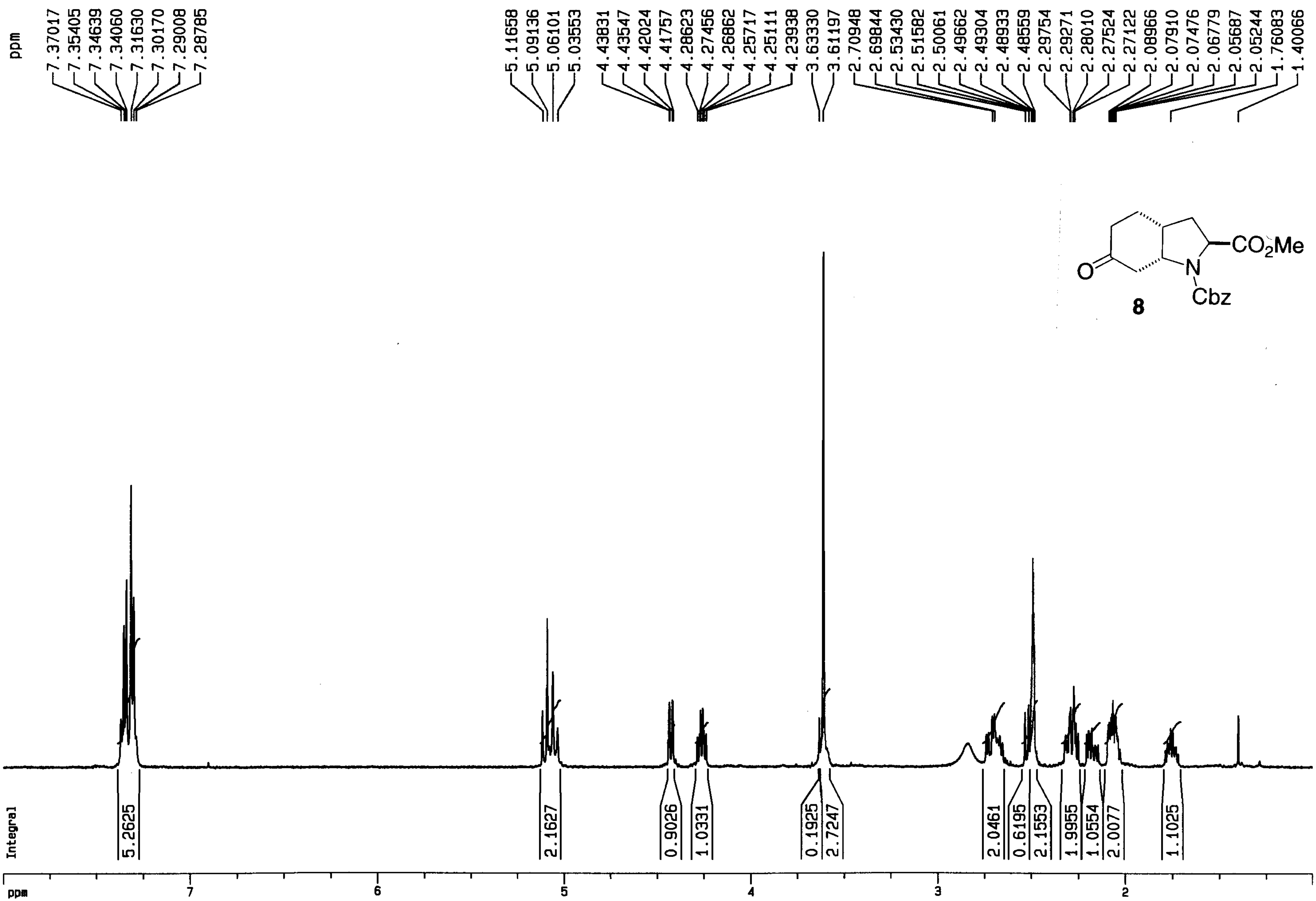
Zn Reduction - CDCl3



Zn Reduction - CDCl3

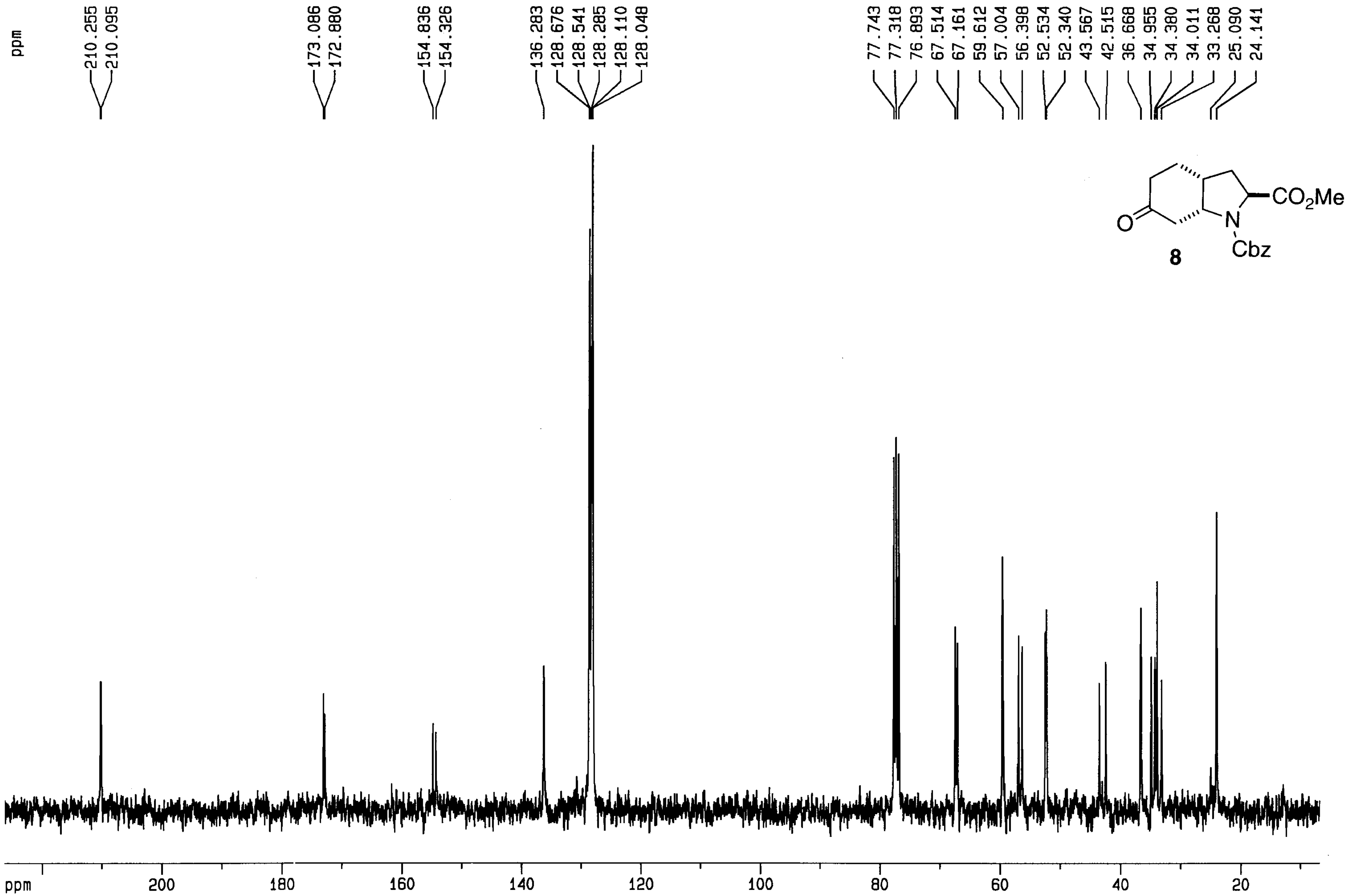


H2/PtO2 (route I) 500 MHz DMSO-d6 380 K

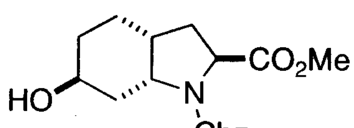


8

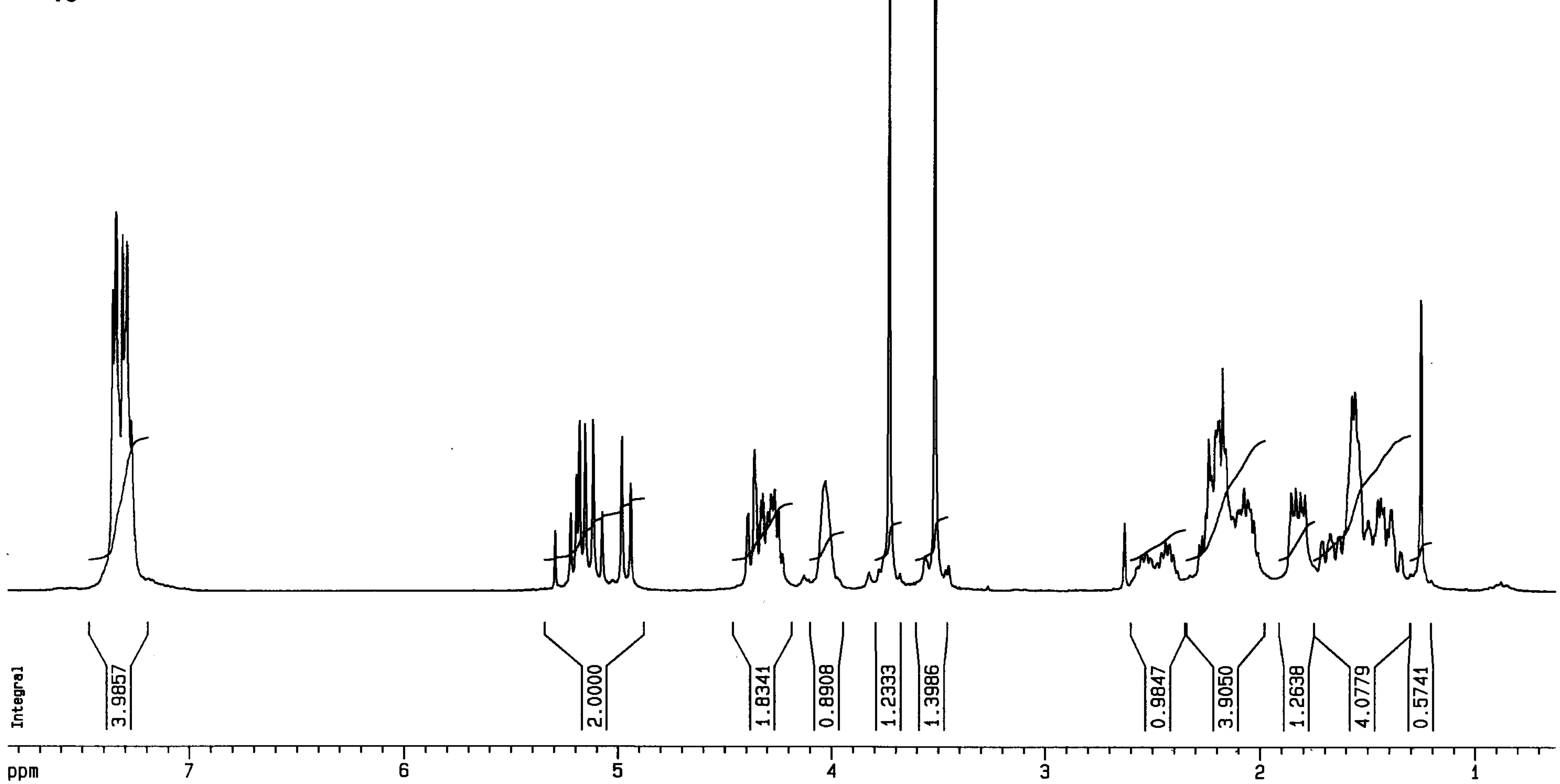
PtO2 Hydrogenation RT/CDCl3

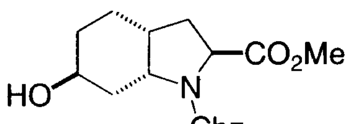


8

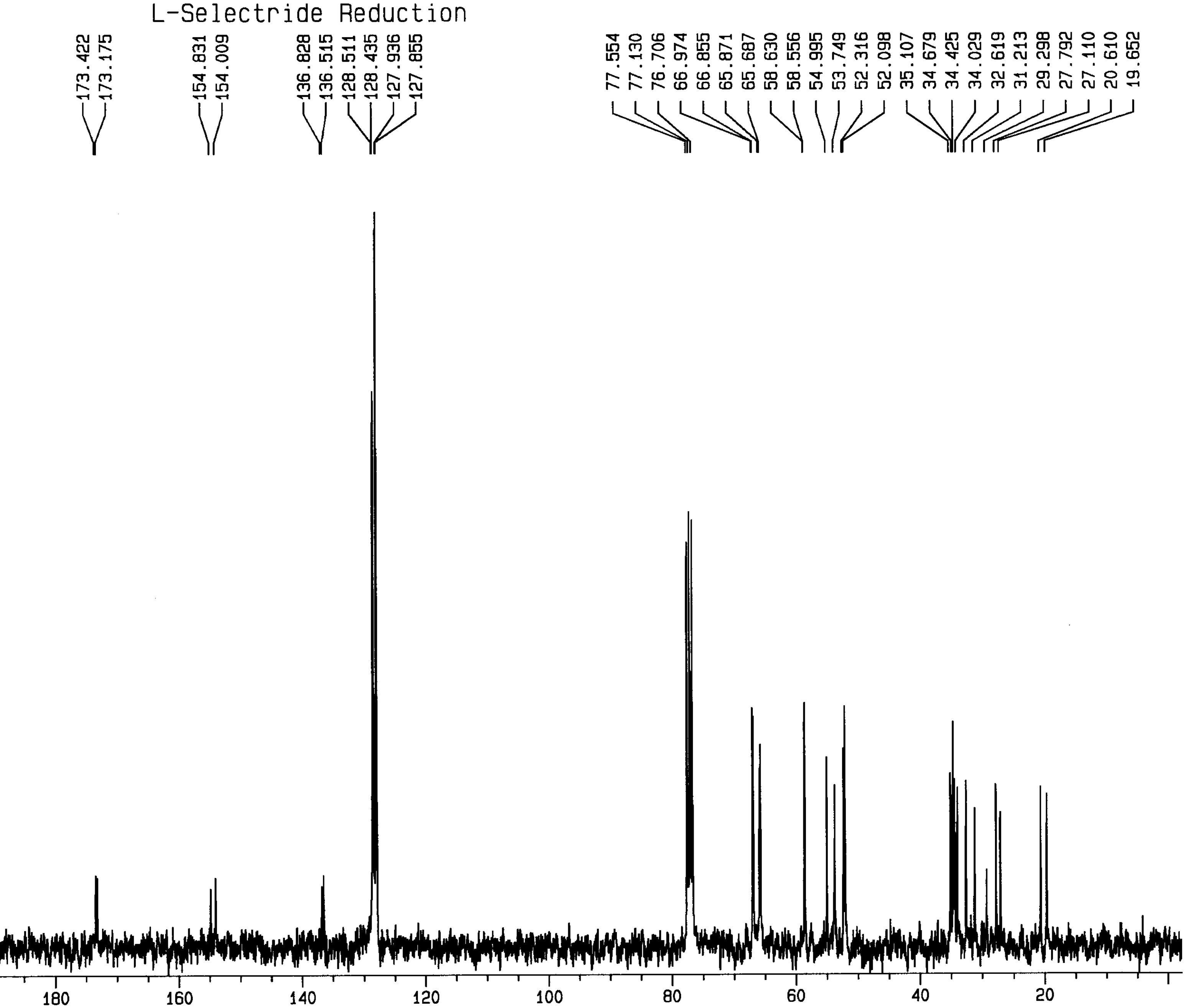


10

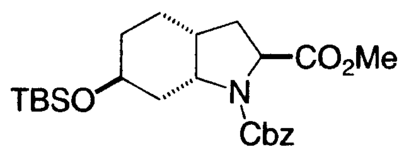

L-Selectride Reduction
ppm
7.35724
7.34279
7.31225
7.29135
7.27124
5.29421
5.22194
5.19490
5.18027
5.15386
5.11693
5.07518
4.98277
4.94161
4.39049
4.36115
4.33072
4.32133
4.29765
4.28420
4.26649
4.24774
4.22825
4.02839
3.72931
3.56352
3.51637
2.63119
2.44010
2.42197
2.23892
2.22643
2.20749
2.19481
2.19163
2.17501
2.16043
2.07659
2.05796
1.85594
1.83491
1.81320
1.79246
1.57354
1.55999
1.54484
1.45455
1.44080
1.42536
1.39126
1.25428
Integral
3.9857
2.0000
1.8341
0.8908
1.2333
1.3986
0.9847
3.9050
1.2638
4.0779
0.5741
ppm
7
6
5
4
3
2
1

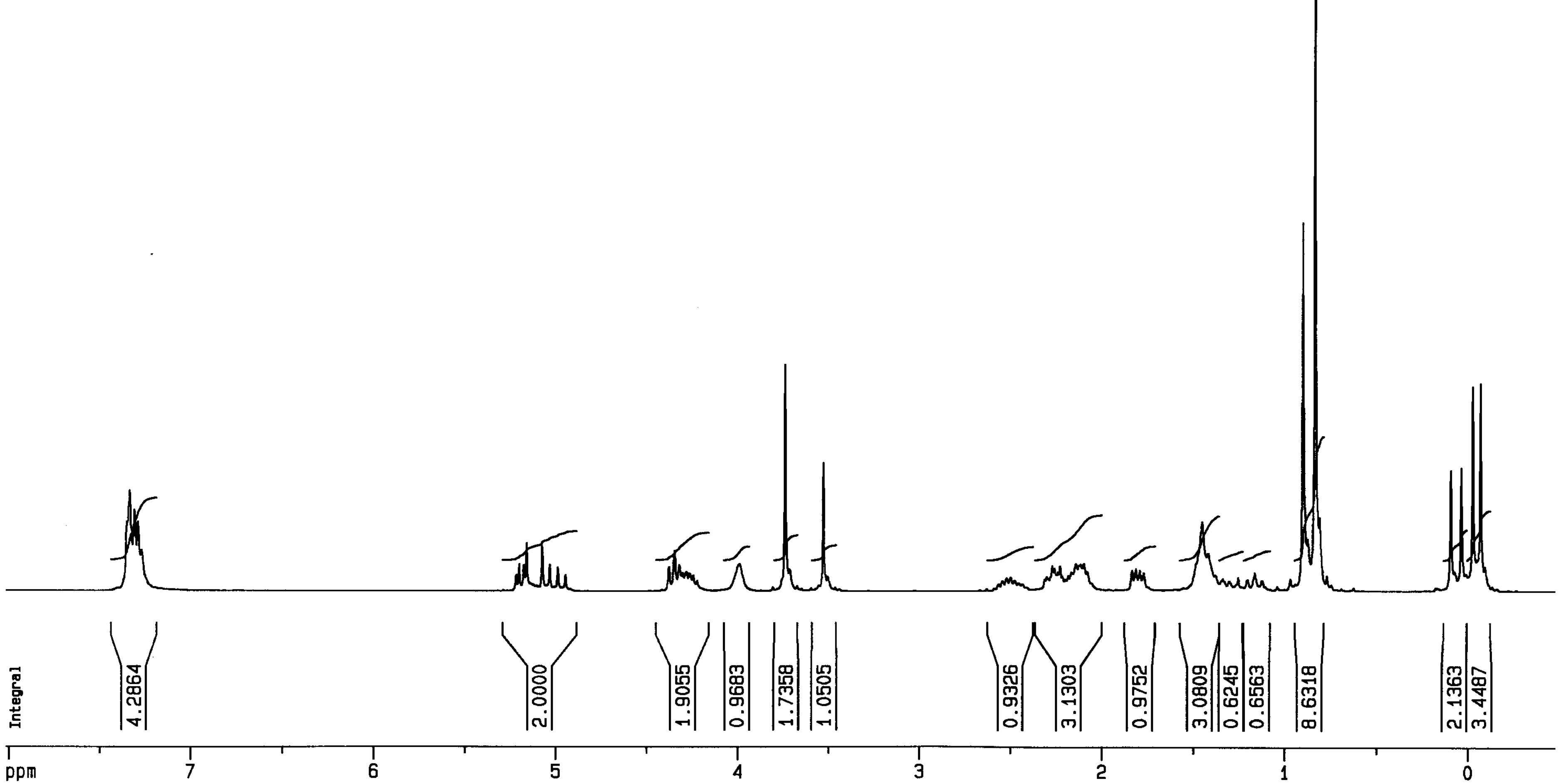

HO
N
CO2Me
Cbz

10

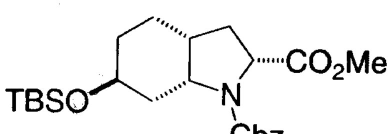

L-Selectride Reduction
ppm
173.422
173.175
154.831
154.009
136.828
136.515
128.511
128.435
127.936
127.855
77.554
77.130
76.706
66.974
66.855
65.871
65.687
58.630
58.556
54.995
53.749
52.316
52.098
35.107
34.679
34.425
34.029
32.619
31.213
29.298
27.792
27.110
20.610
19.652
ppm
200
180
160
140
120
100
80
60
40
20

TBS-ether of L-Selectride Rdn Product

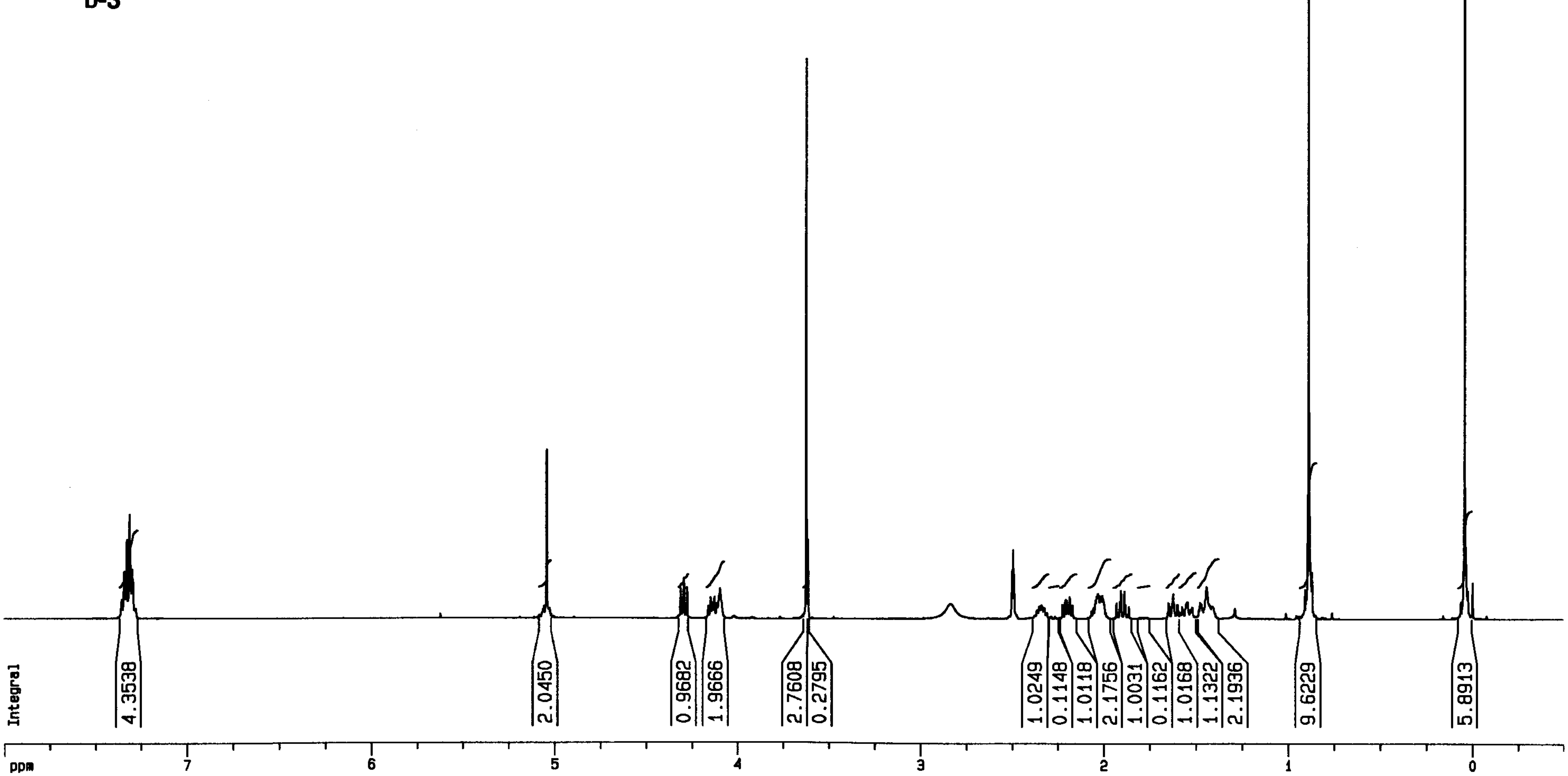




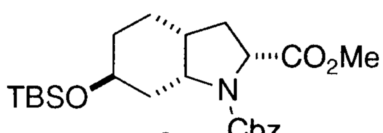
LiNEt2 Epimerization   500 MHZ DMSO-d6 380 K



