Radical Functionalization of Unsaturated Amino Acids: Synthesis of side-chain Fluorinated, Azido-substituted and Hydroxylated Amino Acids

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Electronic Supplementary Information

Methyl (2*S*)-2-{[(*tert*-butoxy)carbonyl]amino}-3-(1-fluorocyclopentyl)propanoate (2a)

Empirical formula	C14 H24 F N O4	
Formula weight	289.34	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 16.1257(6) Å	a = 90°.
	b = 5.0821(2) Å	b = 97.582(2)°.
	c = 19.3075(6) Å	g = 90°.
Volume	1568.46(10) $Å^3$	
Z	4	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	0.806 mm^{-1}	
F(000)	624	
Crystal size	0.320 x 0.120 x 0.120 mm^3	
Theta range for data collection	2.308 to 66.651°.	
Index ranges	-15<=h<=19, -6<=k<=6, -22<=l<=22	
Reflections collected	22527	
Independent reflections	5386 [R(int) = 0.1030]	
Completeness to theta = 67.679°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.86 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5386 / 13 / 379	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0571, wR2 = 0.1104	
R indices (all data)	R1 = 0.1062, wR2 = 0.1295	
Absolute structure parameter	0.00(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.352 and -0.324 e.$Å^{-3}$	

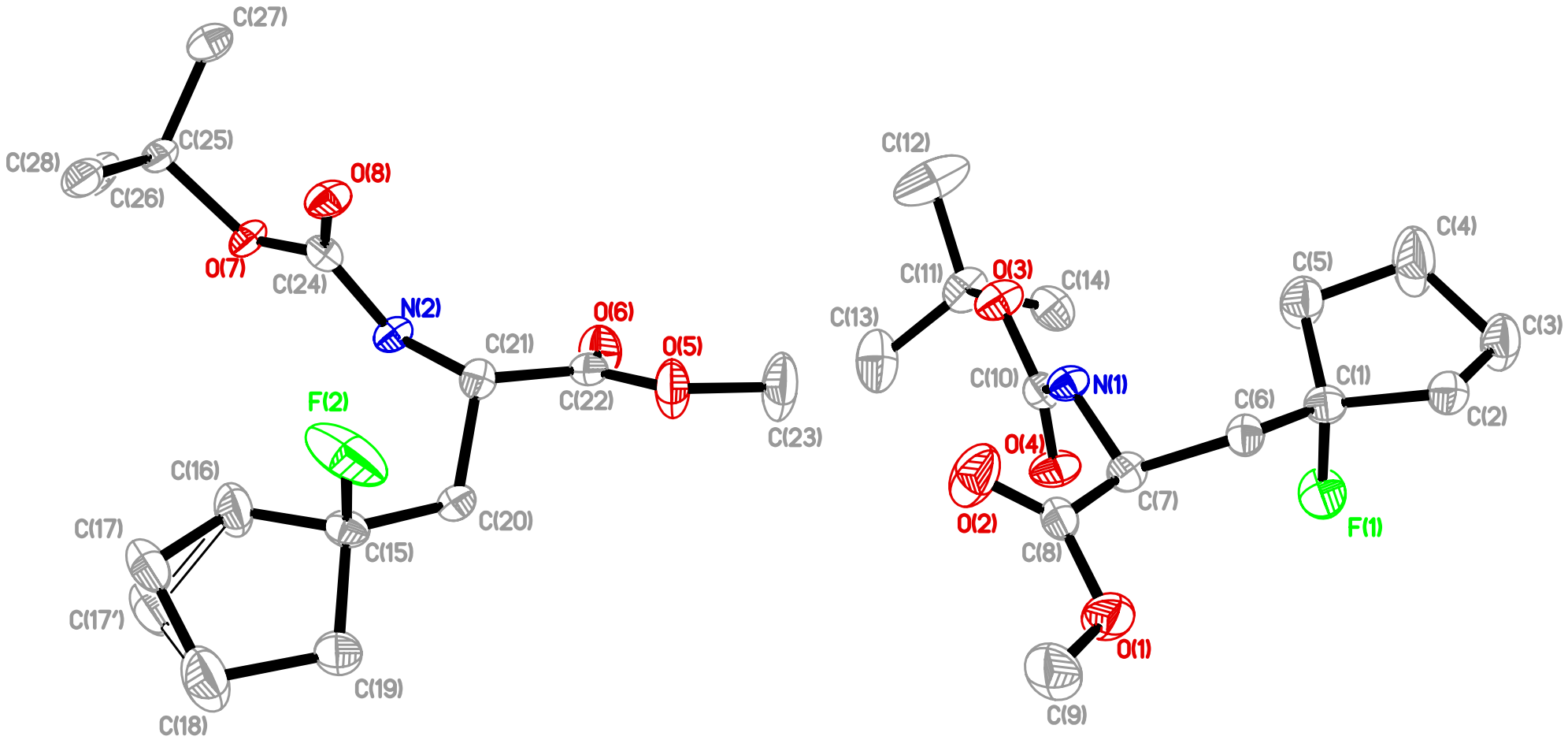


Figure S1. Thermal ellipsoid plot for **2a**, with ellipsoid contour probability at the 50% level.

Methyl (2*S*)-2-{[(*tert*-butoxy)carbonyl]amino}-3-(1,4,4-trifluorocyclohexyl)propanoate (24)

Empirical formula	C15 H24 F3 N O4	
Formula weight	339.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.20190(10) Å	a= 90°.
	b = 11.2334(3) Å	b= 90°.
	c = 28.6154(6) Å	g = 90°.
Volume	1672.14(7) $Å^3$	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	1.016 mm^{-1}	
F(000)	720	
Crystal size	0.400 x 0.130 x 0.100 mm^3	
Theta range for data collection	3.089 to 66.605°.	
Index ranges	-6<=h<=5, -13<=k<=13, -34<=l<=34	
Reflections collected	20183	
Independent reflections	2951 [R(int) = 0.0271]	
Completeness to theta = 67.000°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.54	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2951 / 0 / 212	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0646	
R indices (all data)	R1 = 0.0271, wR2 = 0.0656	
Absolute structure parameter	0.00(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.118 and -0.265 $e.Å^{-3}$	

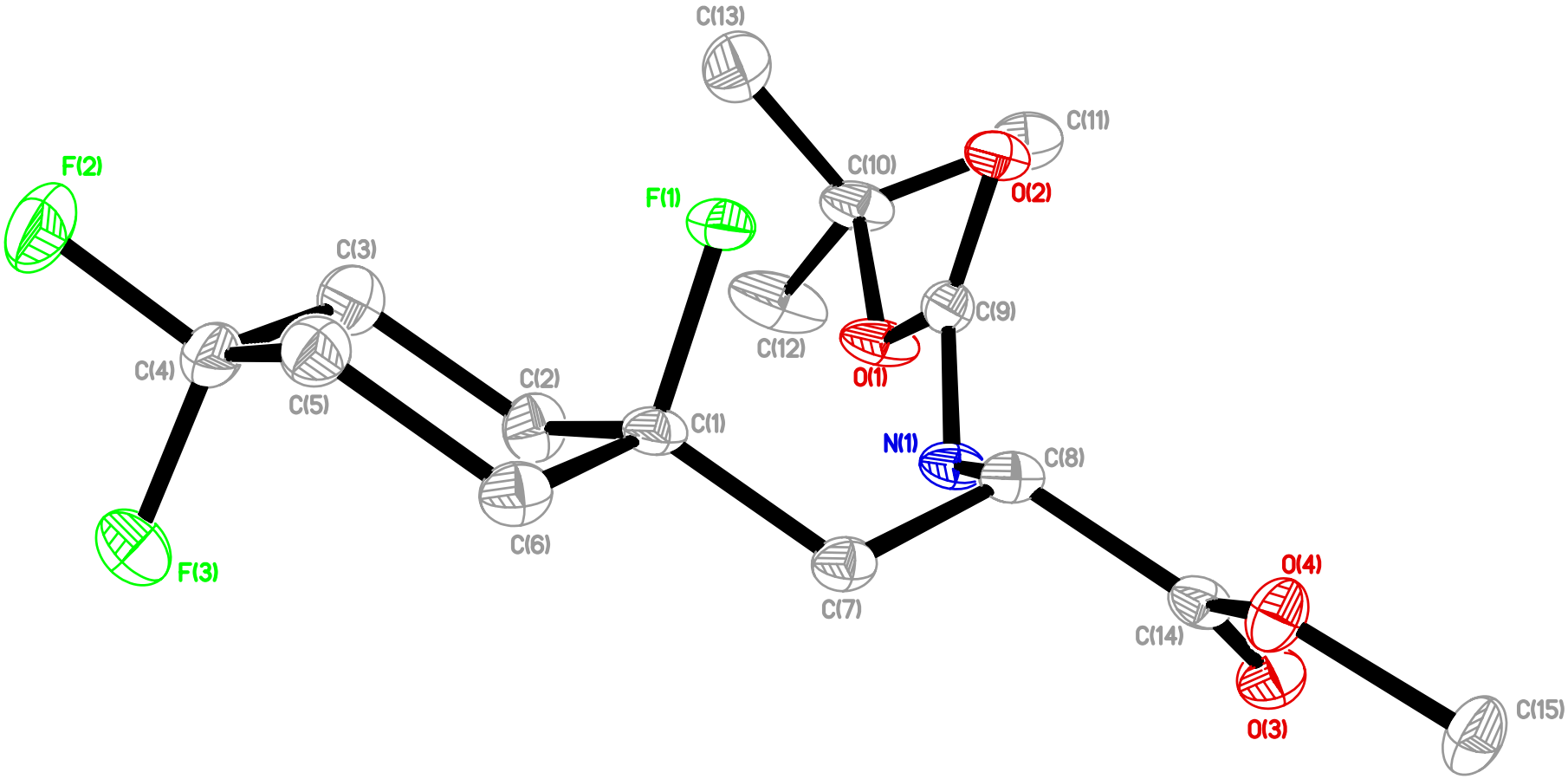


Figure S2. Thermal ellipsoid plot for **24**, with ellipsoid contour probability at the 50% level.

Tert-butyl _N_-[(3_S_)-2-oxo-1-azaspiro[4.5]decan-3-yl]carbamate (40)

Empirical formula	C14 H24 N2 O3	
Formula weight	268.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.8929(4) Å	a = 90°.
	b = 9.6349(6) Å	b = 95.355(4)°.
	c = 13.2171(9) Å	g = 90°.
Volume	747.16(9) $Å^3$	
Z	2	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.678 mm^{-1}	
F(000)	292	
Crystal size	0.120 x 0.100 x 0.020 mm^3	
Theta range for data collection	5.691 to 66.384°.	
Index ranges	-7<=h<=6, -11<=k<=11, -15<=l<=15	
Reflections collected	9664	
Independent reflections	2594 [R(int) = 0.0559]	
Completeness to theta = 66.384°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2594 / 1 / 176	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0788	
R indices (all data)	R1 = 0.0489, wR2 = 0.0828	
Absolute structure parameter	0.02(16)	
Extinction coefficient	0.012(2)	
Largest diff. peak and hole	0.153 and -0.144 e.$Å^{-3}$	

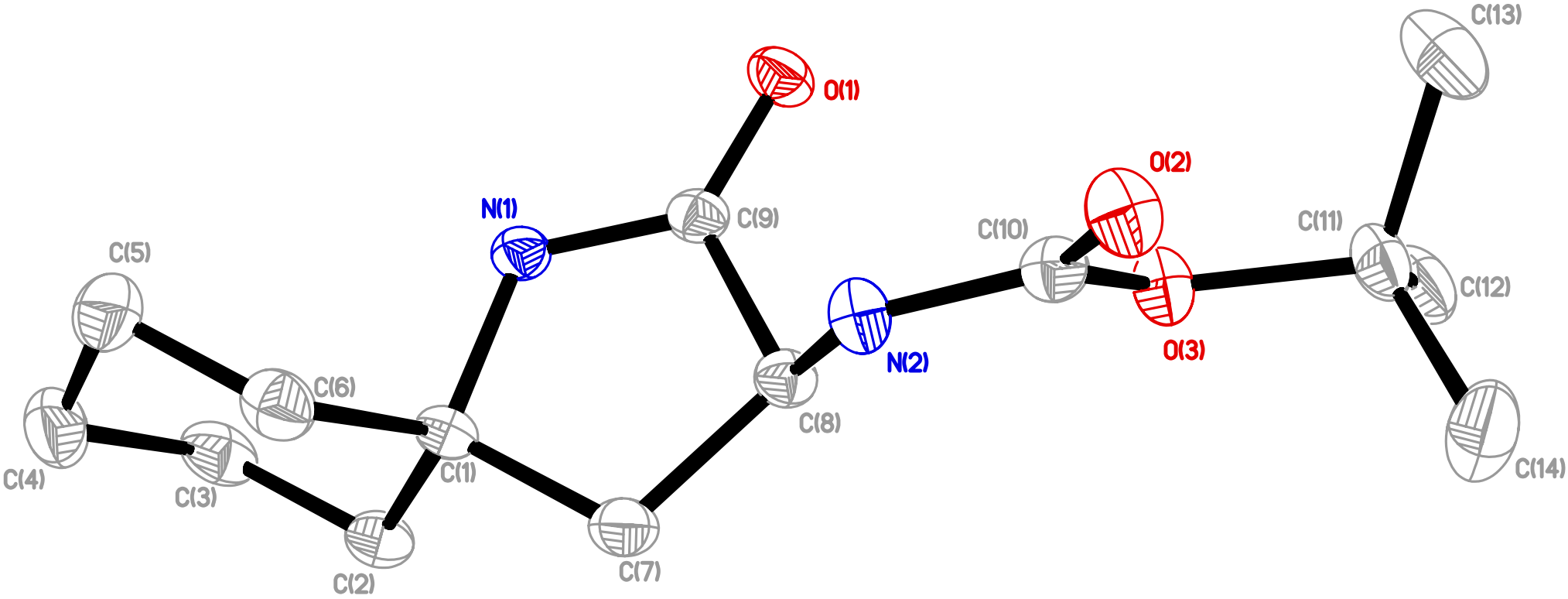
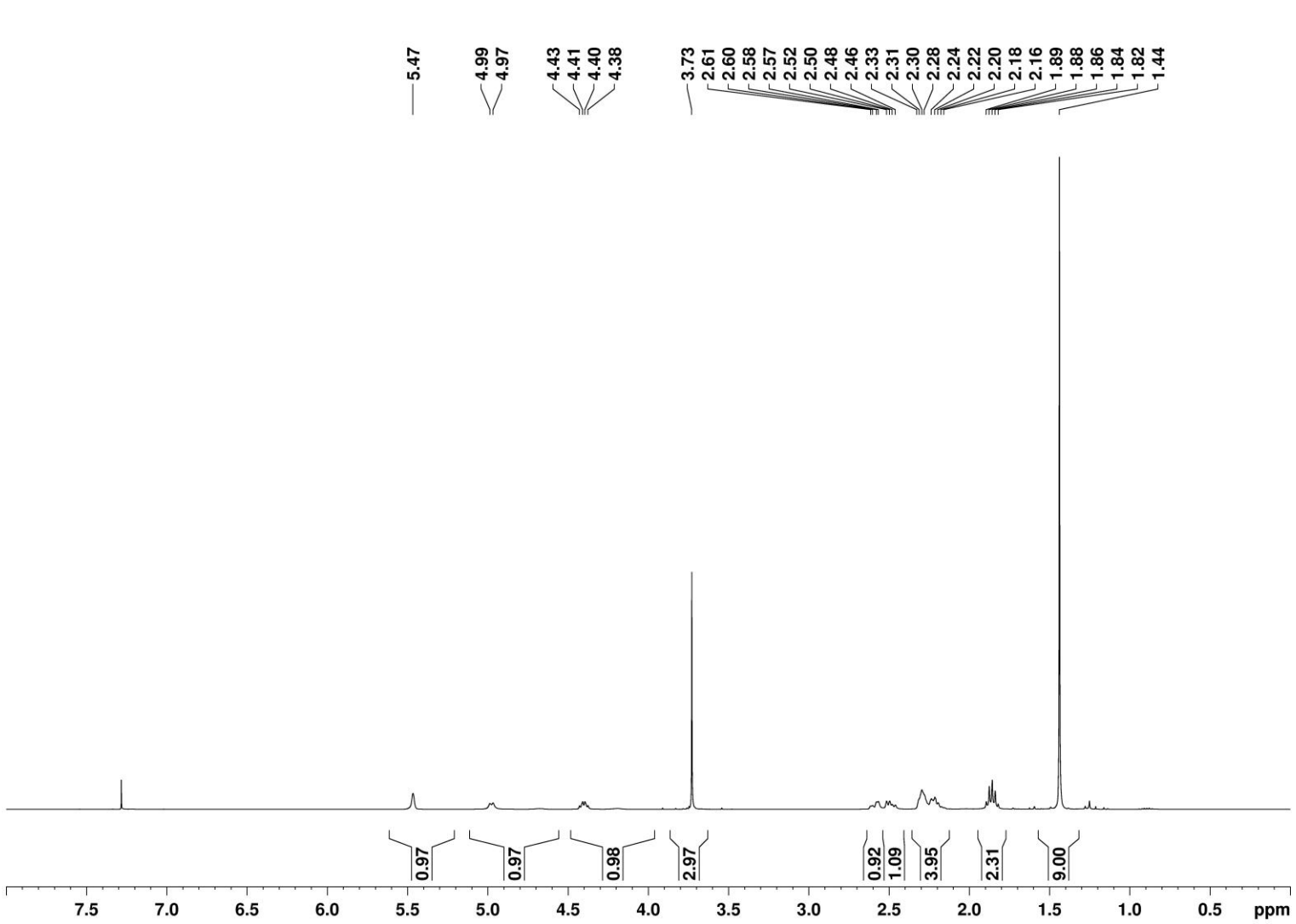
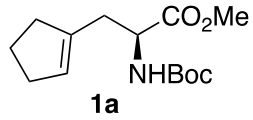


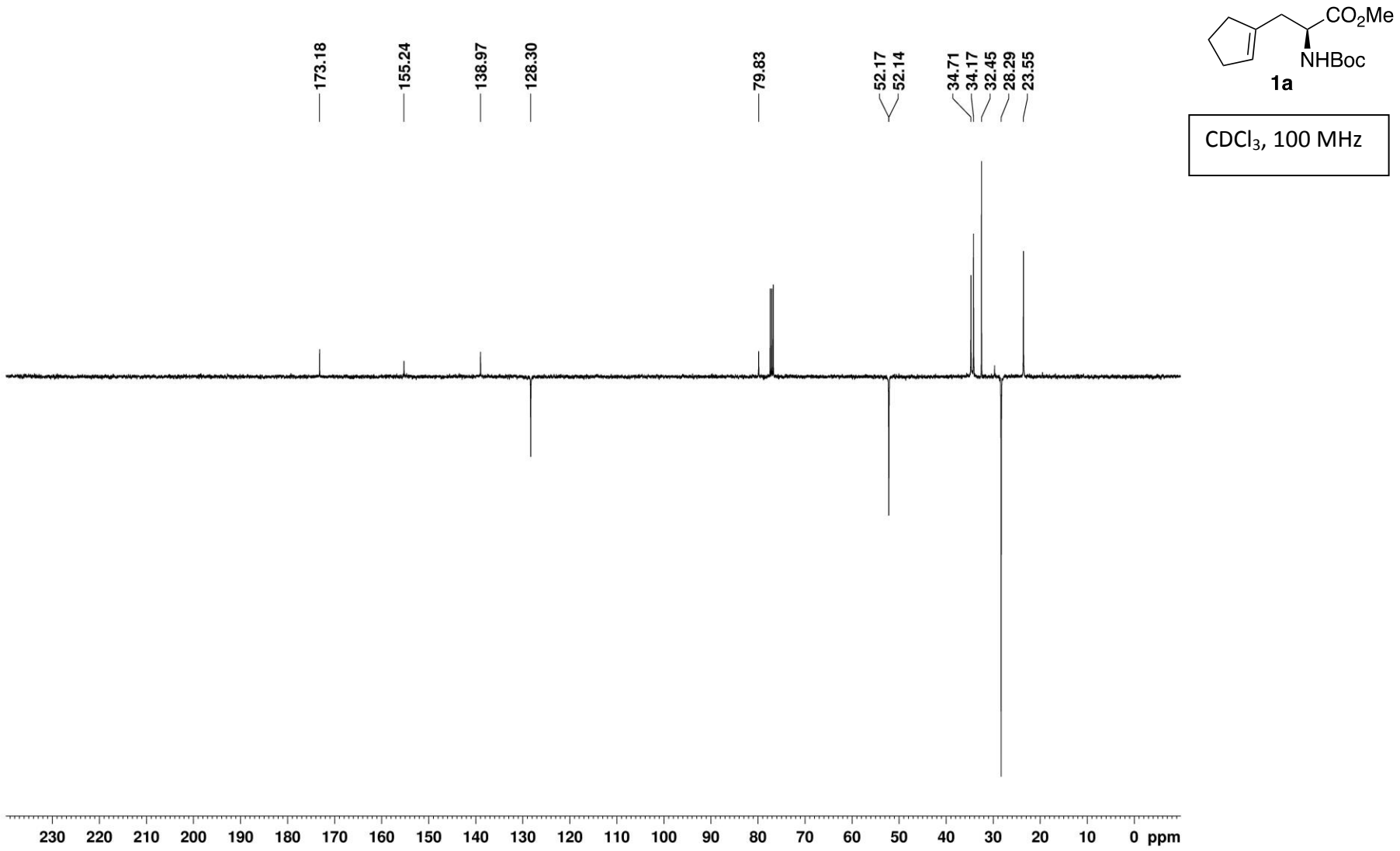
Figure S3. Thermal ellipsoid plot for **40**, with ellipsoid contour probability at the 50% level.

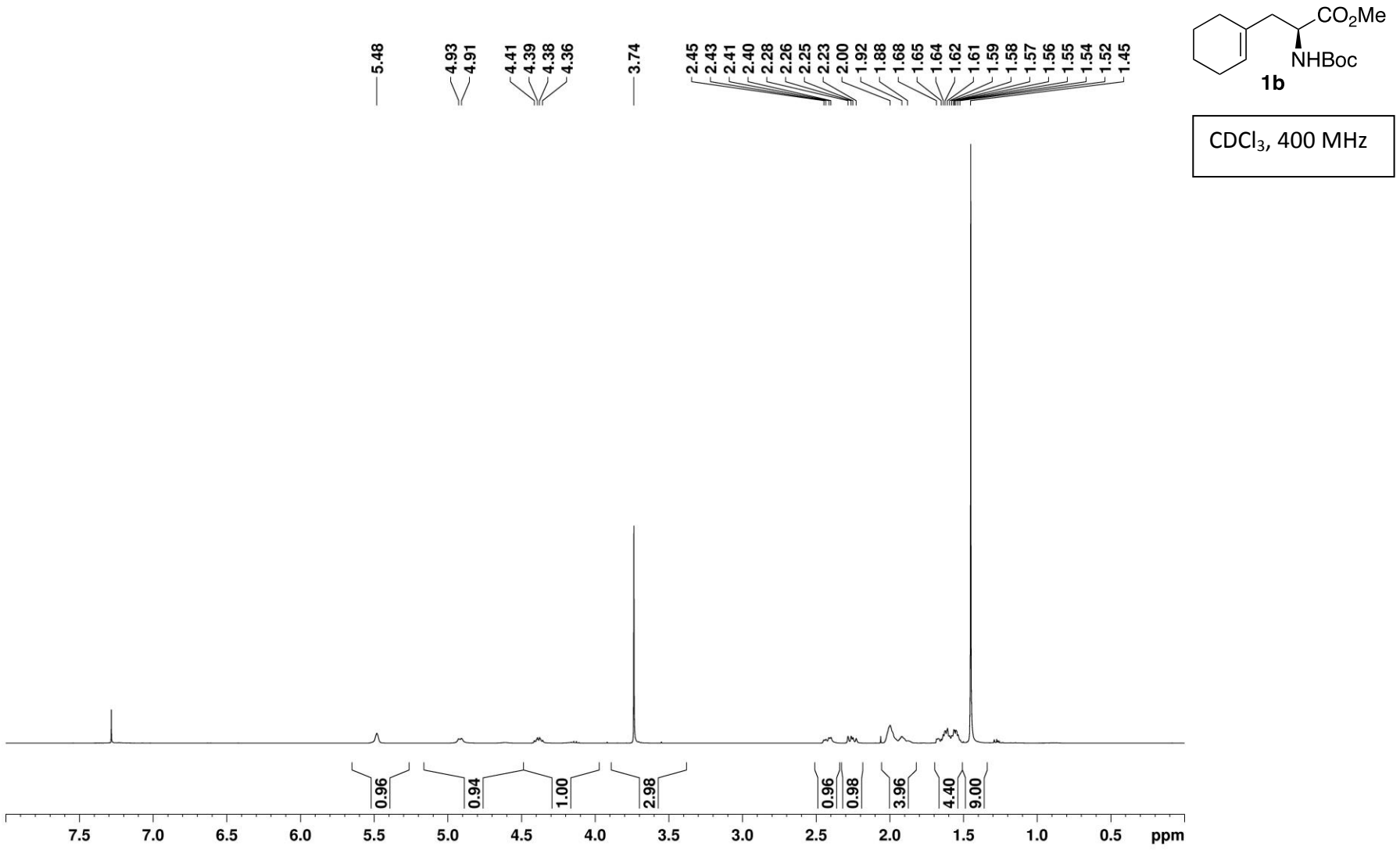




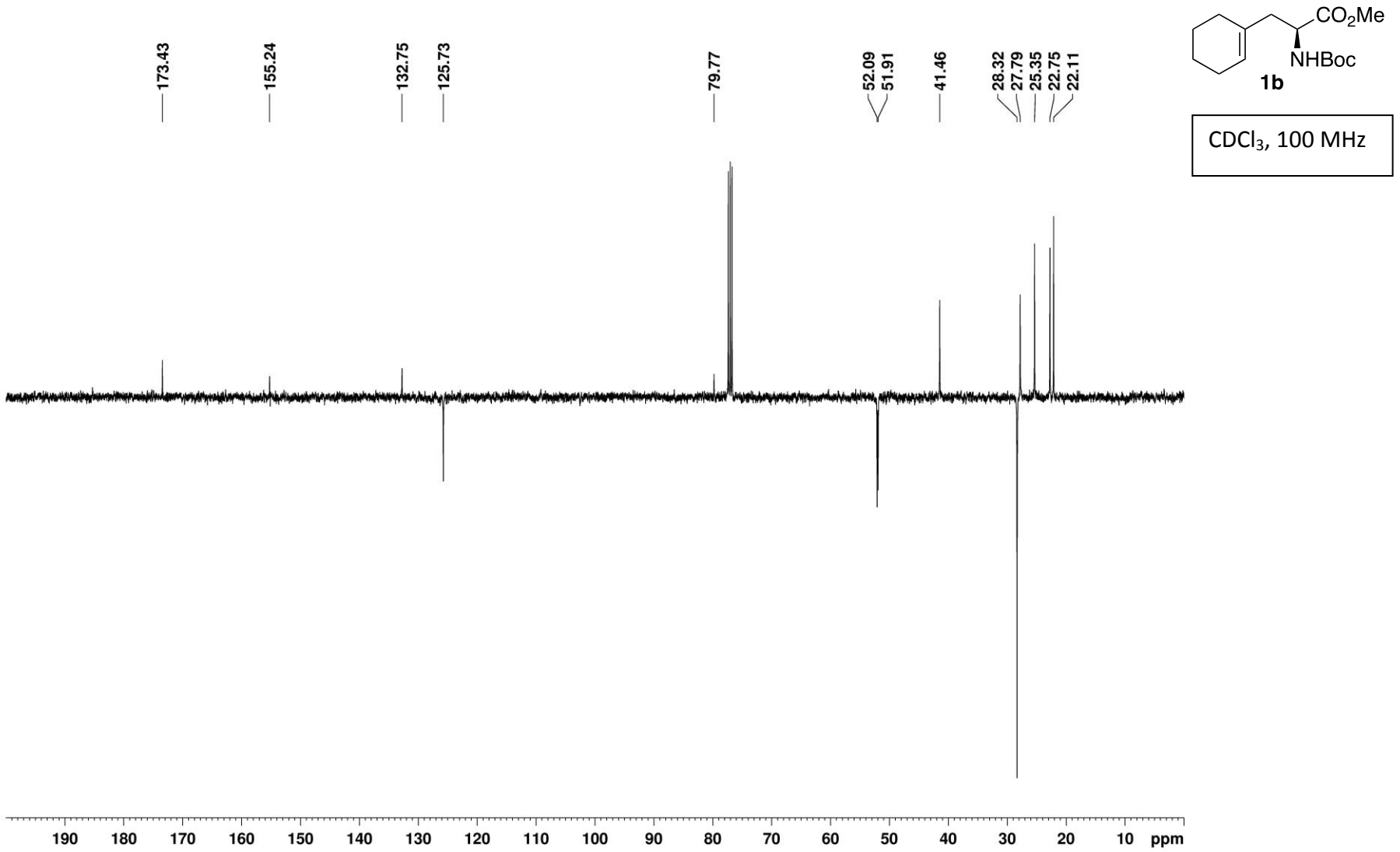
1a

$CDCl_3$, 400 MHz


173.18
155.24
138.97
128.30
79.83
52.17
52.14
34.71
34.17
32.45
28.29
23.55
CO2Me
NHBoc
1a
CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