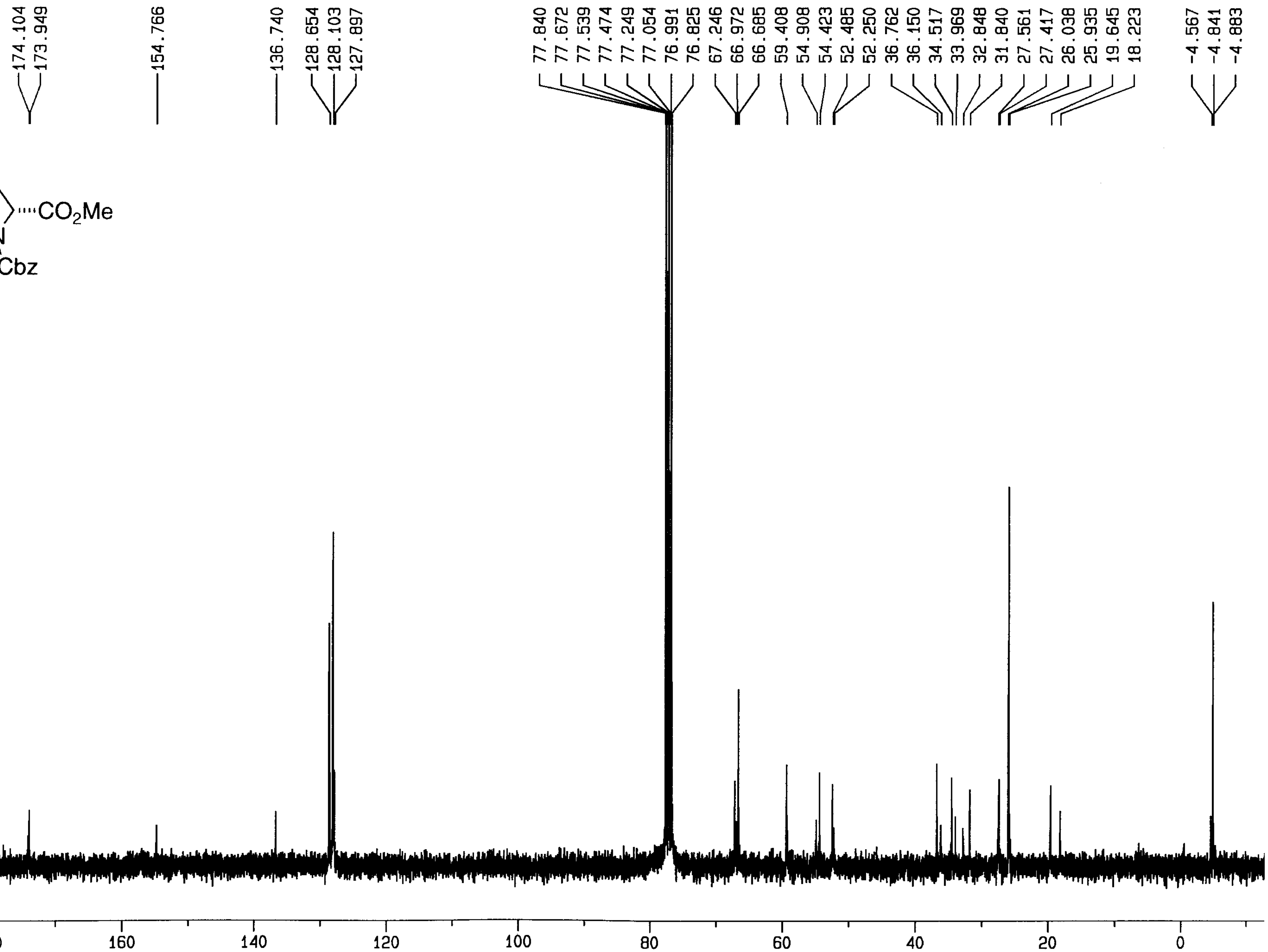
D-3



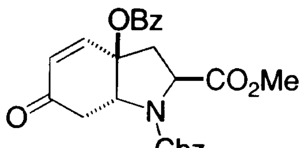
Epimerization Product (18: 1 mixture by 1H NMR, CDCl3, 300 MHz, 300K)



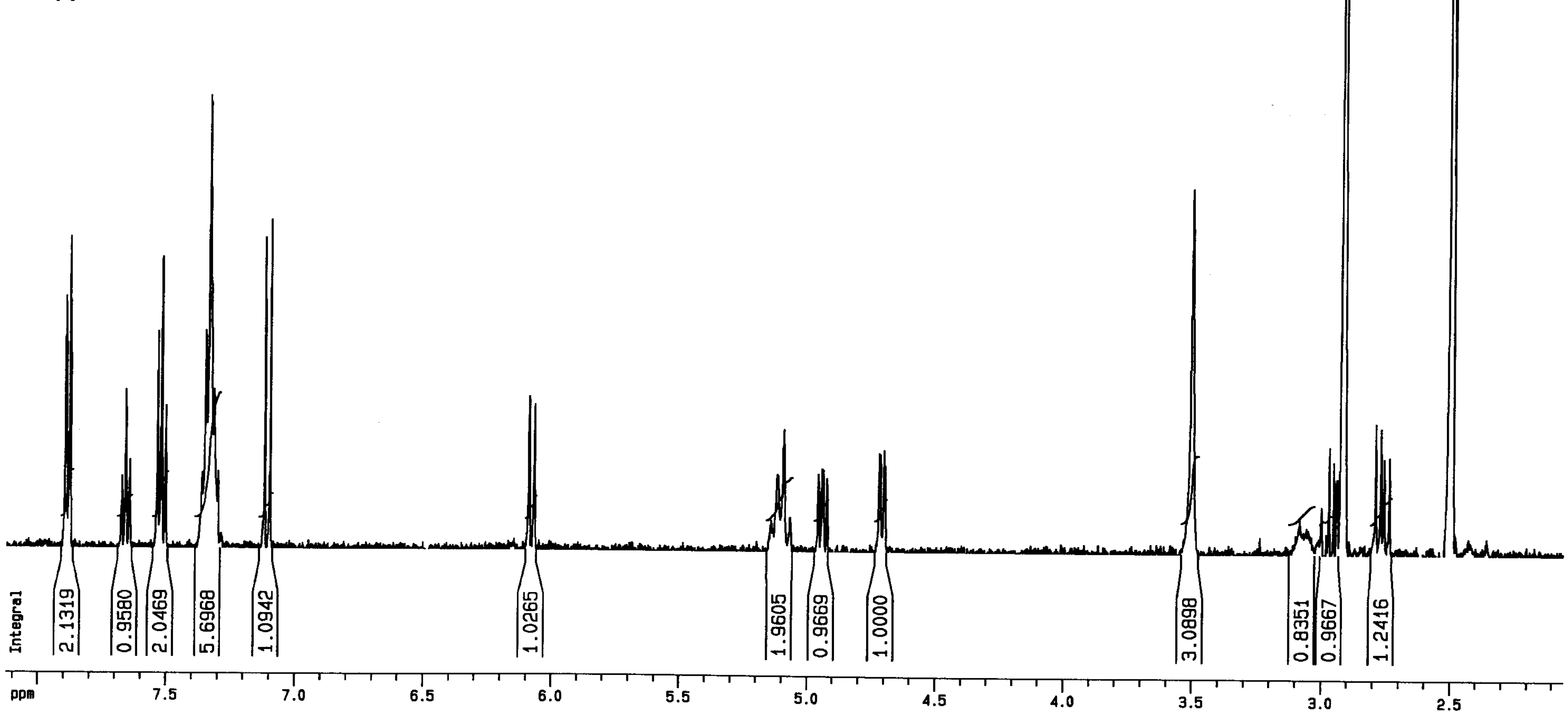
D-3



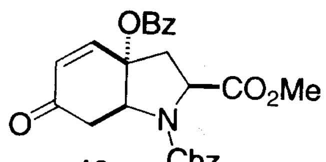
Benzoate of Hydroxyenone dmso-d6 100C 500MHz



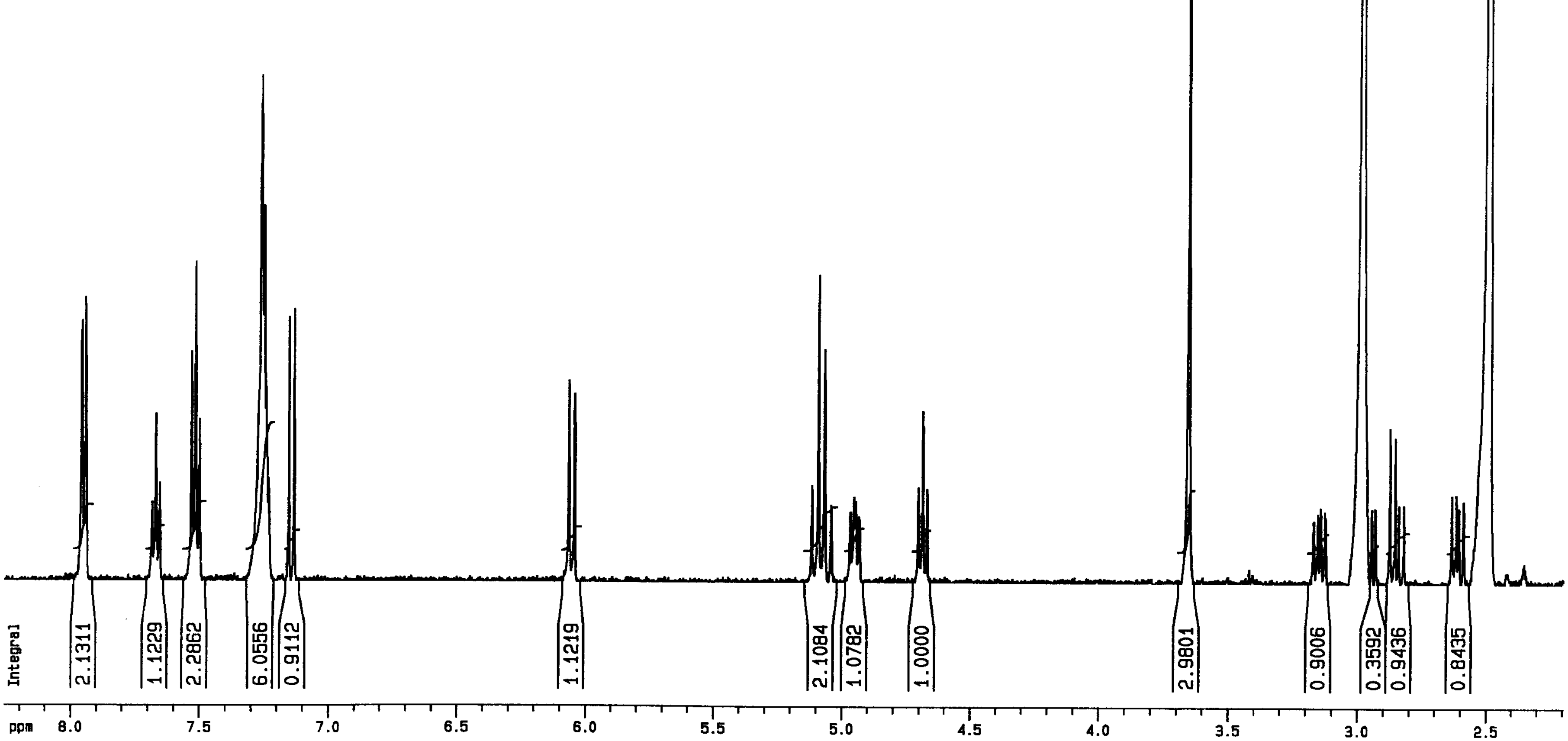
11

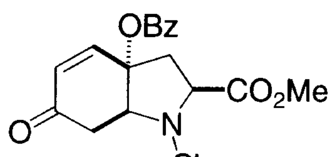


Retro-Michael Equilibration dmso-d6 90C 500MHz delay 12sec

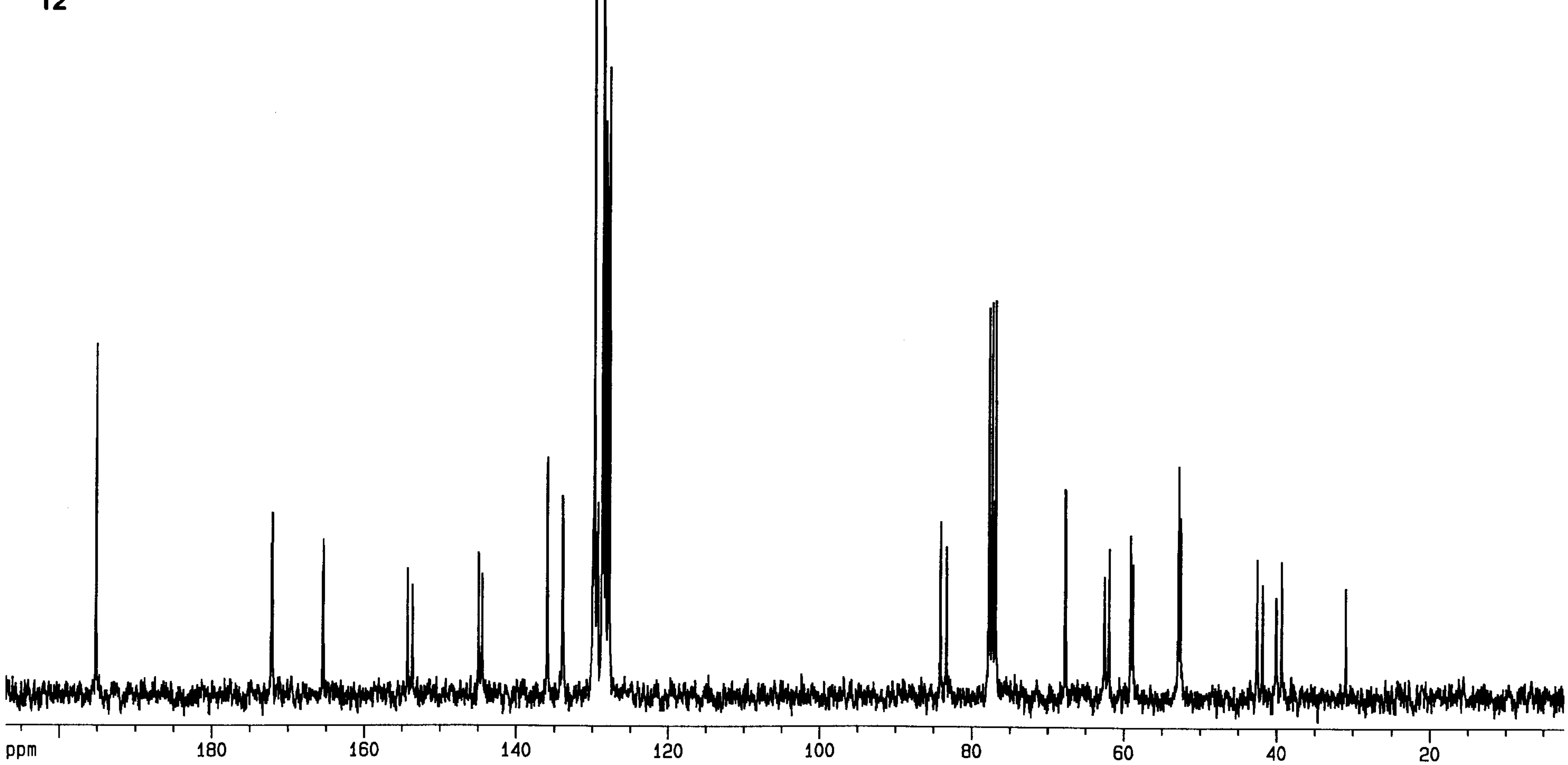


12

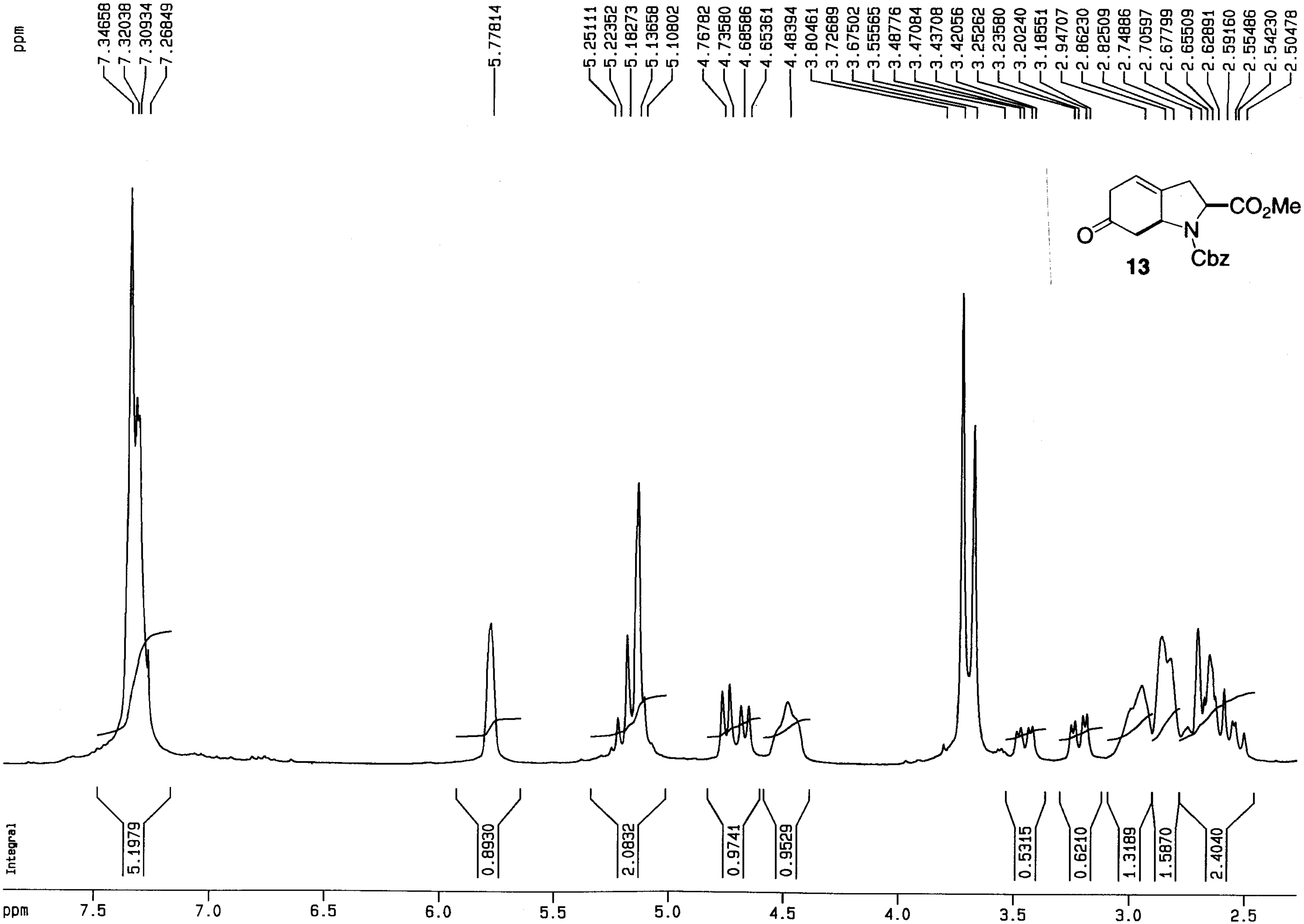



OBz
CO_2Me
N
Cbz

12

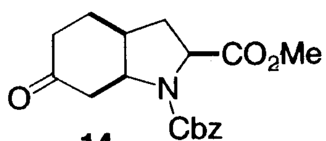

Equilibration Product (CDCl3)
ppm
195.153
172.142
172.021
165.383
154.263
153.627
144.937
144.456
135.910
133.913
129.934
129.755
129.404
129.250
128.691
128.606
128.530
128.252
127.883
127.791
84.110
83.303
77.719
77.292
76.867
67.685
62.490
61.919
59.113
58.813
52.836
52.590
42.553
41.825
40.046
39.336
30.961
ppm
180
160
140
120
100
80
60
40
20

SmI2 Reduction (CDCl3, rt)

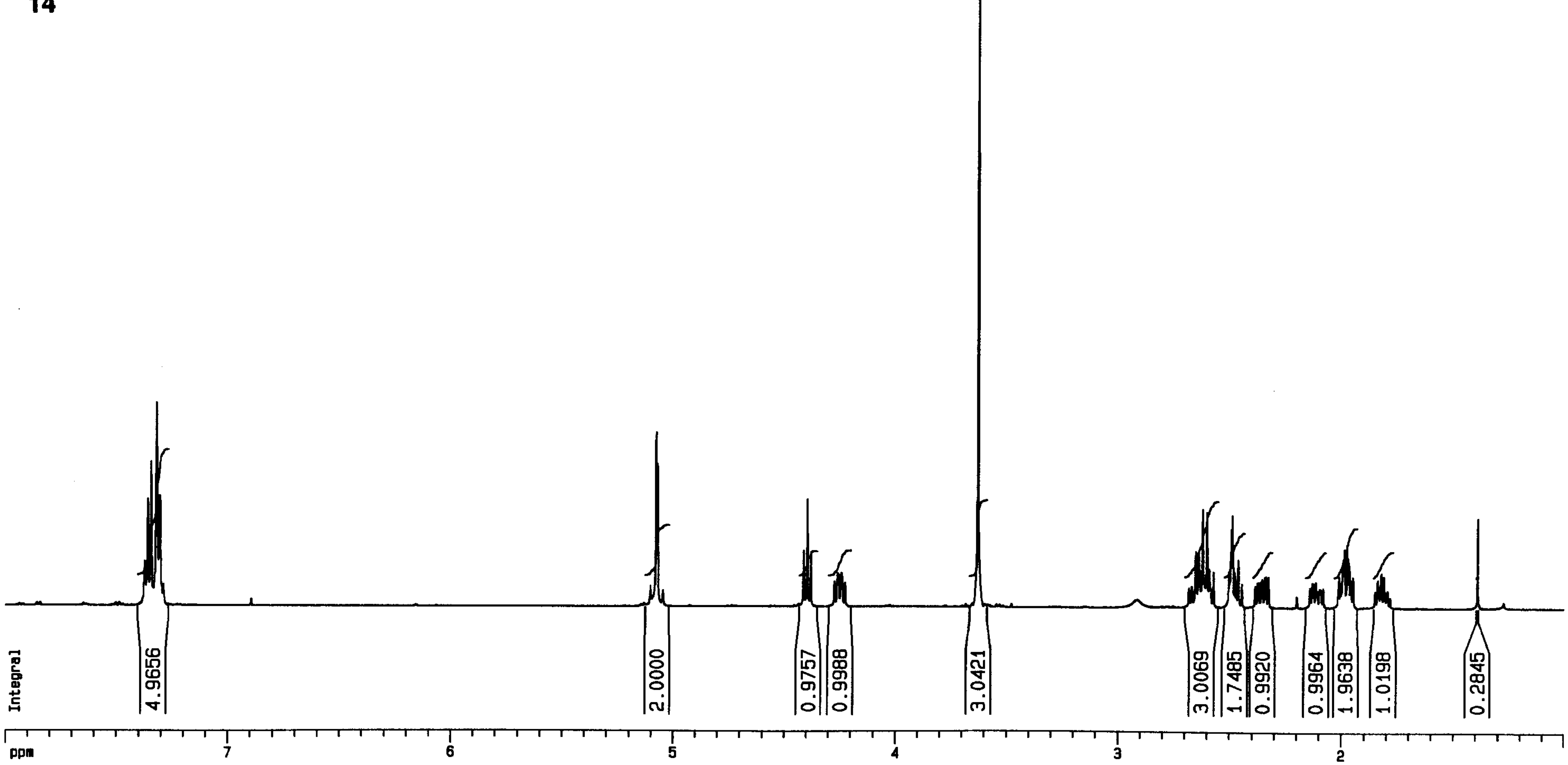


13

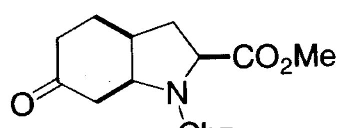
H2/PtO2 (route II) 500 MHz DMSO-d6 360 K