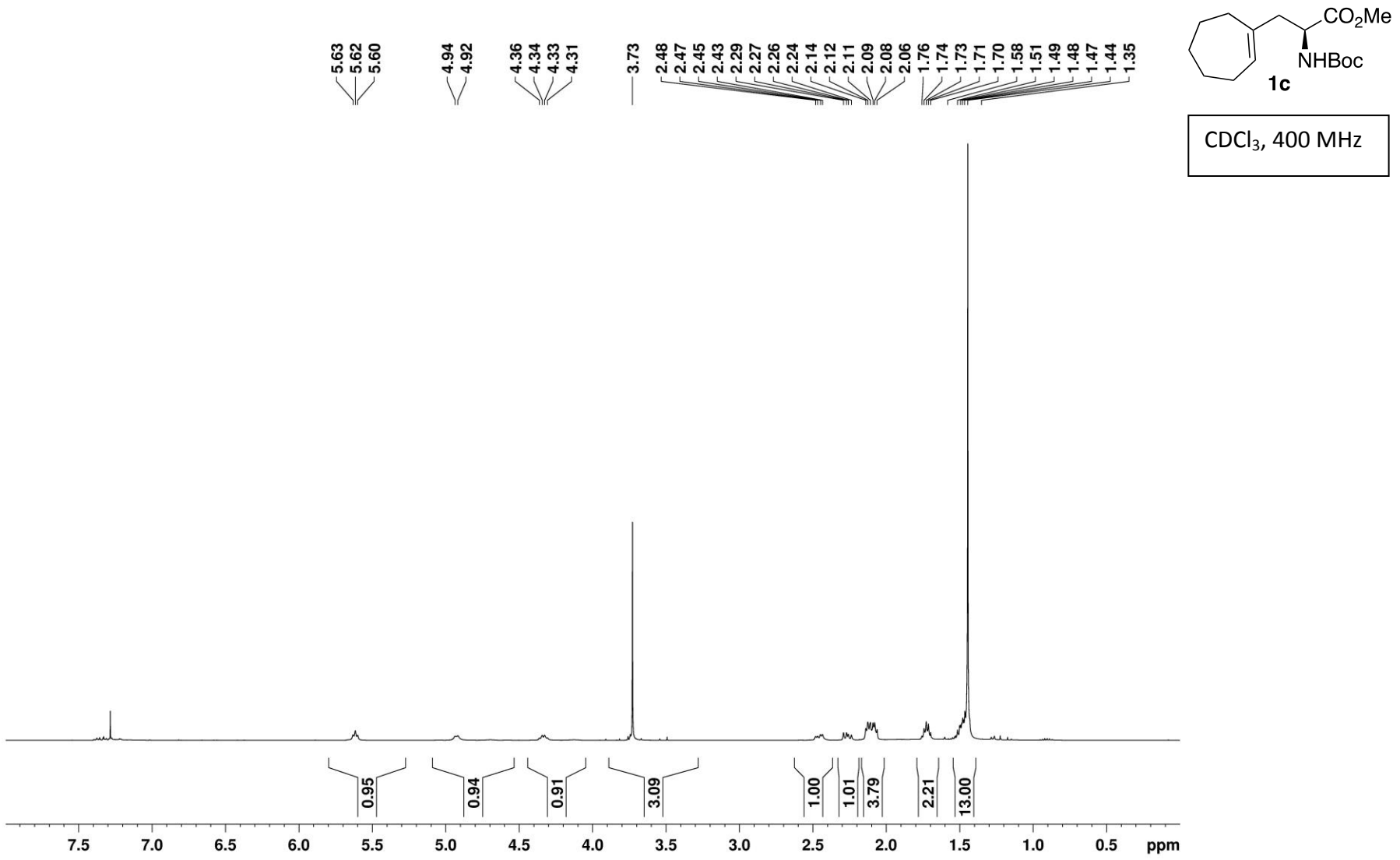


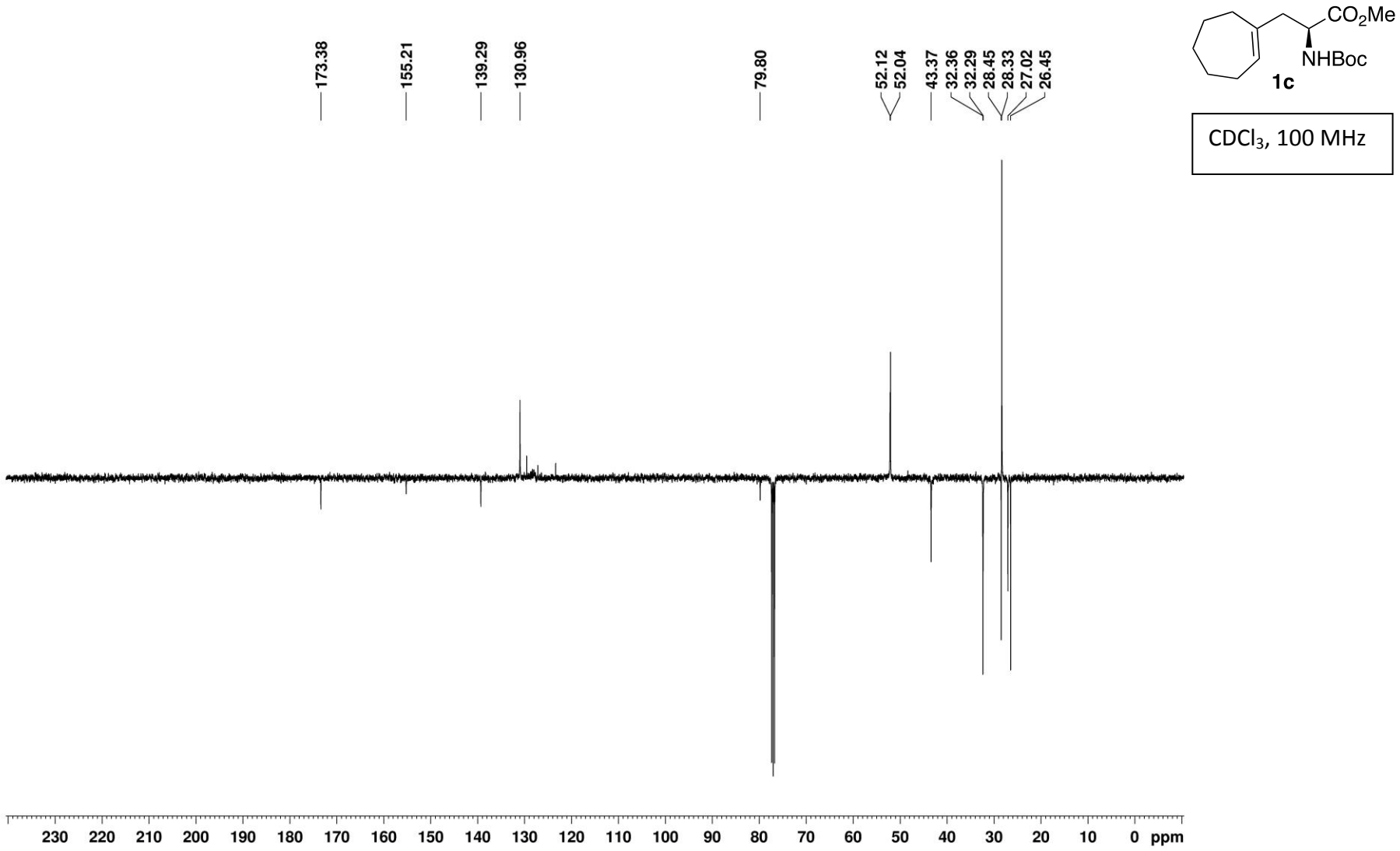
$CDCl_3$, 400 MHz

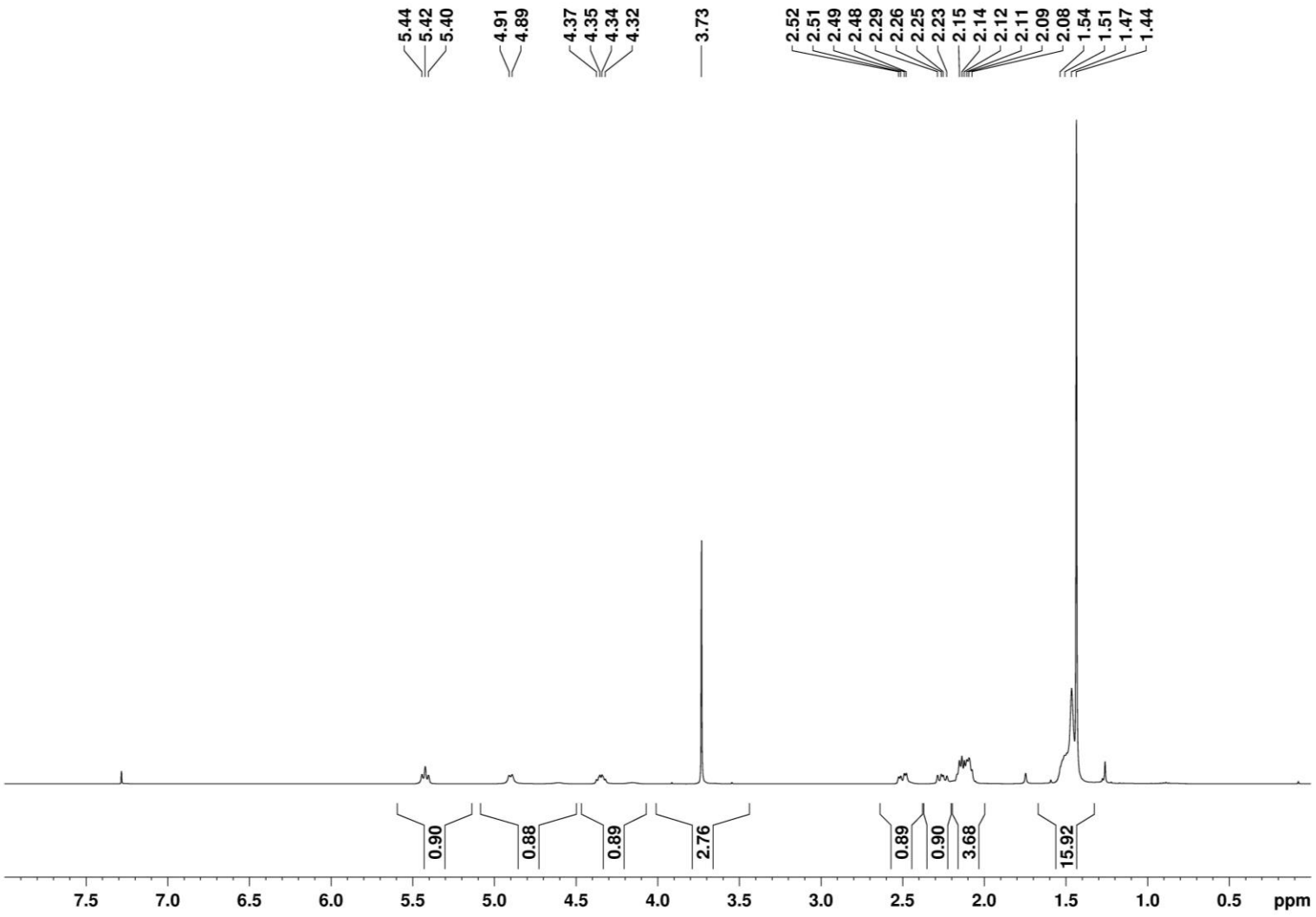


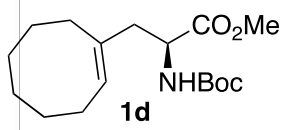
1b

$CDCl_3$, 100 MHz

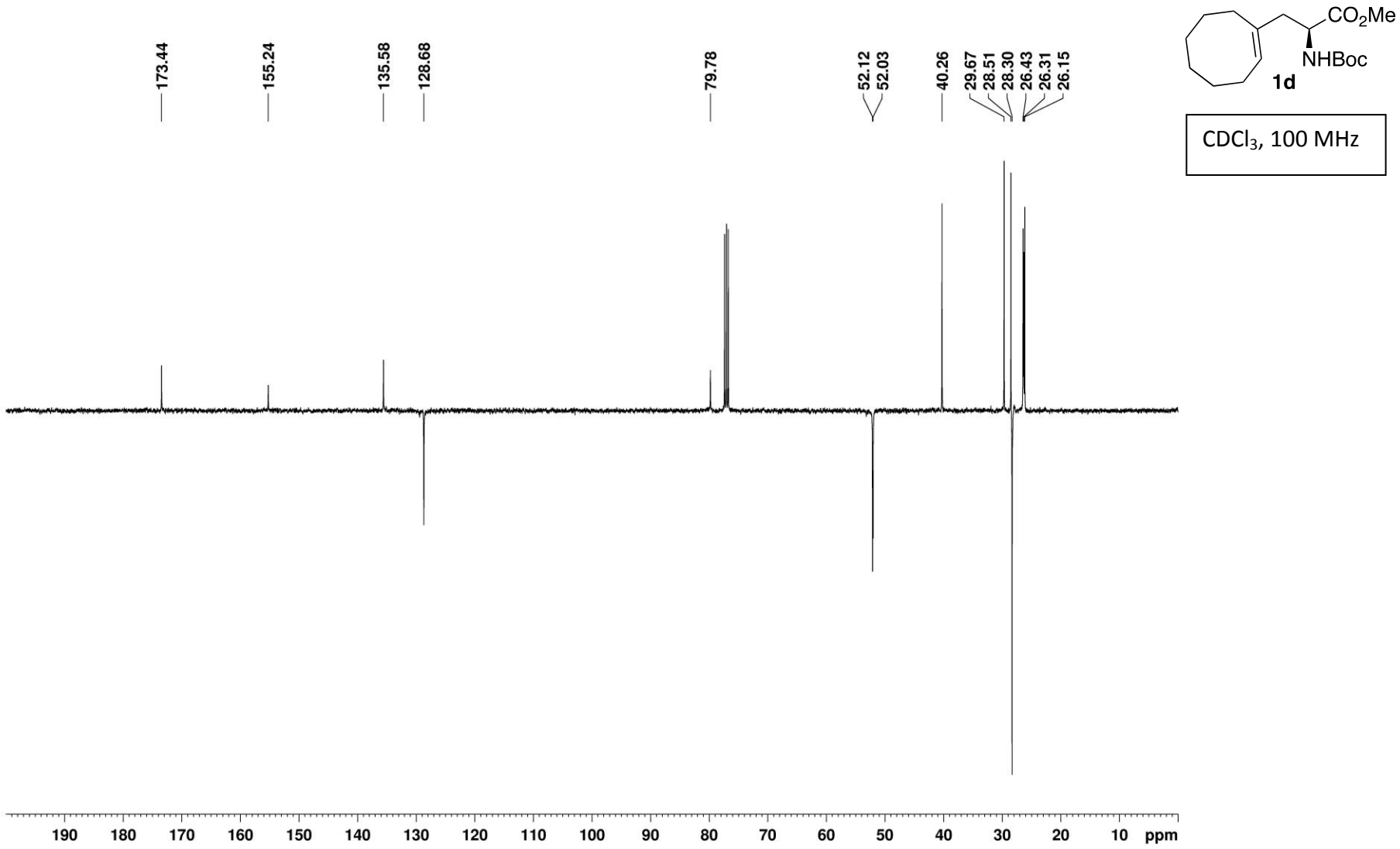

5.63
5.62
5.60
4.94
4.92
4.36
4.34
4.33
4.31
3.73
2.48
2.47
2.45
2.43
2.29
2.27
2.26
2.24
2.14
2.12
2.11
2.09
2.08
2.06
1.76
1.74
1.73
1.71
1.70
1.58
1.51
1.49
1.48
1.47
1.44
1.35
CO2Me
NHBoc
1c
CDCl3, 400 MHz
0.95
0.94
0.91
3.09
1.00
1.01
3.79
2.21
13.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

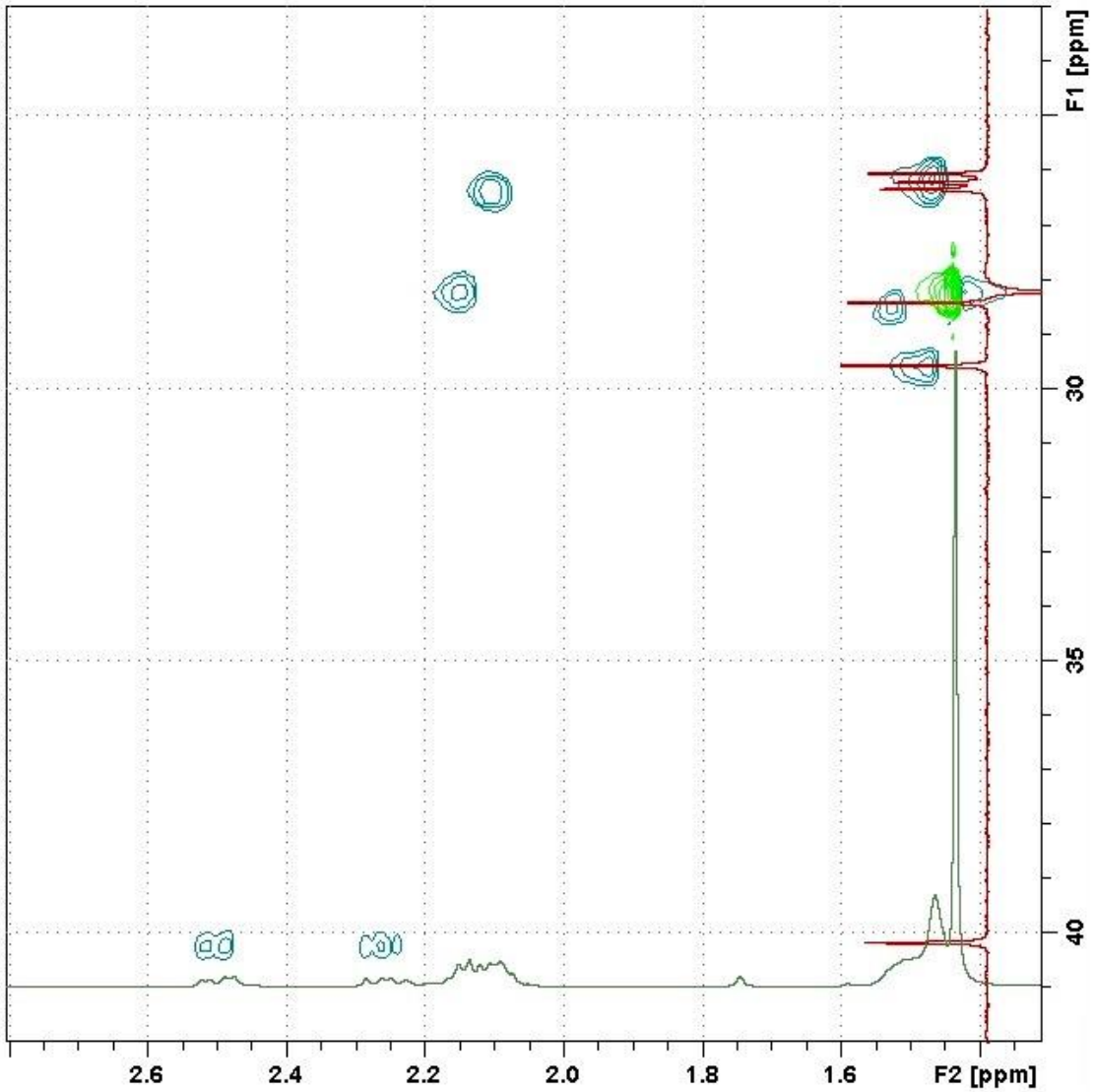

173.38
155.21
139.29
130.96
79.80
52.12
52.04
43.37
32.36
32.29
28.45
28.33
27.02
26.45
CO2Me
NHBoc
1c
CDCl3, 100 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

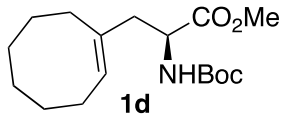




$CDCl_3$, 400 MHz

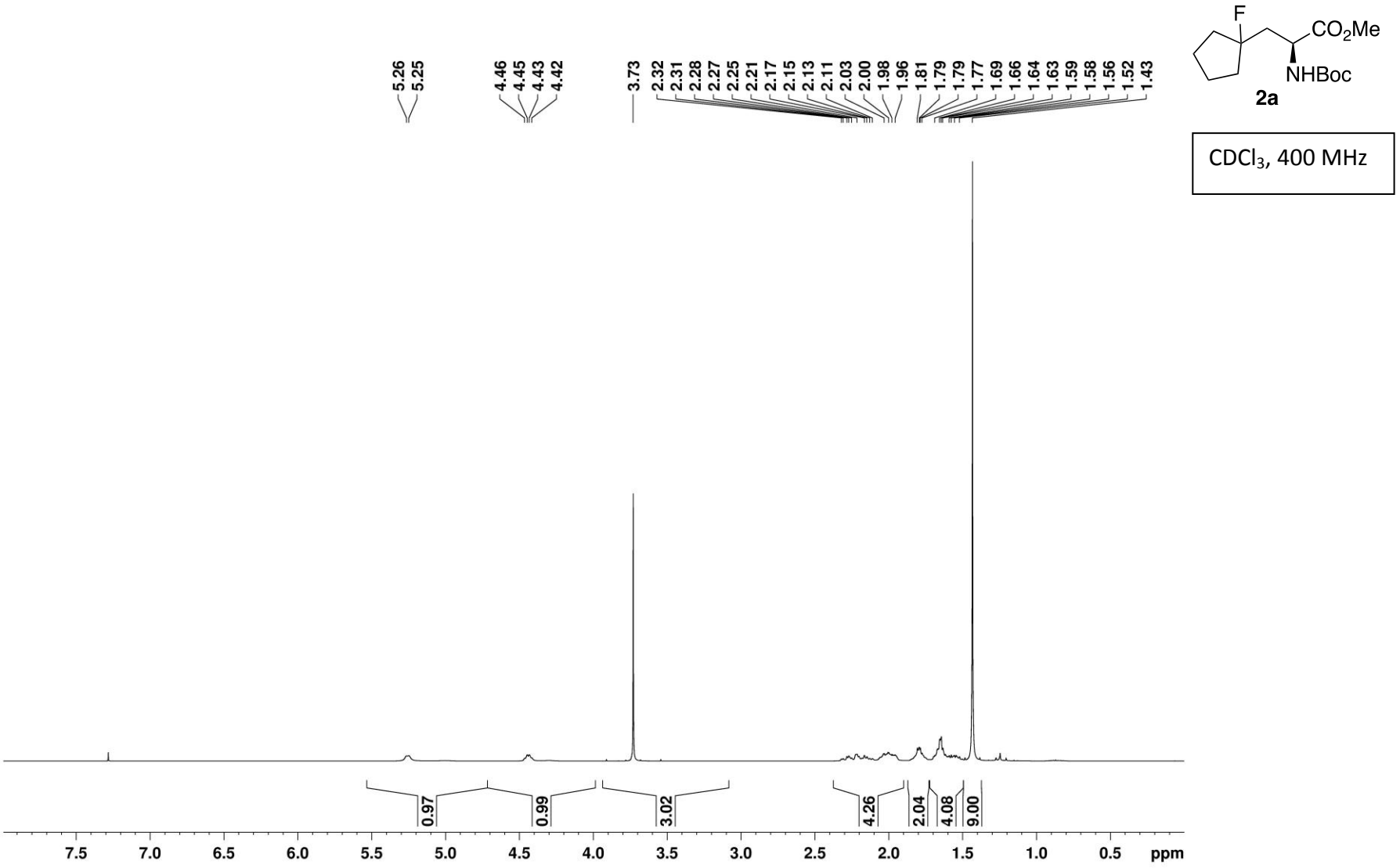

173.44
155.24
135.58
128.68
79.78
52.12
52.03
40.26
29.67
28.51
28.30
26.43
26.31
26.15
CO2Me
NHBoc
1d
CDCl3, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