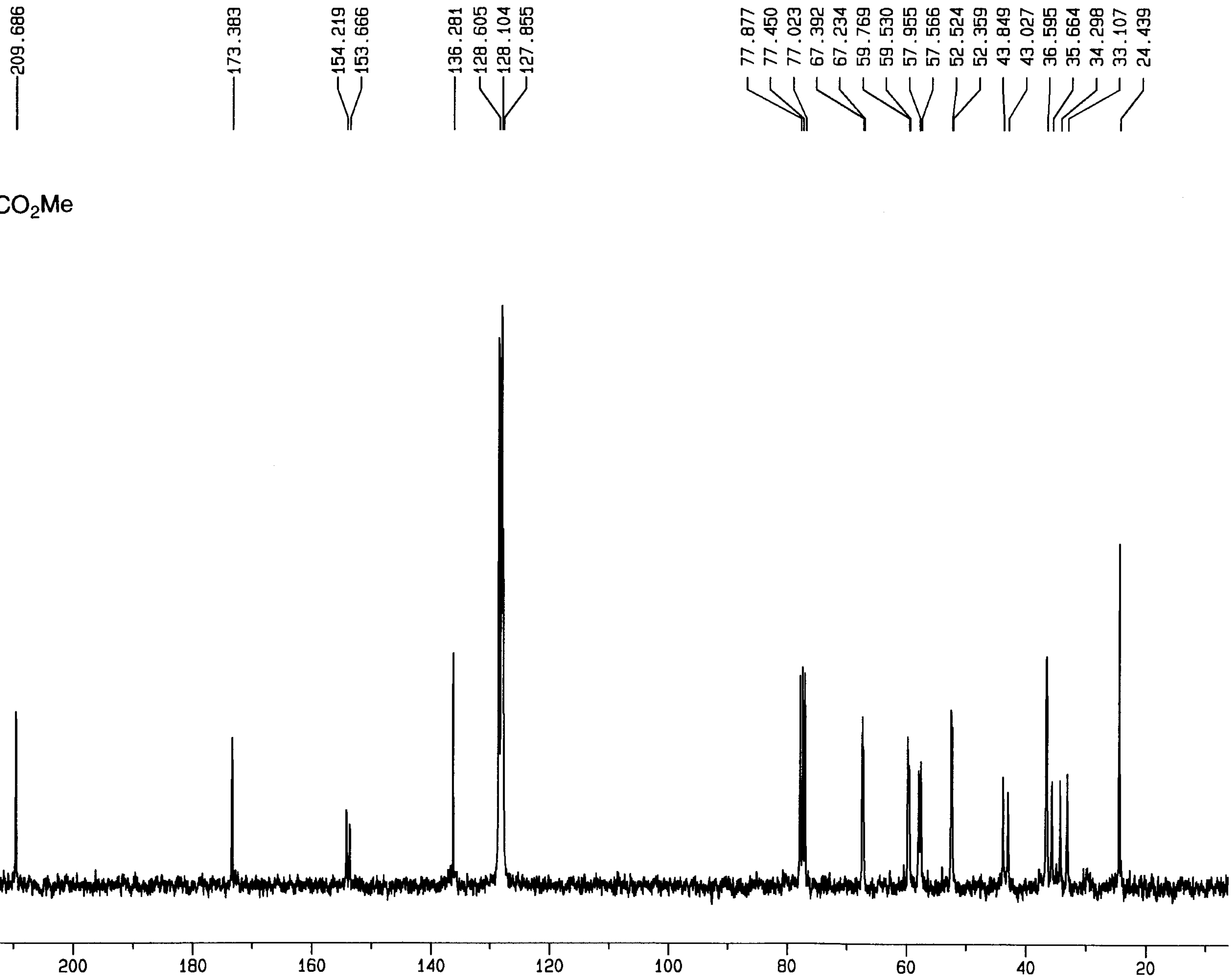
14



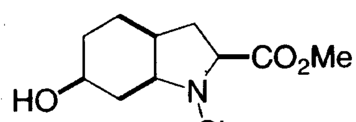
Hydrogenation Product (route II)



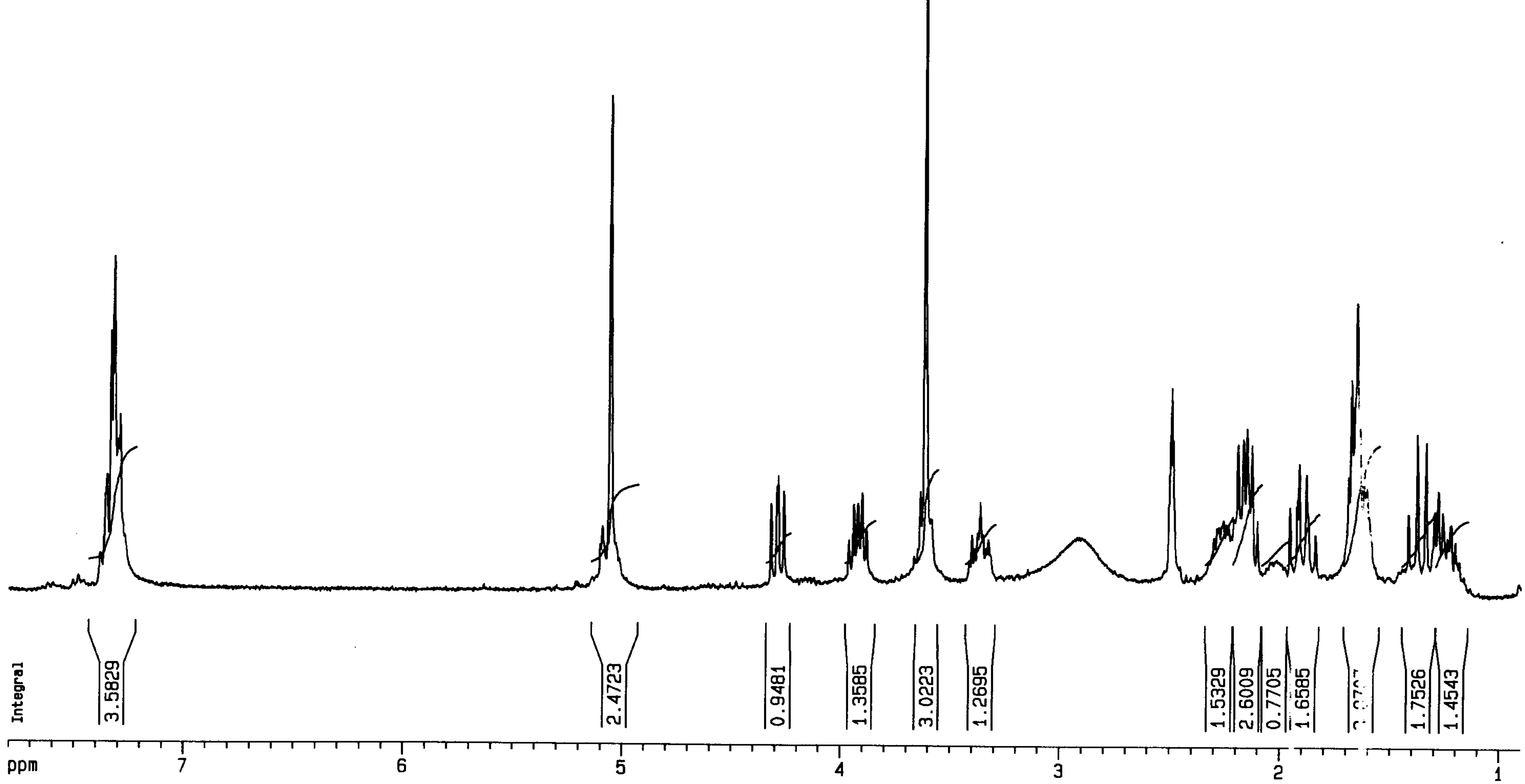
14



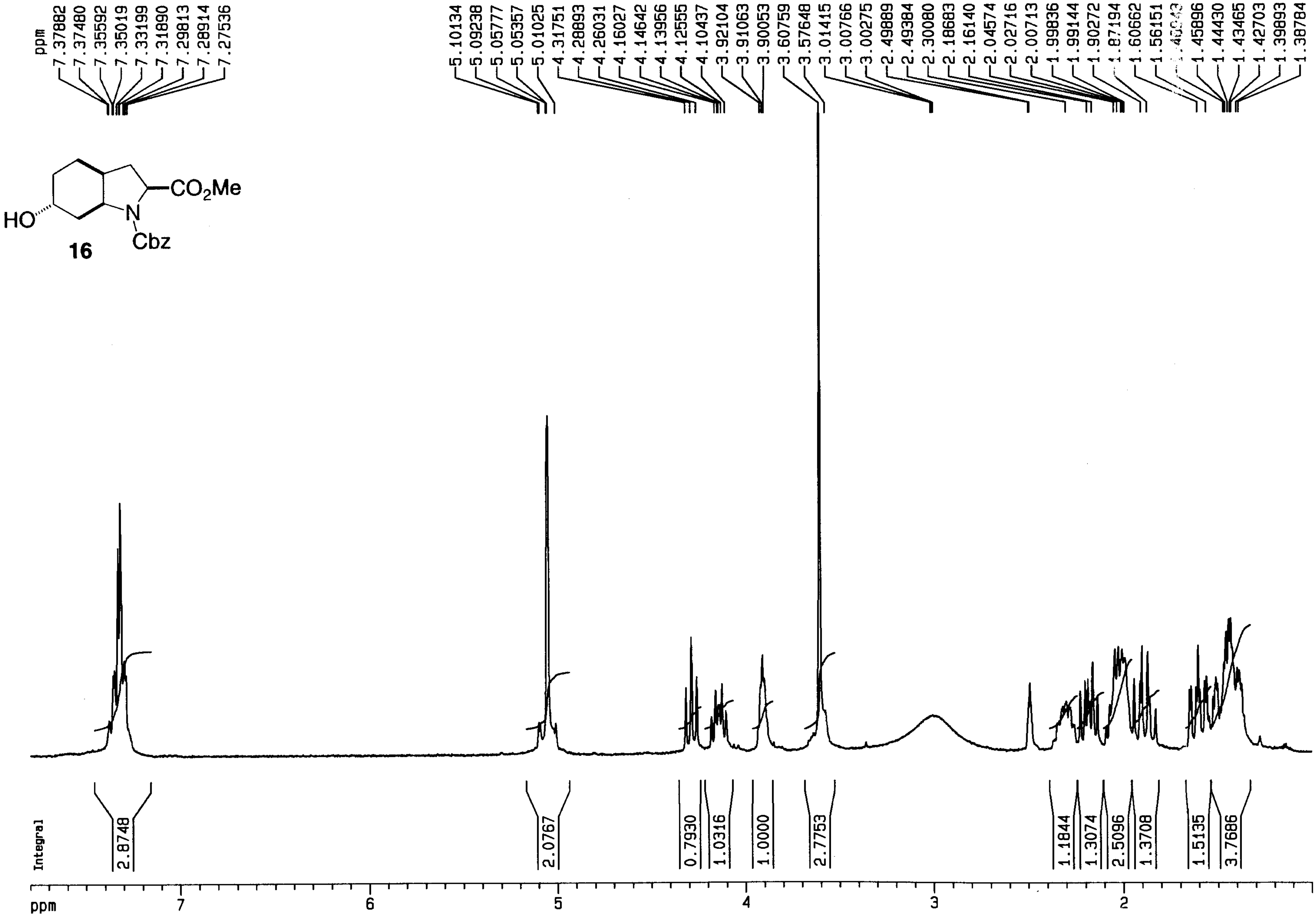
L-Selectride Reduction (minor product, DMSO, 373K)



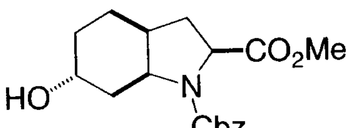
15



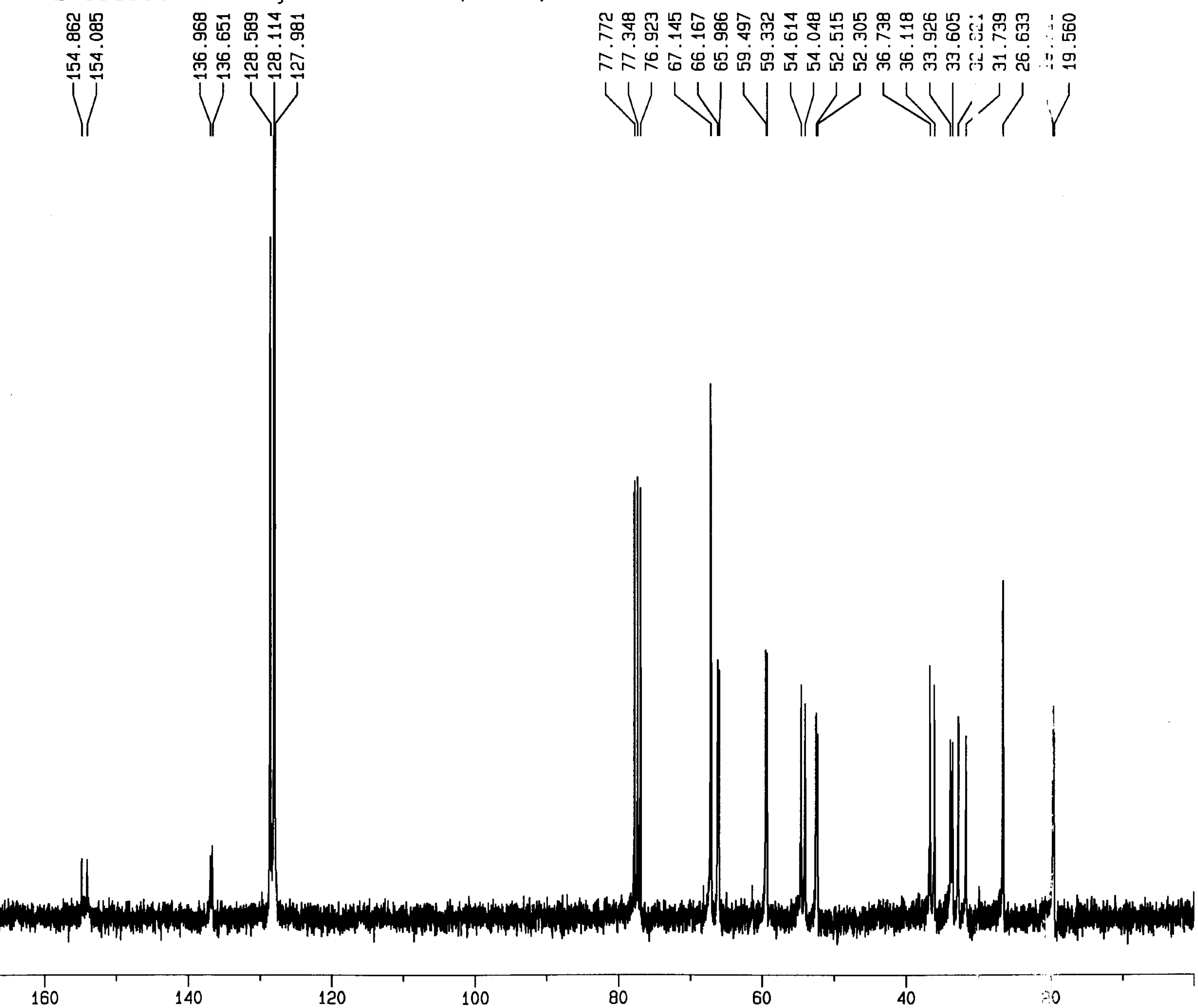
L-Selectride Reduction (major product, DMSO, 373K)



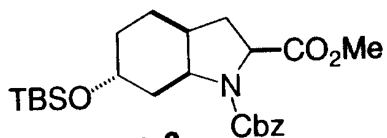
L-Selectride Major Product (CDCl3)



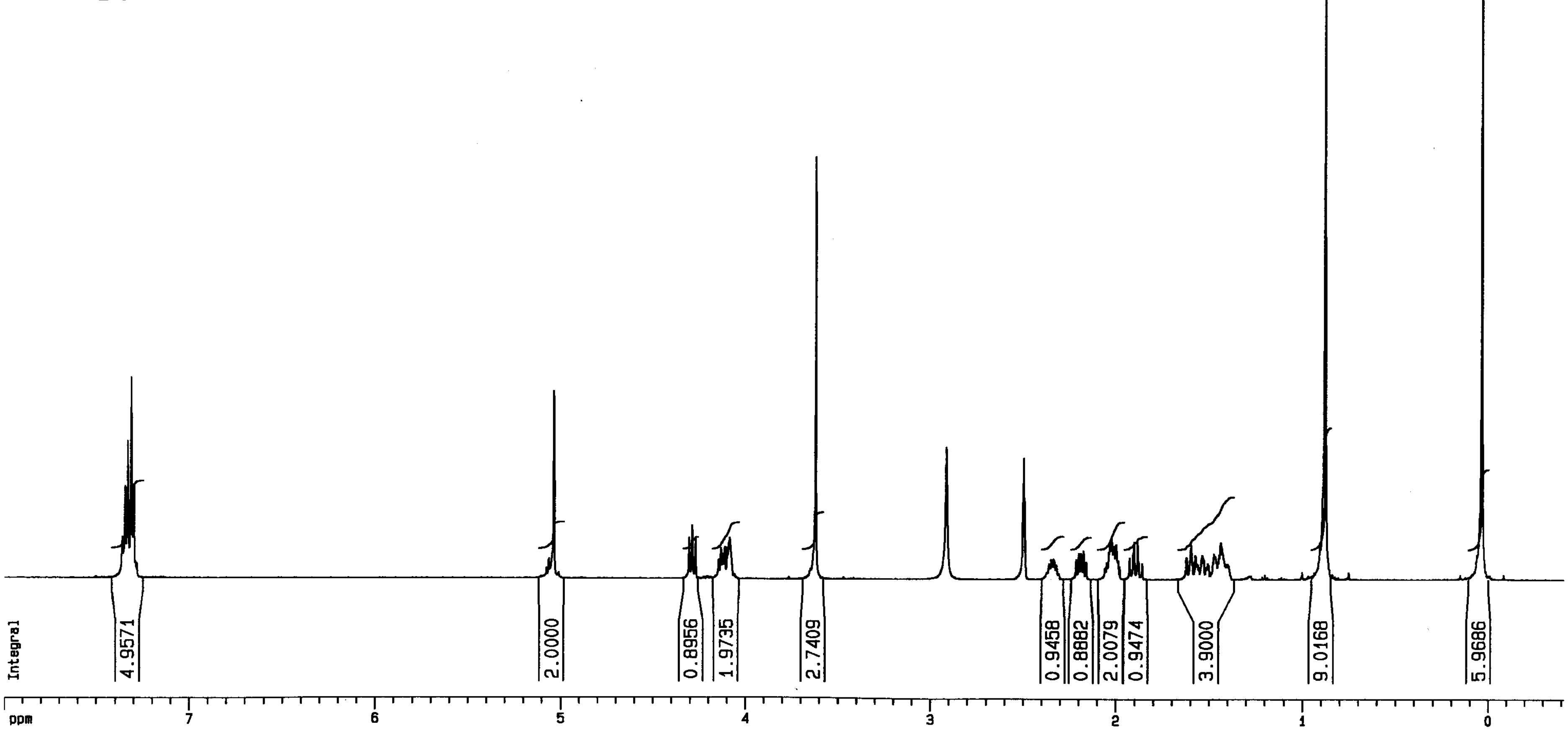
16



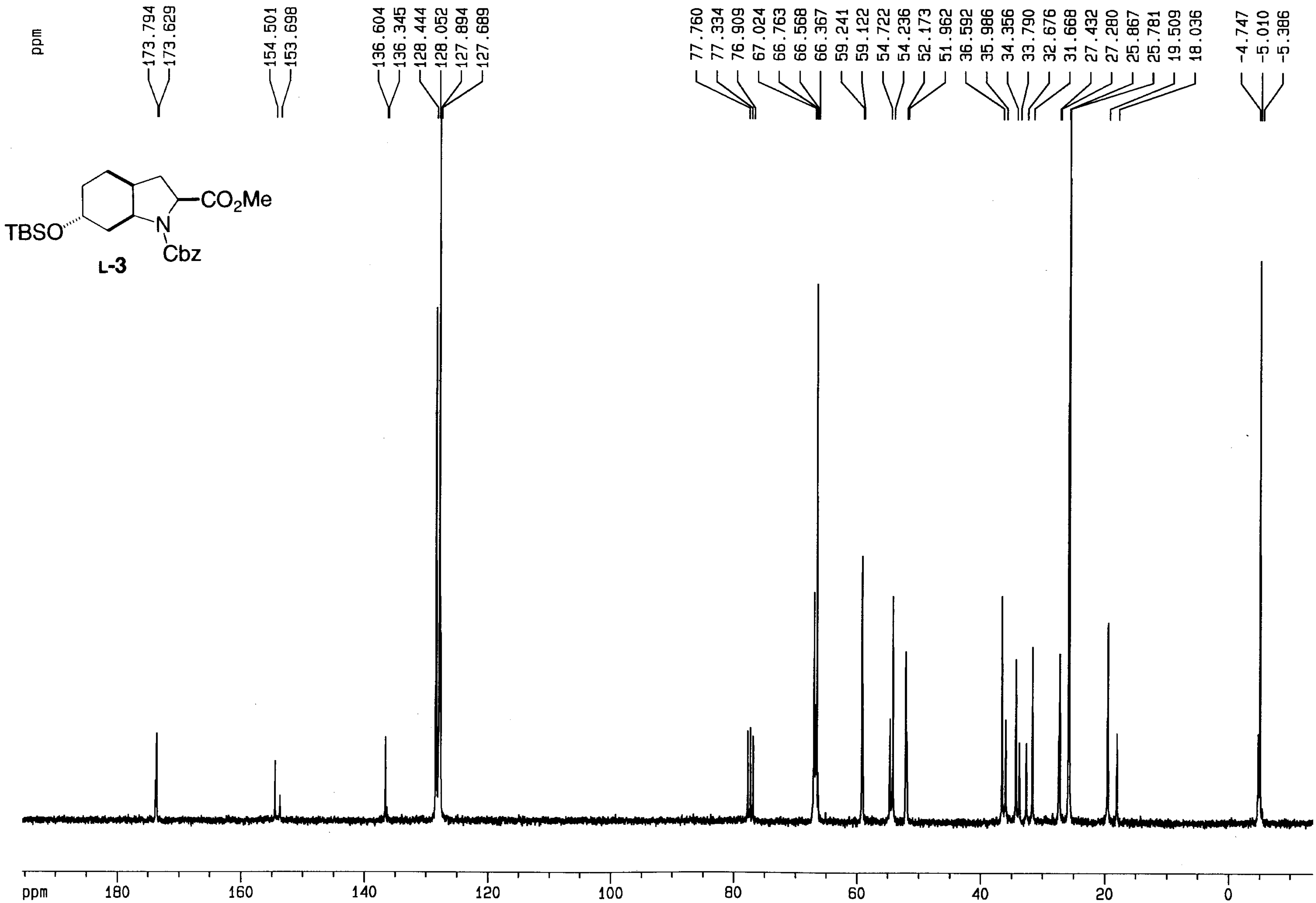
Aeruginosin Core dmso-d6 100C 500MHz 1H delay 12sec 11/1/99