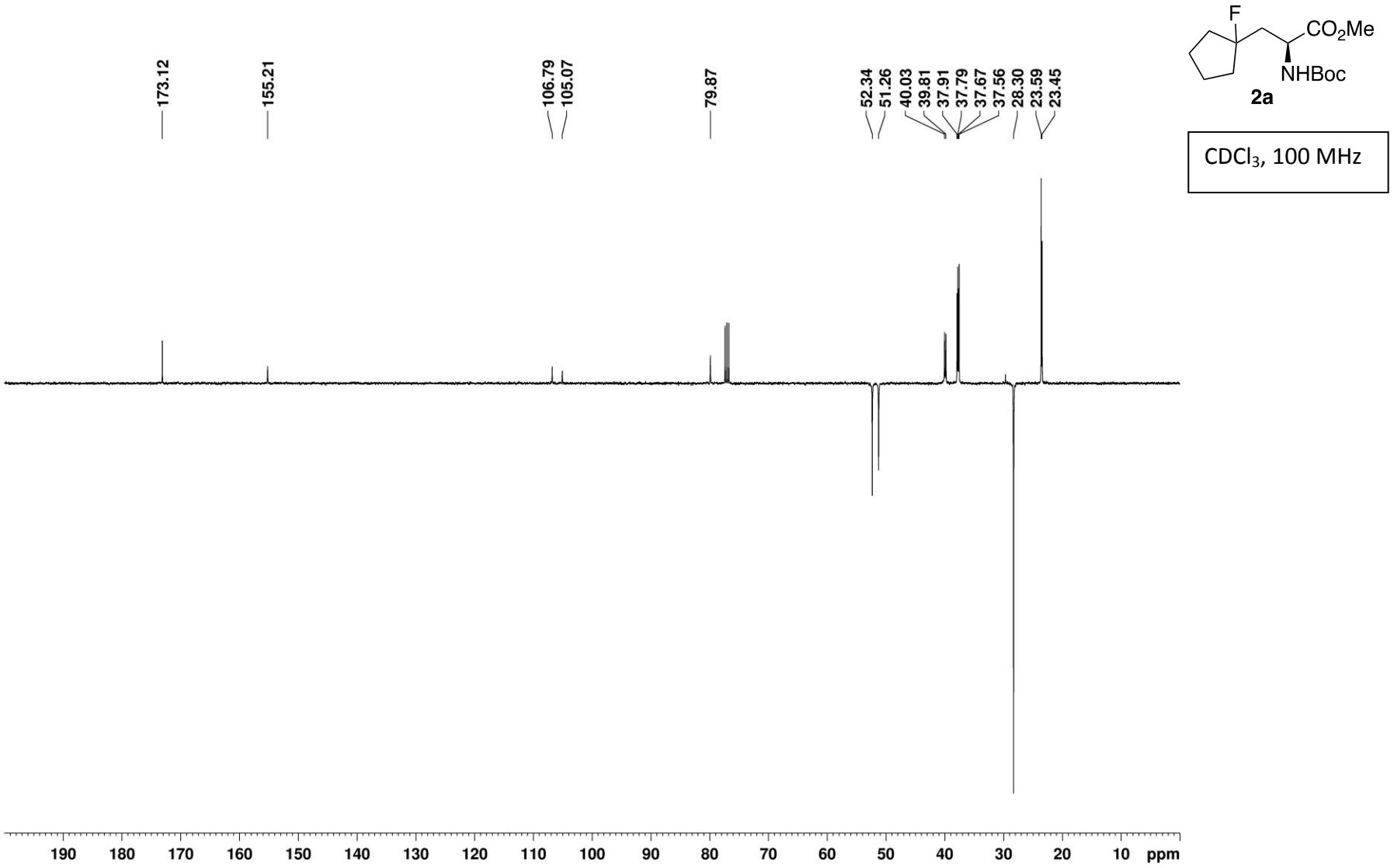




1d

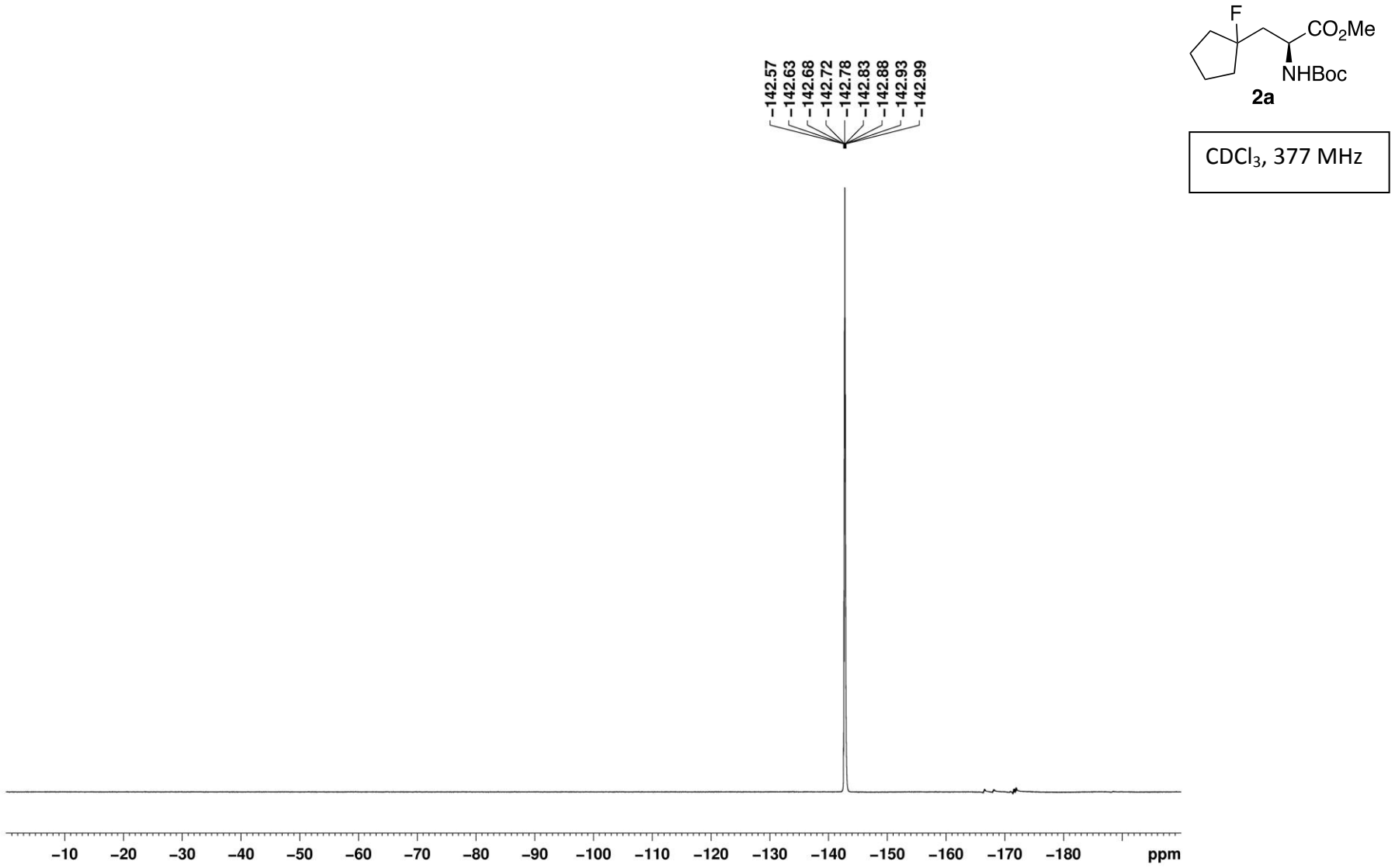
$CDCl_3$, HSQC

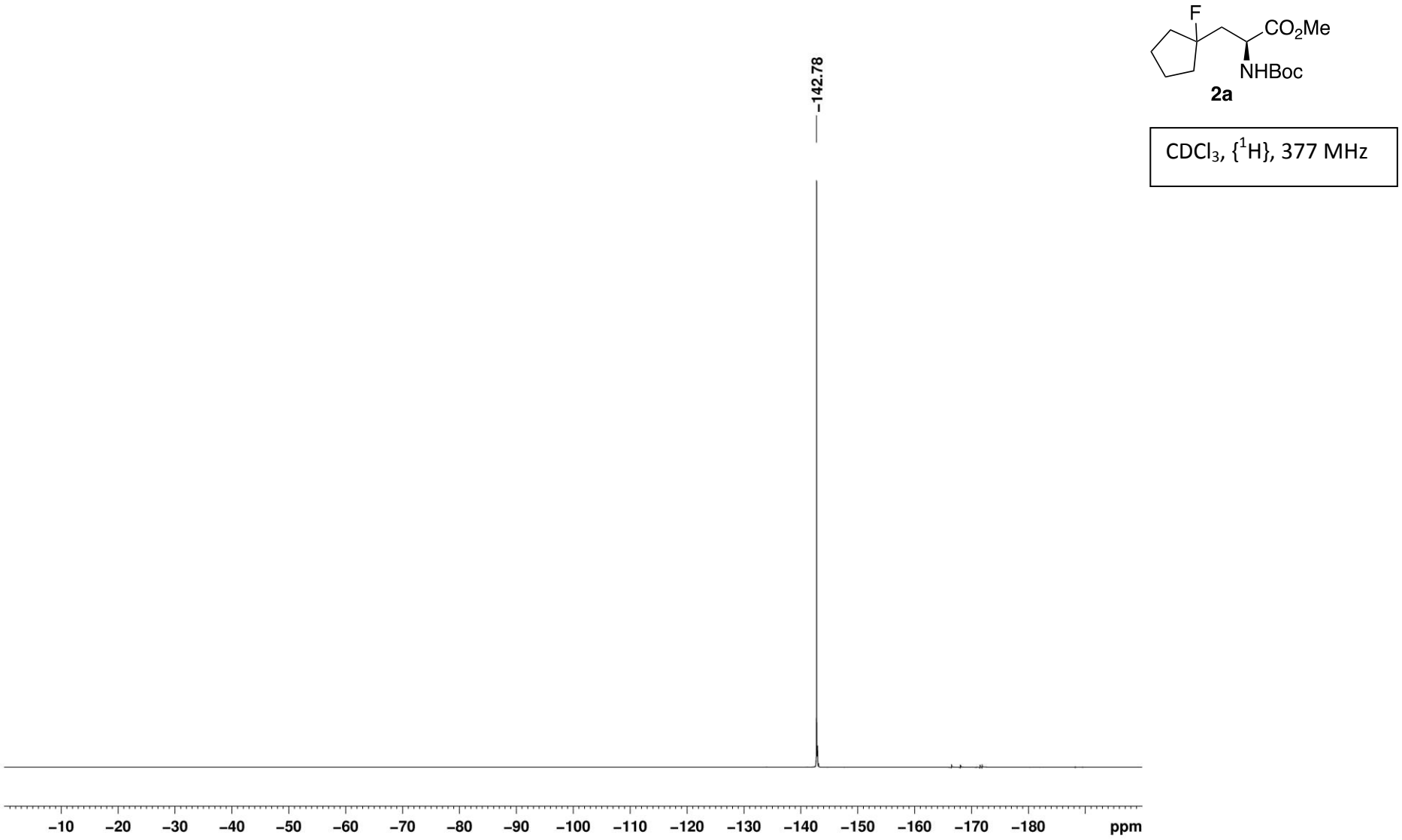

5.26
5.25
4.46
4.45
4.43
4.42
3.73
2.32
2.31
2.28
2.27
2.25
2.21
2.17
2.15
2.13
2.11
2.03
2.00
1.98
1.96
1.81
1.79
1.79
1.77
1.69
1.66
1.64
1.63
1.59
1.58
1.56
1.52
1.43
F
CO2Me
NHBoc
2a
CDCl3, 400 MHz
0.97
0.99
3.02
4.26
2.04
4.08
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

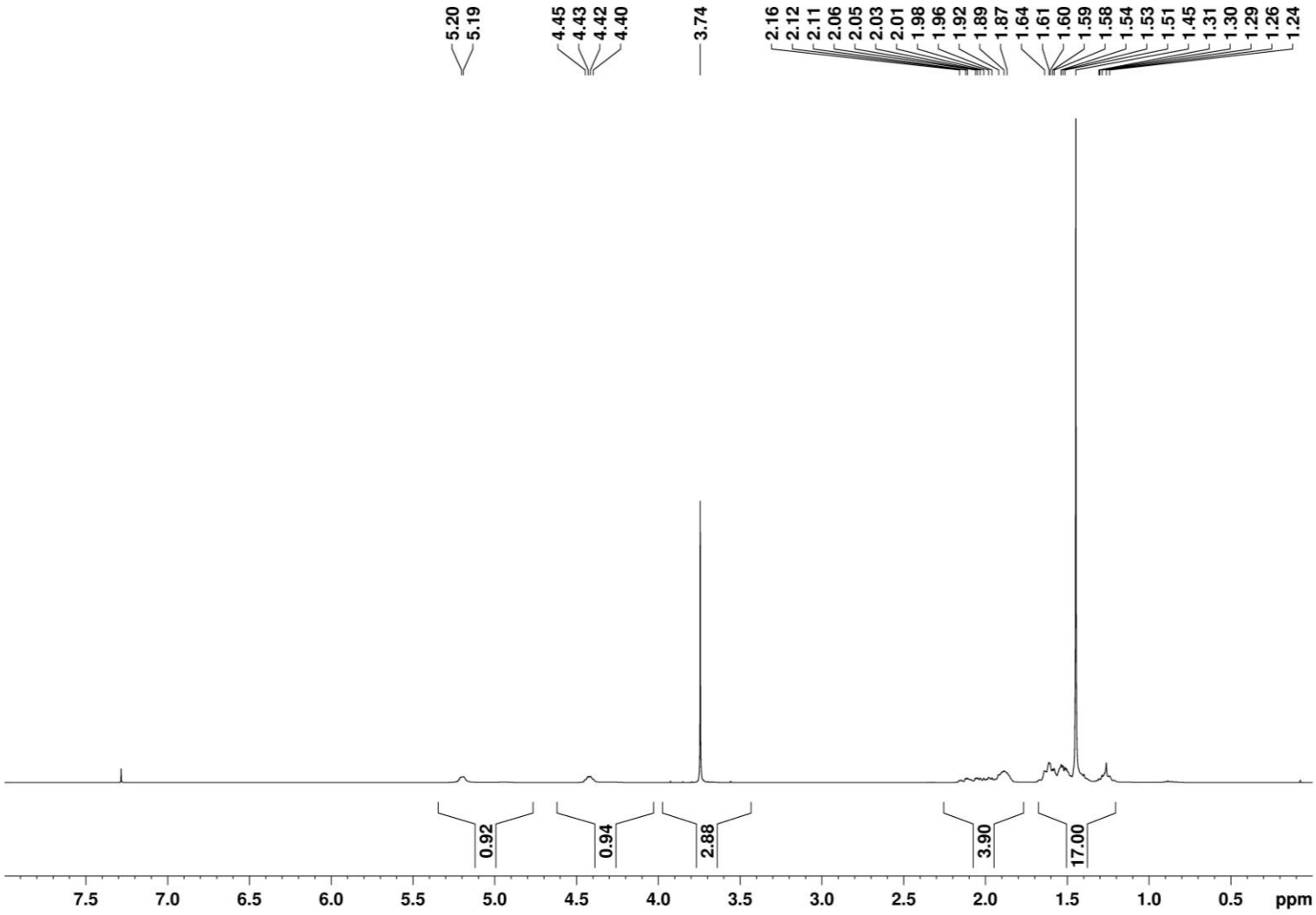


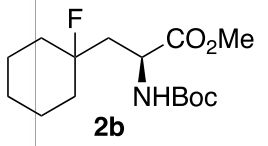
2a

$CDCl_3$, 100 MHz


F
CO2Me
NHBoc
2a
CDCl3, 377 MHz
-142.57
-142.63
-142.68
-142.72
-142.78
-142.83
-142.88
-142.93
-142.99
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

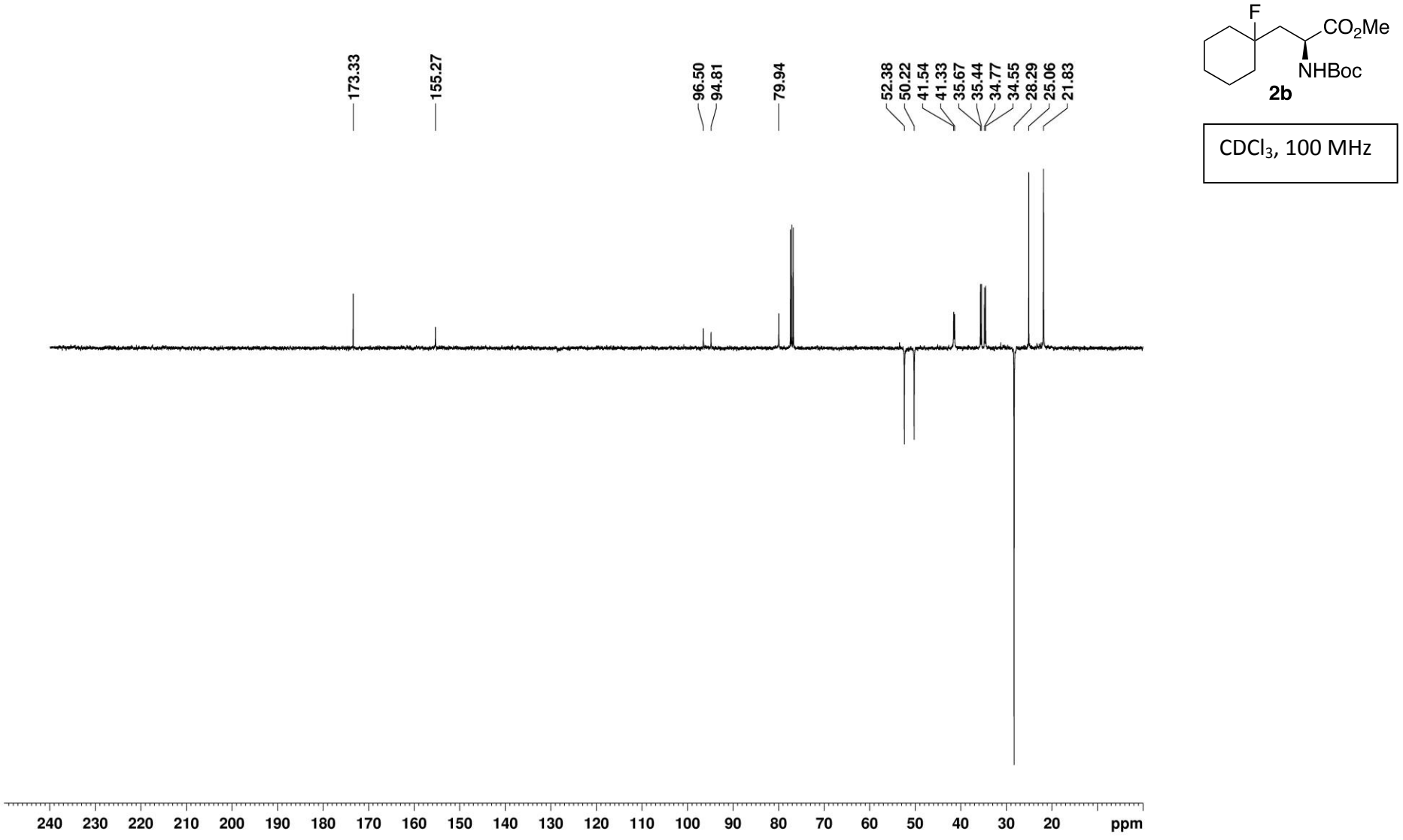

F
CO2Me
NHBoc
2a
-142.78
CDCl3, {1H}, 377 MHz
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm





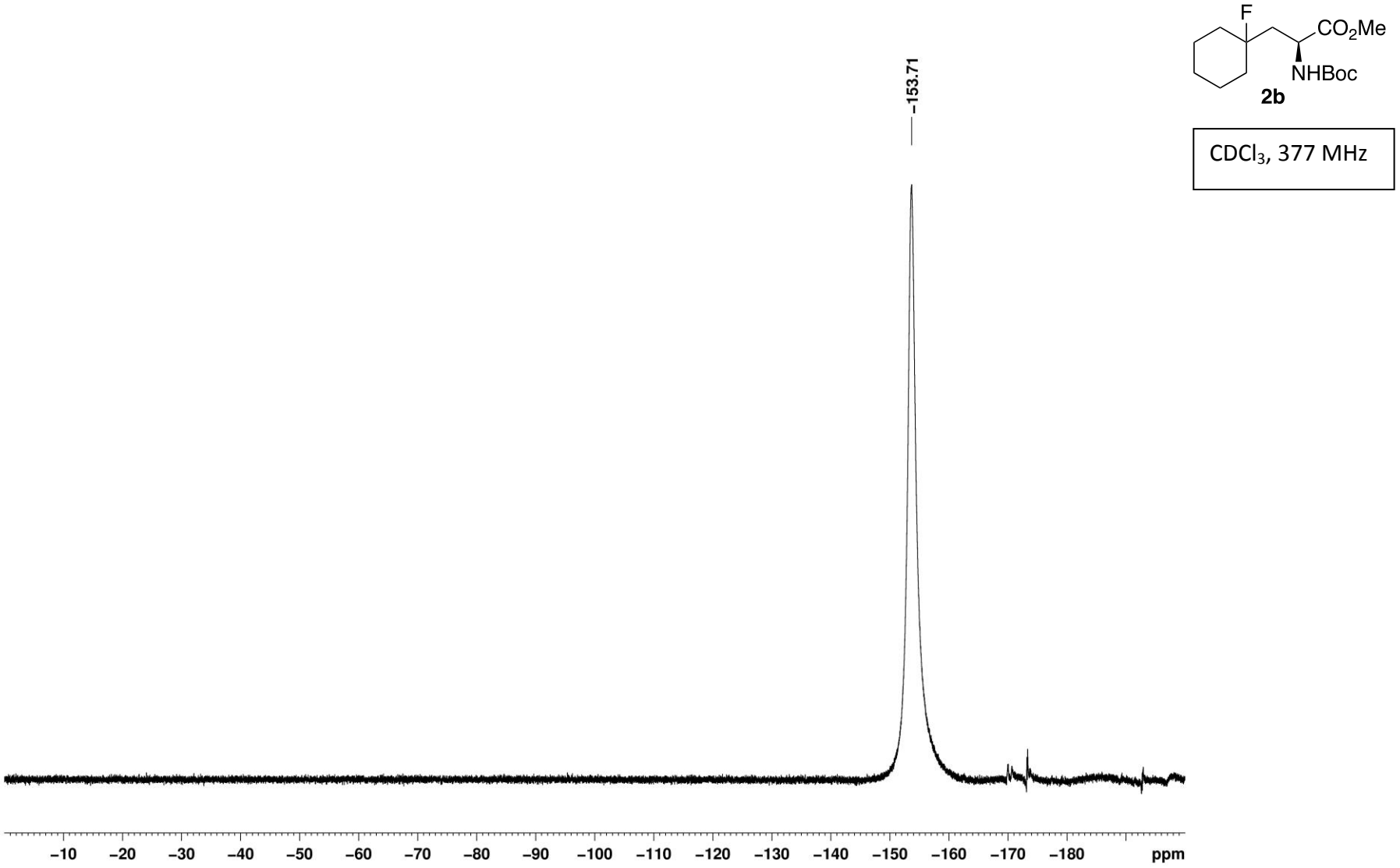
2b

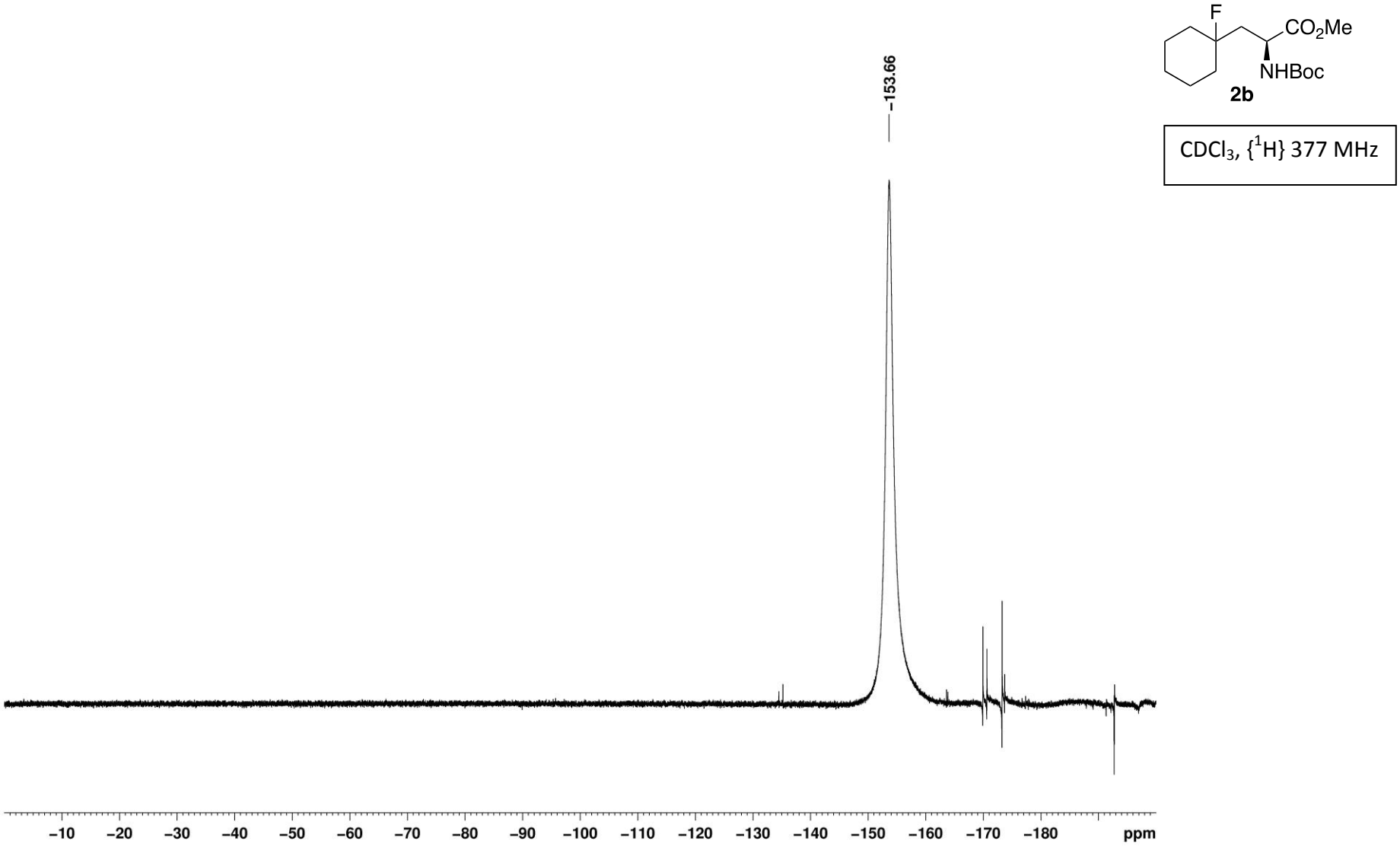
$CDCl_3$, 400 MHz

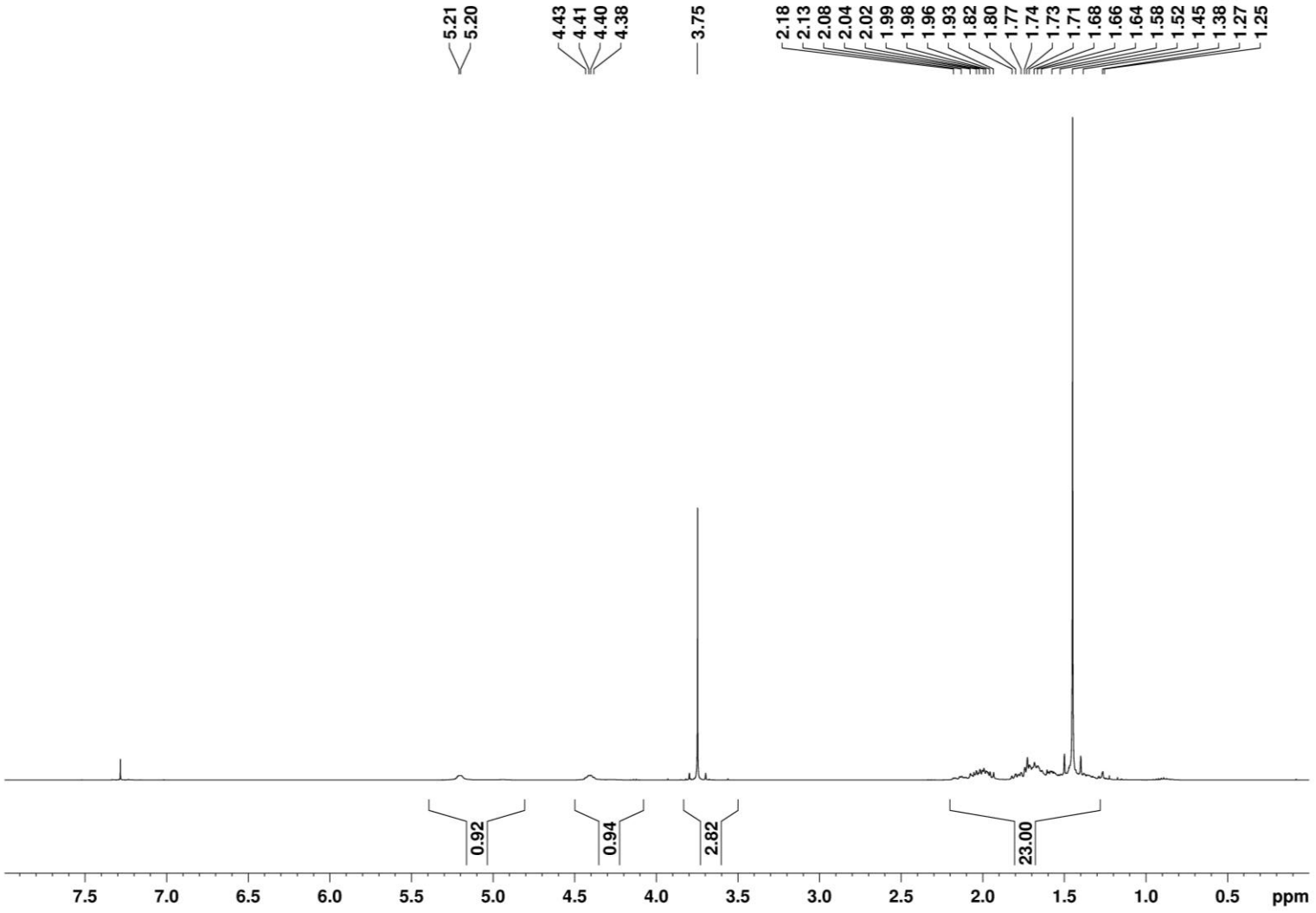


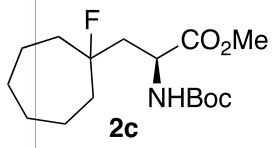
2b

$CDCl_3$, 100 MHz

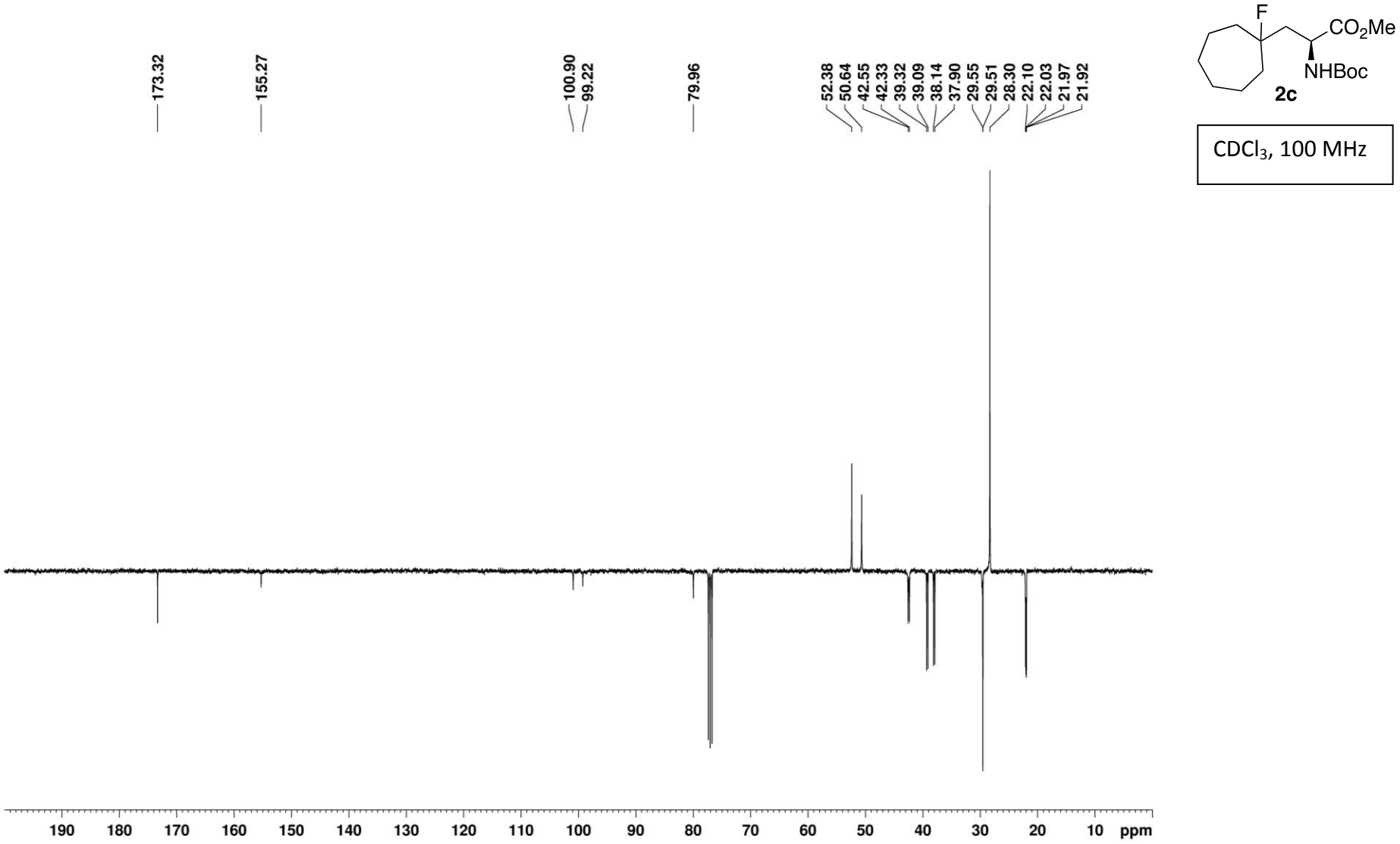

F
CO2Me
NHBoc
2b
CDCl3, 377 MHz
-153.71
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