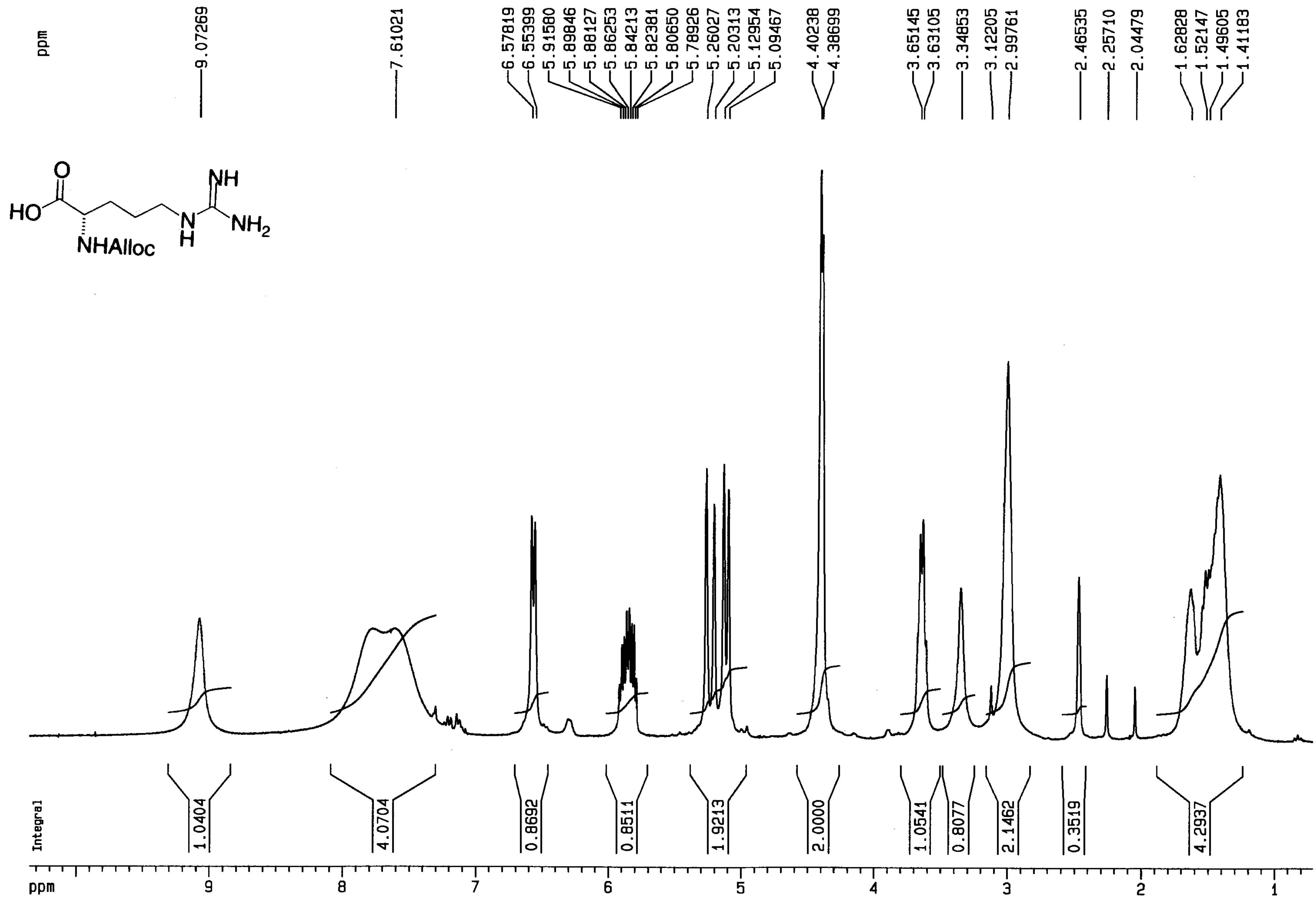
L-3



Aeruginosin Core (CDCl3, 300K)

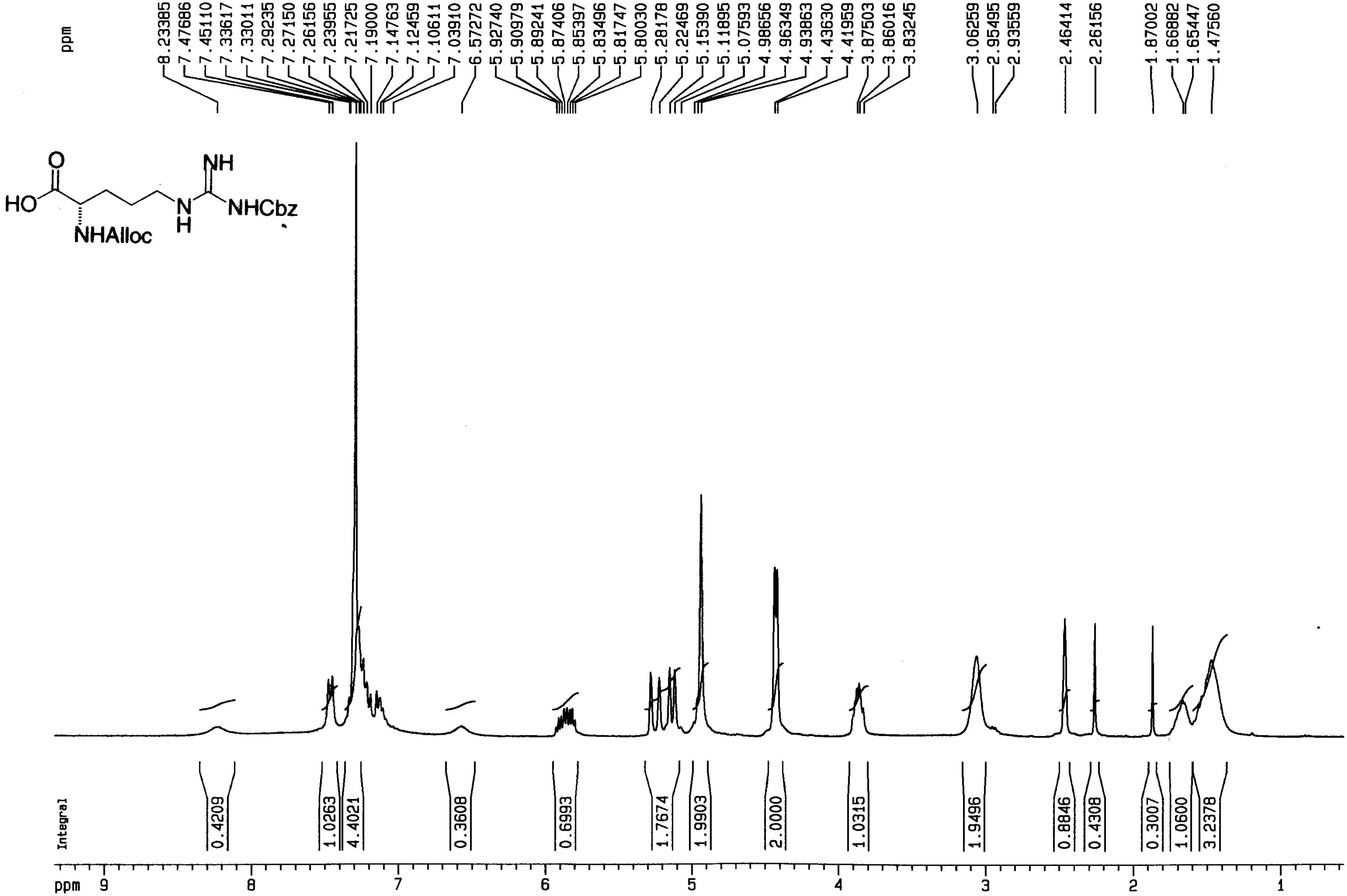


Alloc-L-Arg

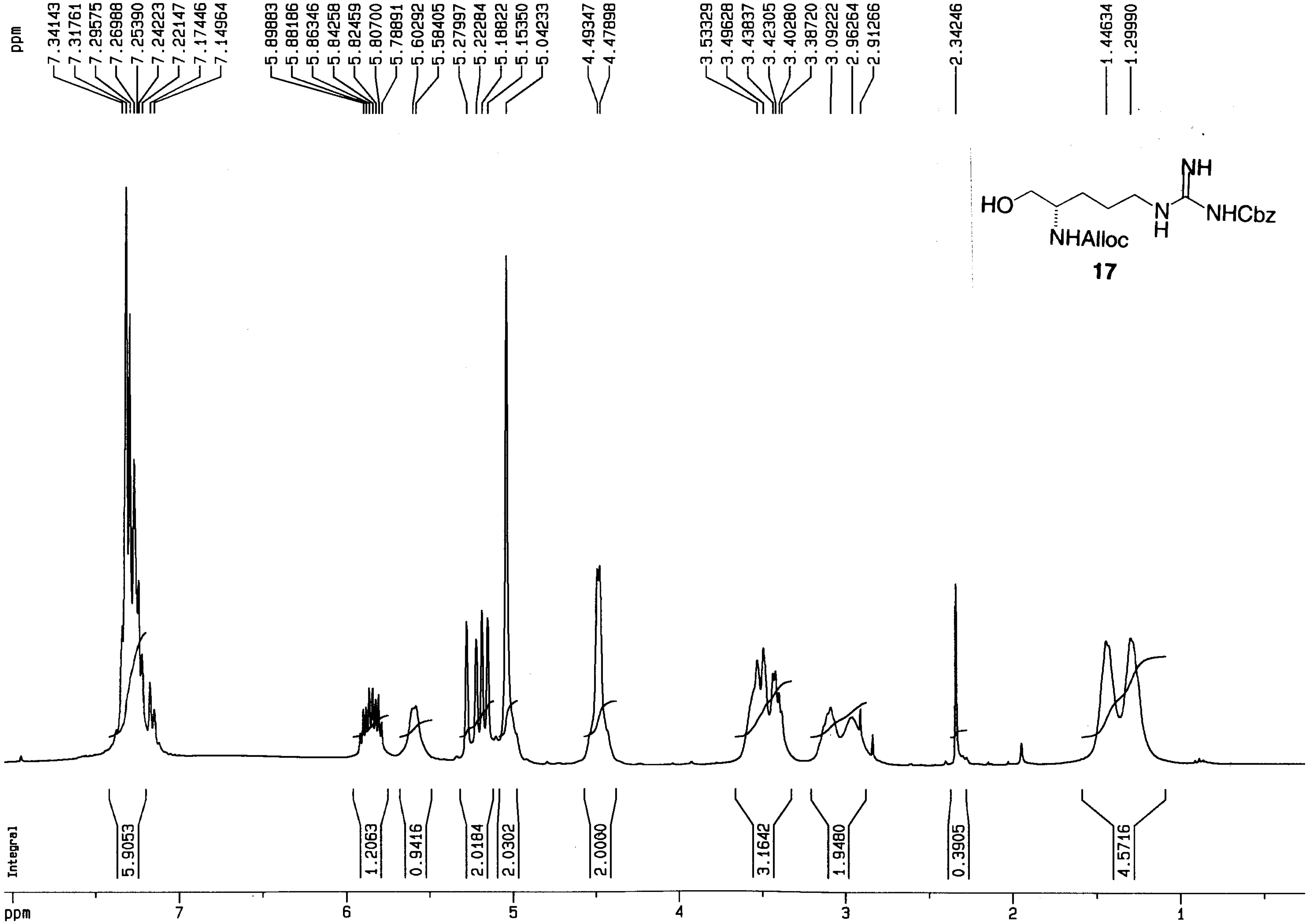


ppm
9.07269
7.61021
6.57819
6.55399
5.91580
5.89846
5.88127
5.86253
5.84213
5.82381
5.80650
5.78926
5.26027
5.20313
5.12954
5.09467
4.40238
4.38699
3.65145
3.63105
3.34853
3.12205
2.99761
2.46535
2.25710
2.04479
1.62828
1.52147
1.49605
1.41183
HO
O
NHAlloc
N
H
NH
NH2
Integral
1.0404
4.0704
0.8692
0.8511
1.9213
2.0000
1.0541
0.8077
2.1462
0.3519
4.2937
ppm
9
8
7
6
5
4
3
2
1

Alloc-Arg(Cbz)-OH

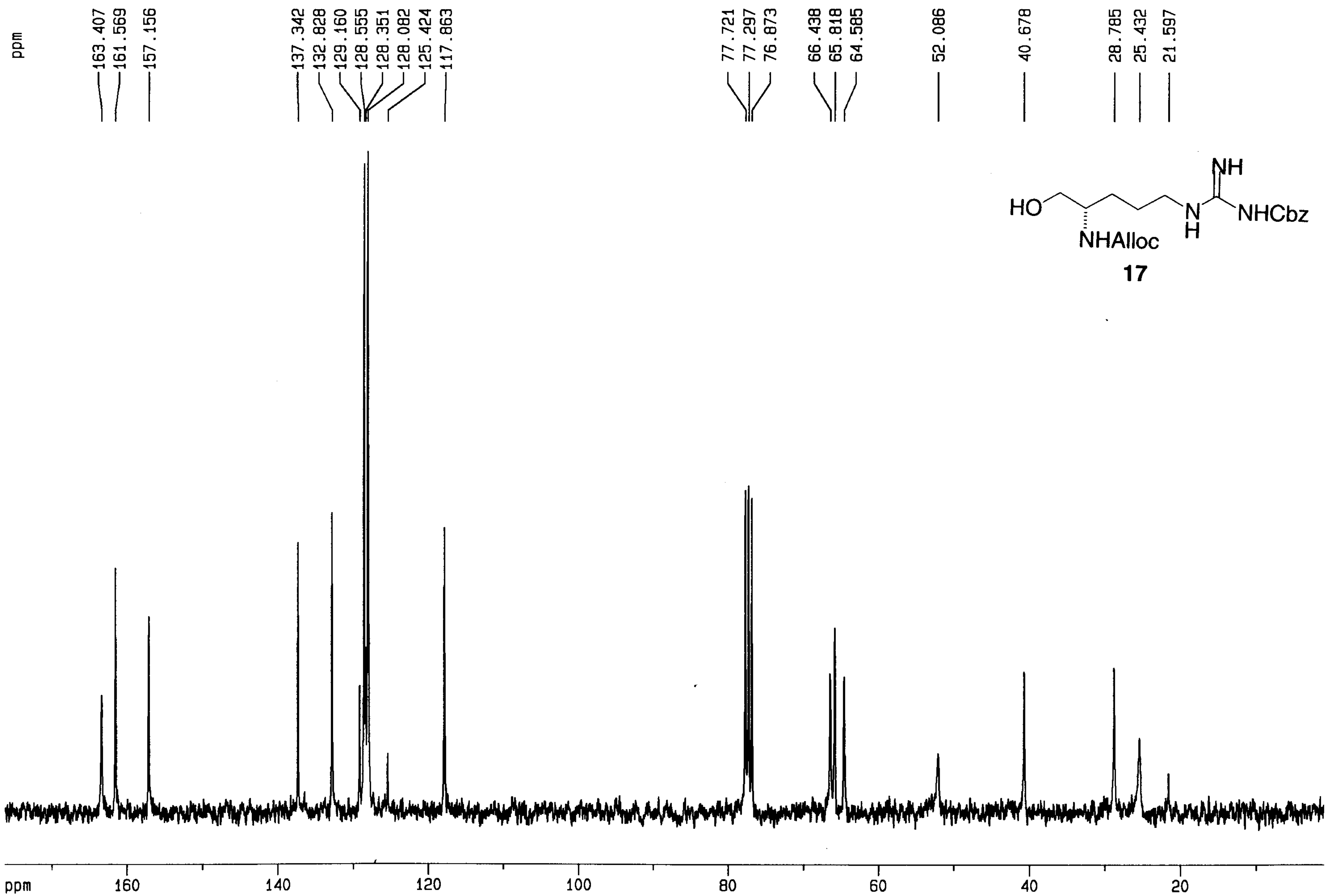


Alloc-L-Arg(Cbz)-CH2OH (CDCl3)



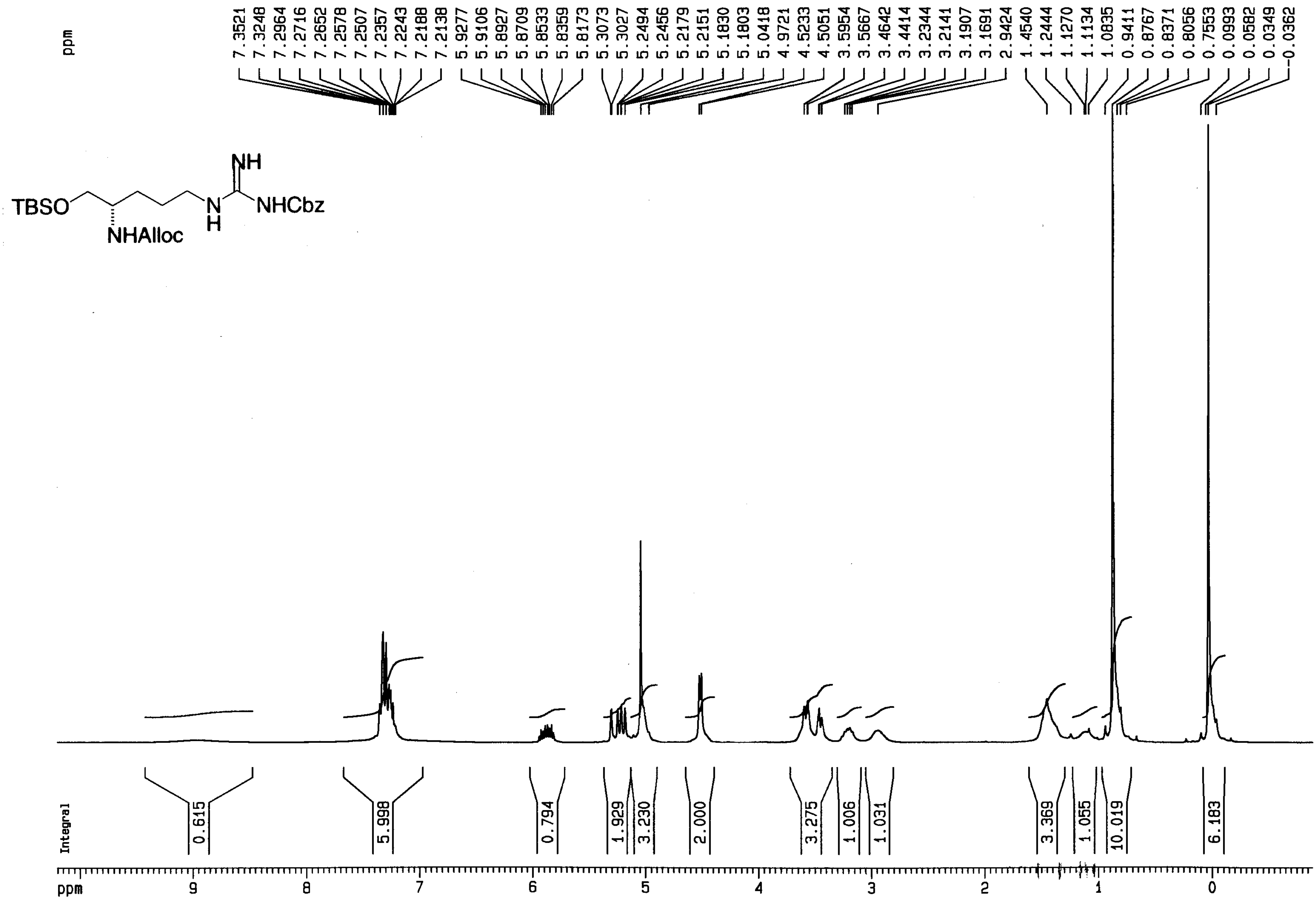
17

Alloc-L-Arg(Cbz)-CH2OH (CDCl3)

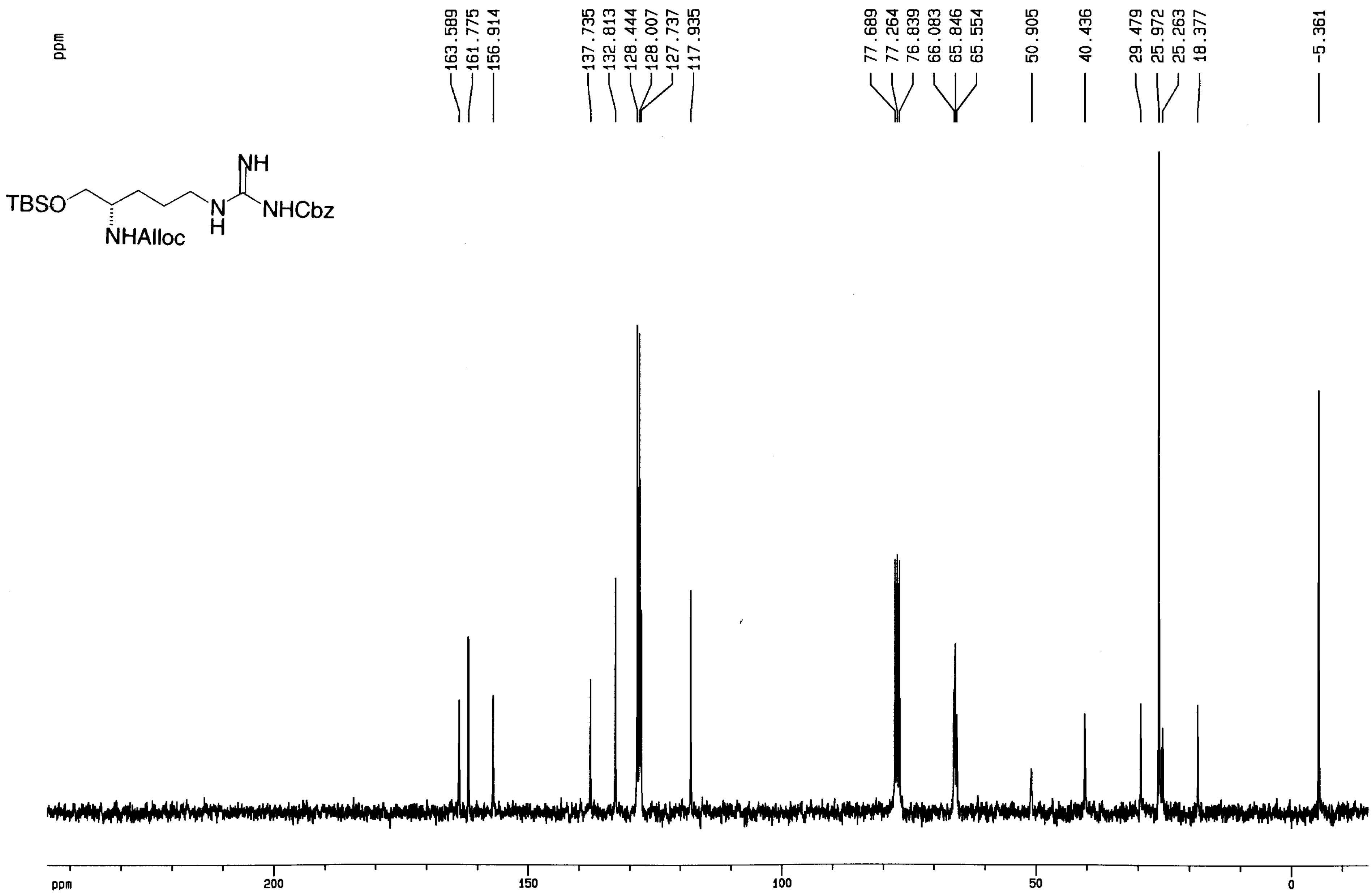


17

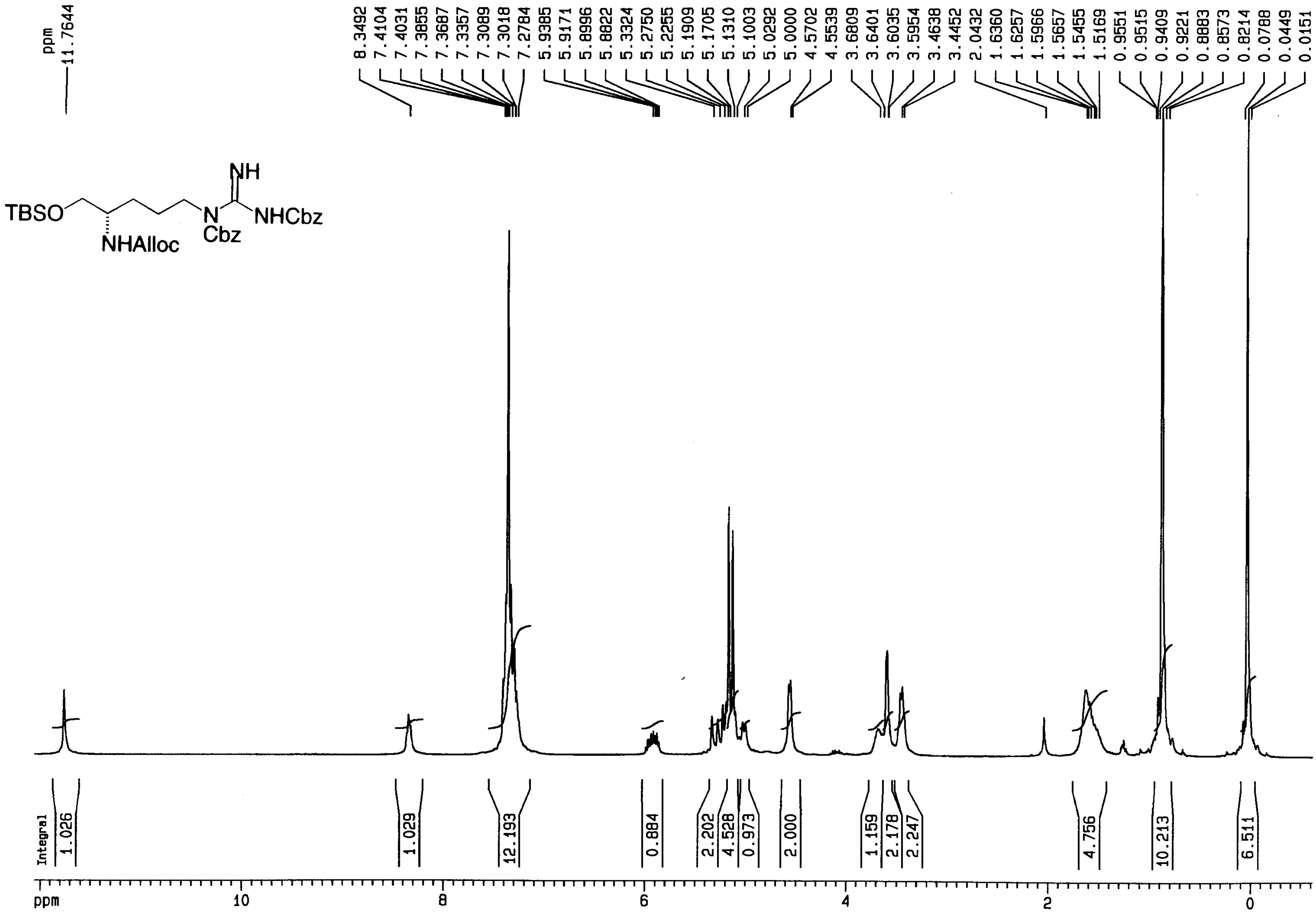
Alloc-L-Arg(Cbz)-CH2OTBS



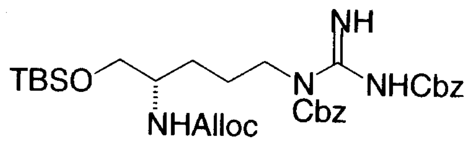
Alloc-L-Arg(Cbz)-CH2OTBS

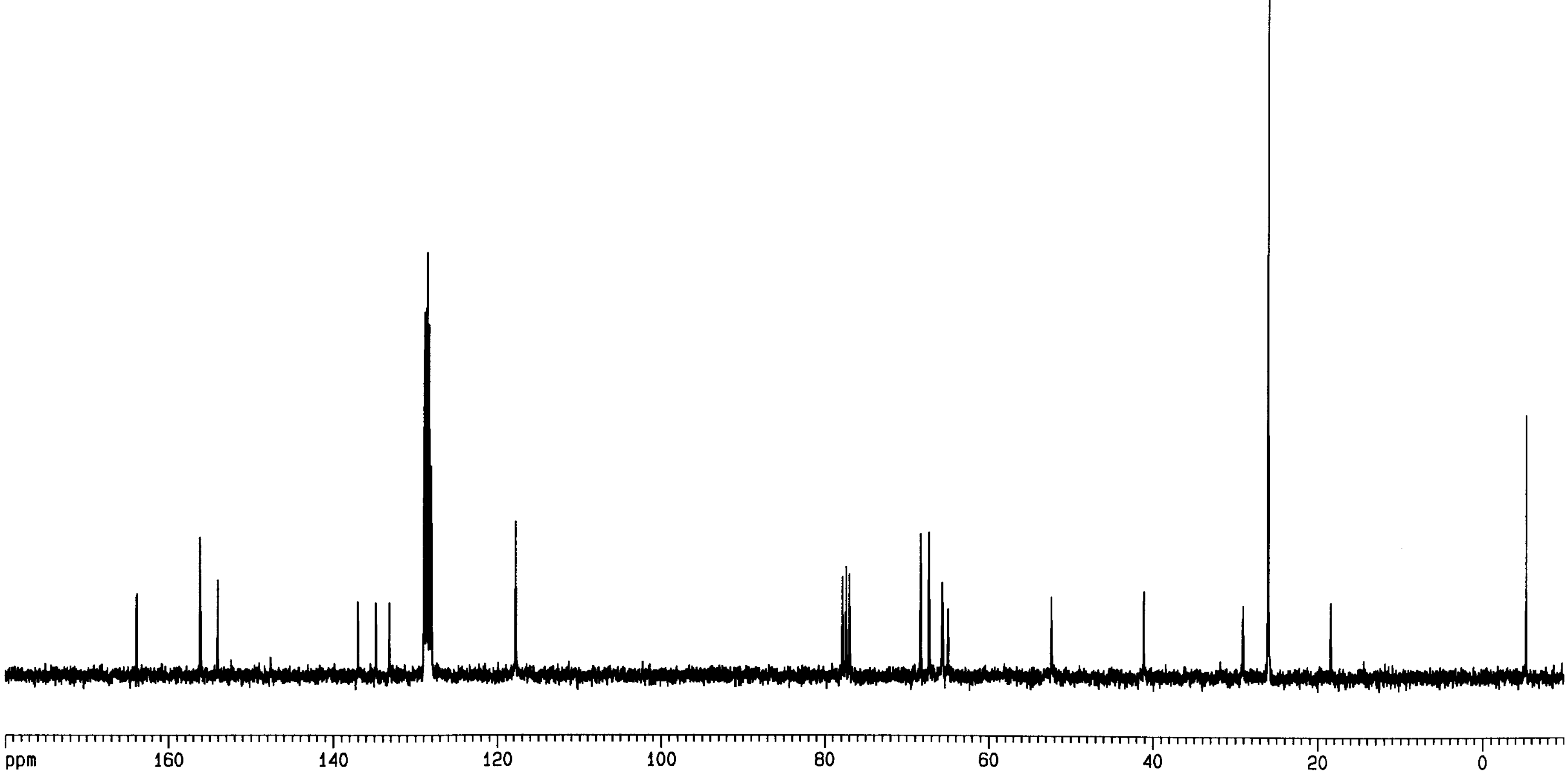


Alloc-Arg(Cbz)2-CH2OTBS CDCl3 300 MHz rt

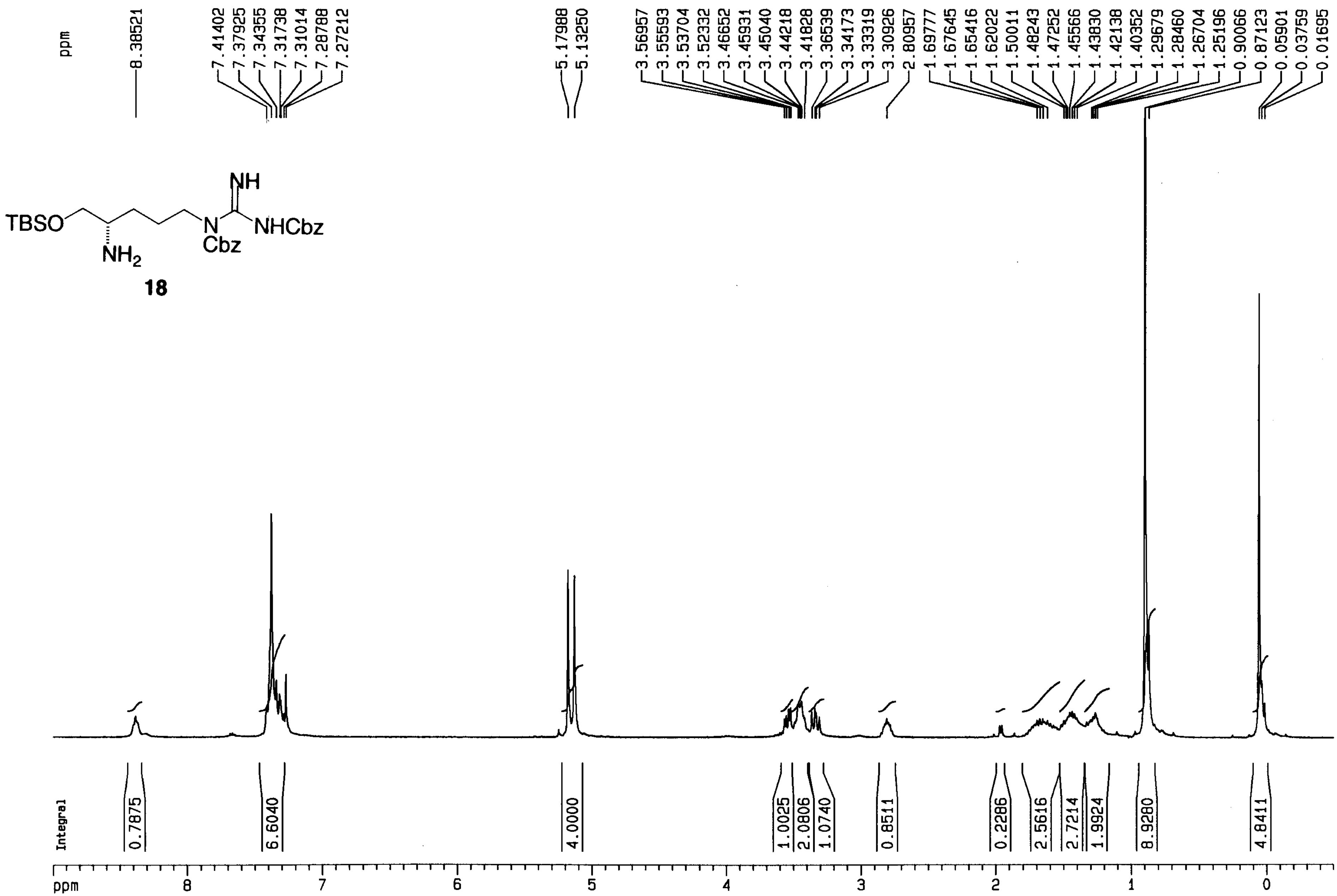


Alloc-Argol(Cbz2)-OTBS 75 MHz CDCl3 rt

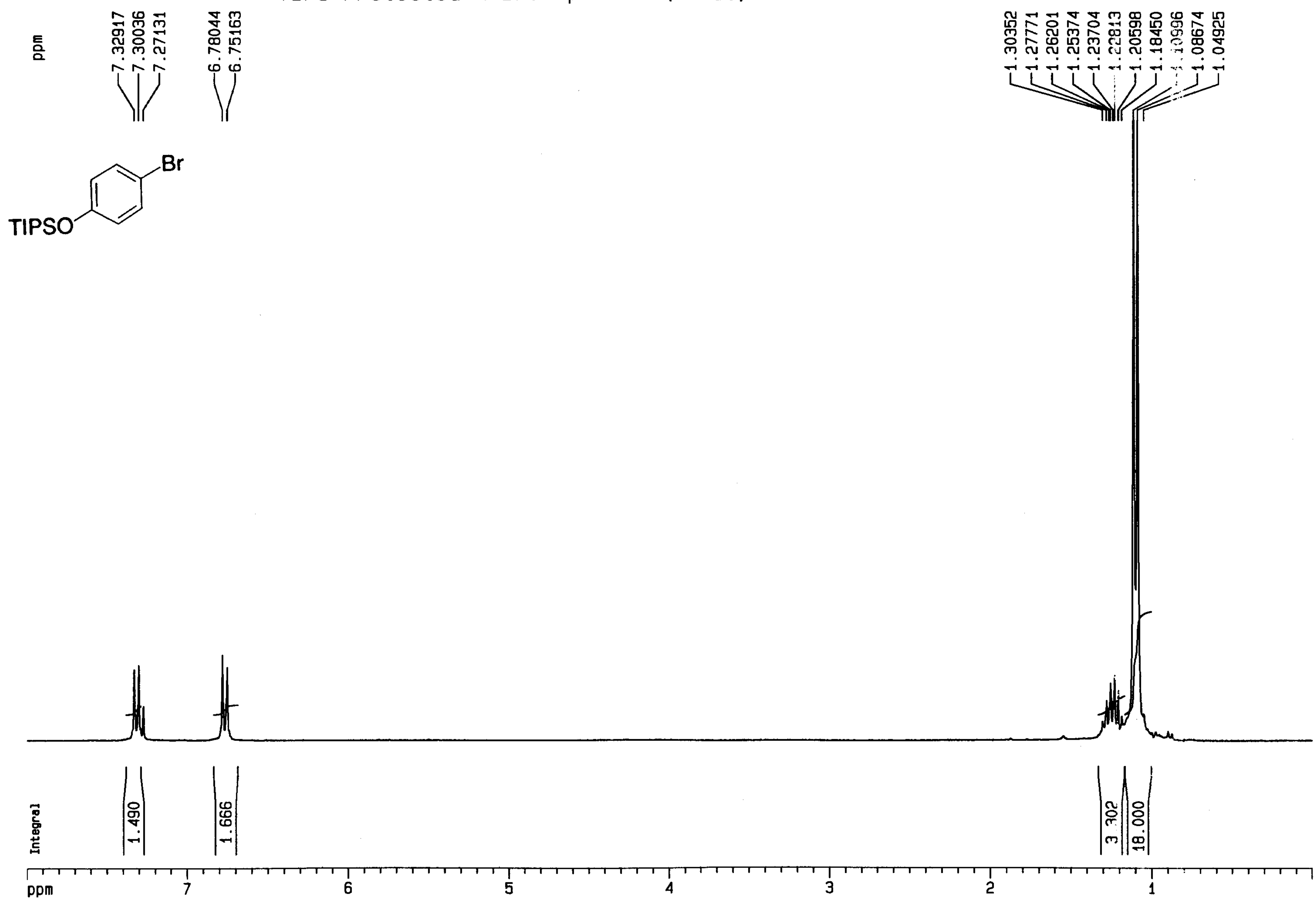




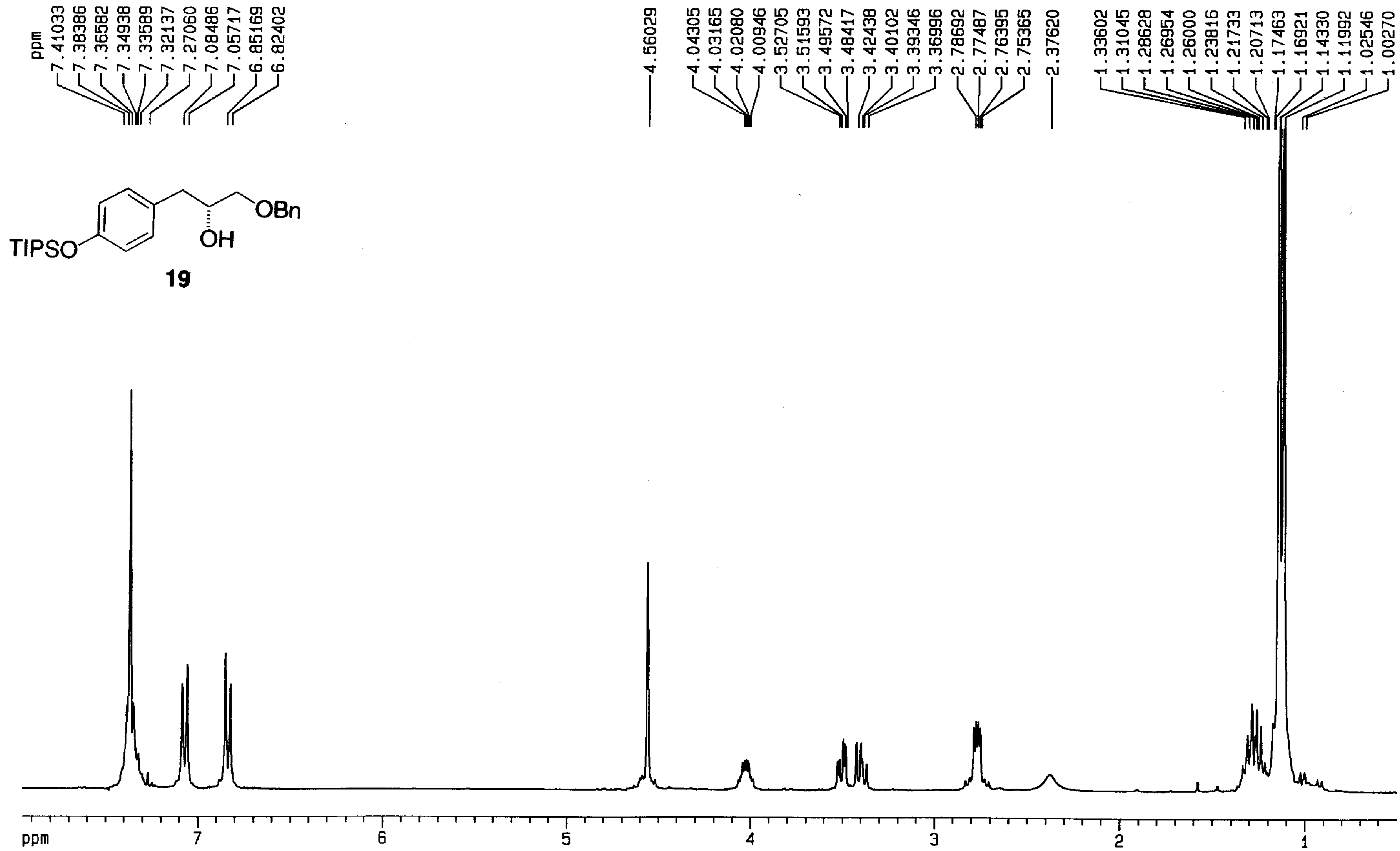
L-Arg (Cbz) 2-CH2OTBS (300MHz, CDCl3)



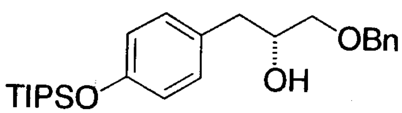
TIPS-Protected 4-Bromophenol (CDCl3)



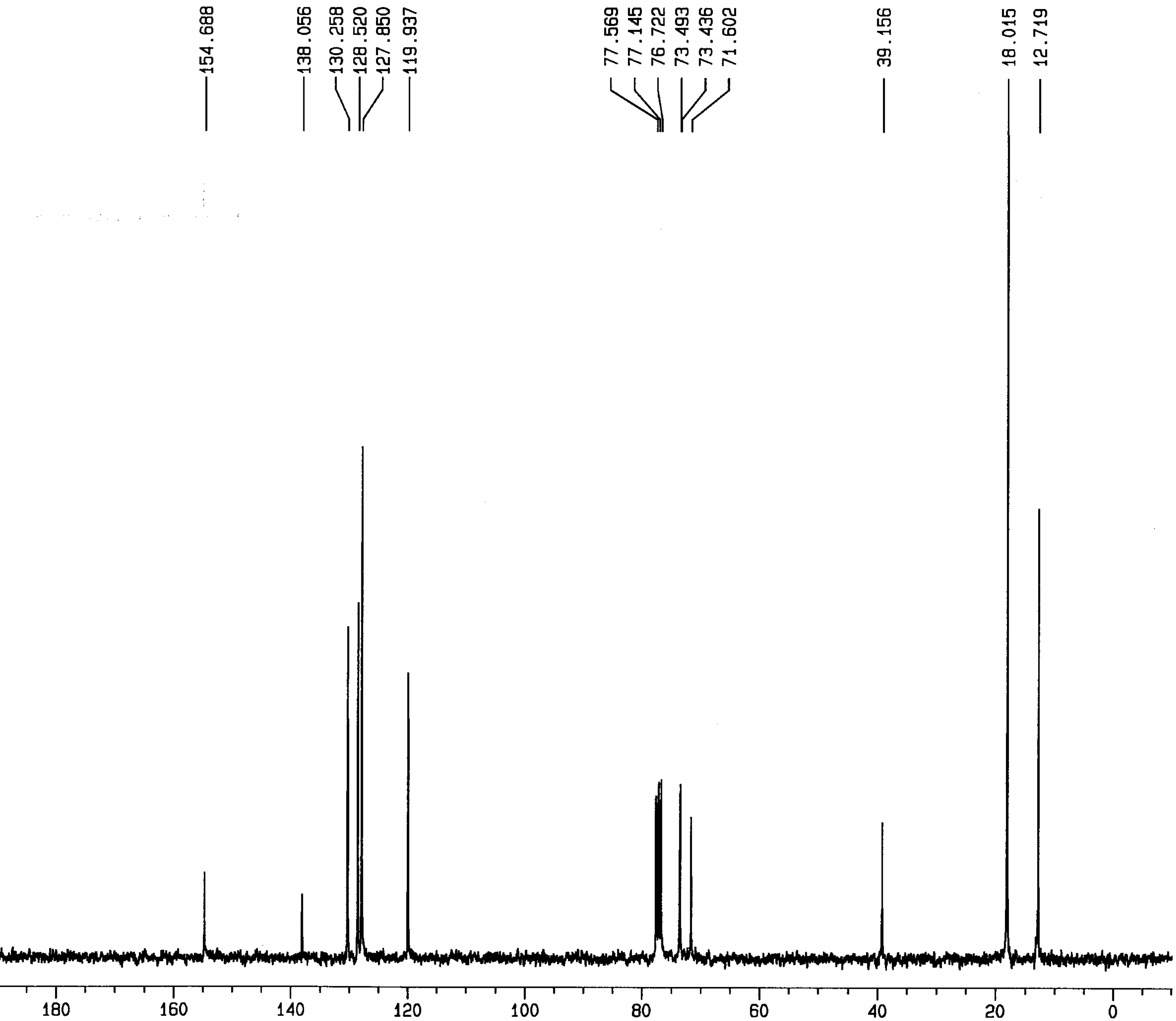
TIPS-Bromophenol + Benzyl Glycidol



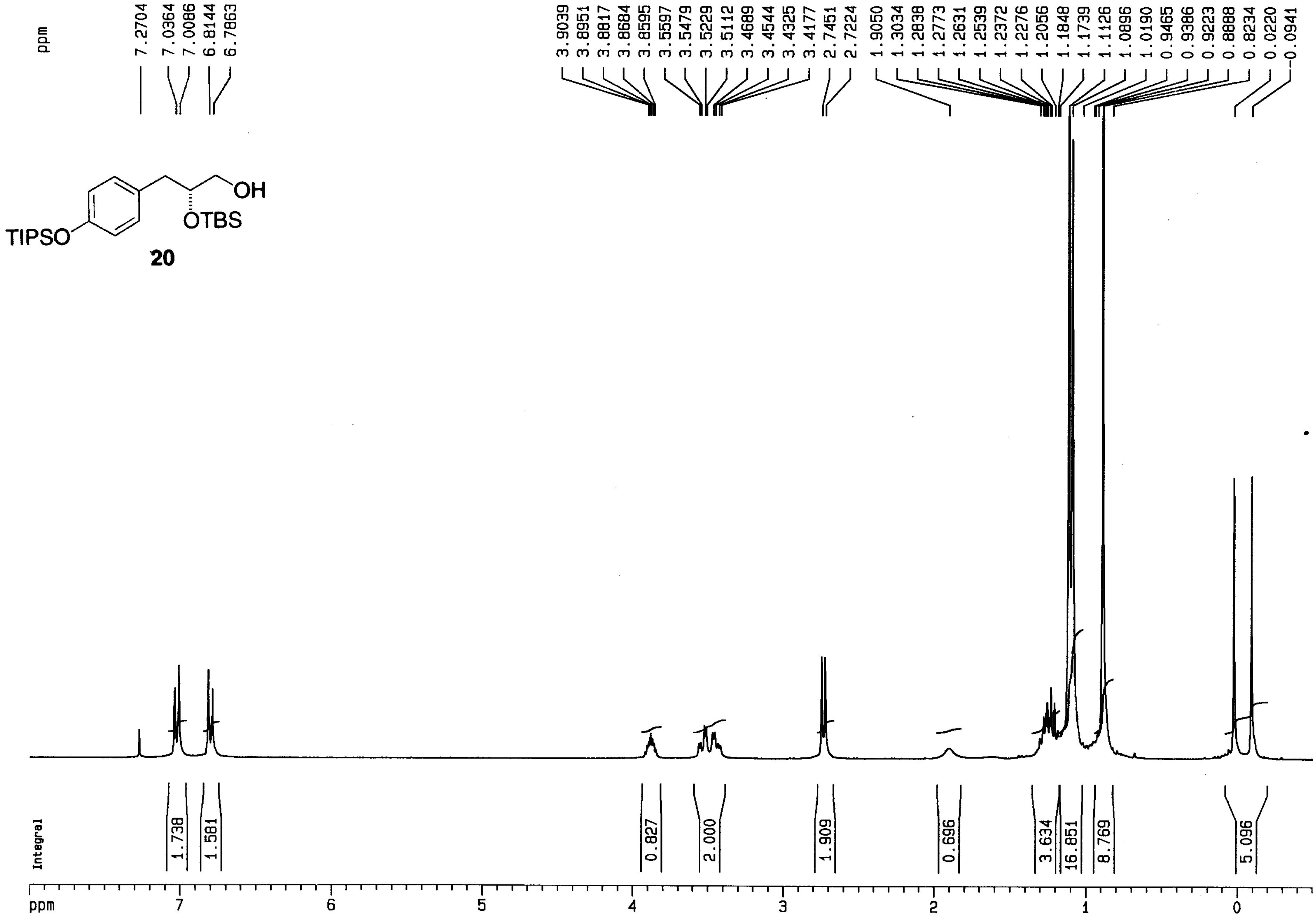
TIPS-Bromophenol + Benzyl Glycidol (delay 6 sec)