F
CO2Me
NHBoc
2b
CDCl3, {1H} 377 MHz
-153.66
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm



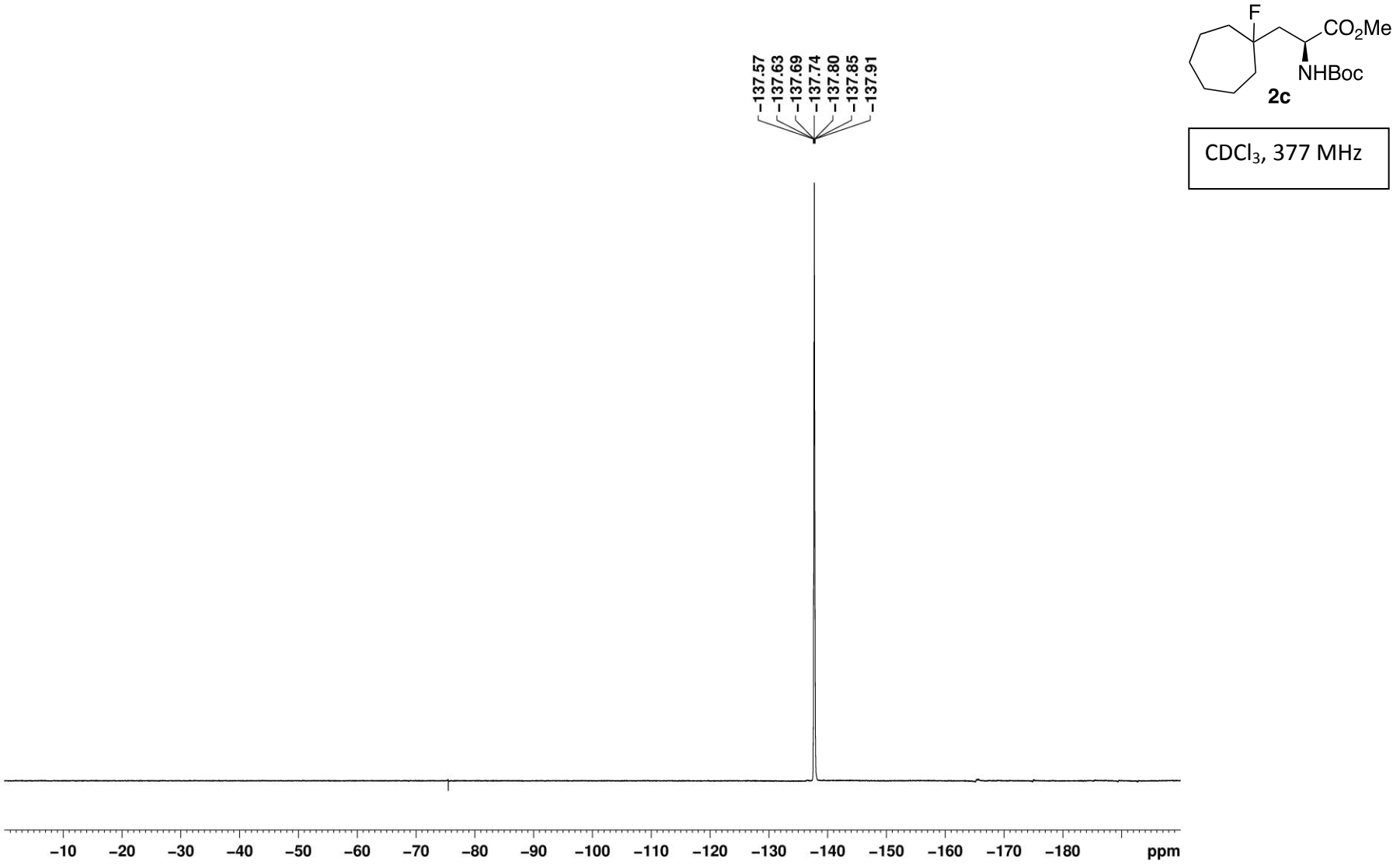


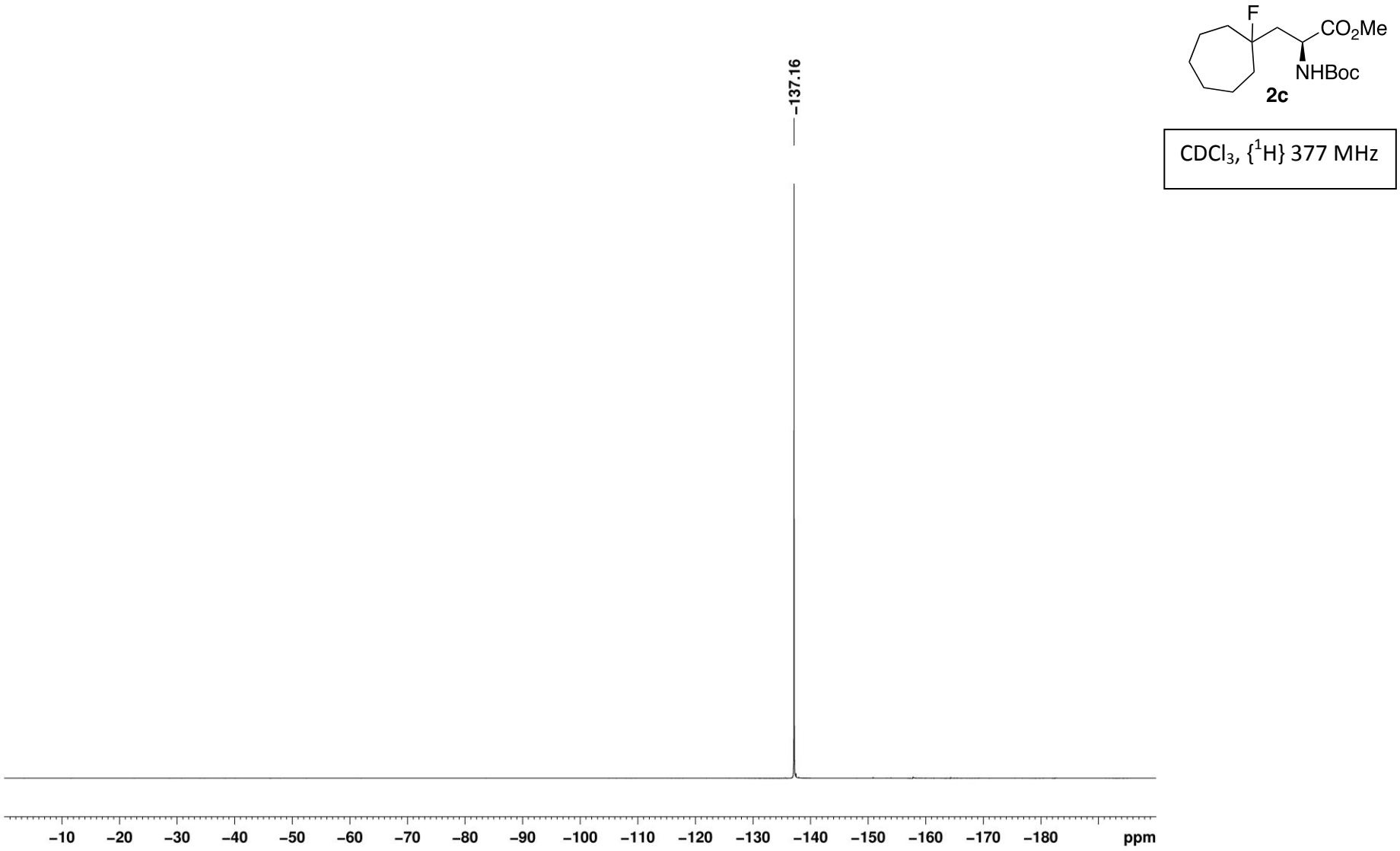
$CDCl_3$, 400 MHz

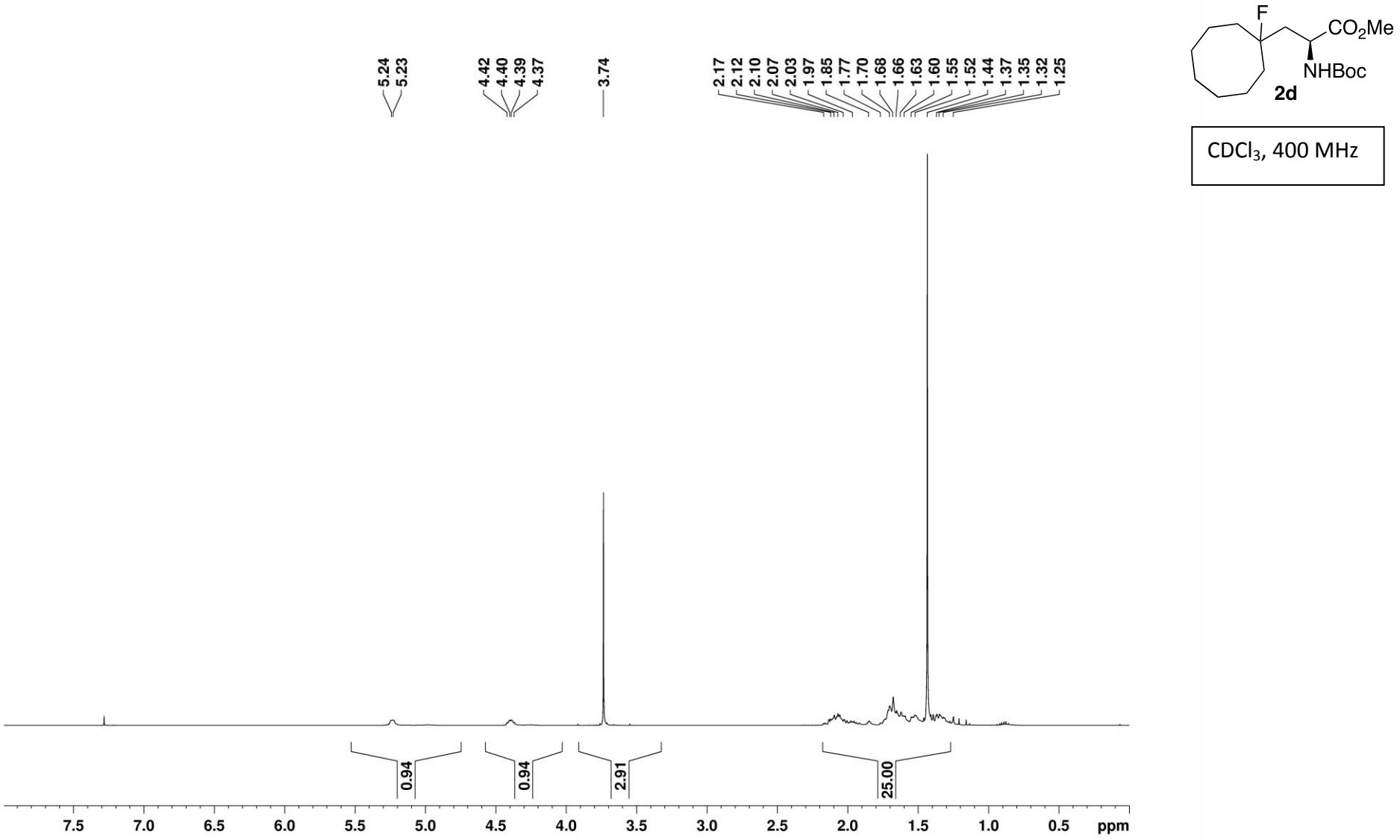


2c

$CDCl_3$, 100 MHz

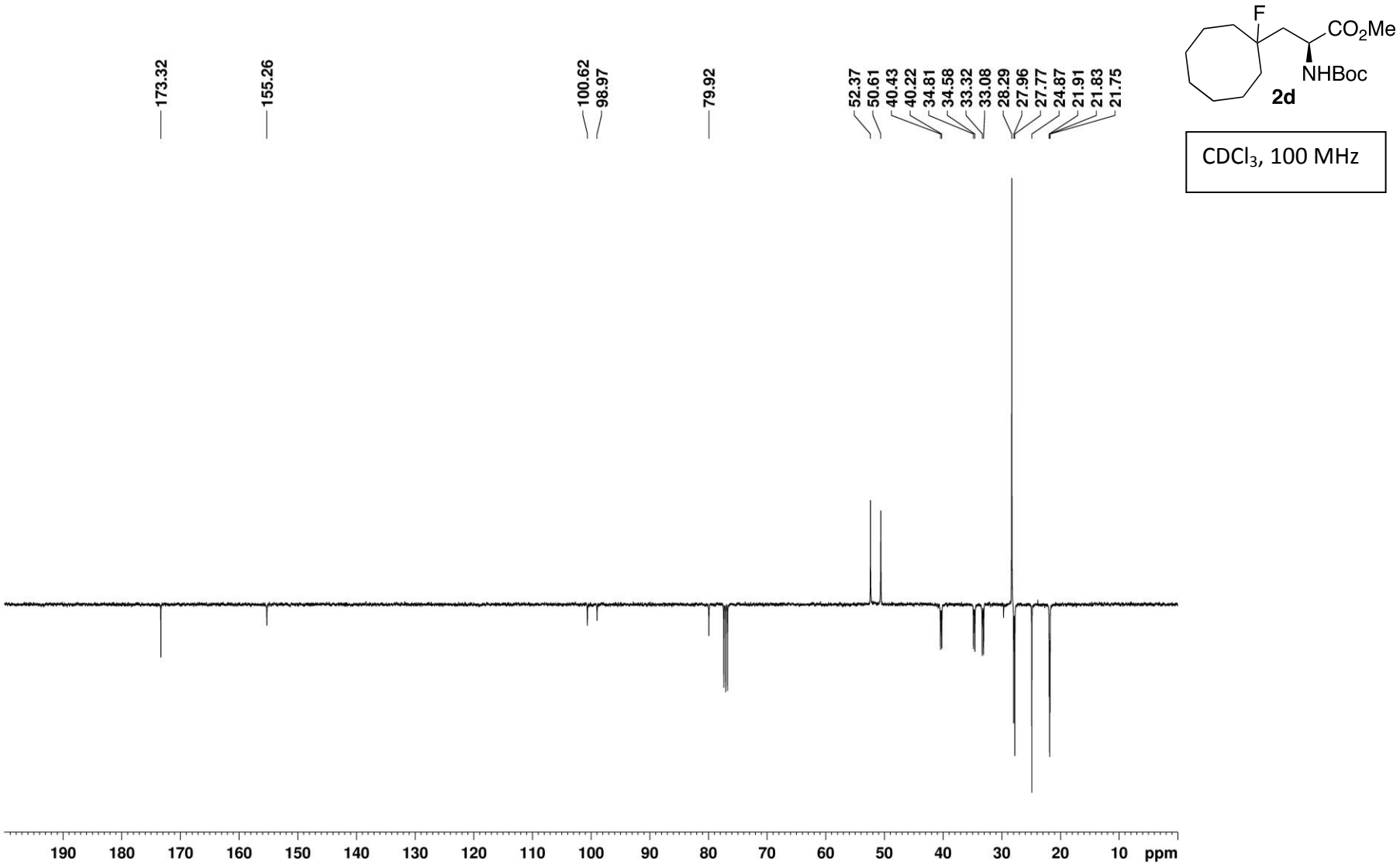

F
CO2Me
NHBoc
2c
CDCl3, 377 MHz
-137.57
-137.63
-137.69
-137.74
-137.80
-137.85
-137.91
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

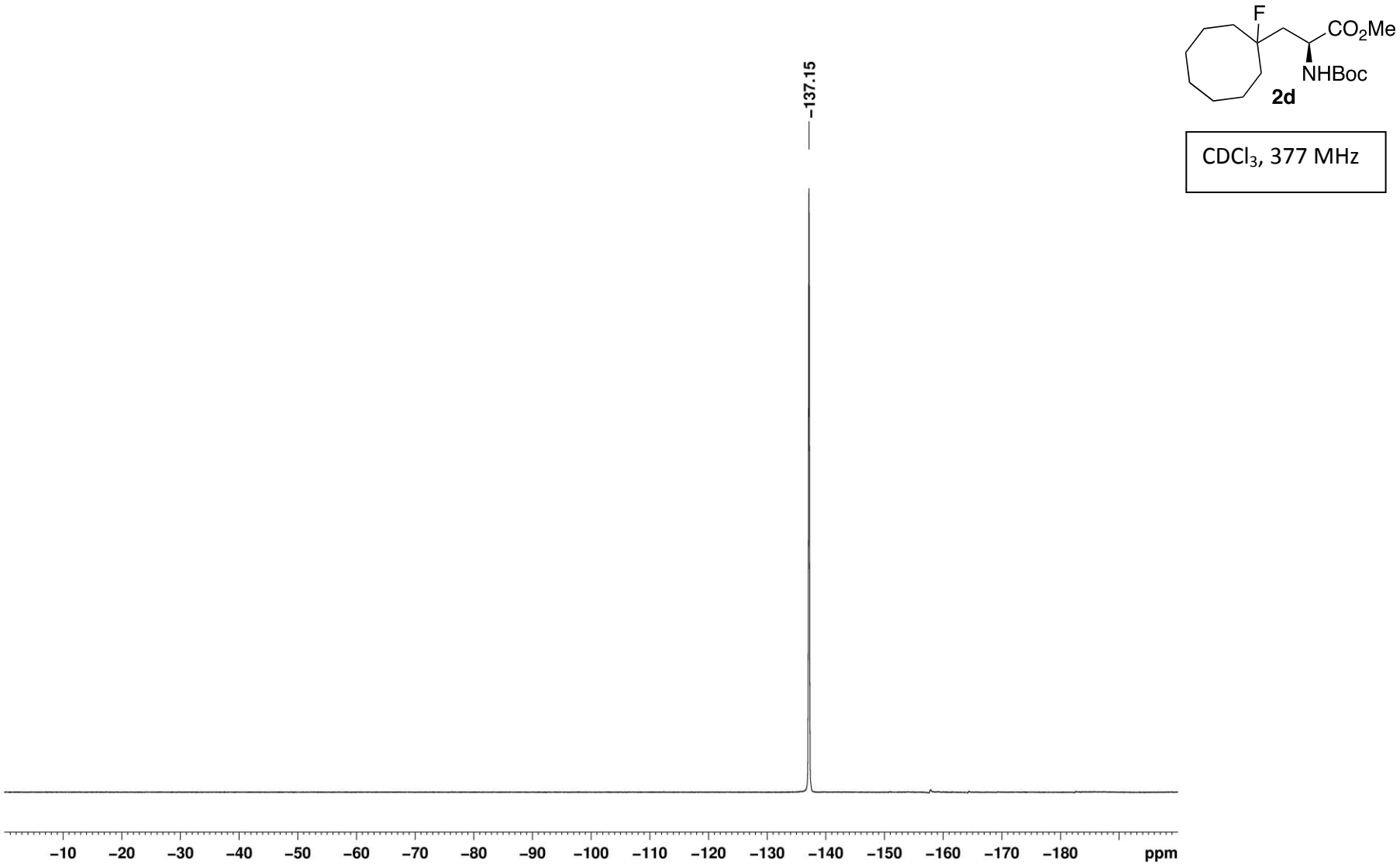

F
CO2Me
NHBoc
2c
CDCl3, {1H} 377 MHz
-137.16
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

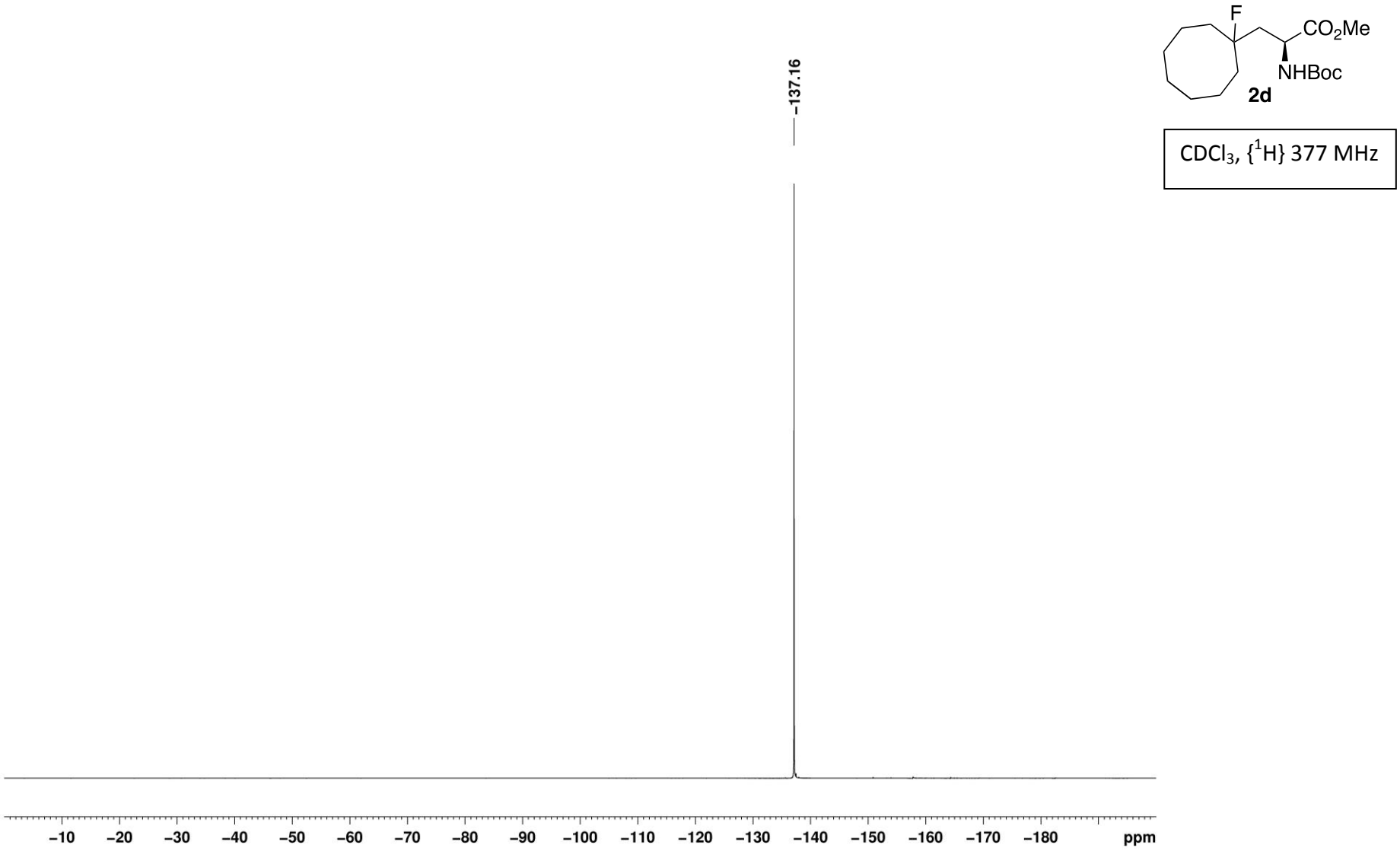


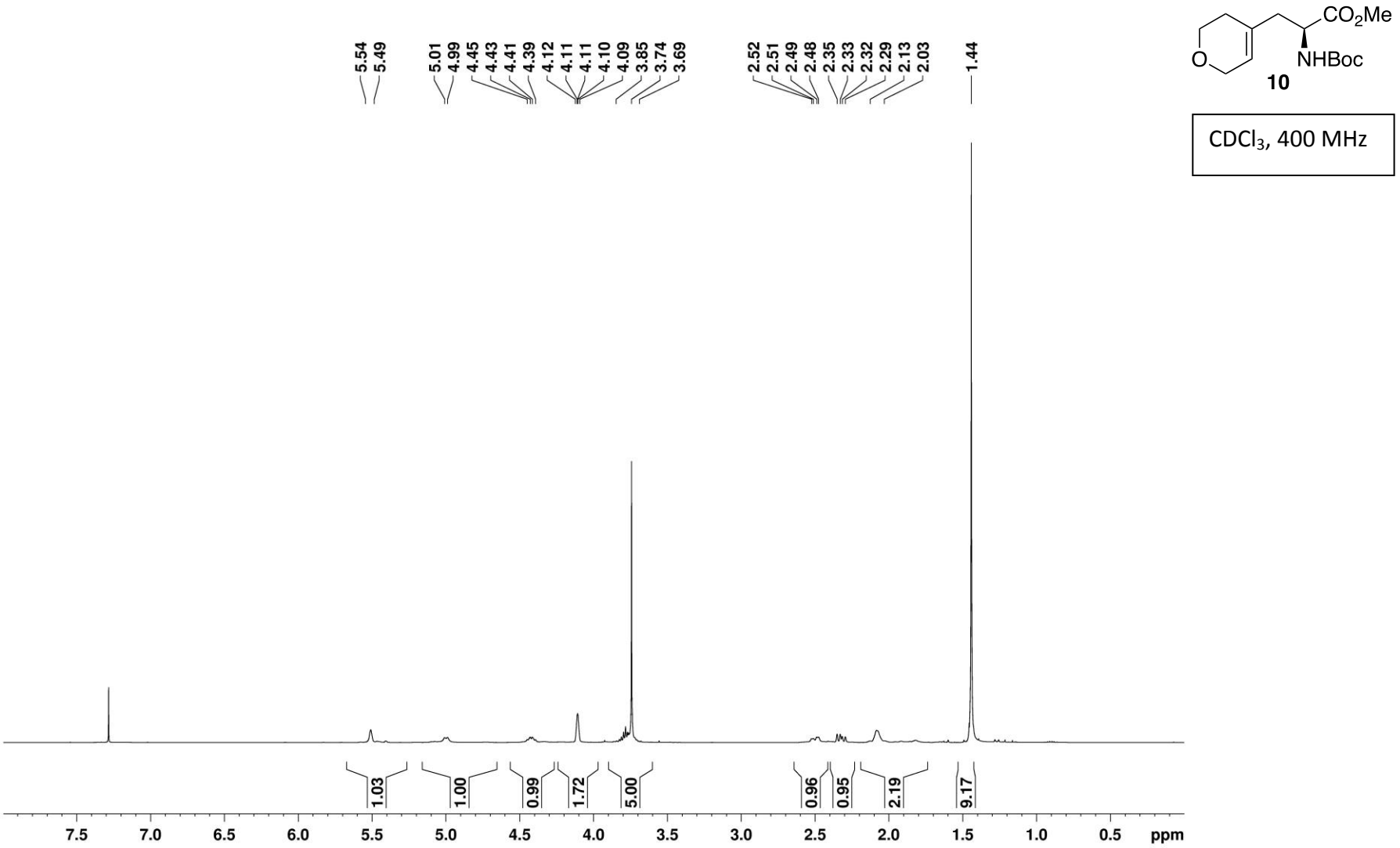
2d

$CDCl_3$, 400 MHz


173.32
155.26
100.62
98.97
79.92
52.37
50.61
40.43
40.22
34.81
34.58
33.32
33.08
28.29
27.96
27.77
24.87
21.91
21.83
21.75
F
CO2Me
NHBoc
2d
CDCl3, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

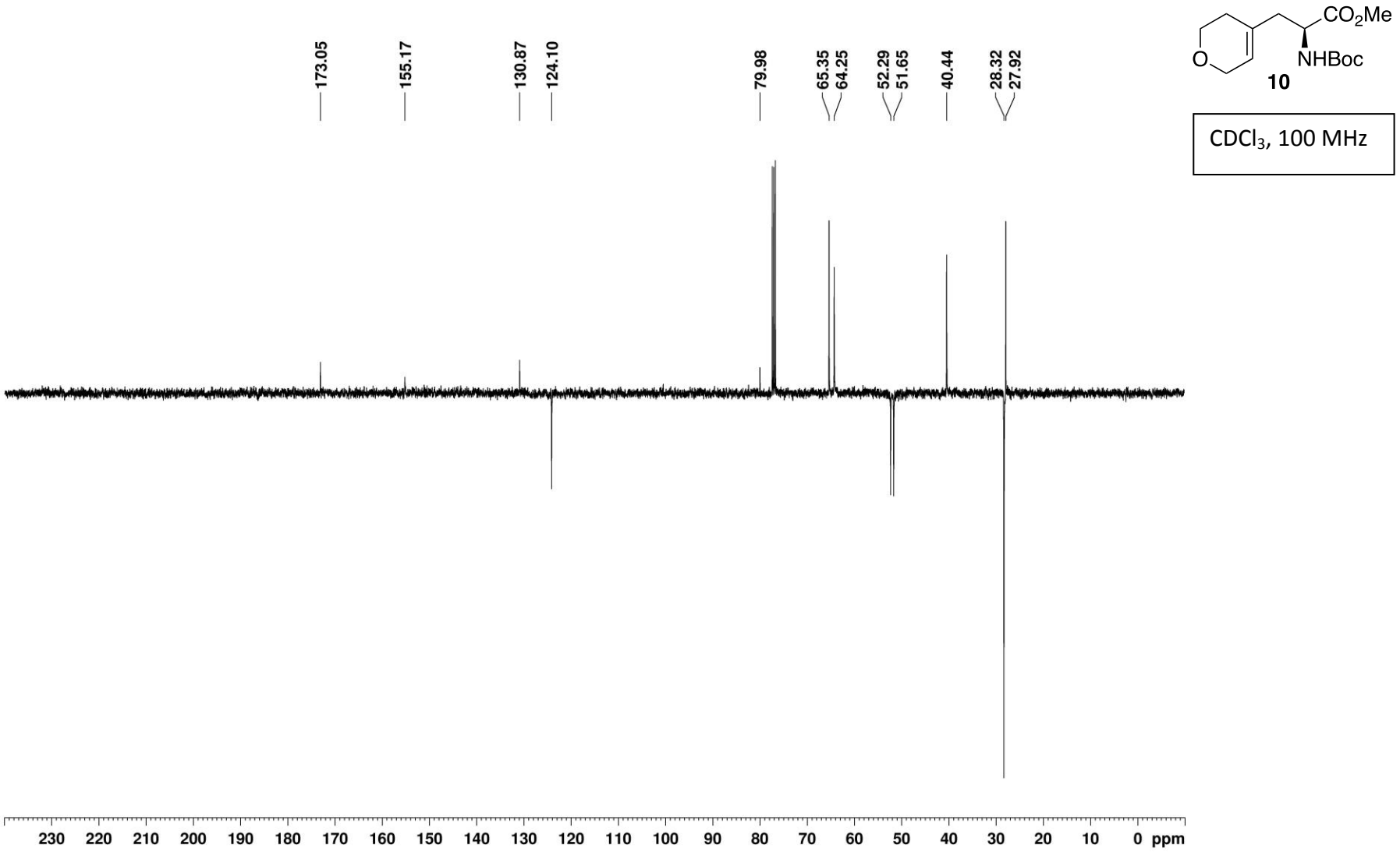

F
CO2Me
NHBoc
2d
CDCl3, 377 MHz
-137.15
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm


F
CO2Me
NHBoc
2d
CDCl3, {1H} 377 MHz
-137.16
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm