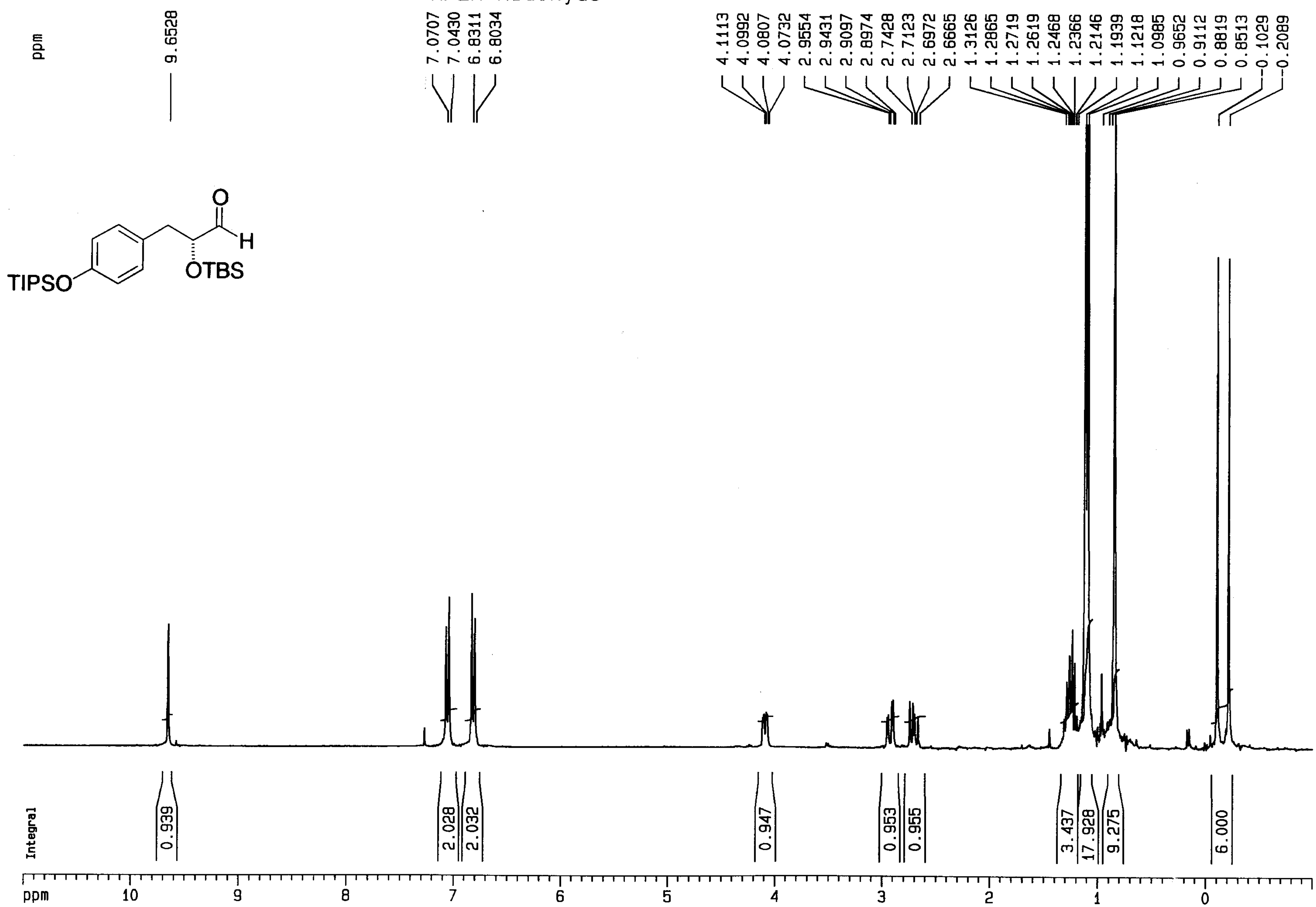
19

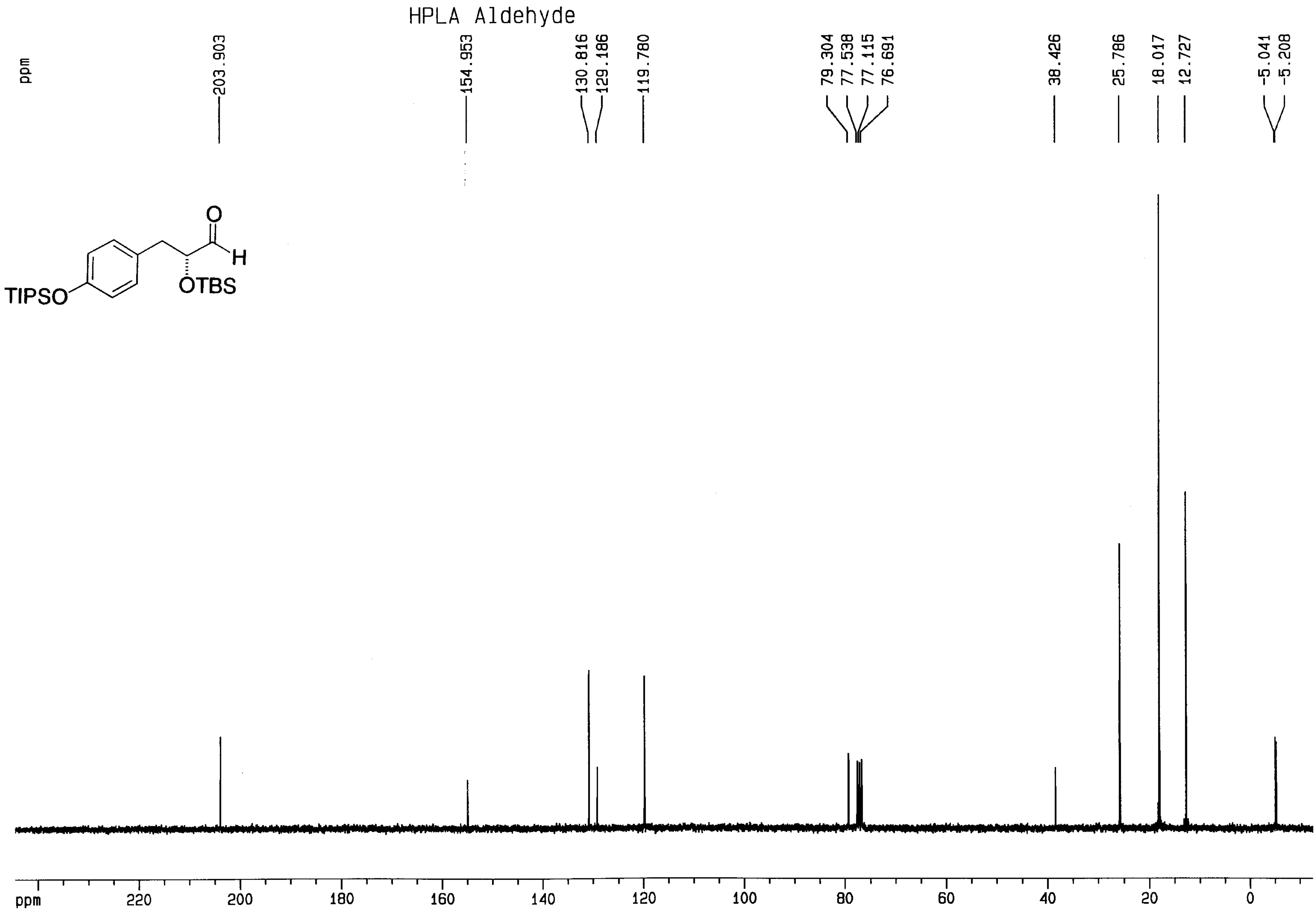


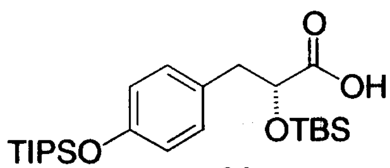
TIPS/TBS HPLA alcohol



HPLA Aldehyde

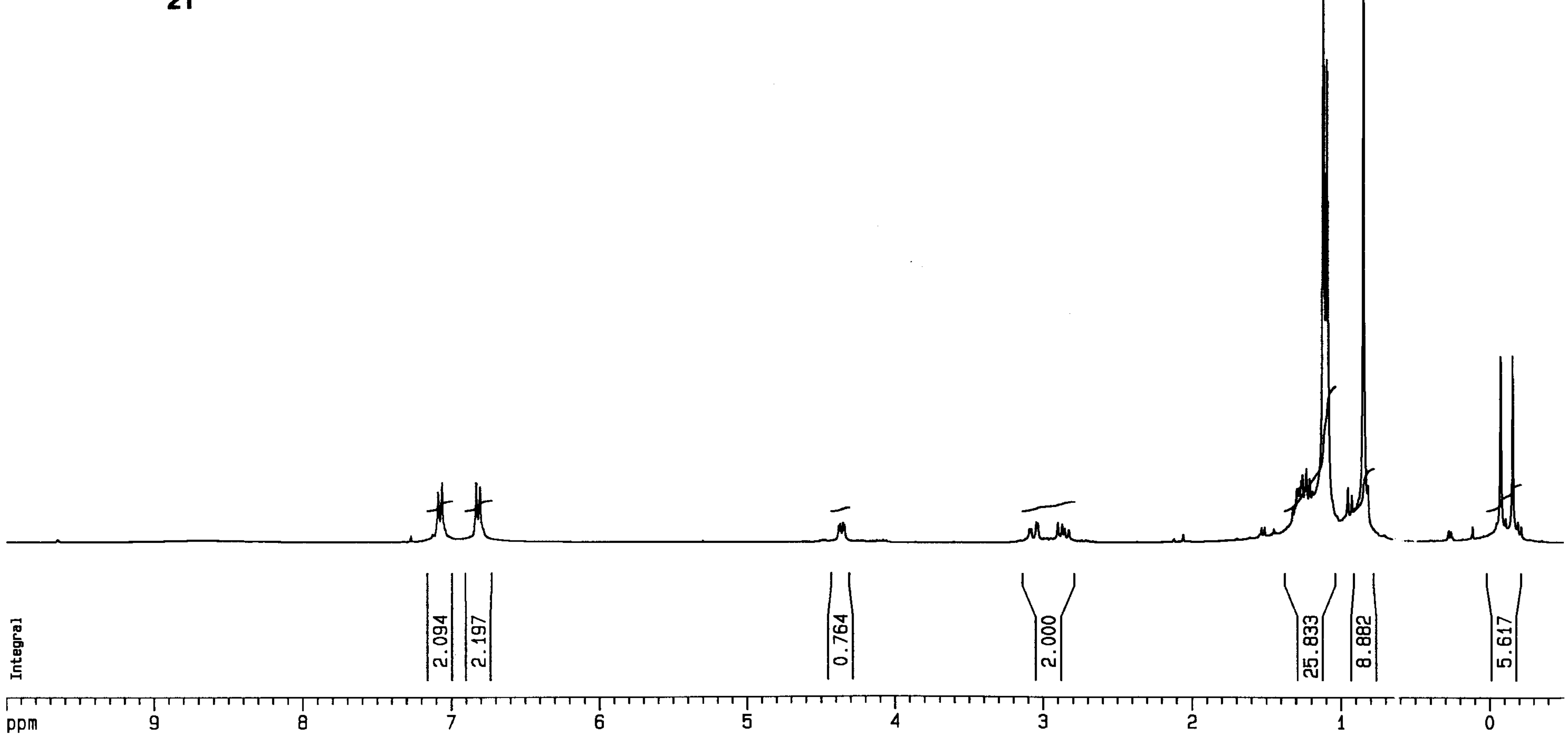



HPLA Aldehyde
ppm
203.903
154.953
130.816
129.186
119.780
79.304
77.538
77.115
76.691
38.426
25.786
18.017
12.727
-5.041
-5.208
O
H
TIPSO
OTBS
ppm
220
200
180
160
140
120
100
80
60
40
20
0

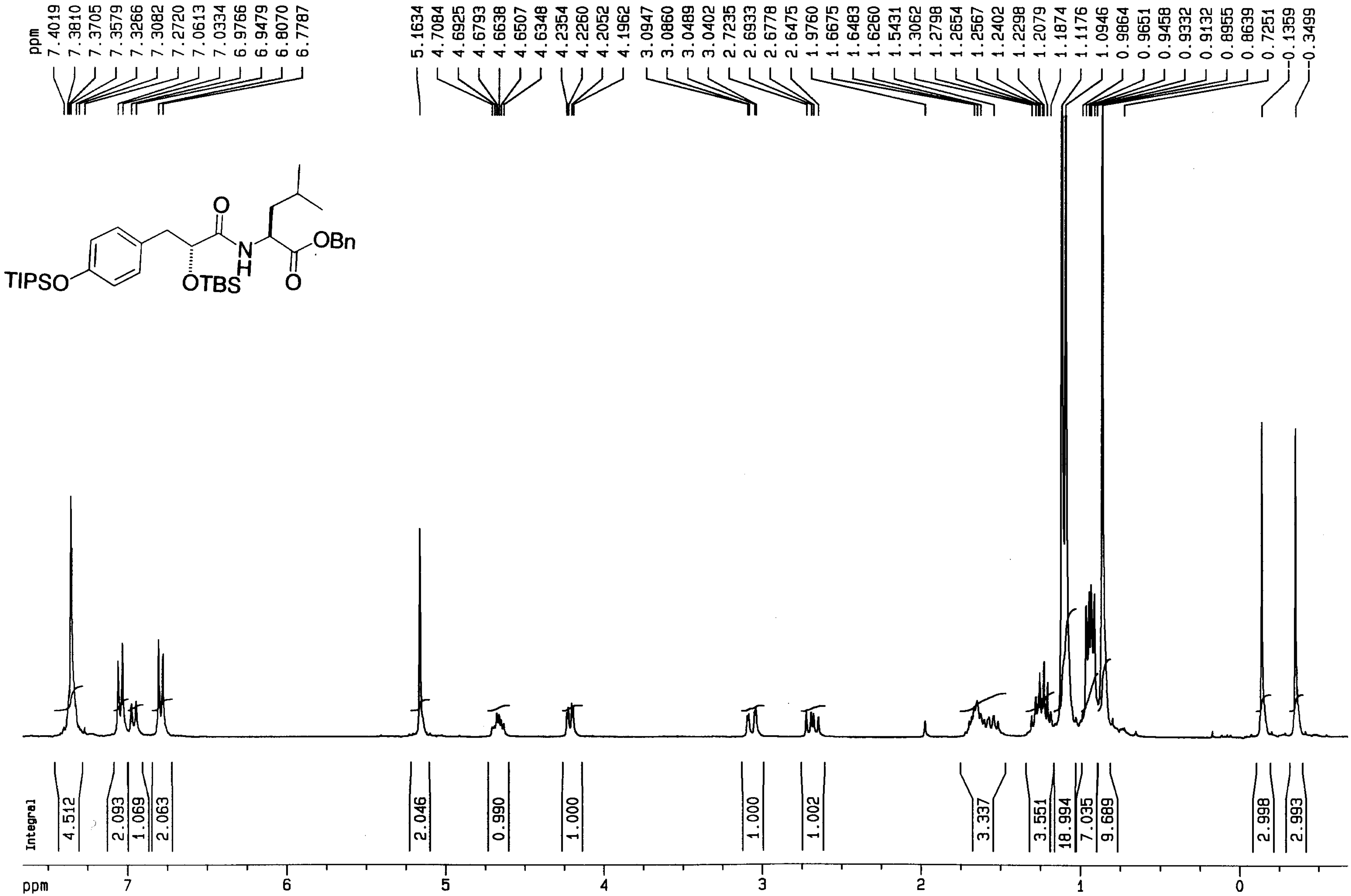


21

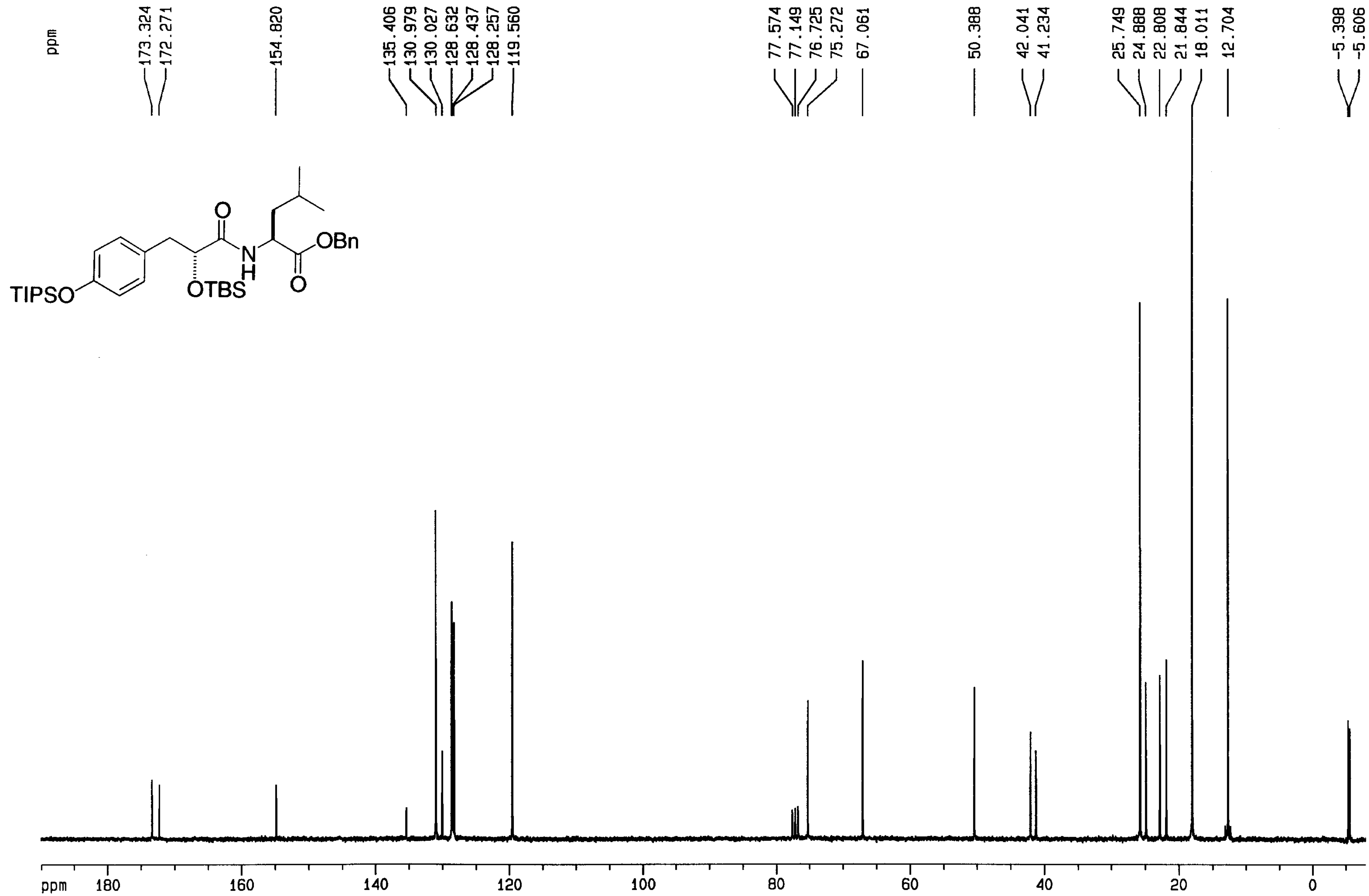
Crude TIPS/TBS HPLA



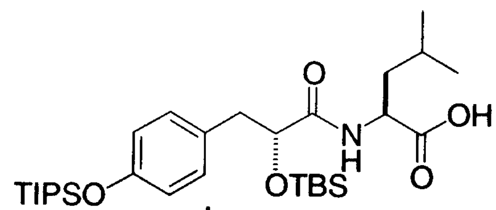
D-Hpla(TIPS, TBS)-L-Leu-OBn 300 MHz, CDCl3, rt



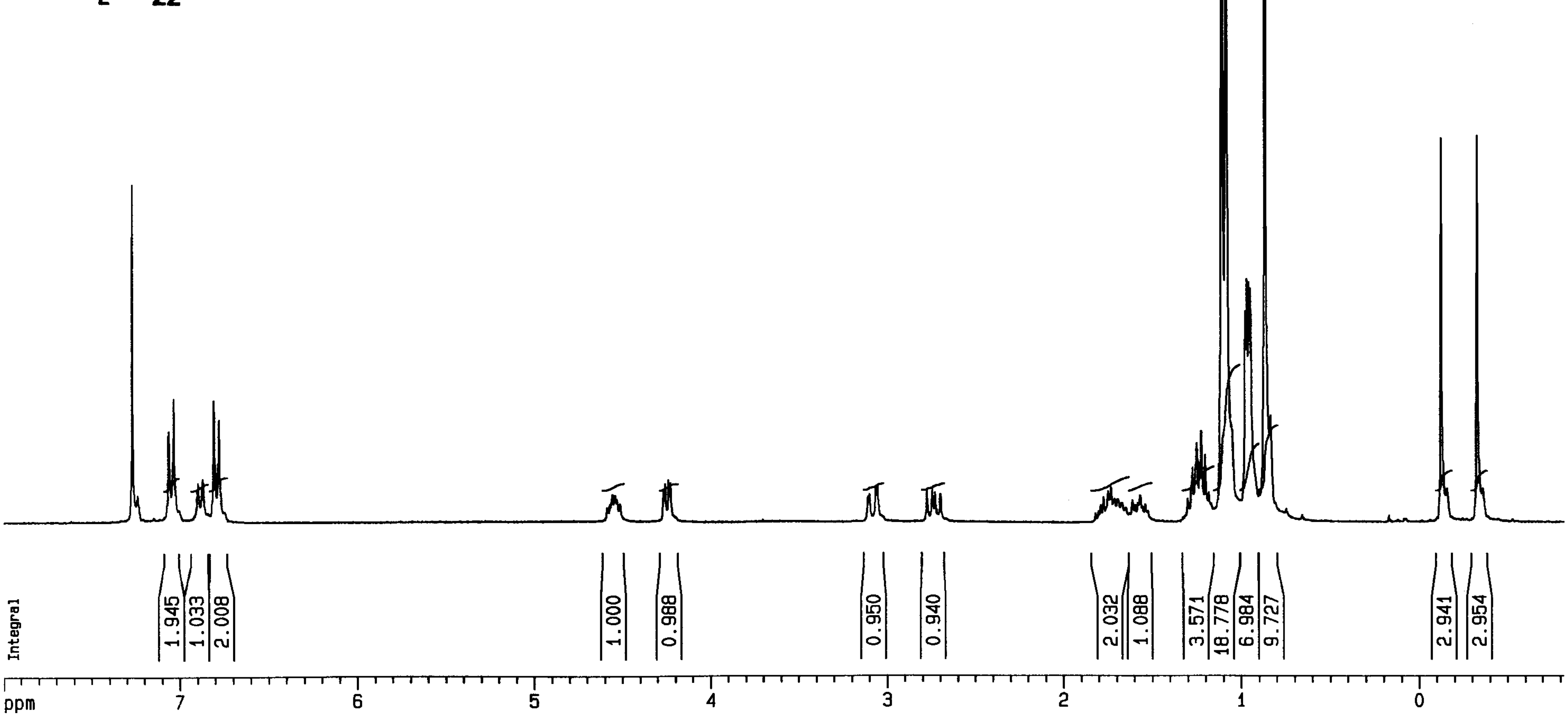
D-Hpla (TIPS, TBS) -L-Leu-OBn 300 MHz, CDCl3, rt