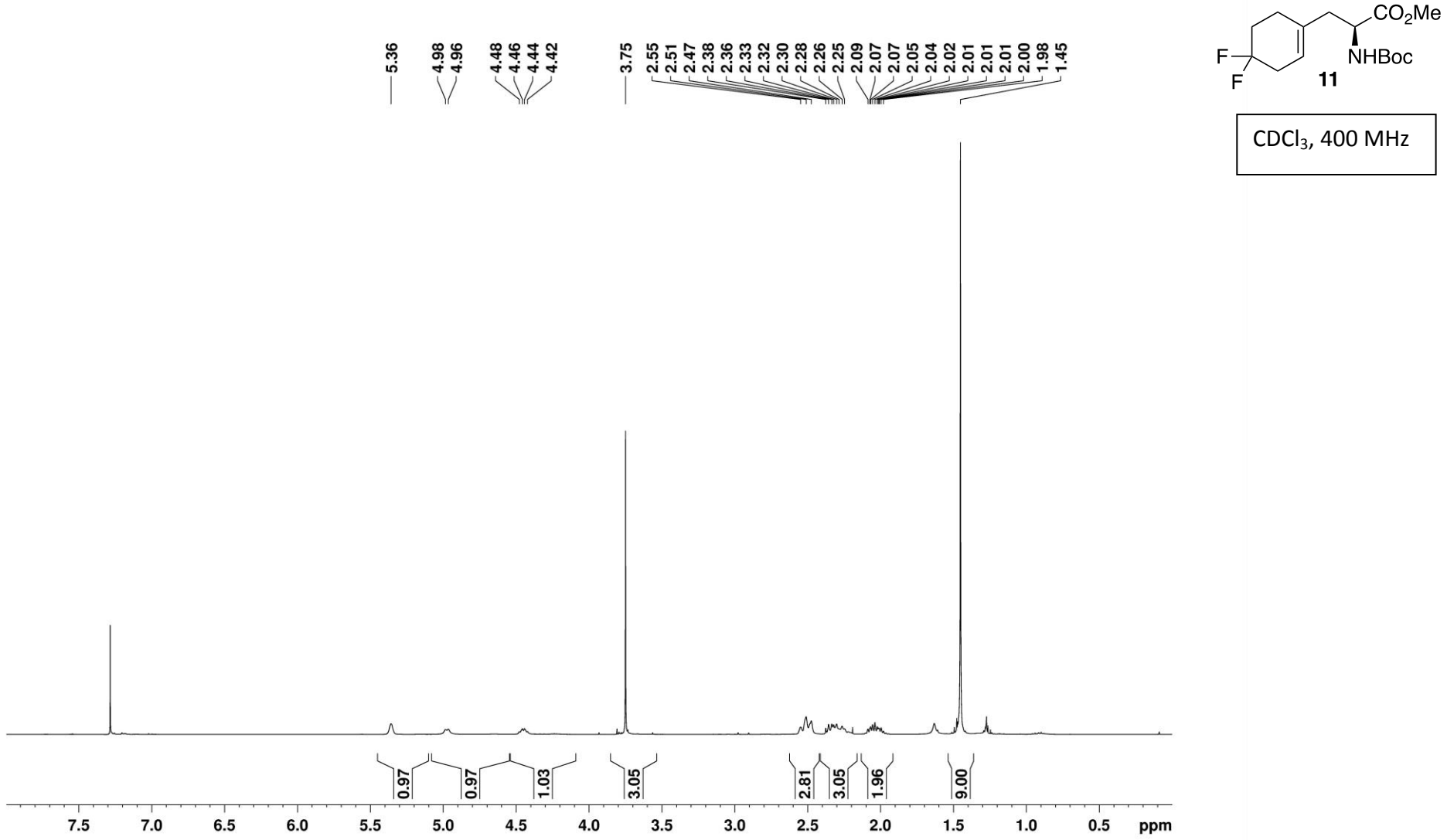
10

$CDCl_3$, 400 MHz

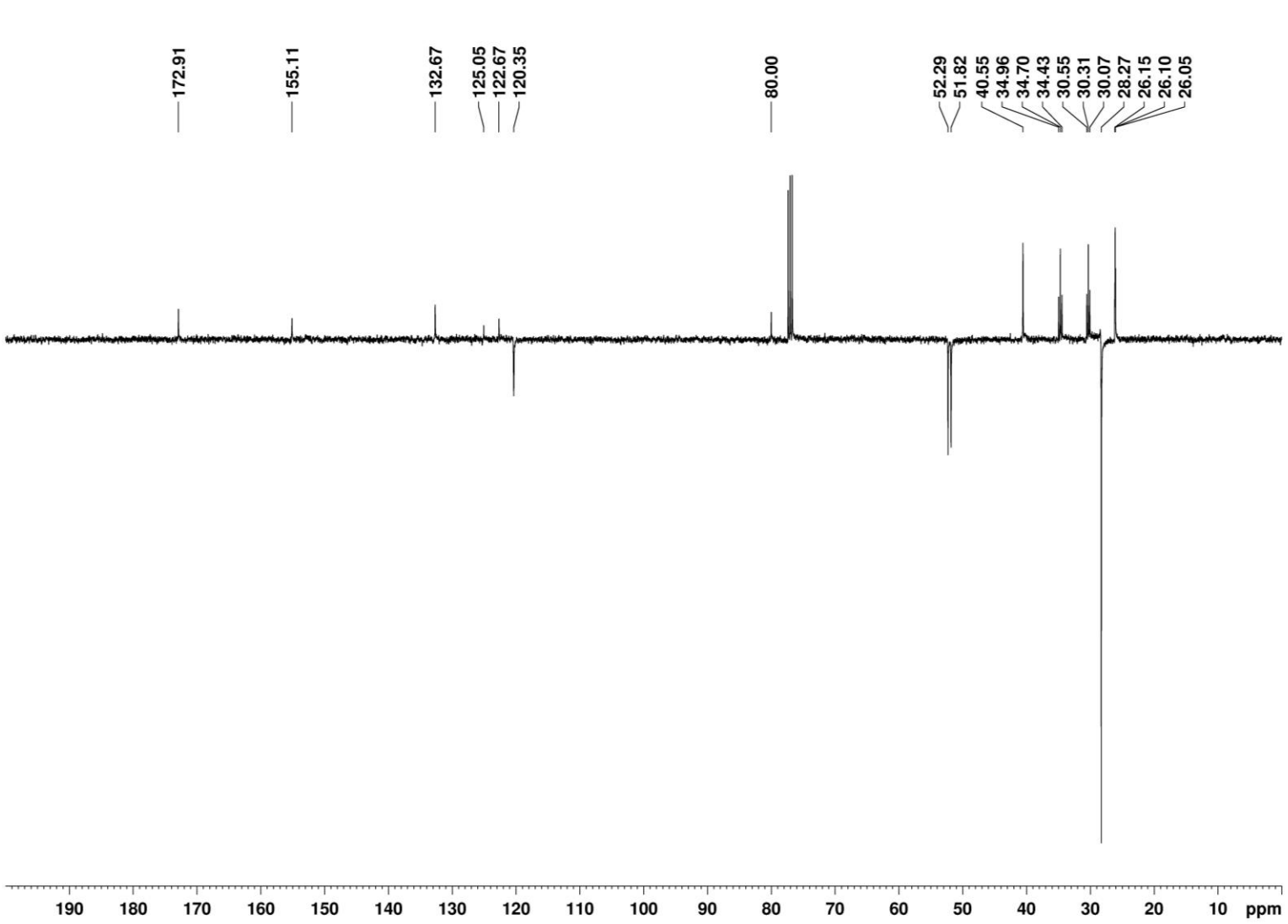


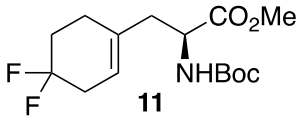
10

$CDCl_3$, 100 MHz

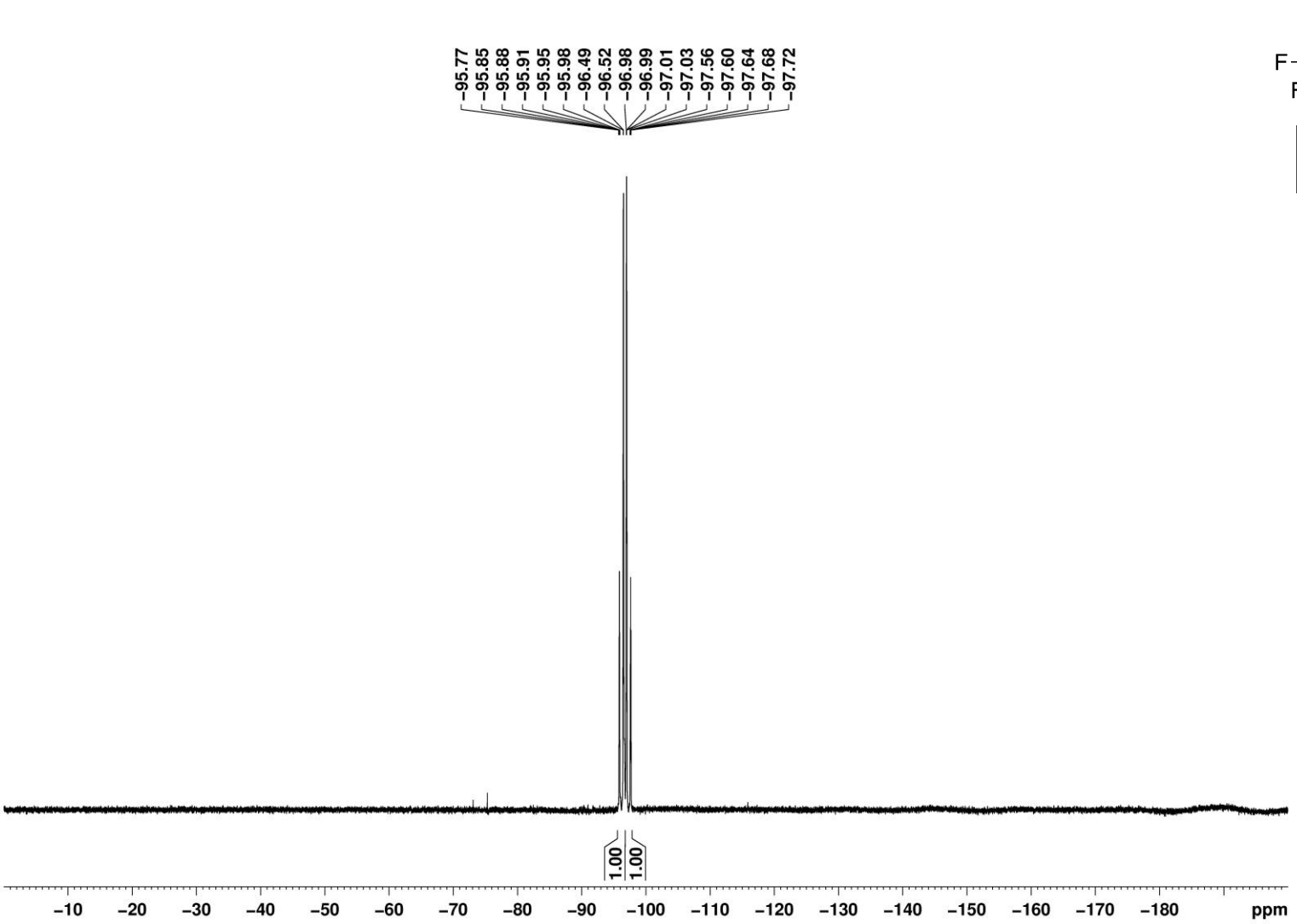


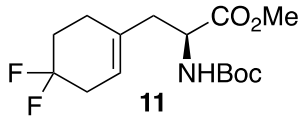
$CDCl_3$, 400 MHz



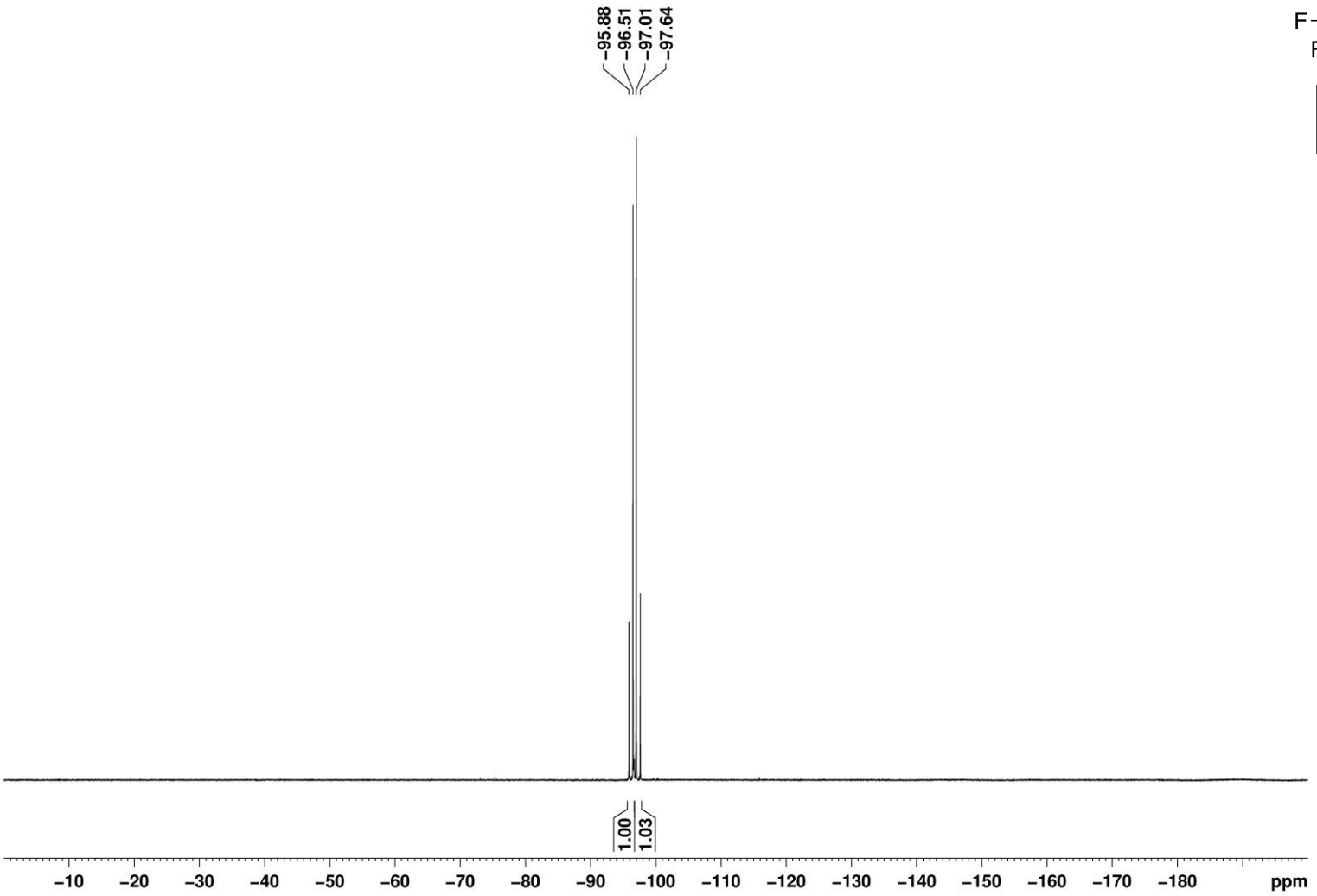


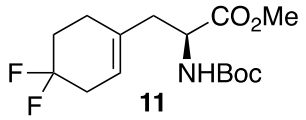
$CDCl_3$, 100 MHz





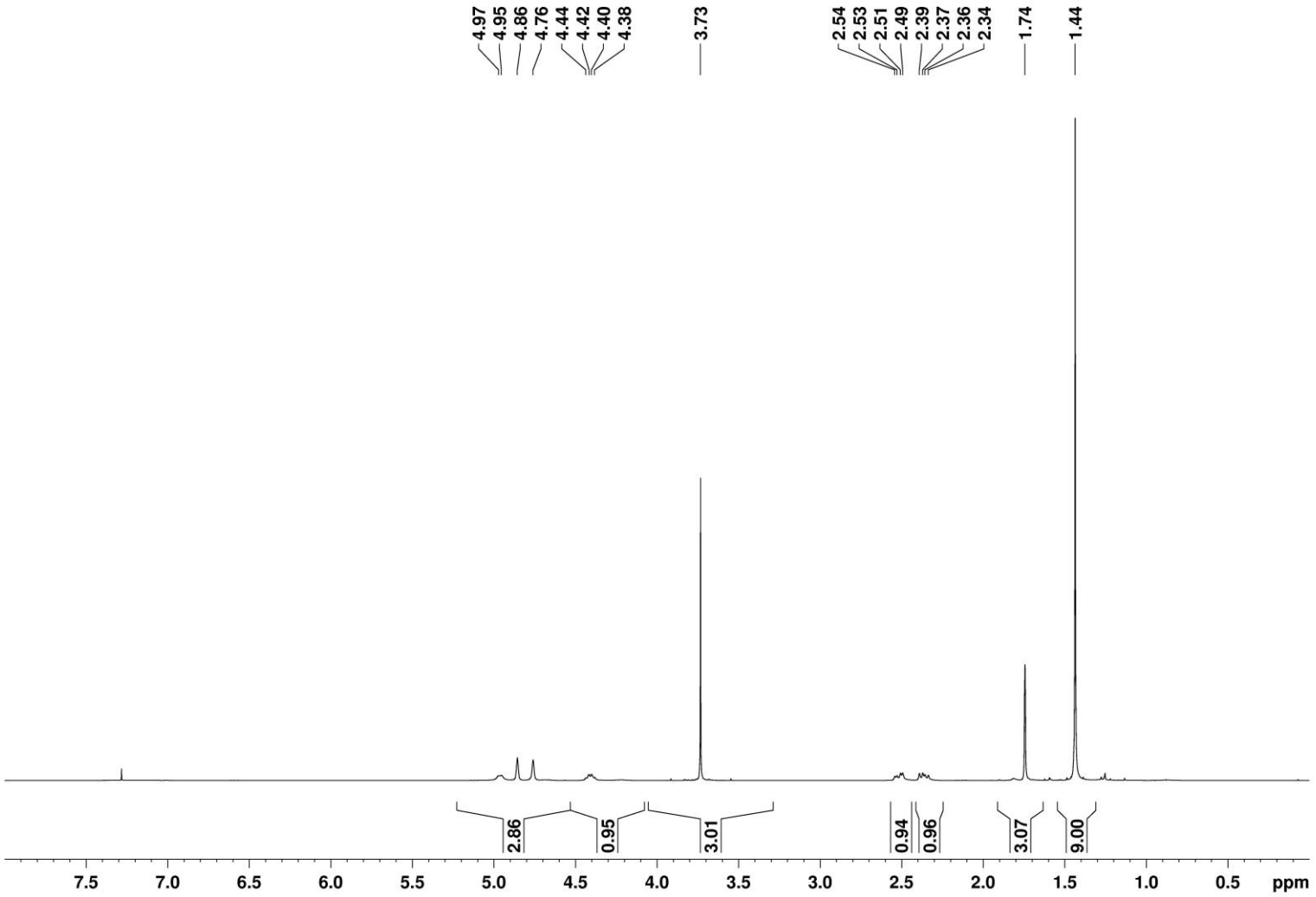
$CDCl_3$, 377 MHz

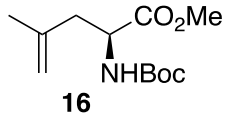




11

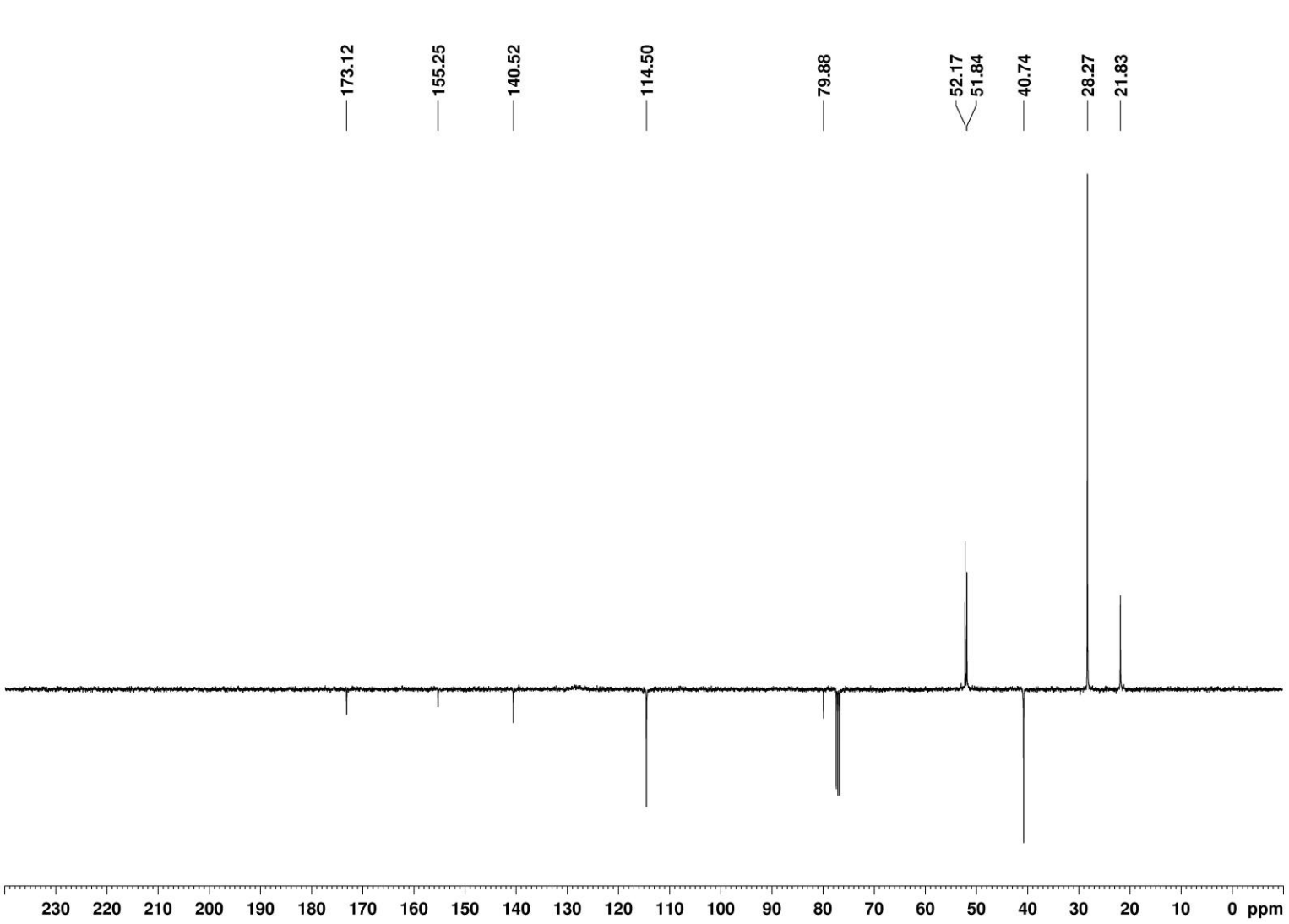
$CDCl_3$, $\{^1H\}$ 377 MHz

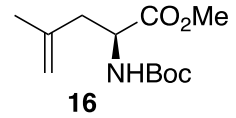




16

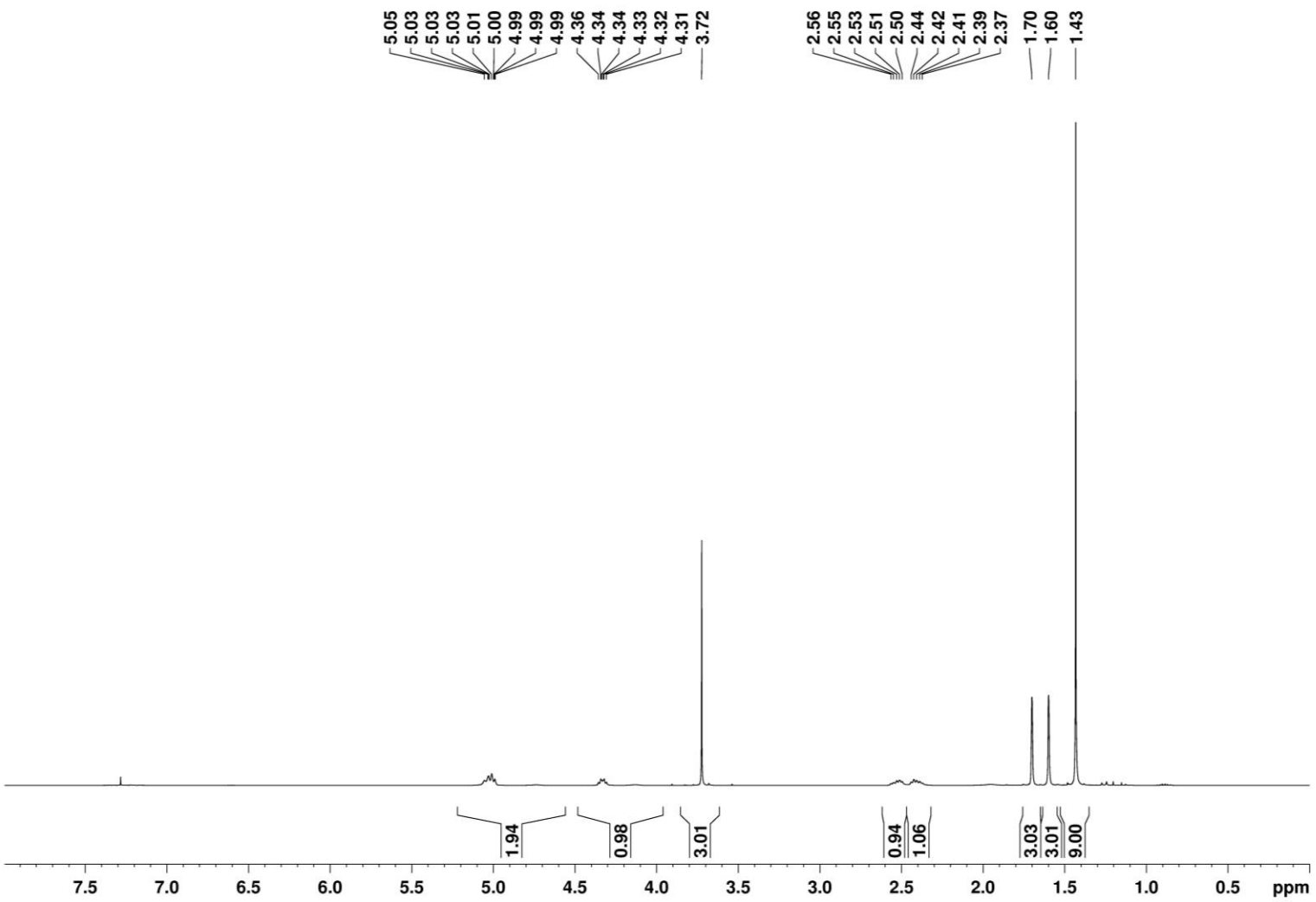
$CDCl_3$, 400 MHz

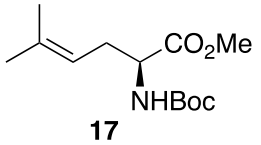




16

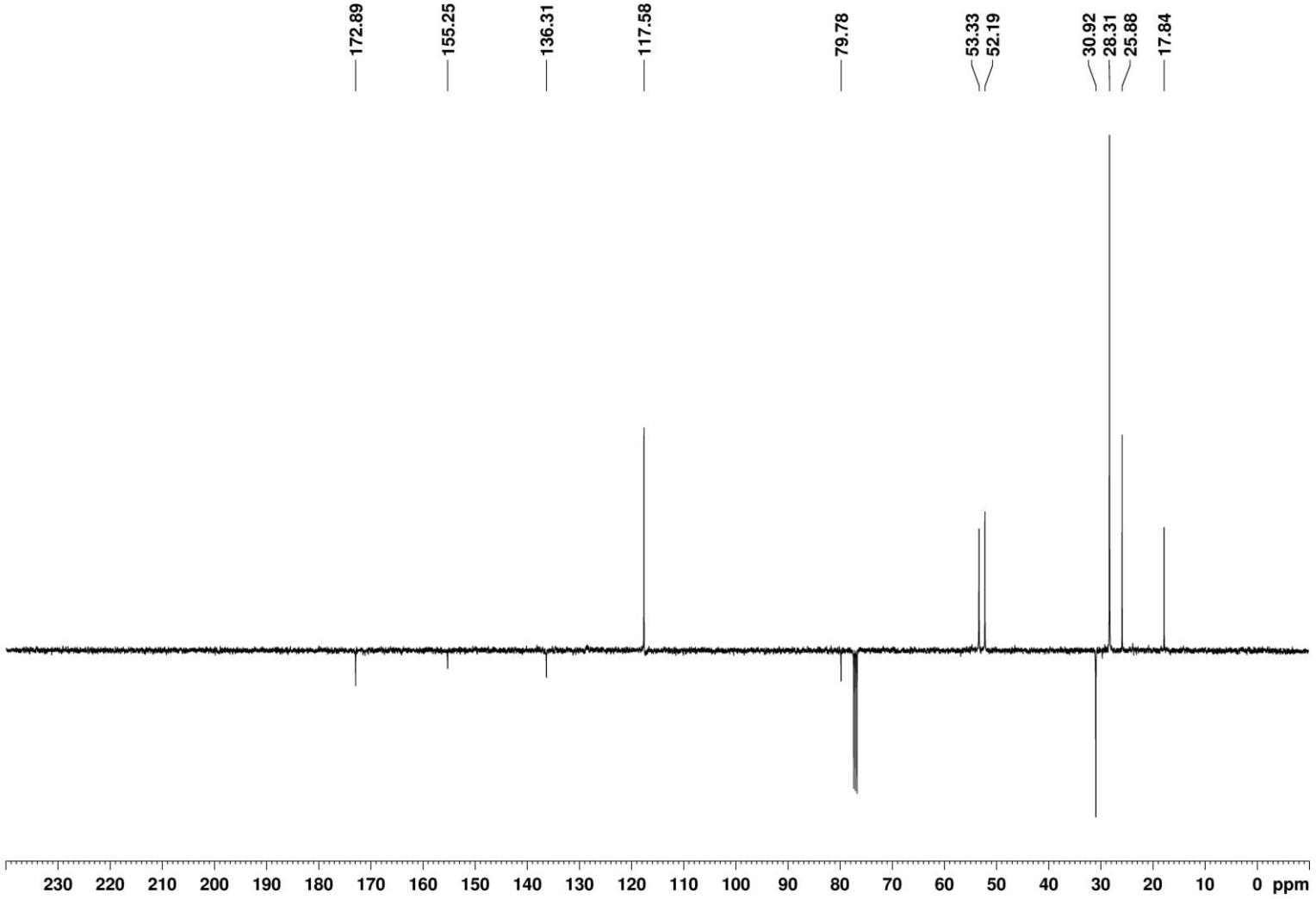
$CDCl_3$, 100 MHz

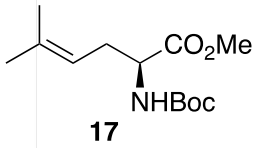




17

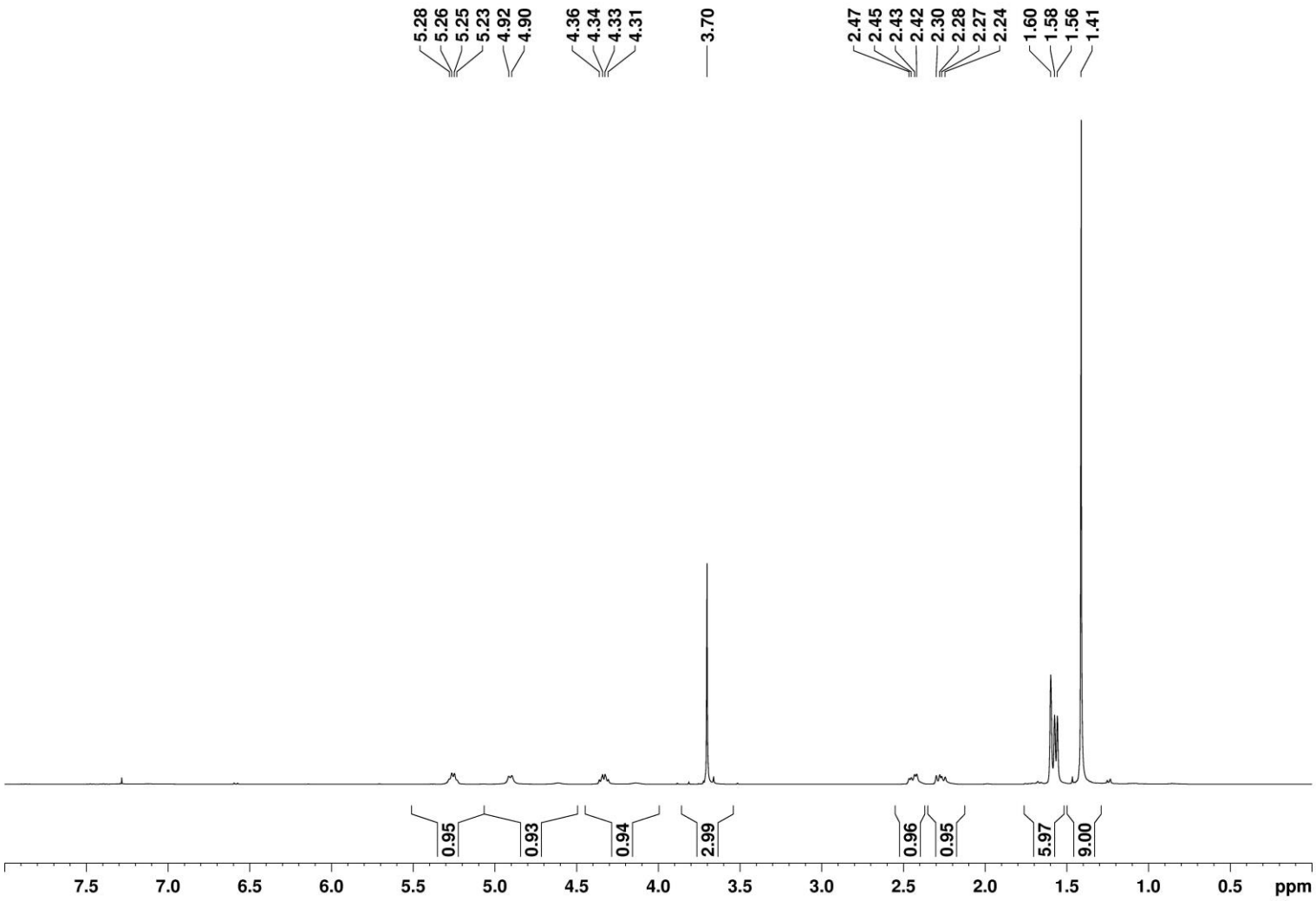
$CDCl_3$, 400 MHz