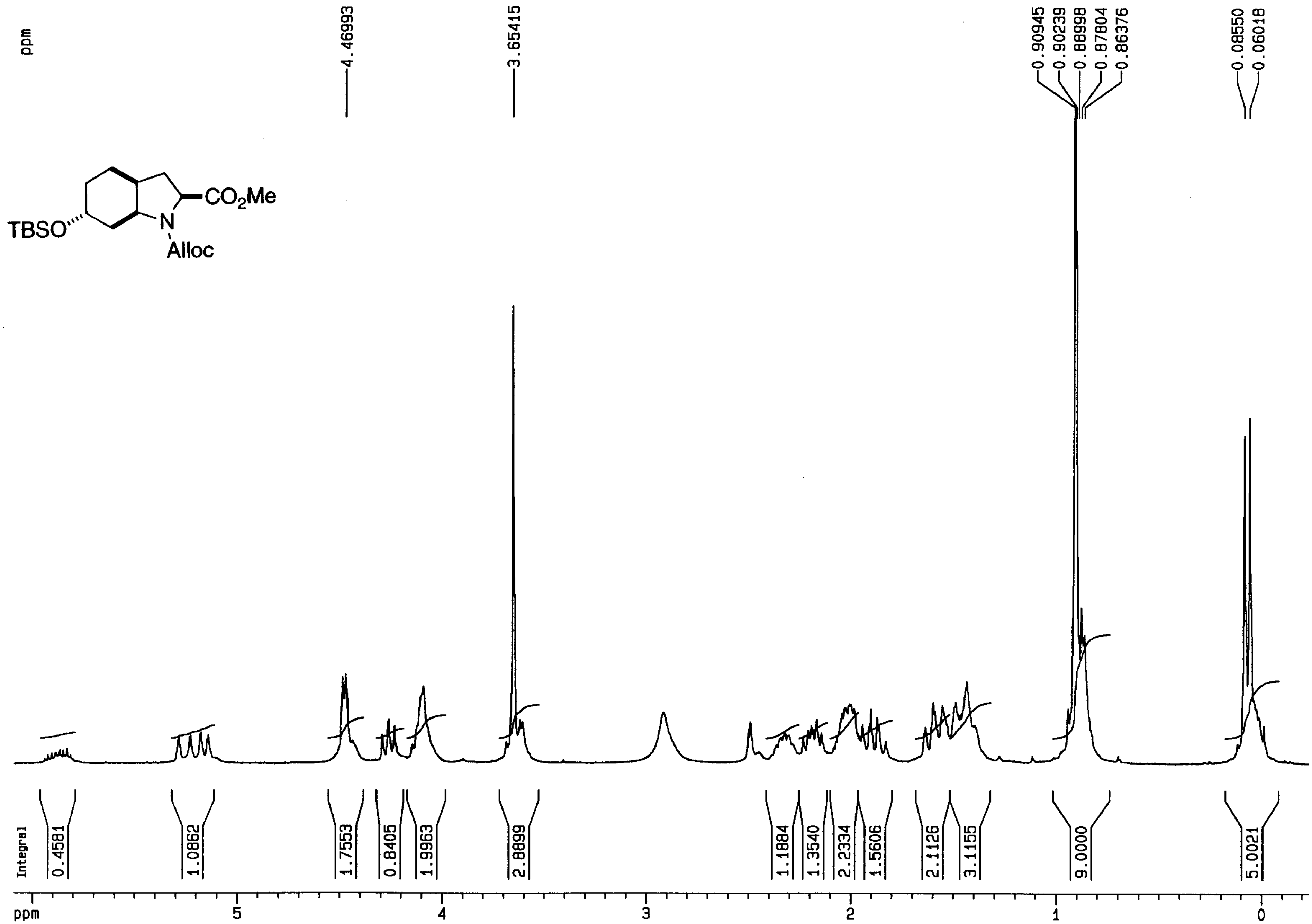
D-Hpla(TIPS, TBS)-L-Leu-OH (H2, Pd/C, EtOH) 300 MHz CDCl3



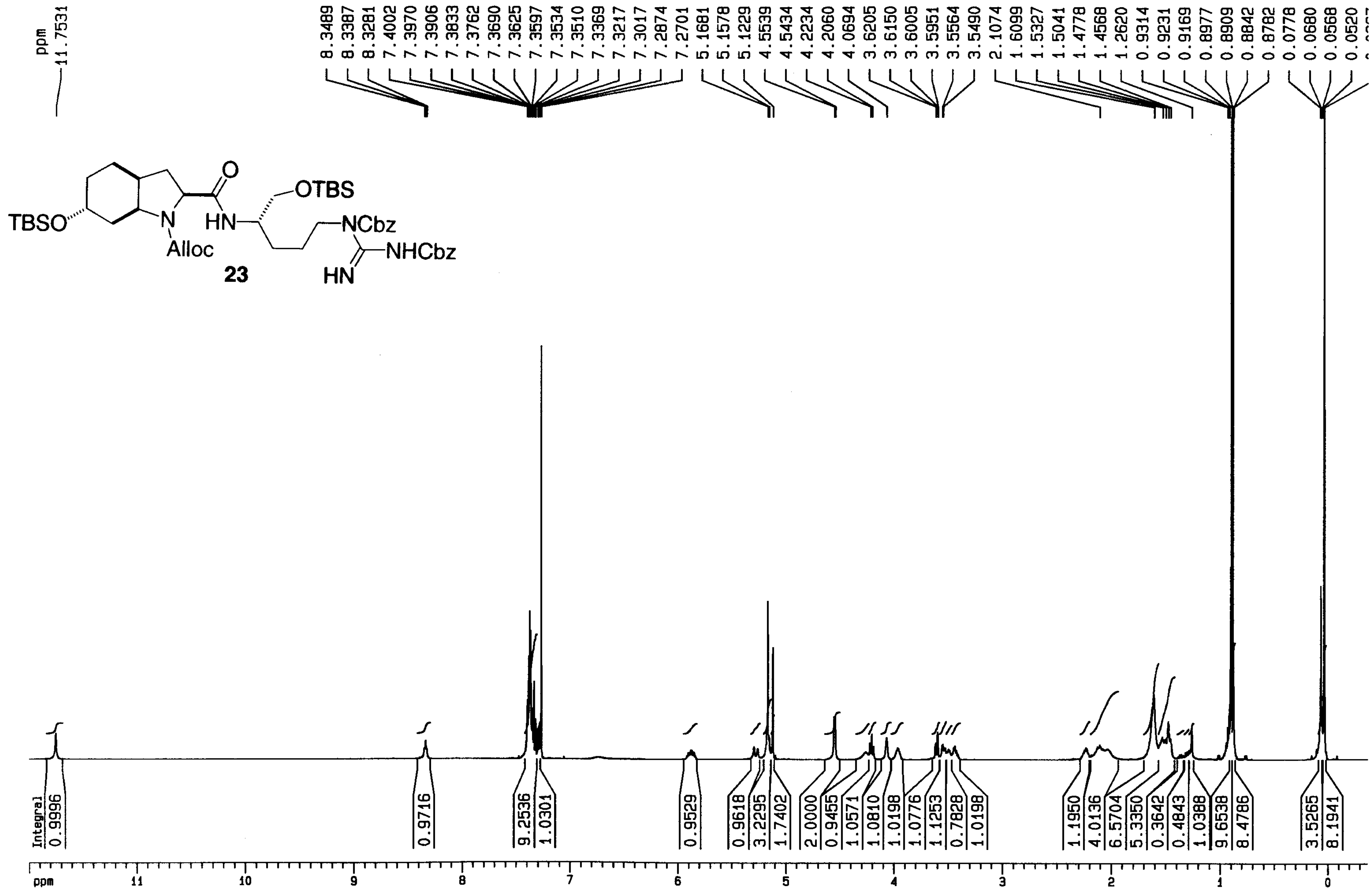
L^{Leu}-22



Alloc-Choi (TBS) -OMe   DMSO-d6   300 MHz   340 K

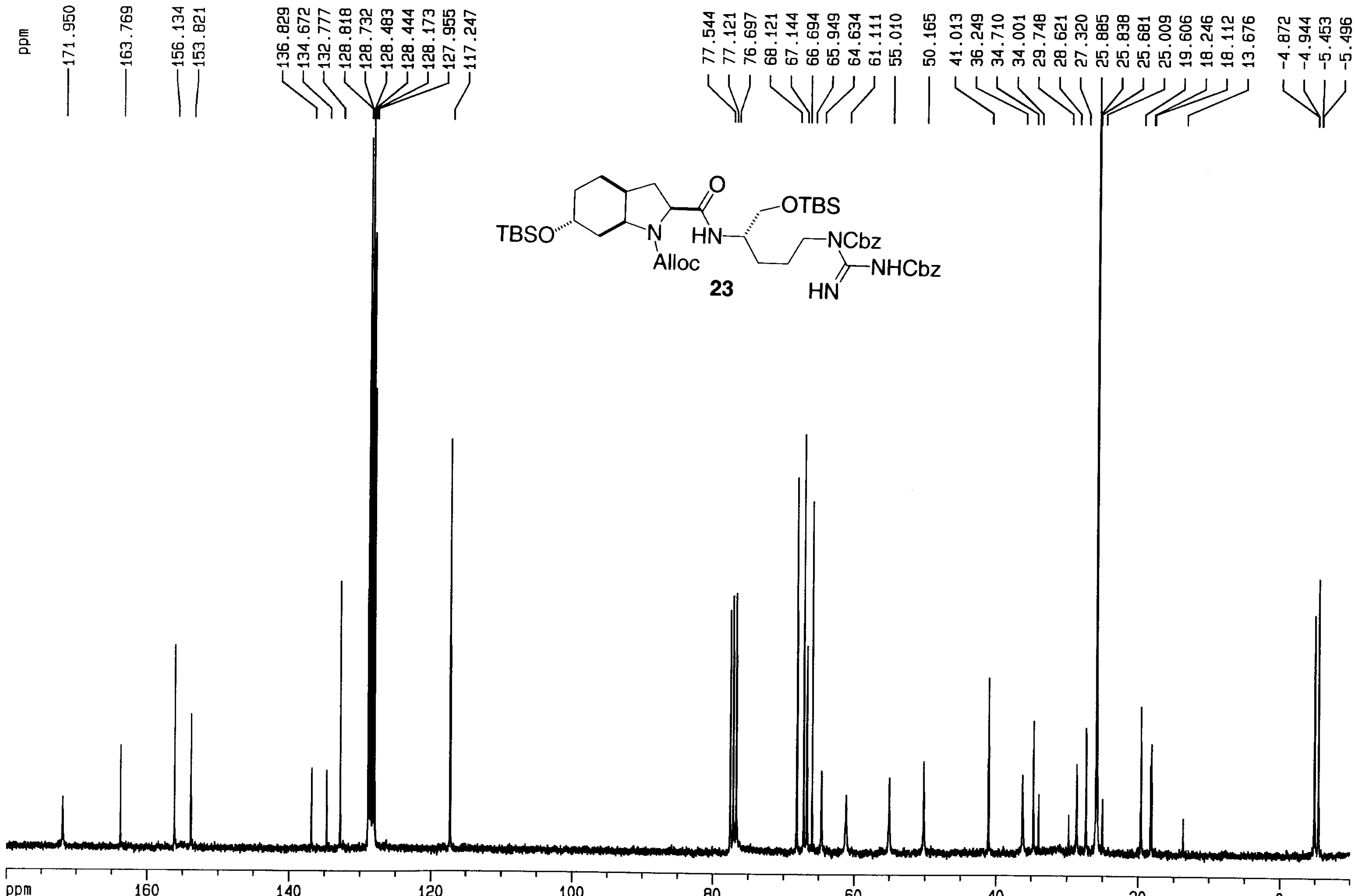


Alloc-Choi(TBS)-Argol(Cbz2)-OTBS 500 MHz CDCl3 rt

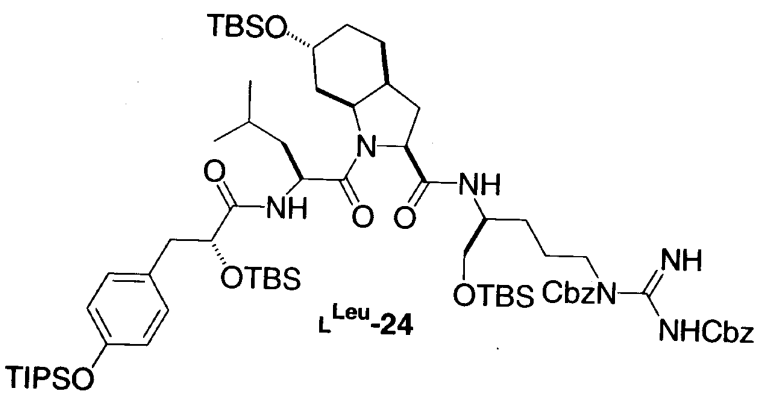


Alloc-Choi(TBS)-Argol(Cbz2)-OTBS   75 MHz CDCl3 rt

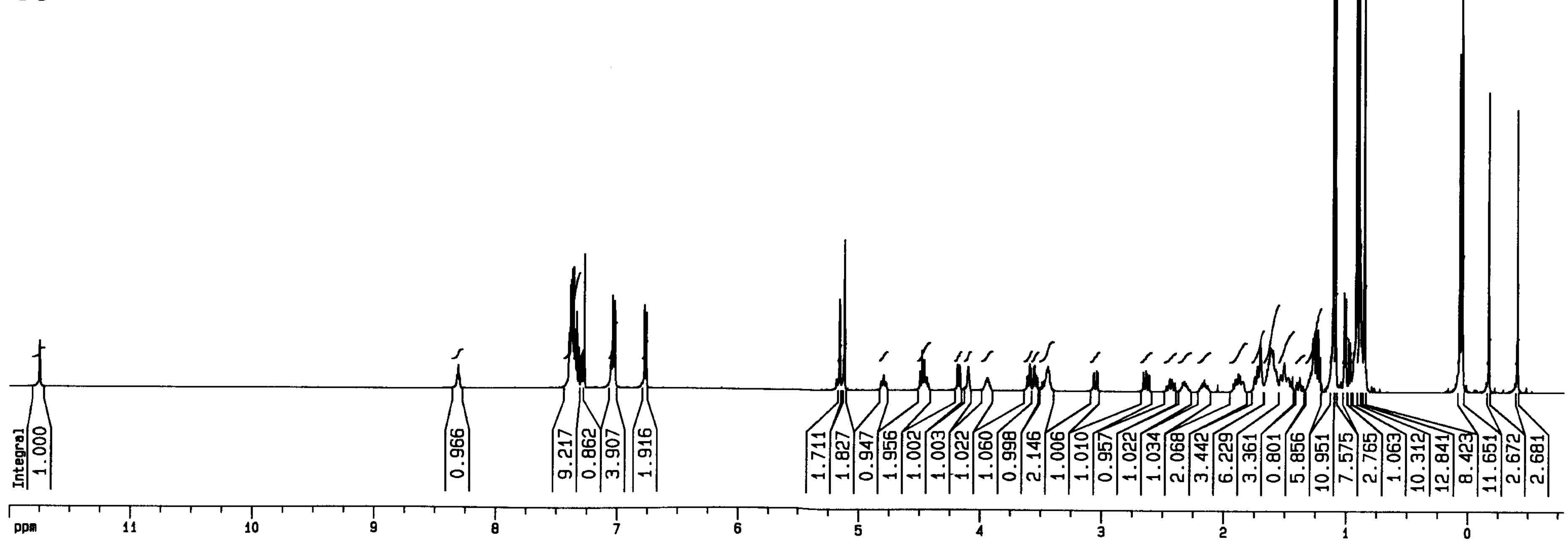
23



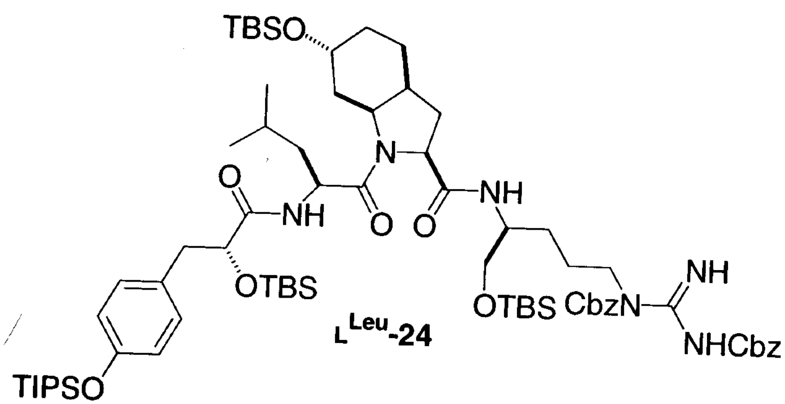
Hpla(TIPS, TBS)-L-Leu-Choi(TBS)-Argol(Cbz2)-OTBS 500 MHz CDCl3 rt



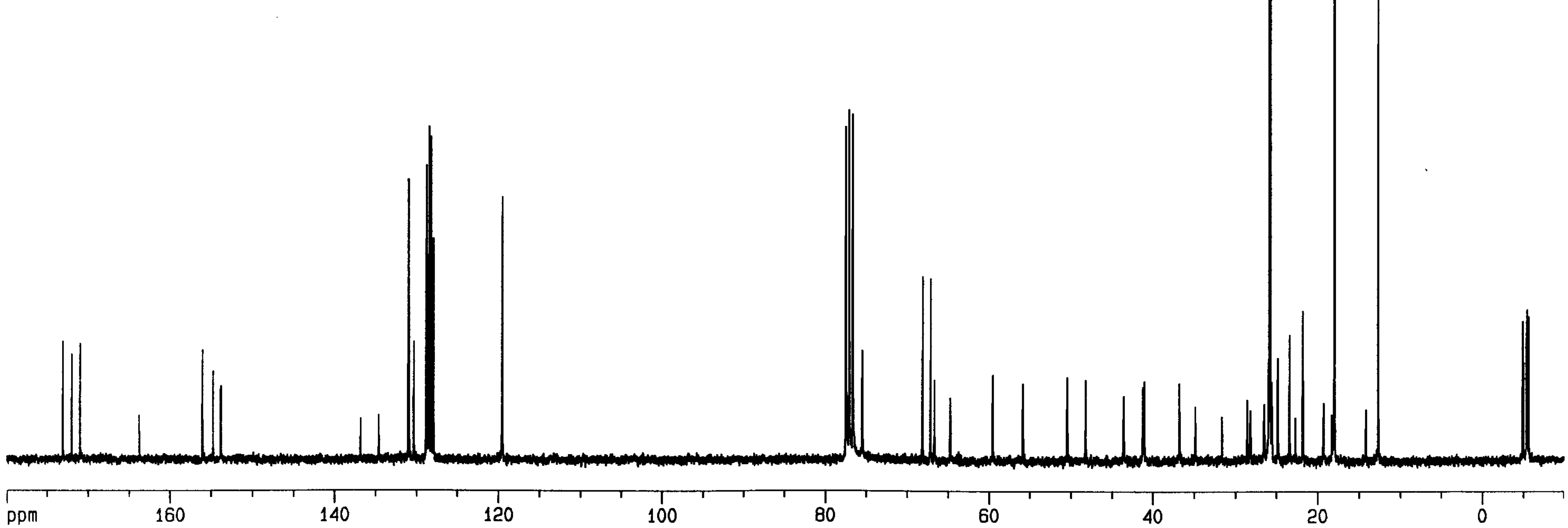
L^{Leu}-24



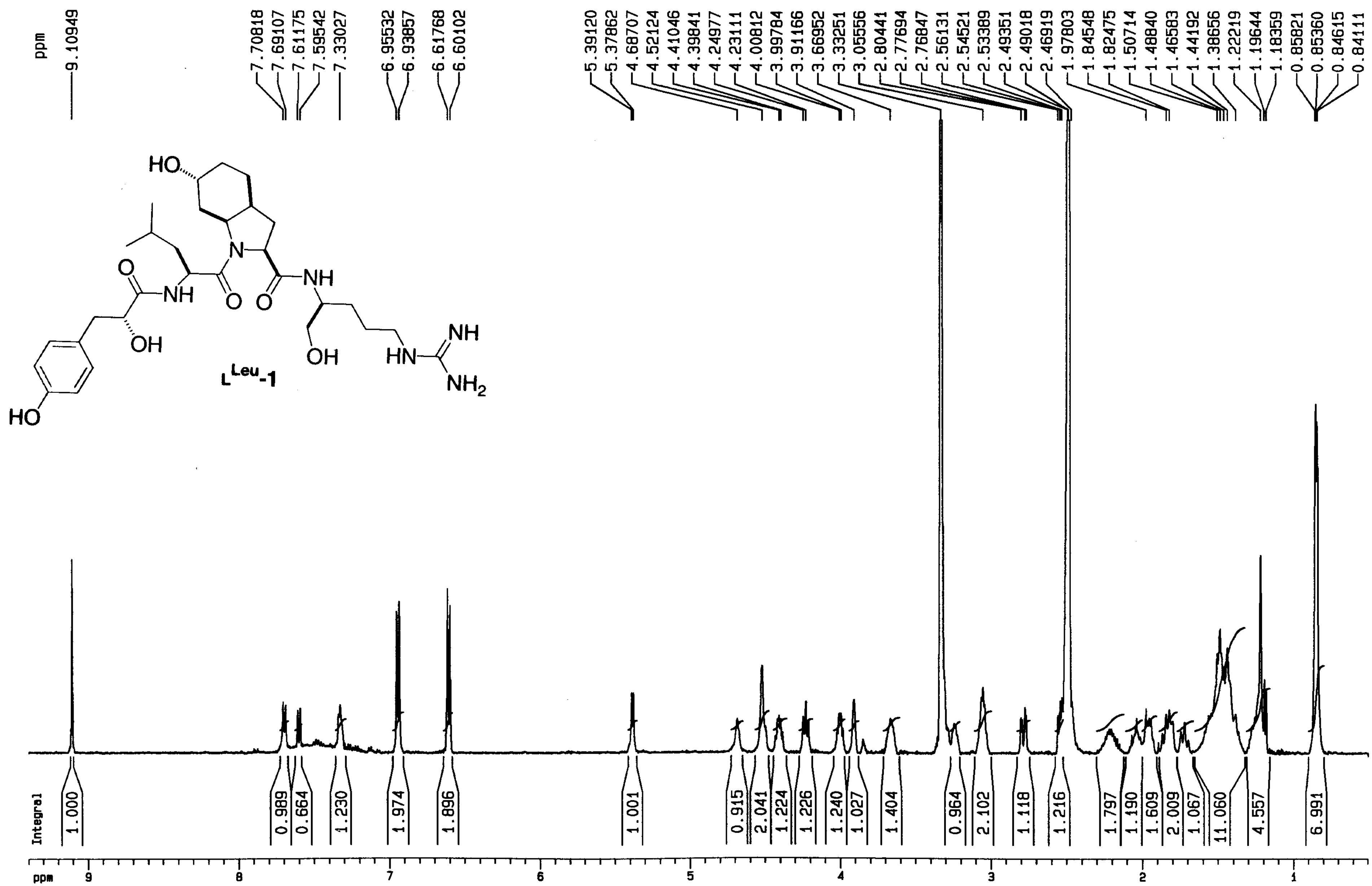
Hpla (TIPS, TBS) -Leu-Choi (TBS) -Argol (Cbz2) -OTBS 75 MHz CDCl3 rt



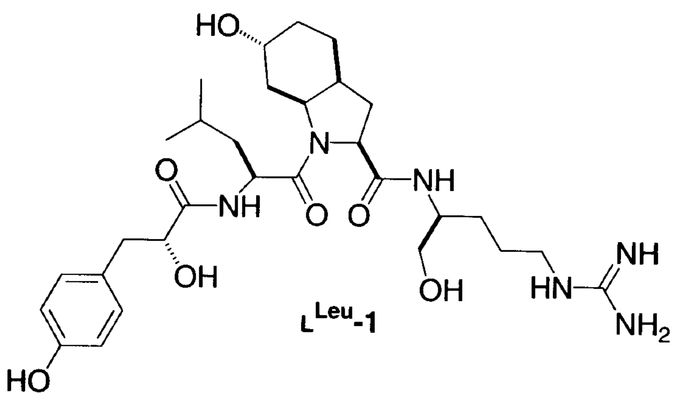
L^{Leu}-24



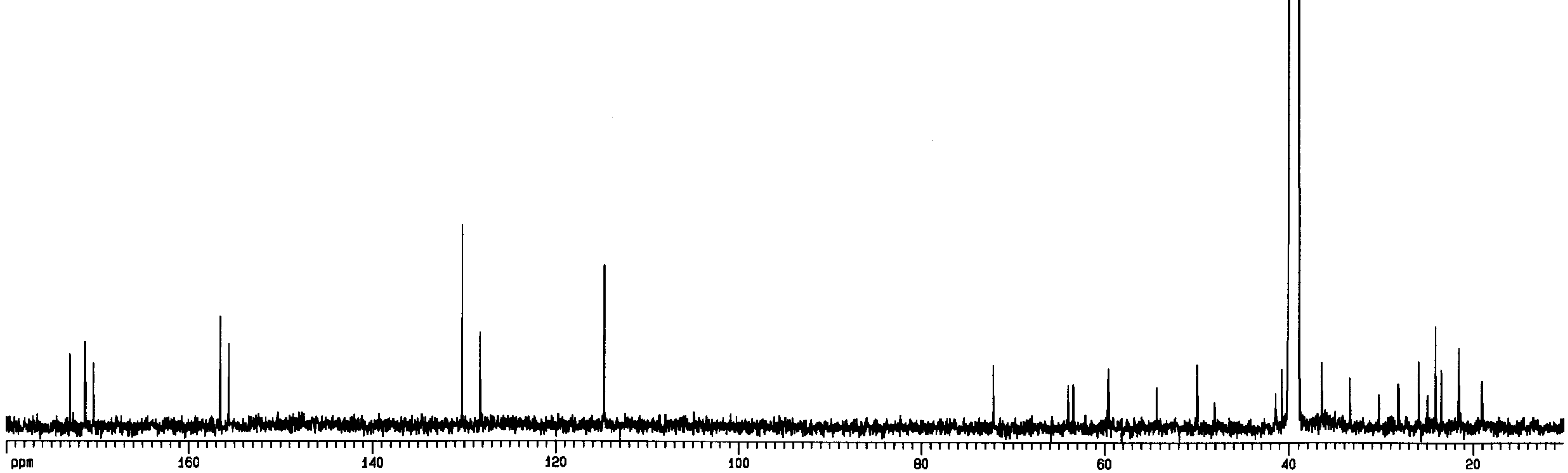
L-Leu Aeruginosin 298-A 1H NMR 500MHz DMSO-d6 rt