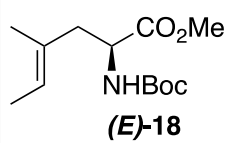




17

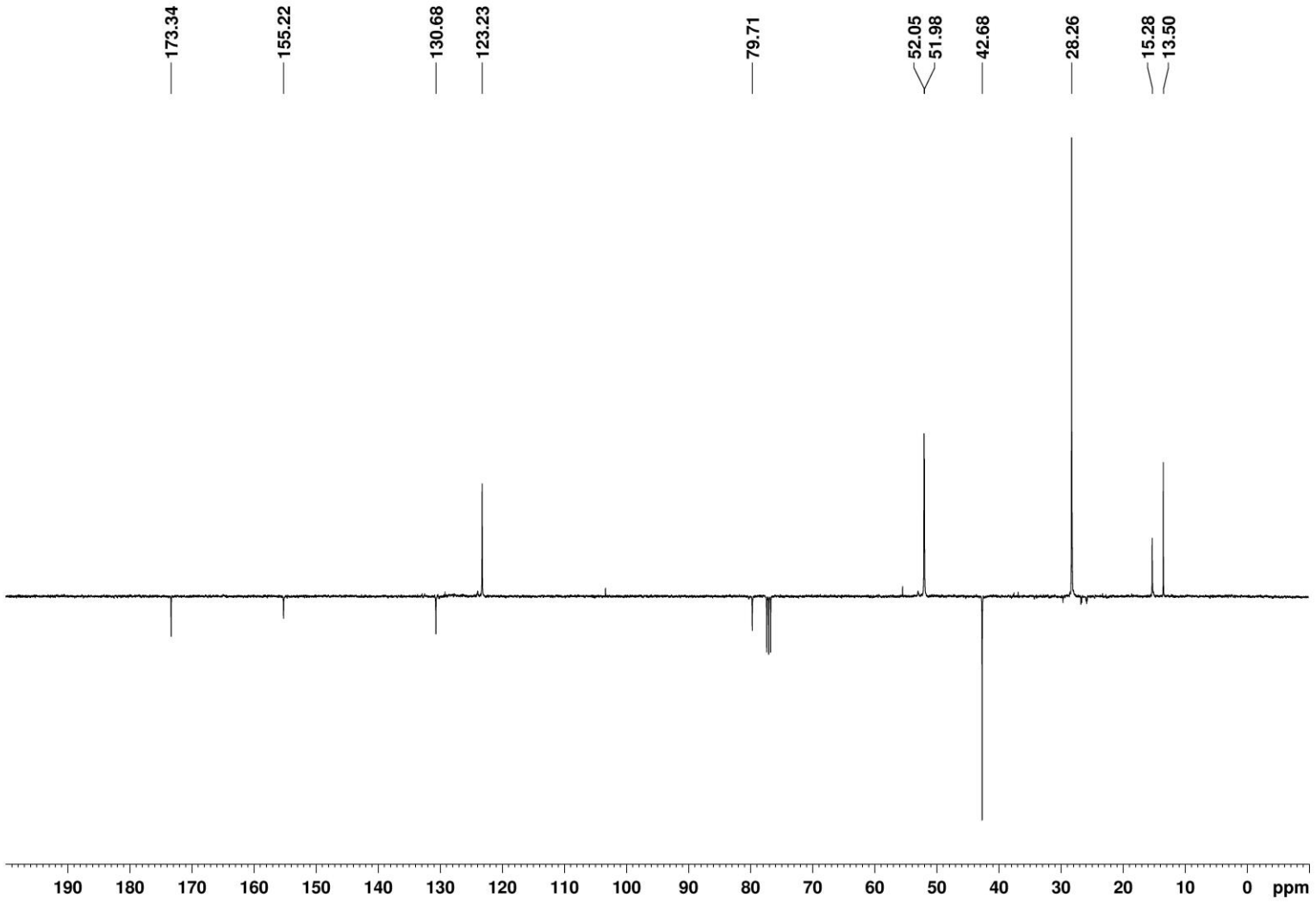
$CDCl_3$, 100 MHz

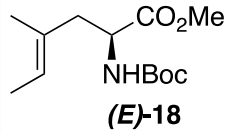




***(E)*-18**

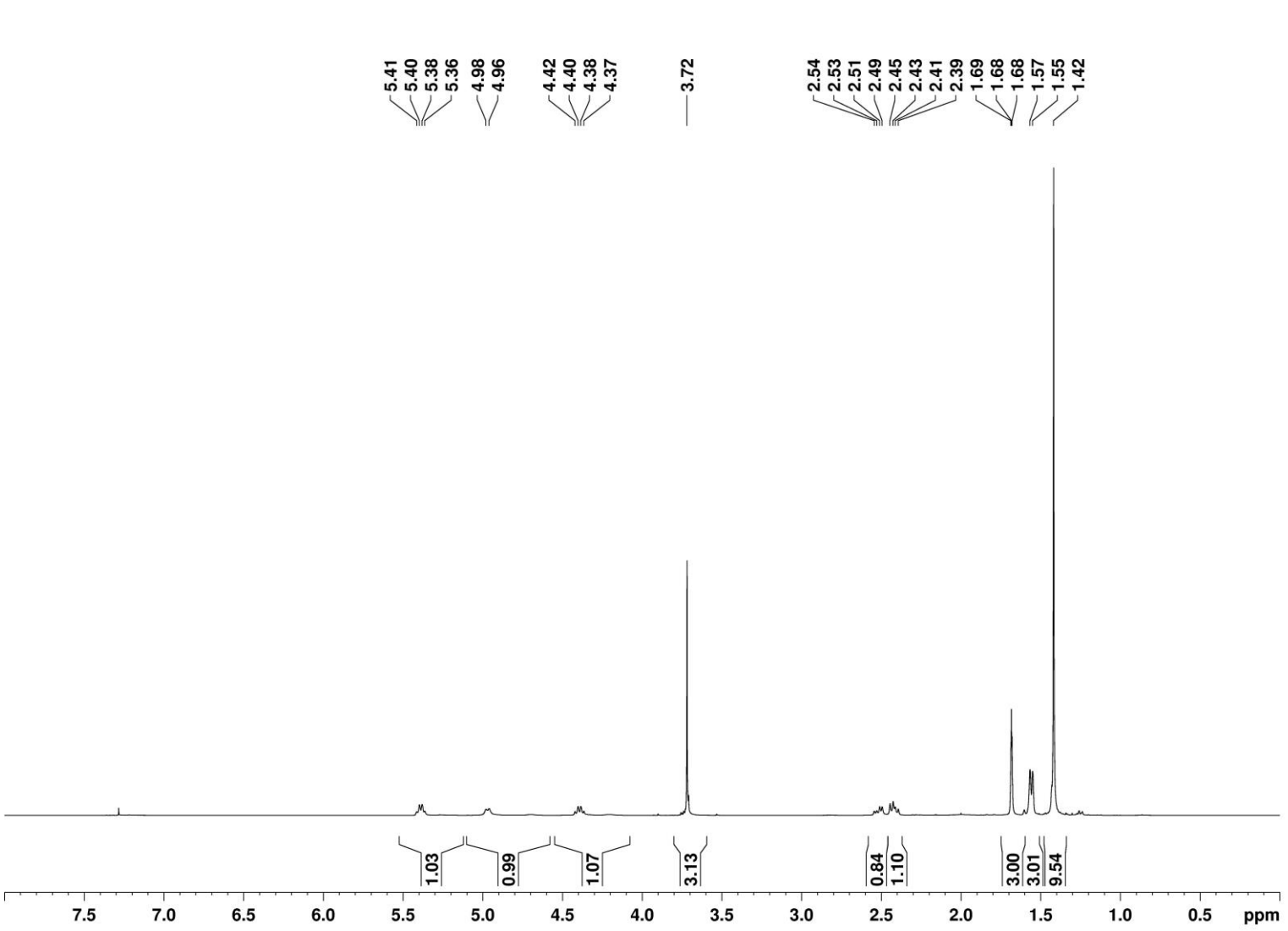
$CDCl_3$, 400 MHz

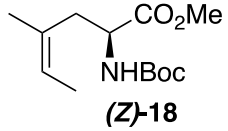




***(E)*-18**

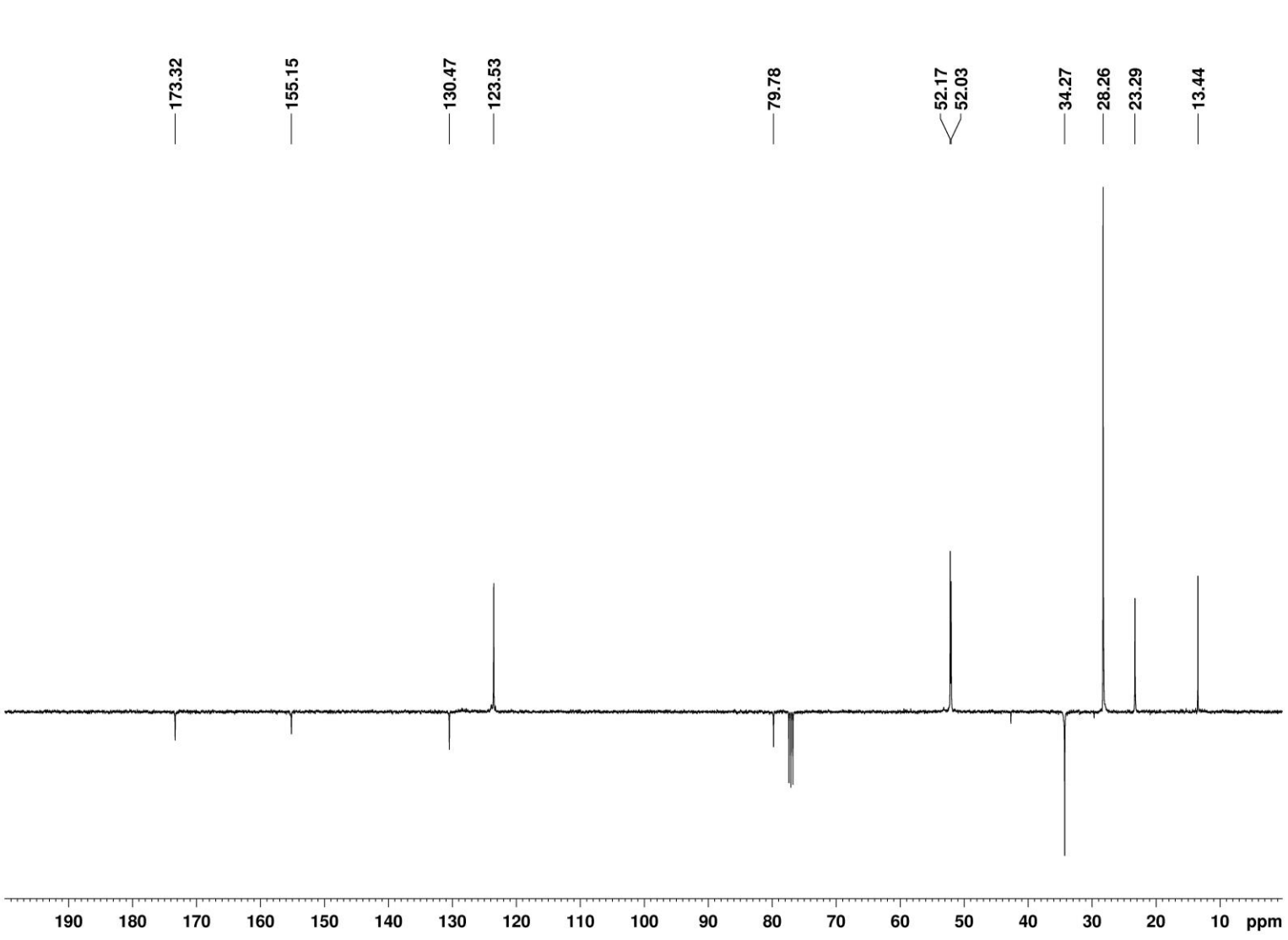
$CDCl_3$, 100 MHz

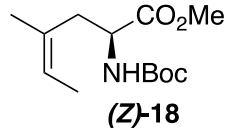




***(Z)*-18**

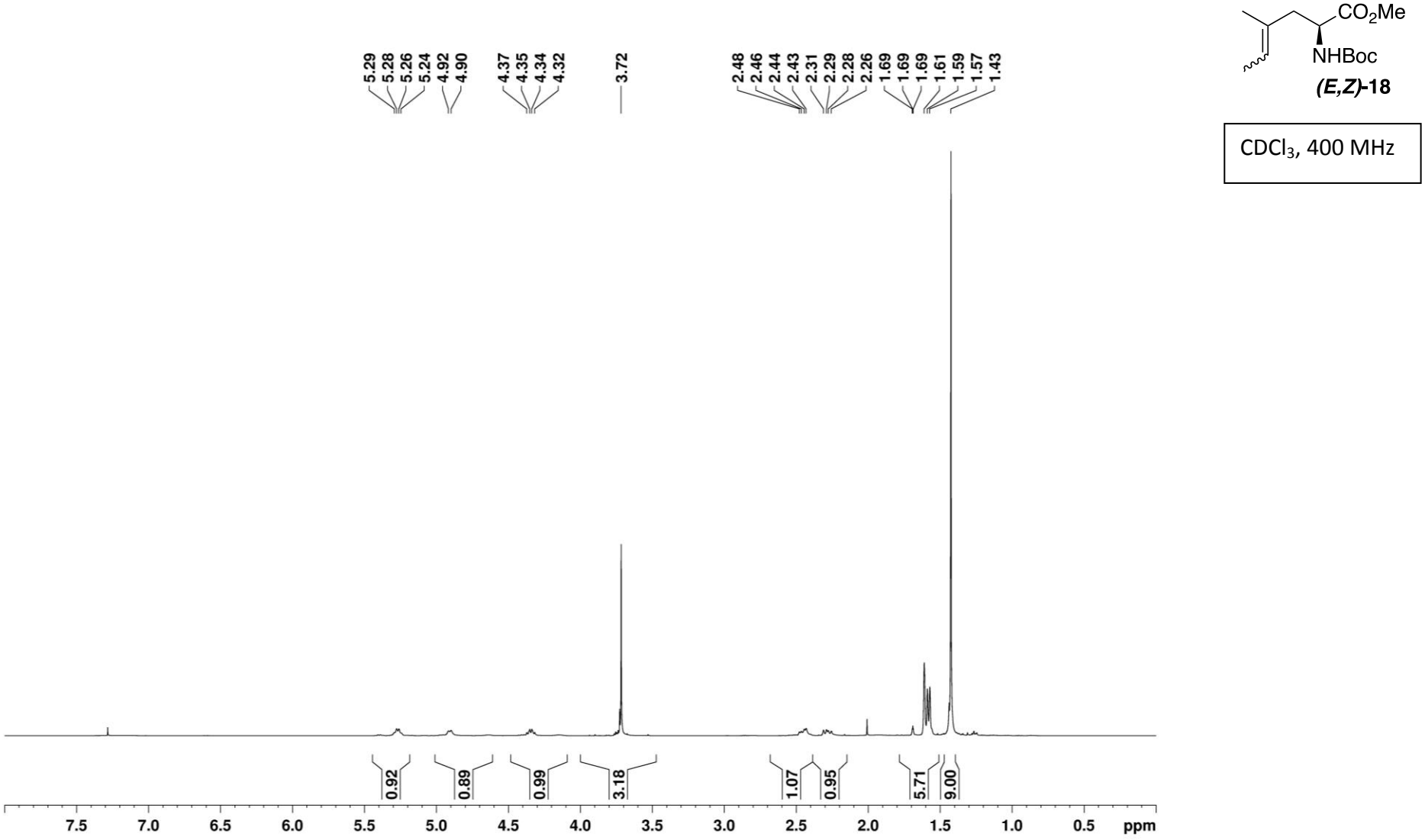
$CDCl_3$, 400 MHz





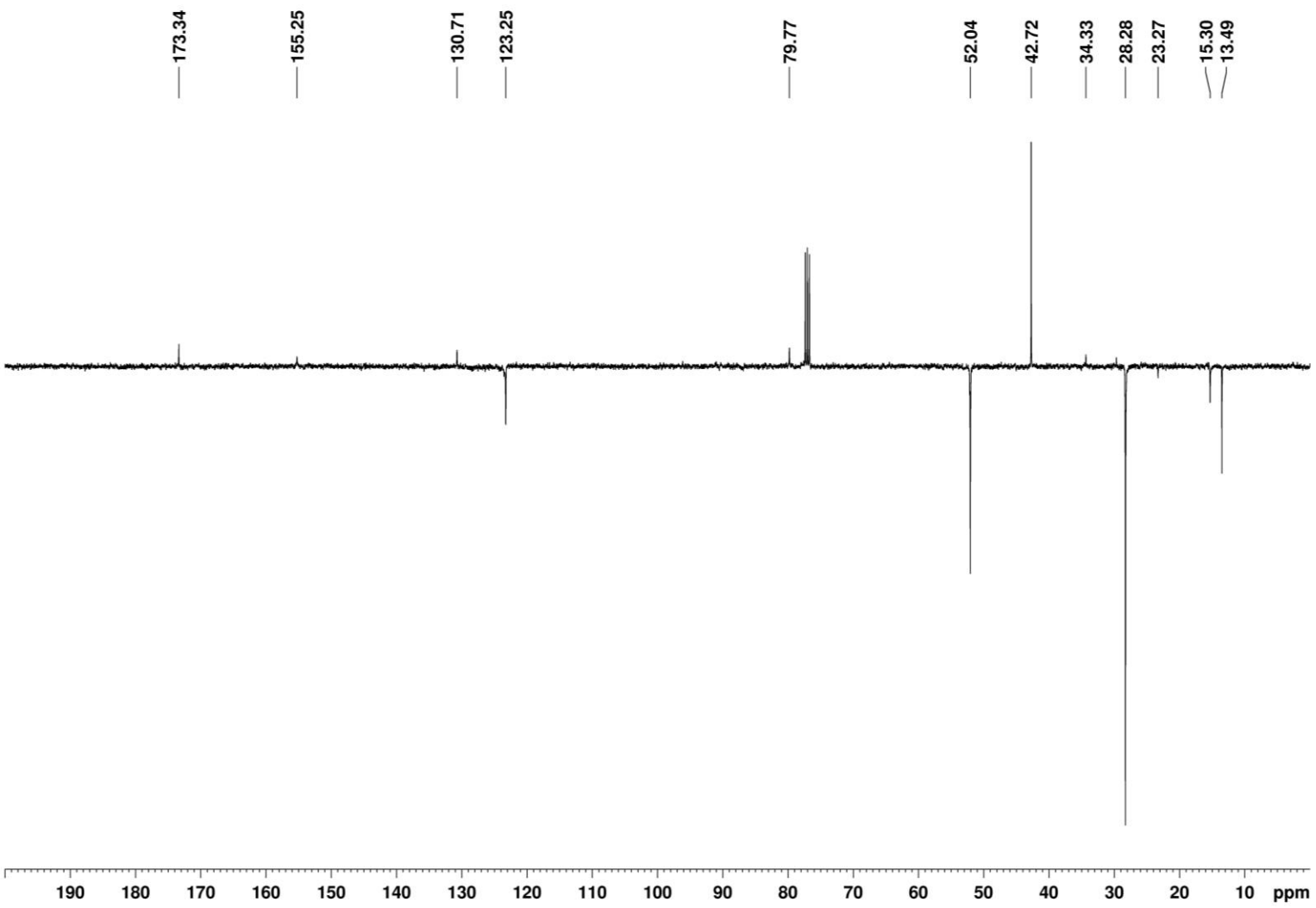
***(Z)*-18**

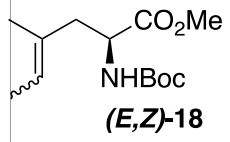
$CDCl_3$, 100 MHz



***(E,Z)*-18**

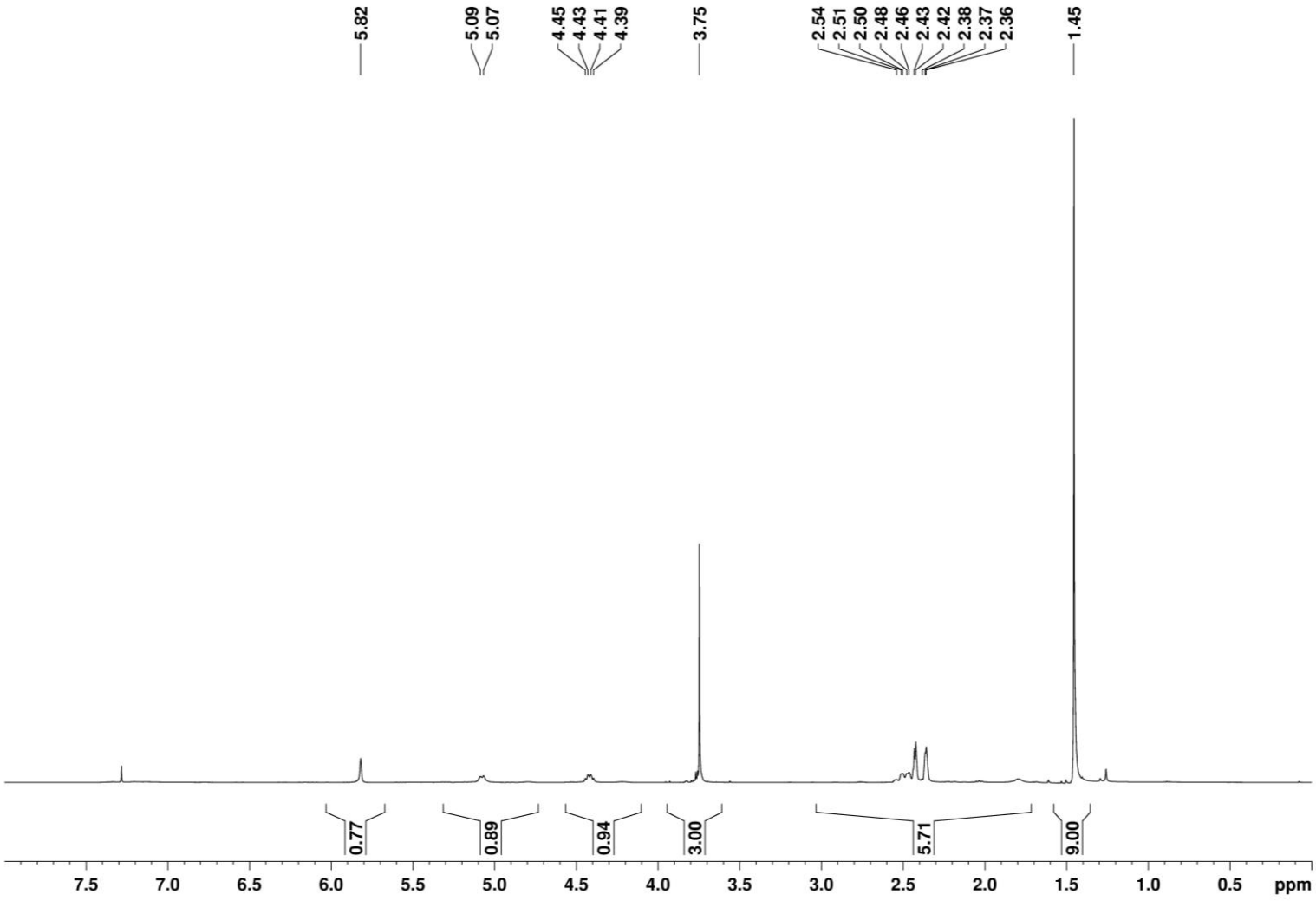
$CDCl_3$, 400 MHz

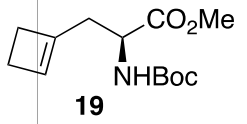




***(E,Z)*-18**

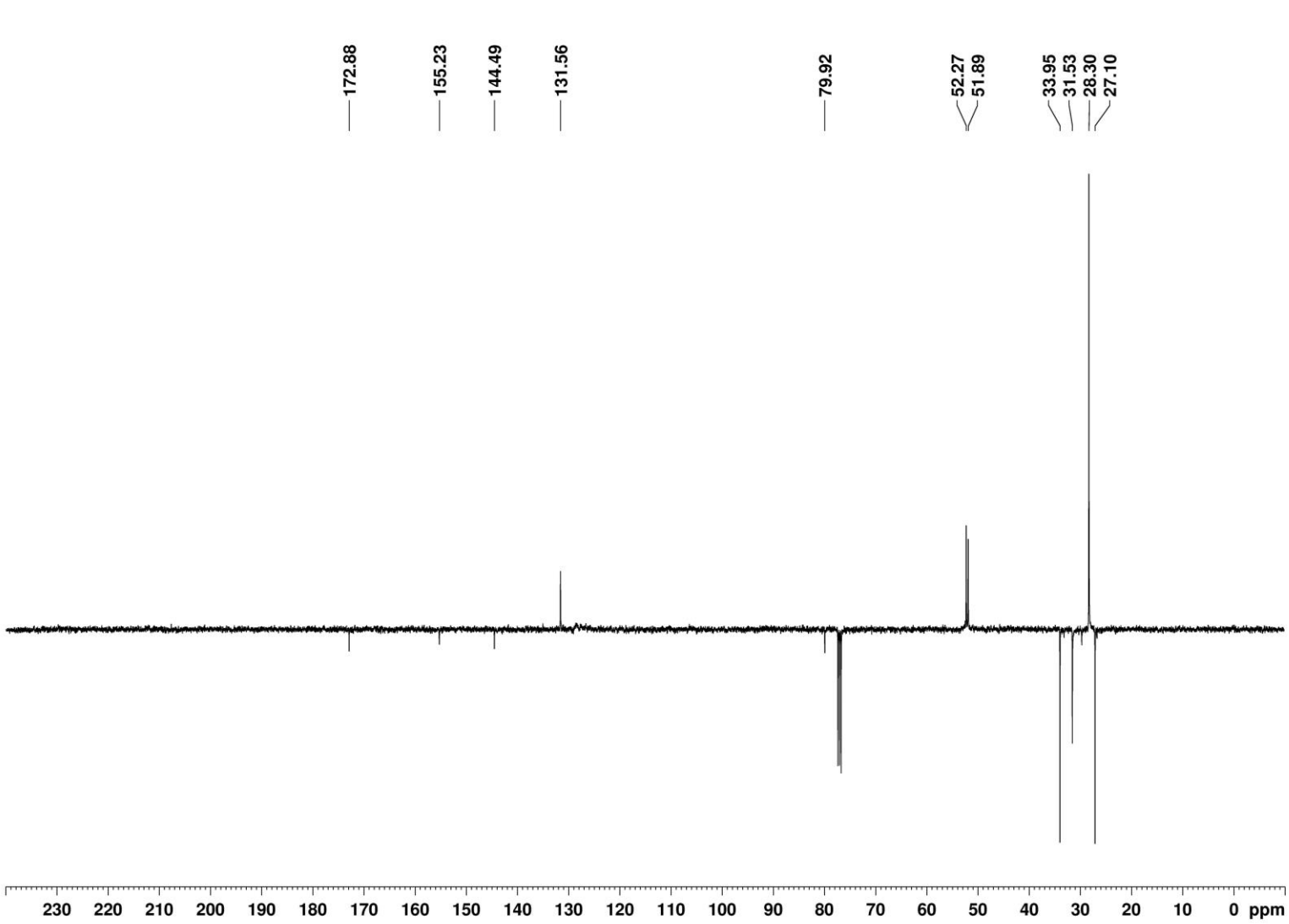
$CDCl_3$, 100 MHz

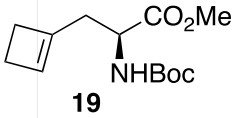




19

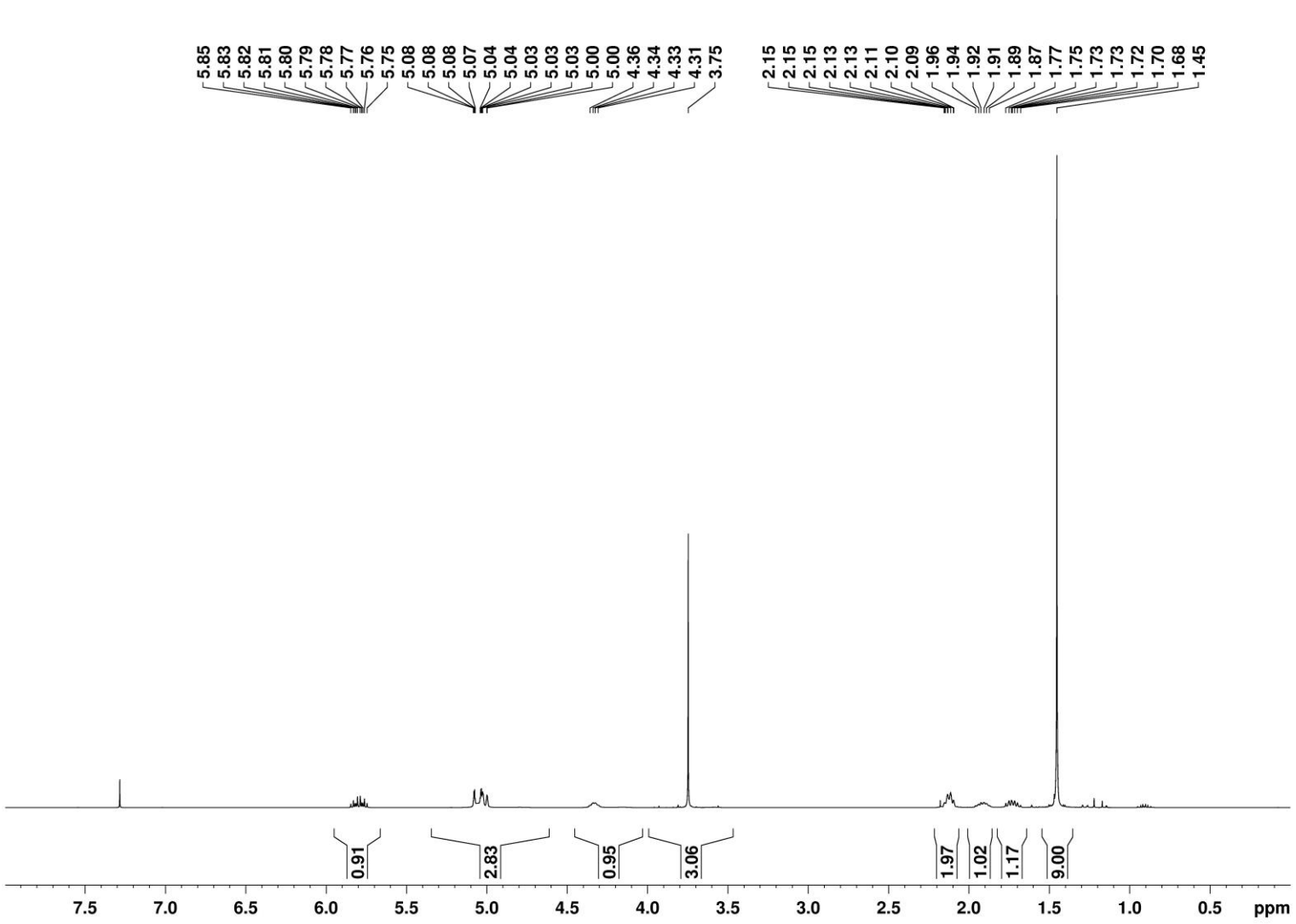