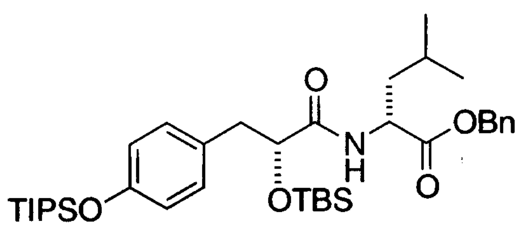
L-Leu Aeruginosin 298-A   13C NMR 125 MHz DMSO-d6 rt

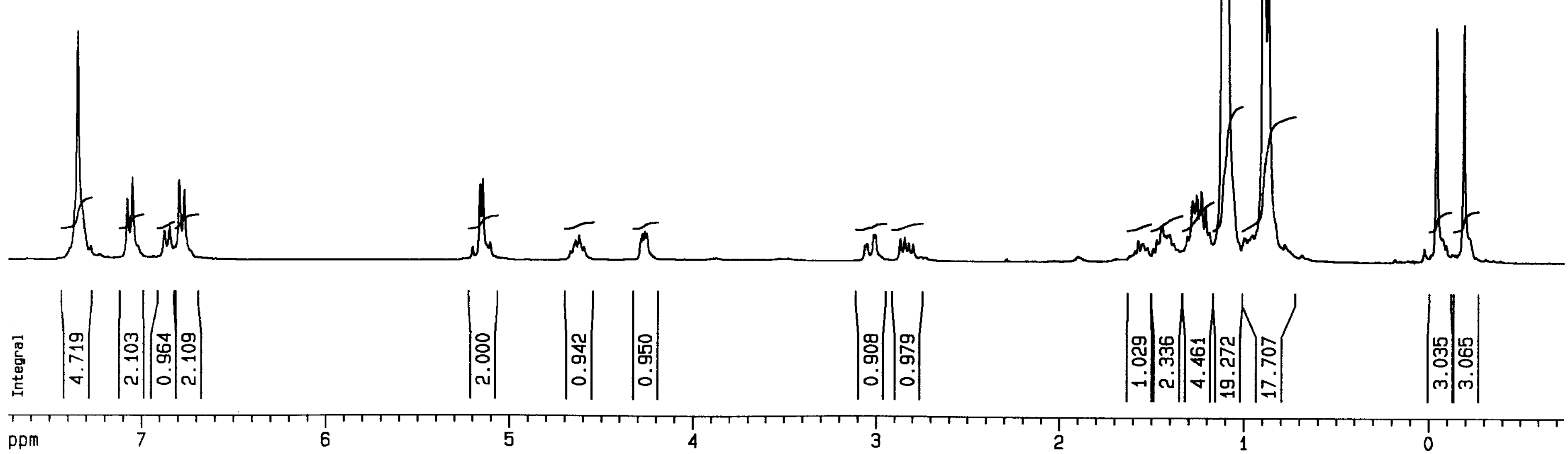


L^{Leu}-1

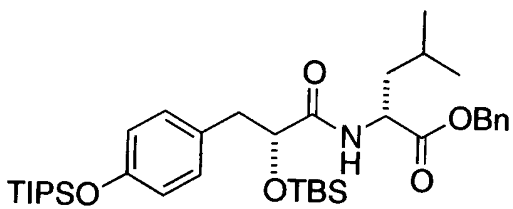


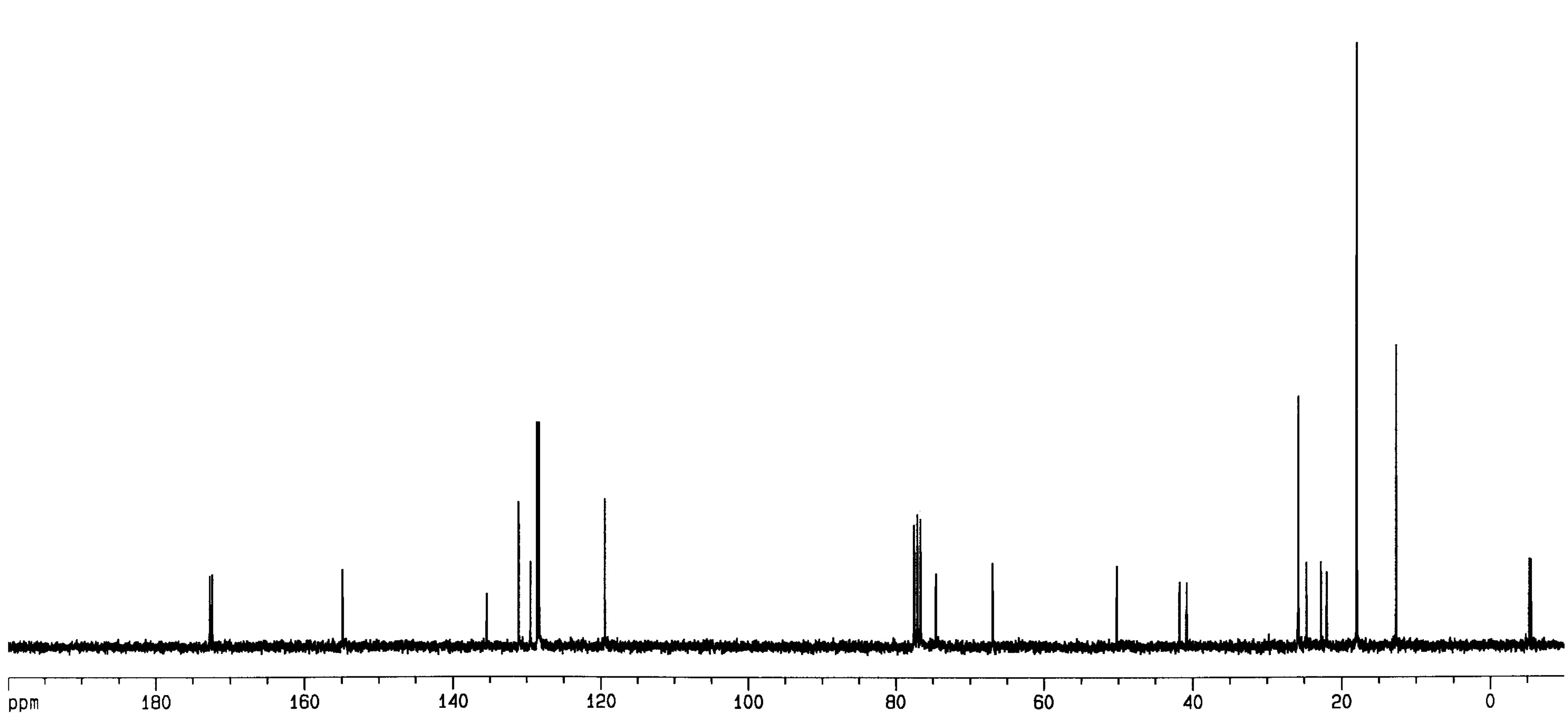
D-Hpla(TIPS, TBS)-D-Leu-OBn   300 MHz CDCl3 rt



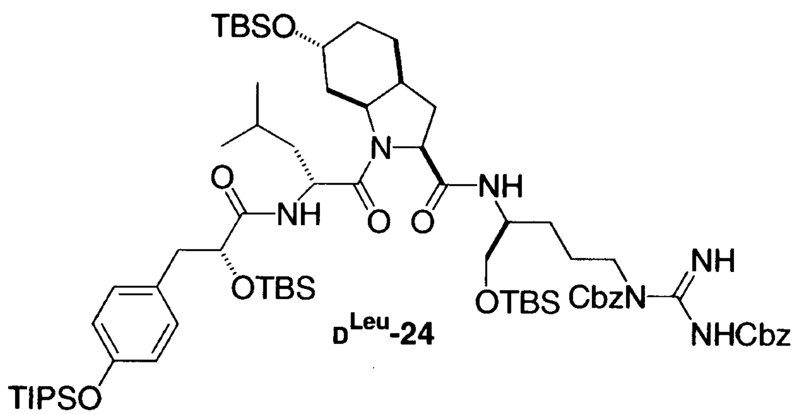


D-Hpla (TIPS, TBS) -D-Leu-OBn   75 MHz CDCl3 rt

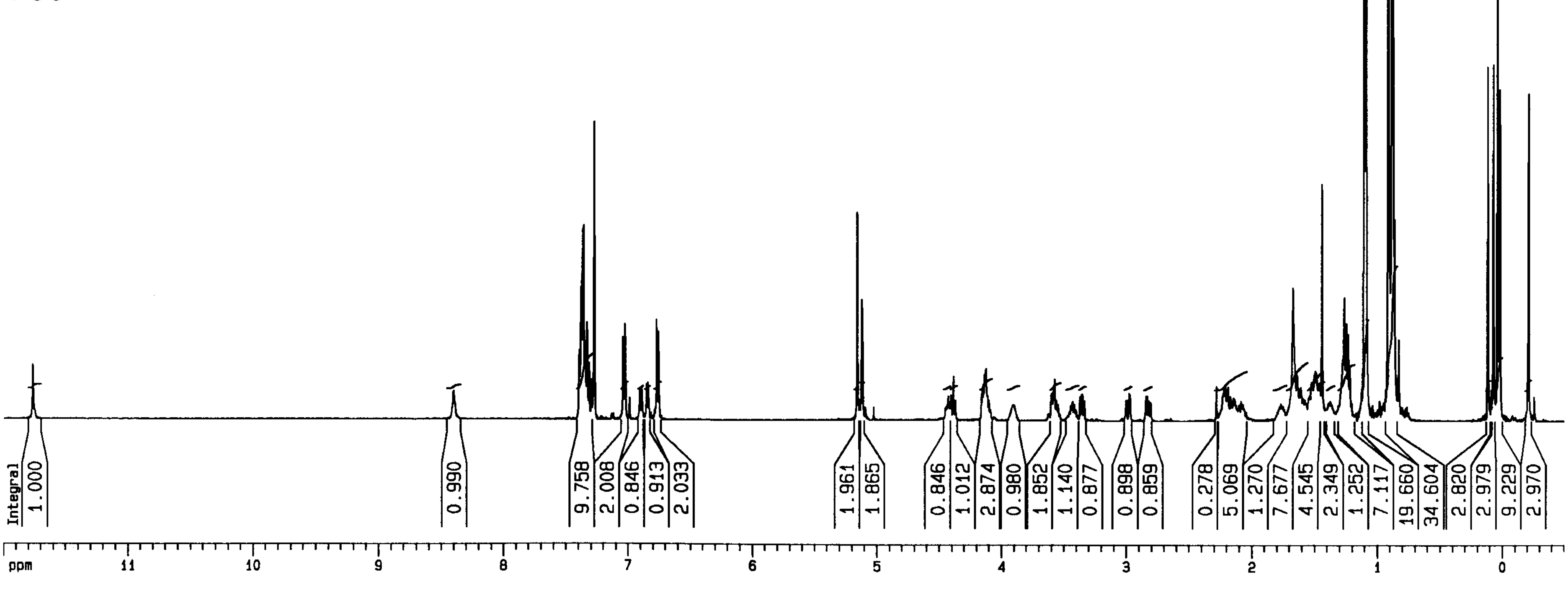




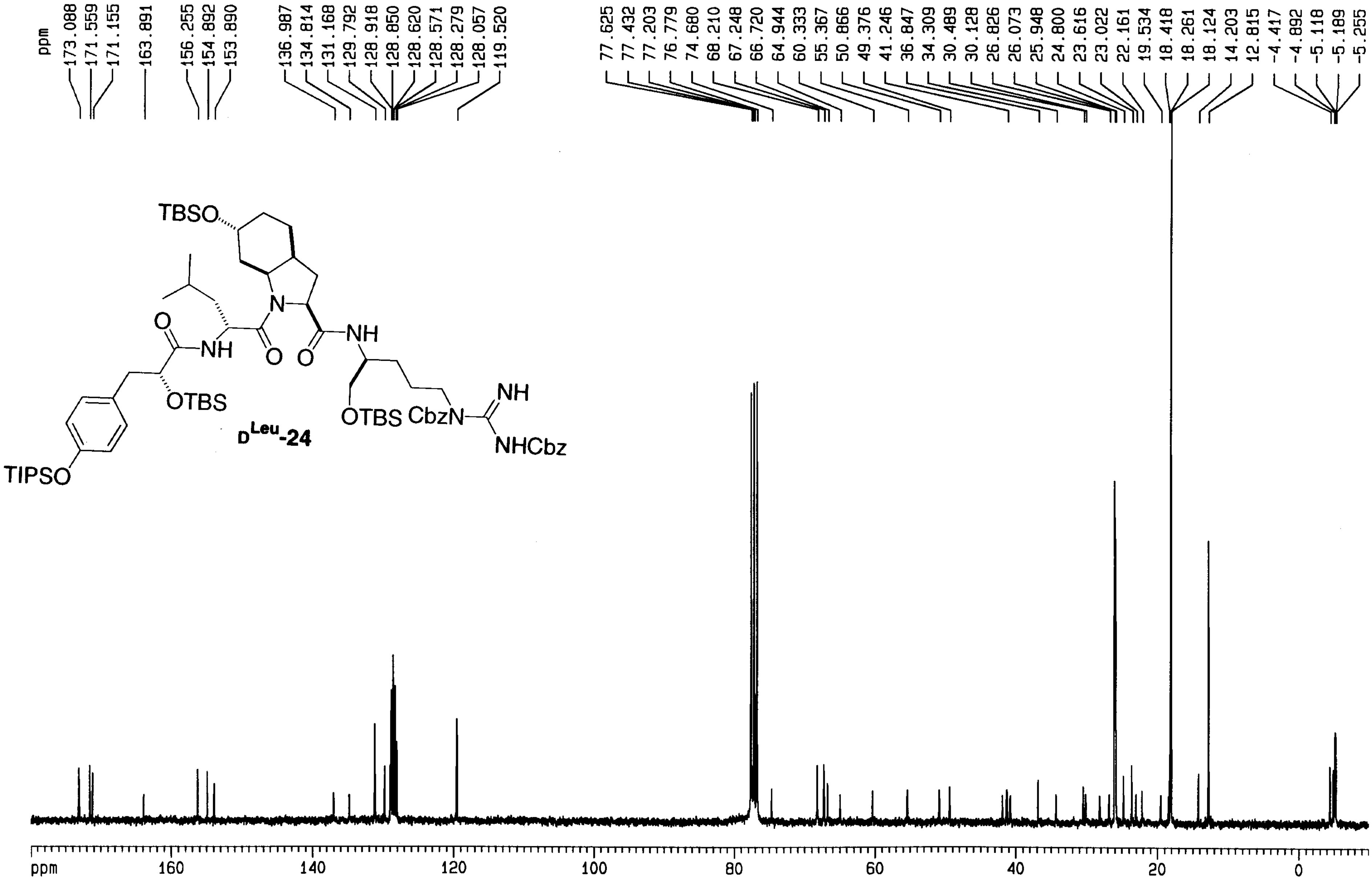
D-Hpla(TIPS, TBS)-D-Leu-Choi(TBS)-Argol(Cbz2)-OTBS 500 MHz CDCl3 rt



$_{D}^{Leu}$-24

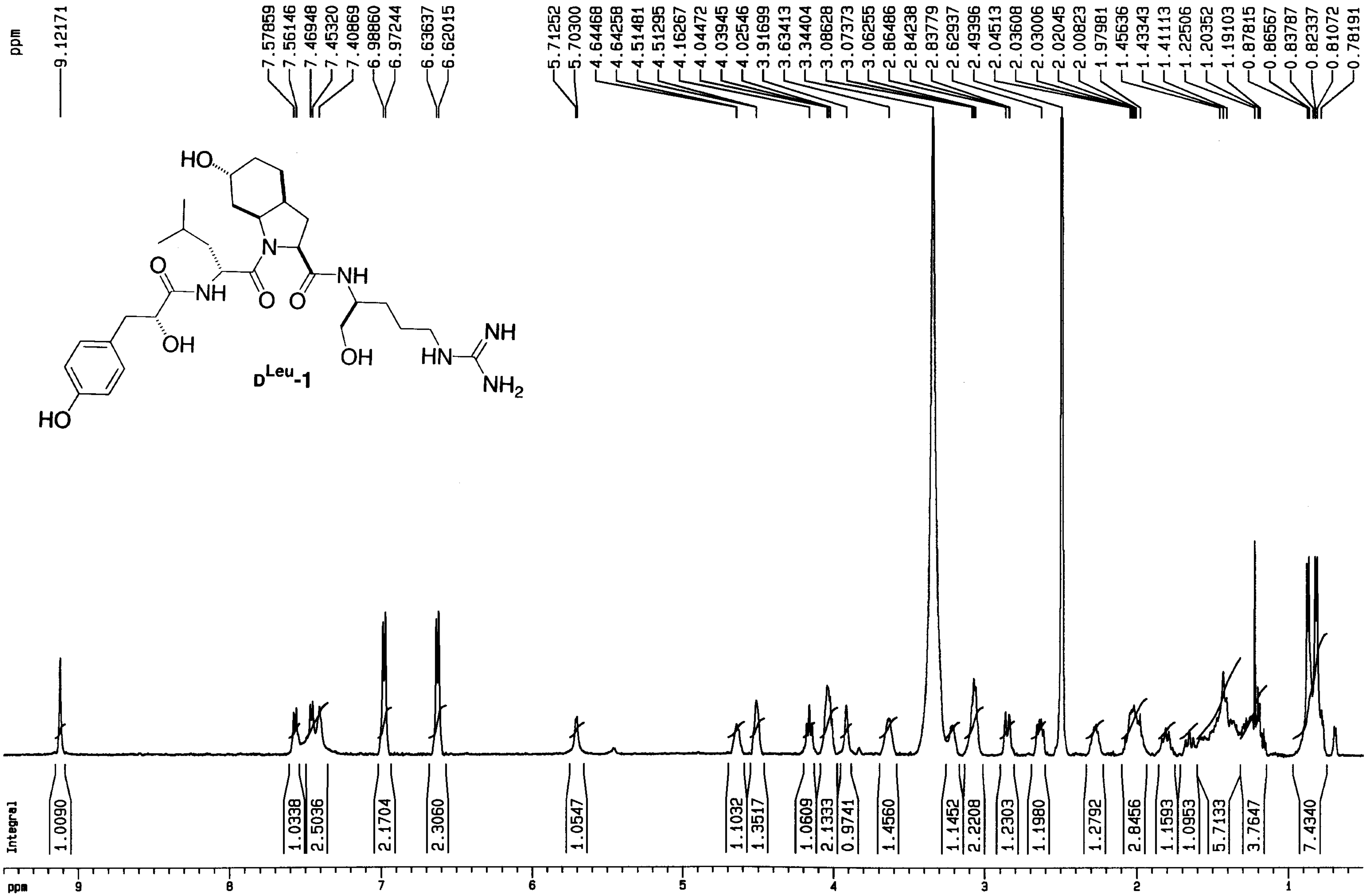


D-Hpla(TIPS, TBS)-D-Leu-Choi(TBS)-Argol(Cbz2)-OTBS 75 MHz CDCl3 rt



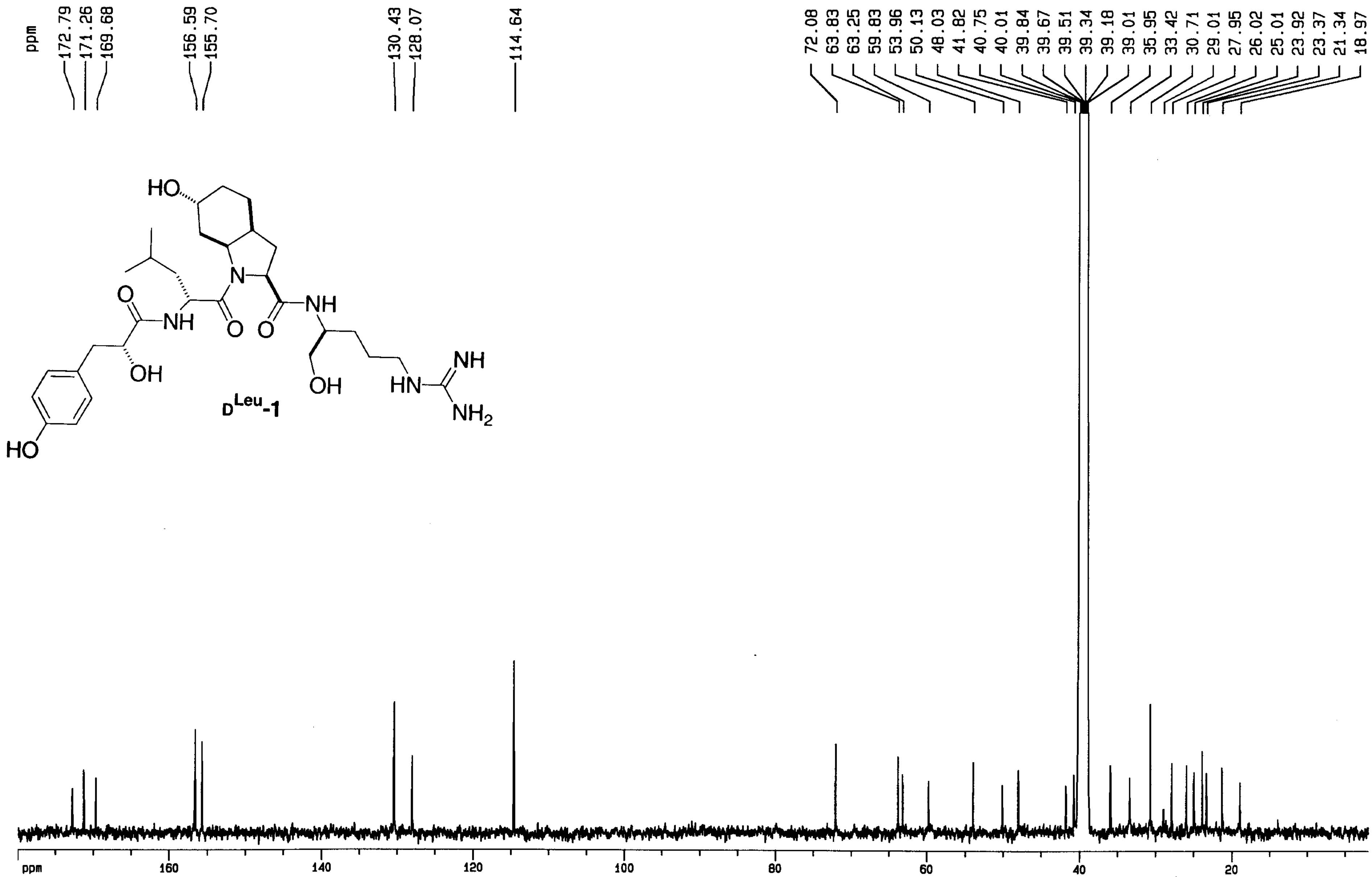
D^{Leu}-24

D-Leu Aeruginosin 298A 1H NMR 500 MHz DMSO-d6 rt



DLeu-1

D-Leu Aeruginosin 298A 13C NMR 125MHz DMSO-d6 rt



$_D$Leu-1

Natural
Aeruginosin 298-A