$CDCl_3$, 400 MHz

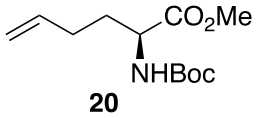




19

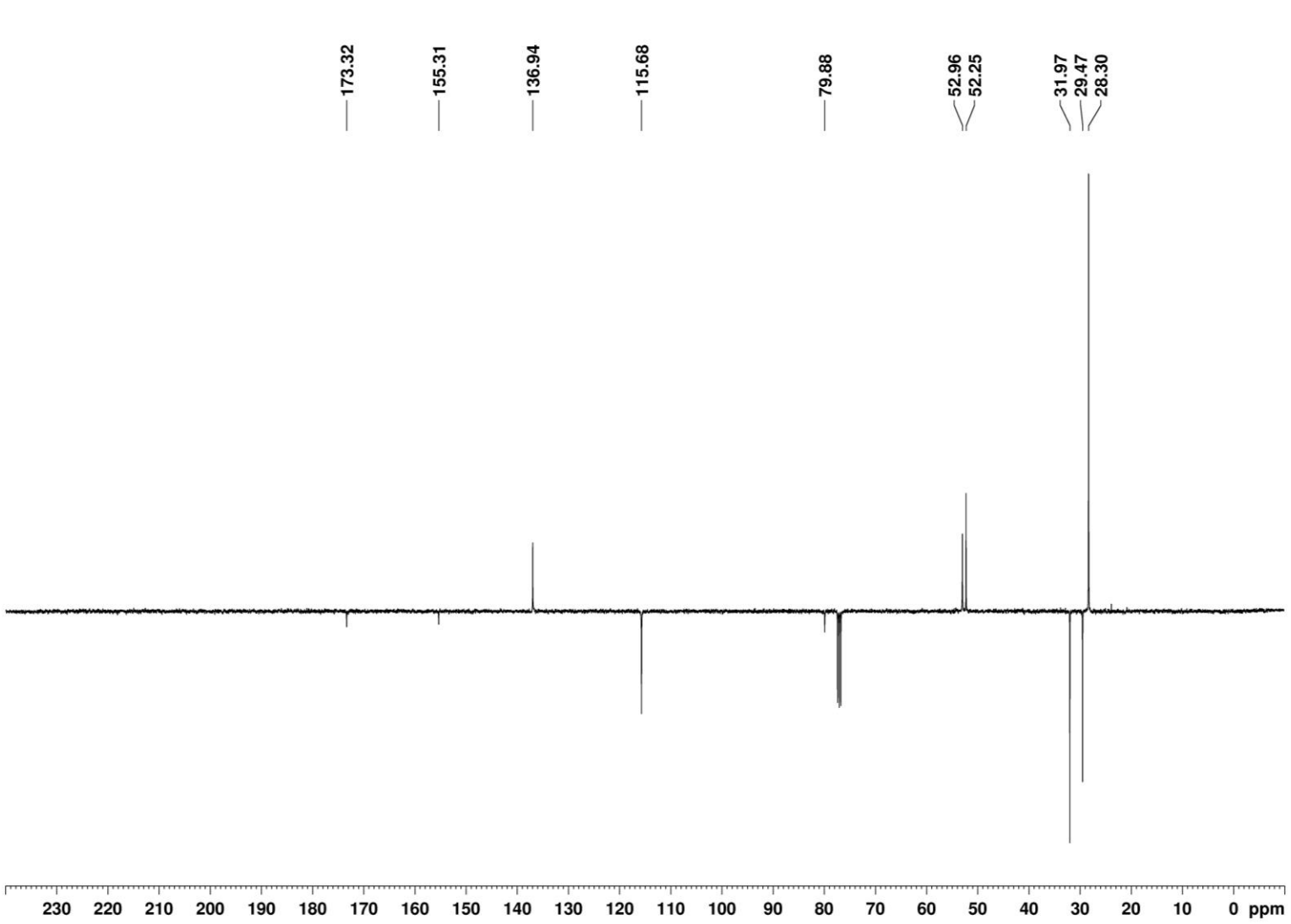
$CDCl_3$, 100 MHz

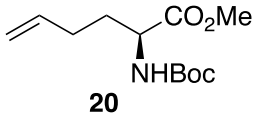




20

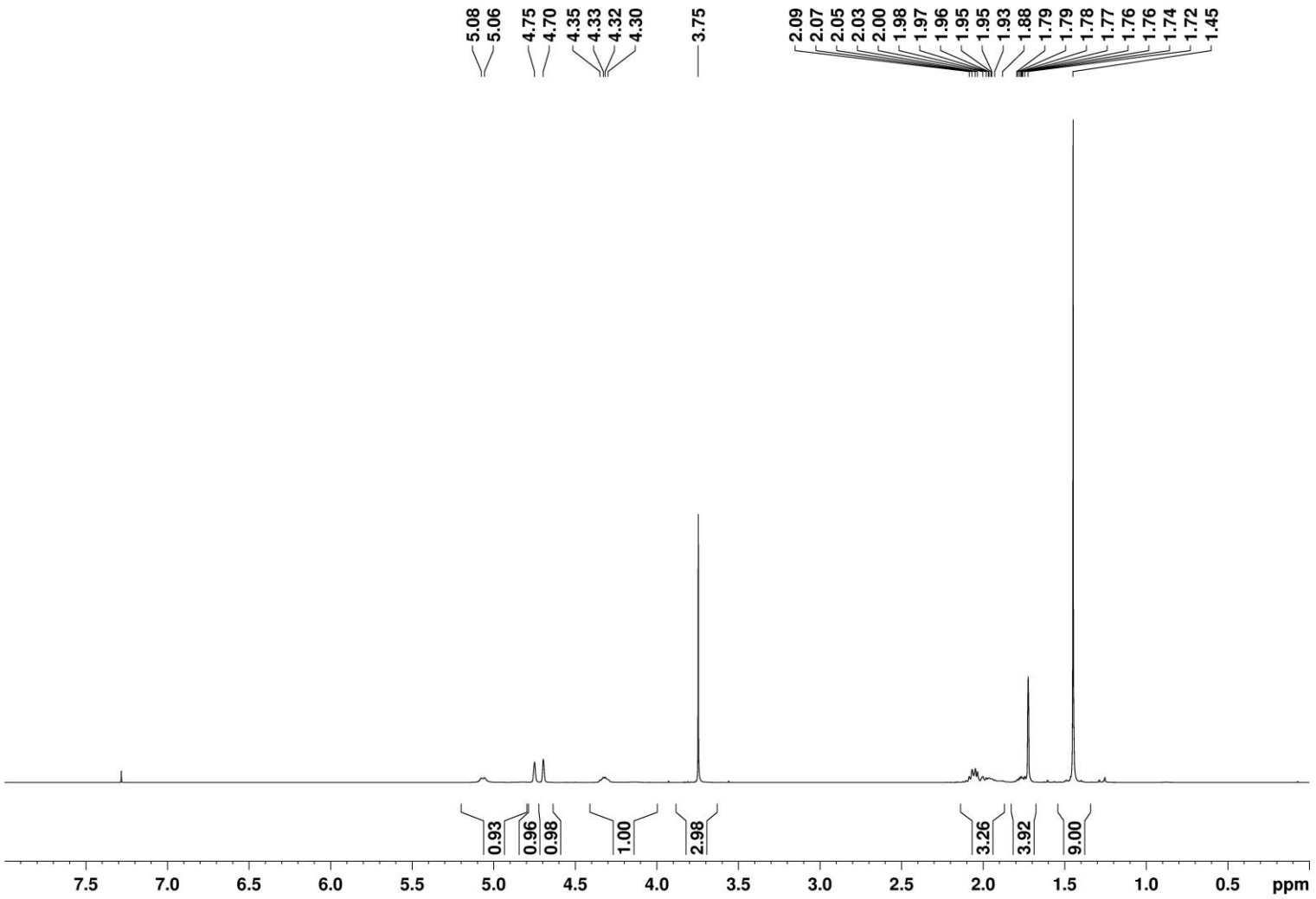
$CDCl_3$, 400 MHz

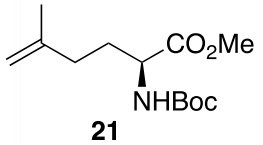




20

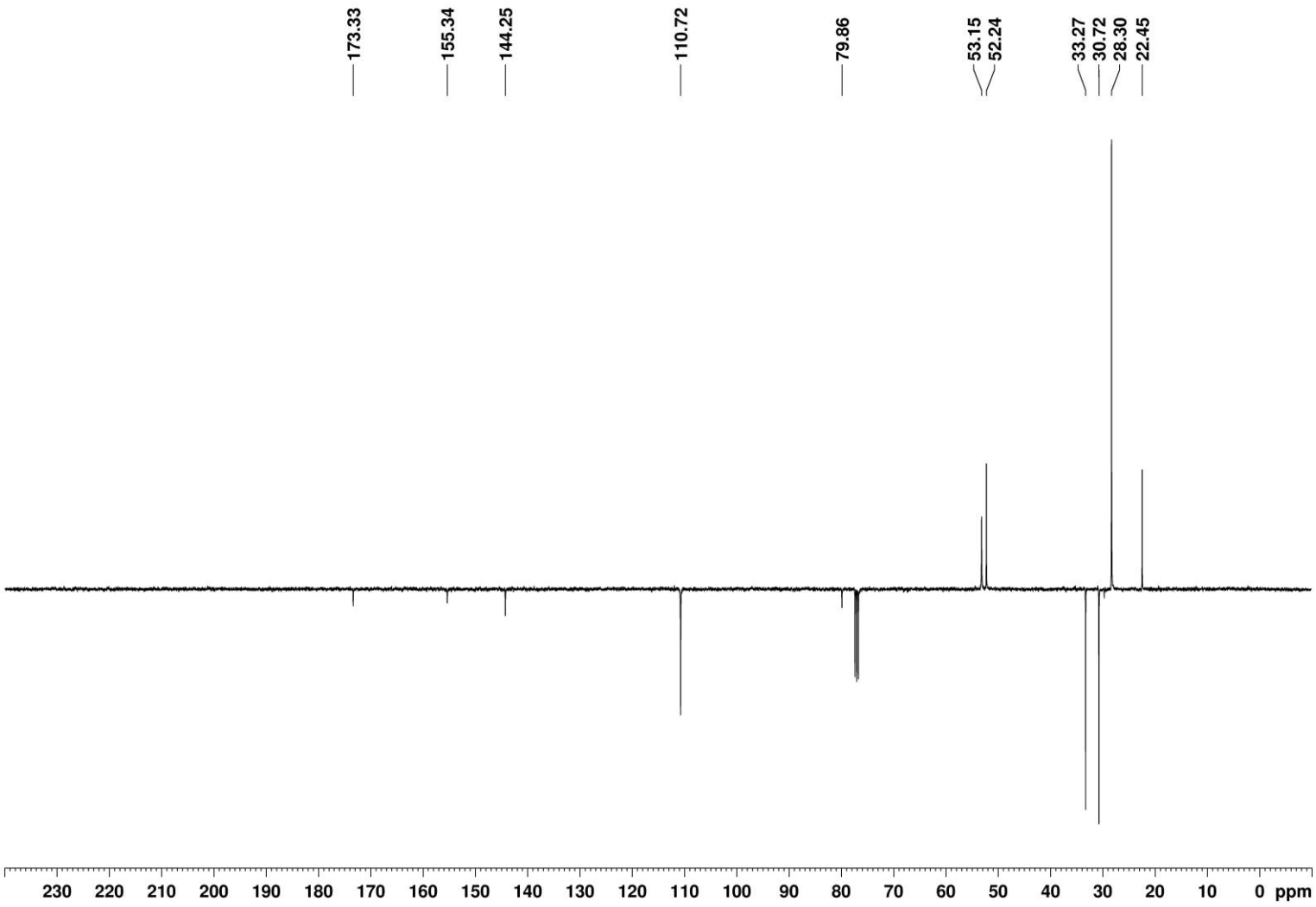
$CDCl_3$, 100 MHz

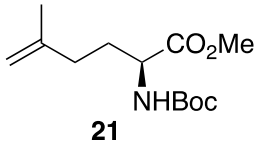




21

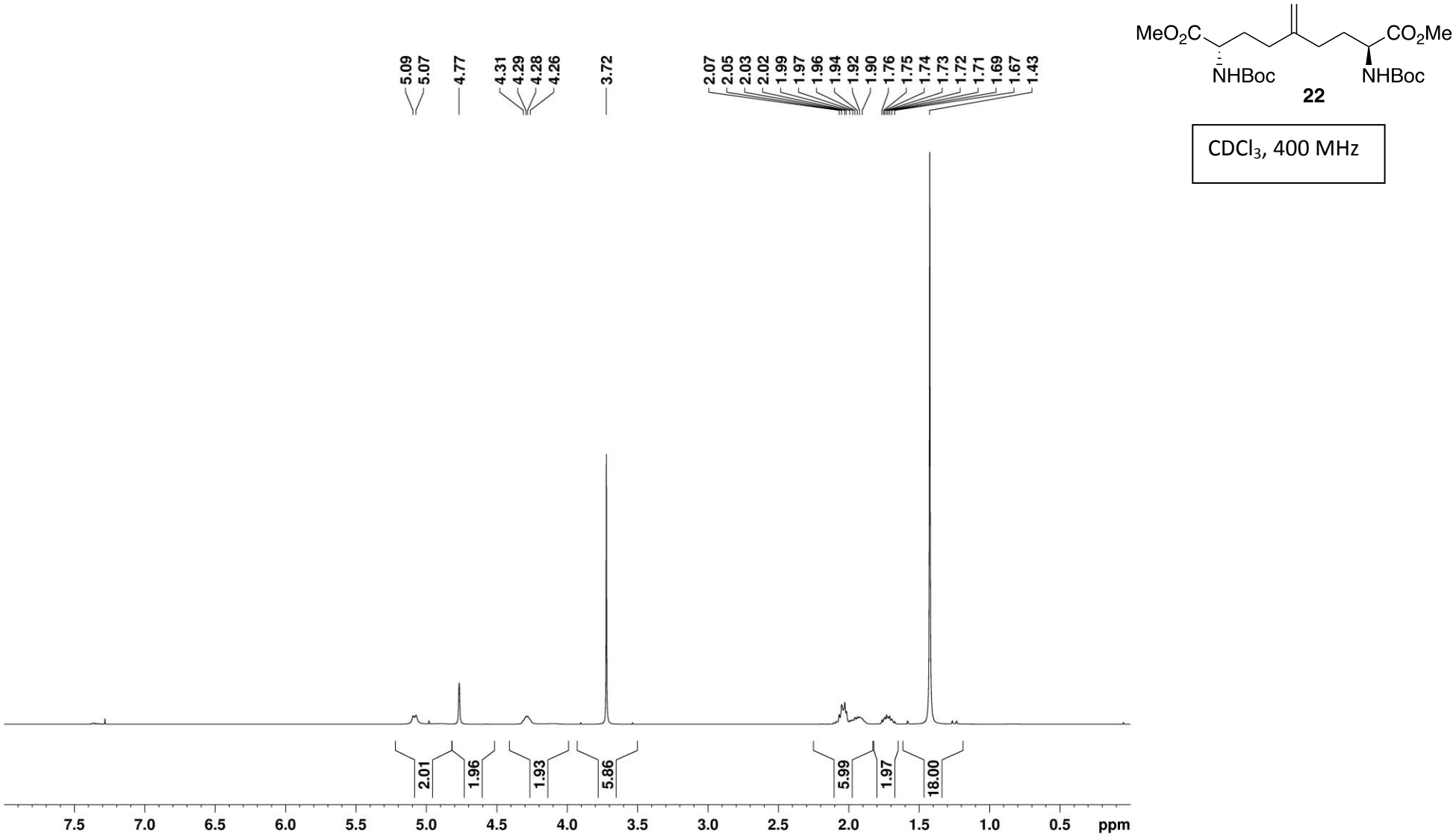
$CDCl_3$, 400 MHz





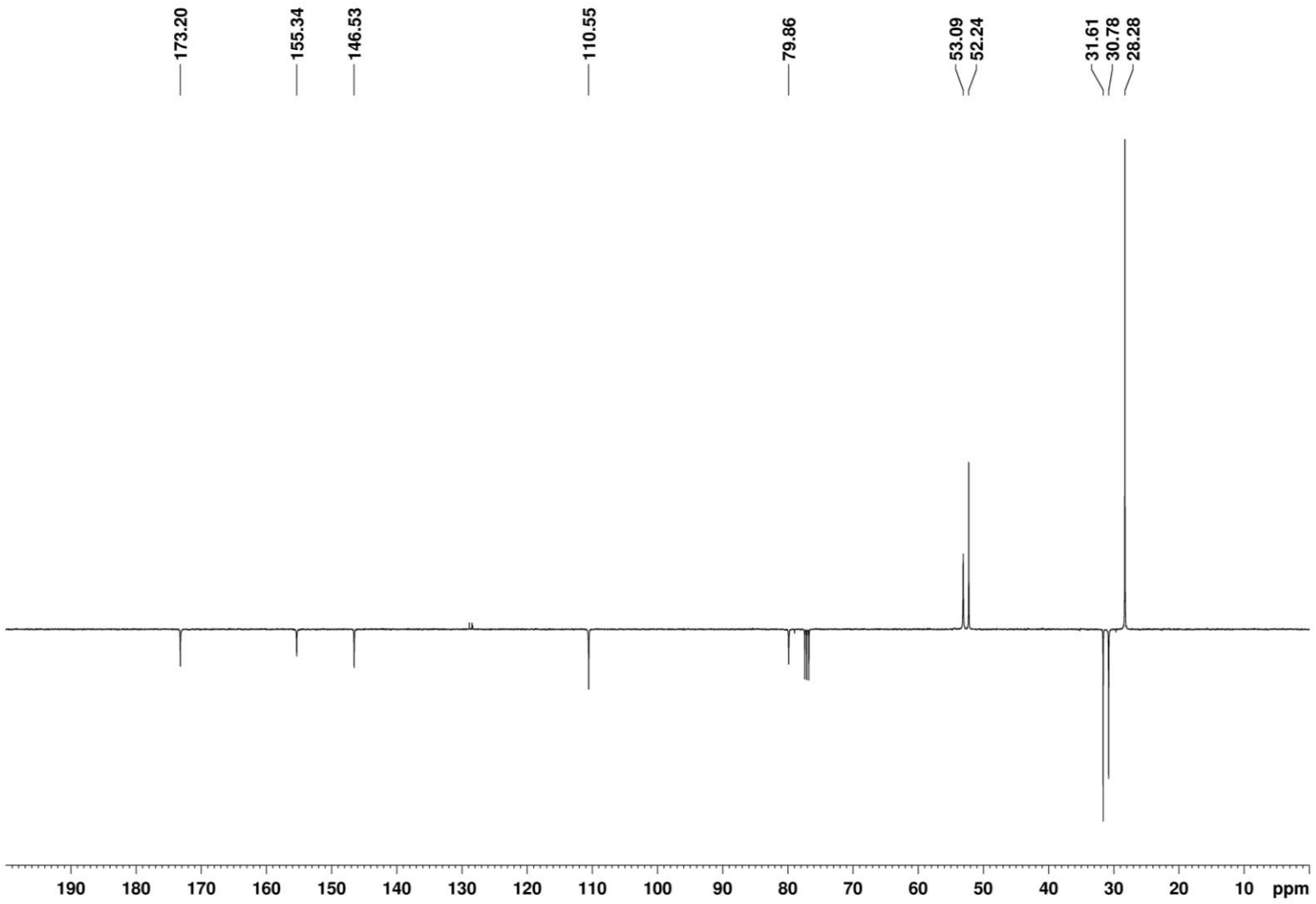
21

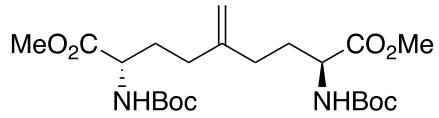
$CDCl_3$, 100 MHz



22

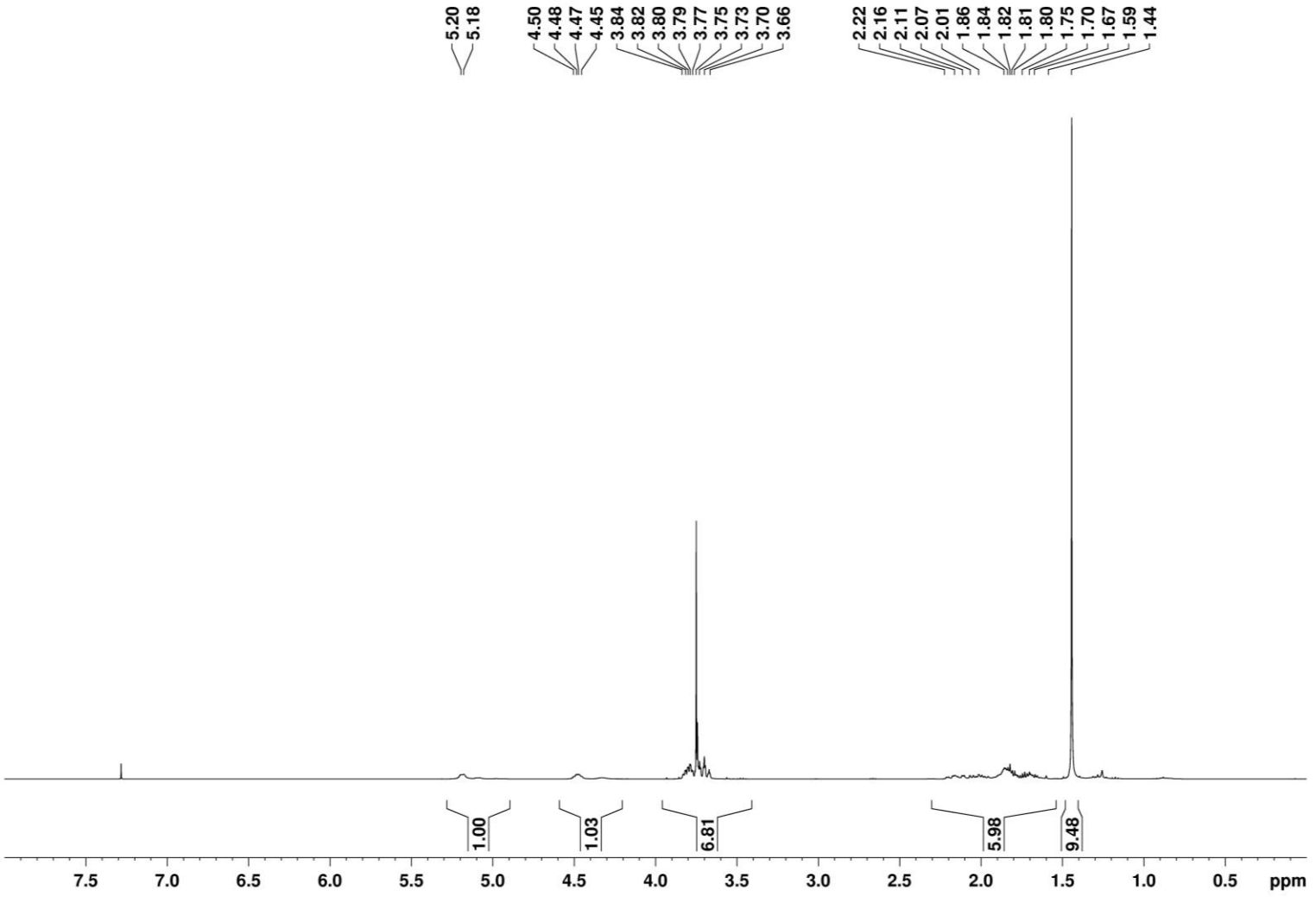
$CDCl_3$, 400 MHz

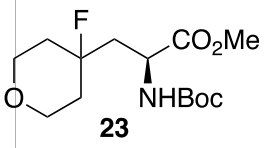




22

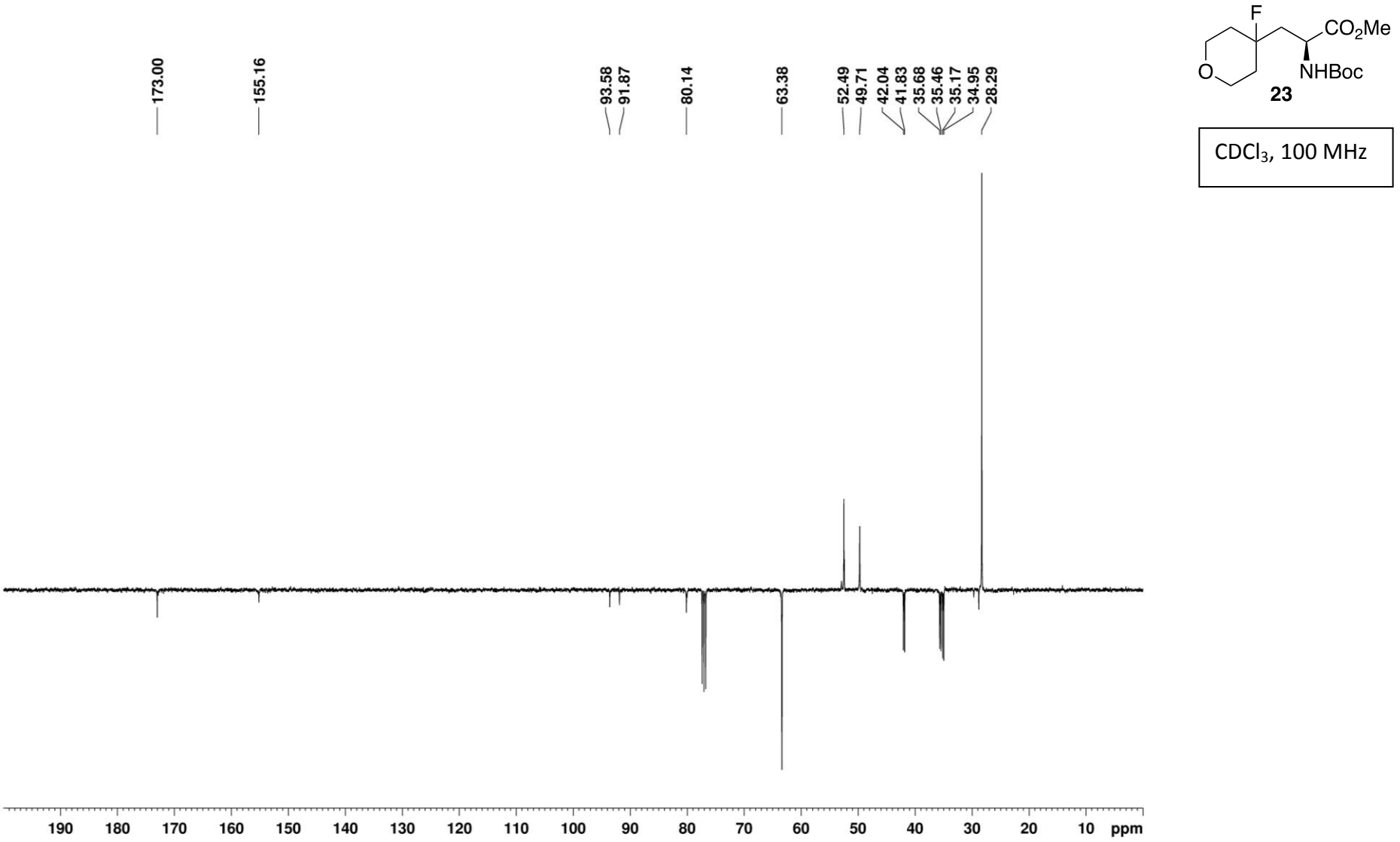
$CDCl_3$, 100 MHz





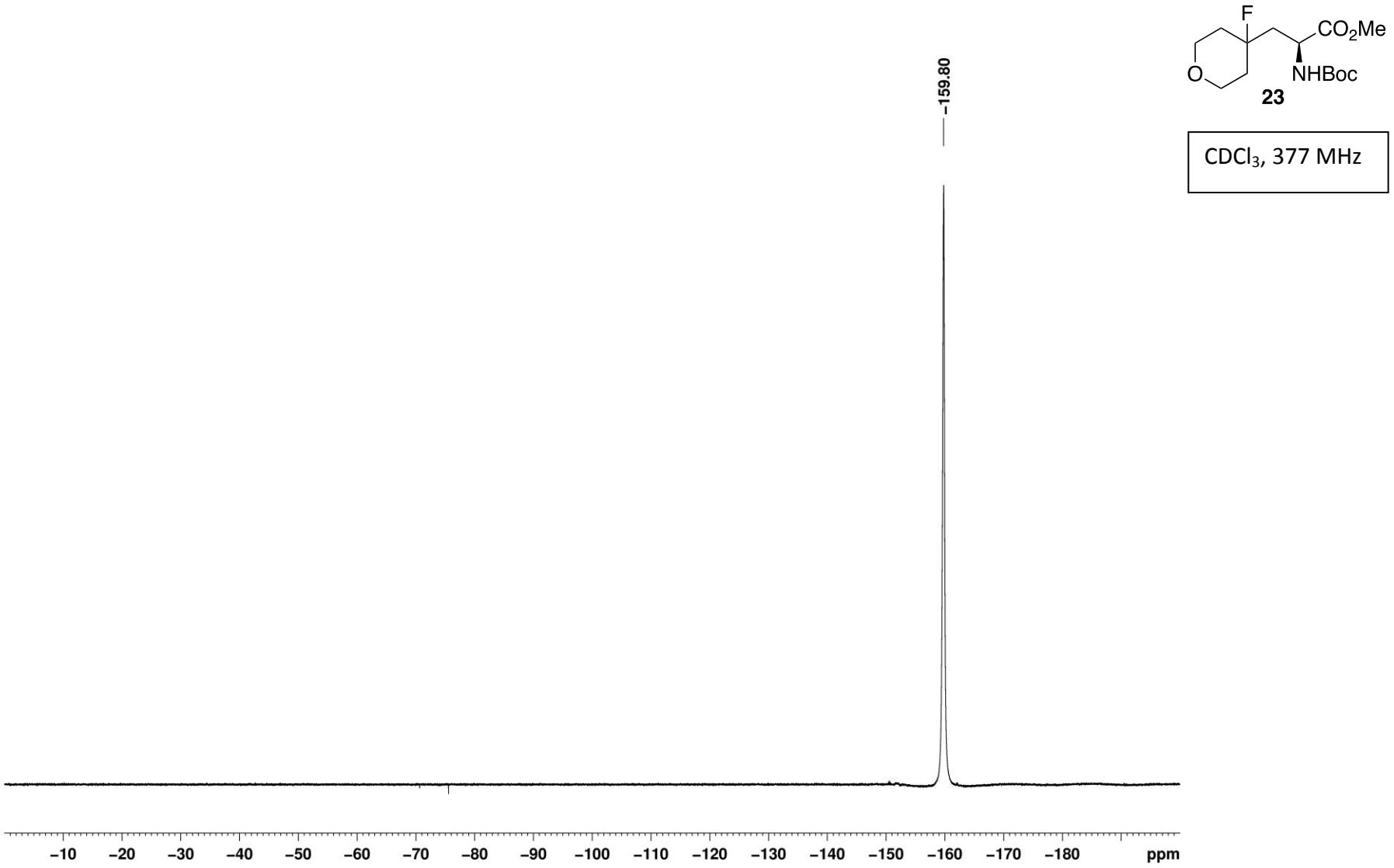
23

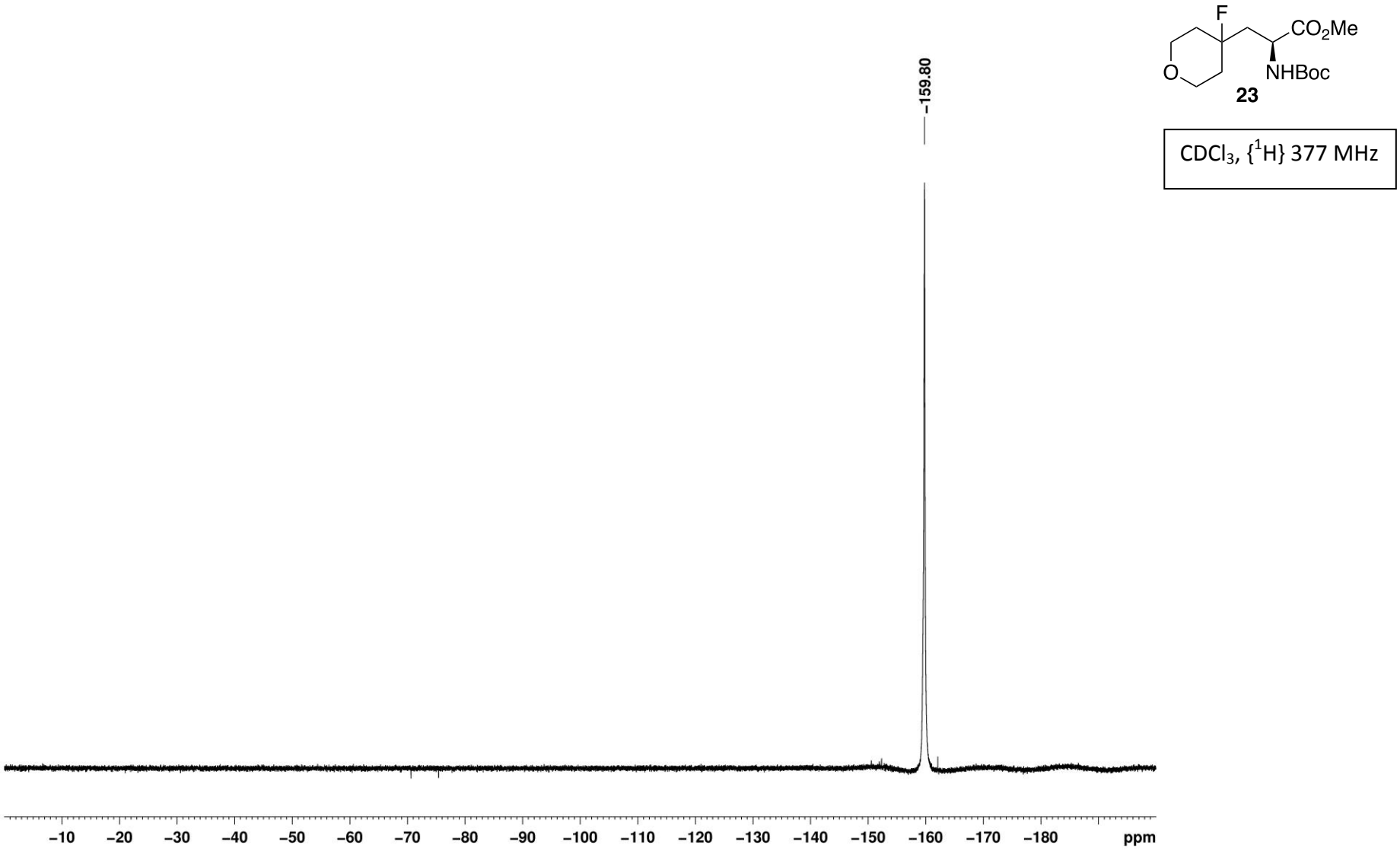
$CDCl_3$, 400 MHz

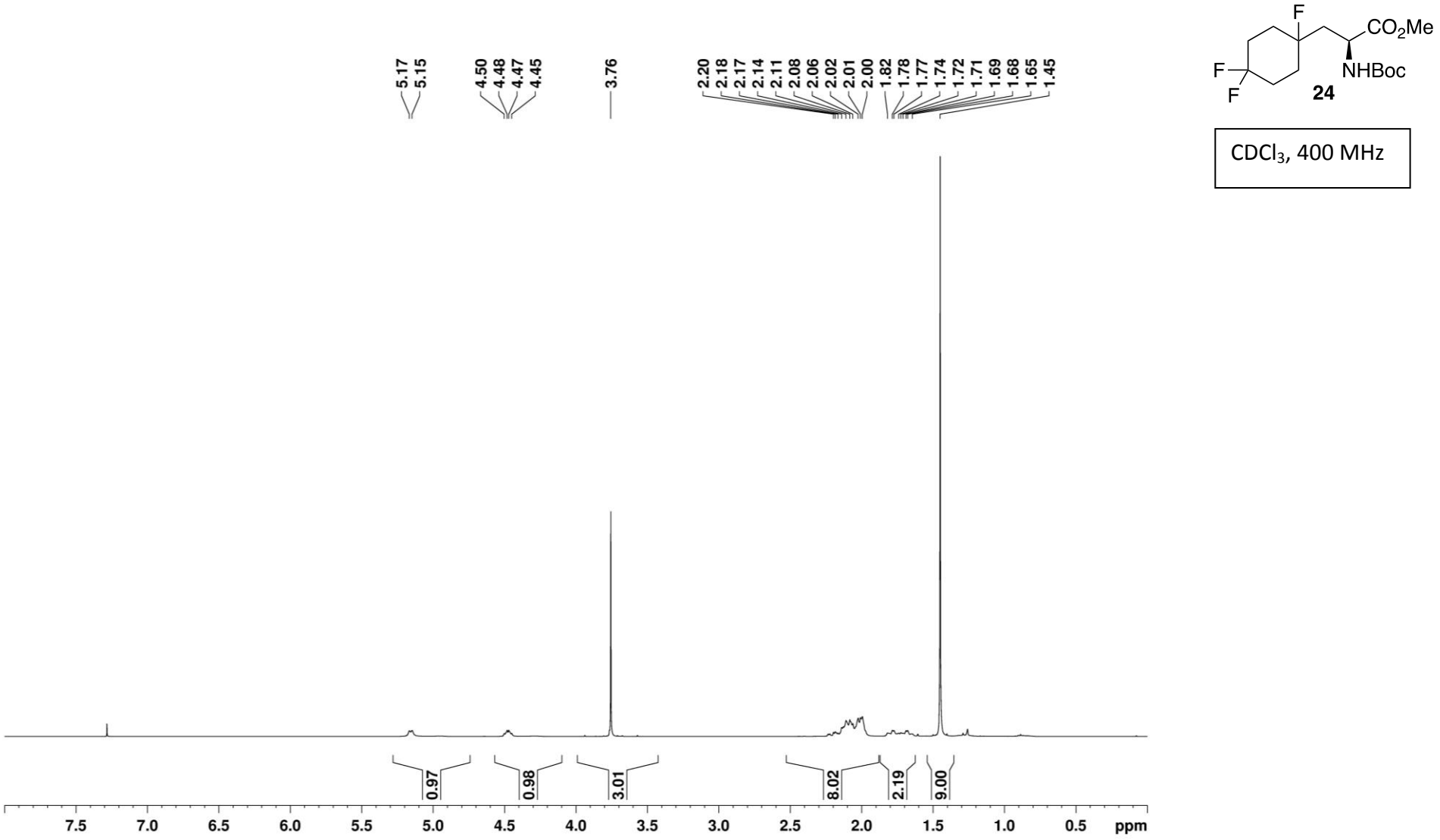


23

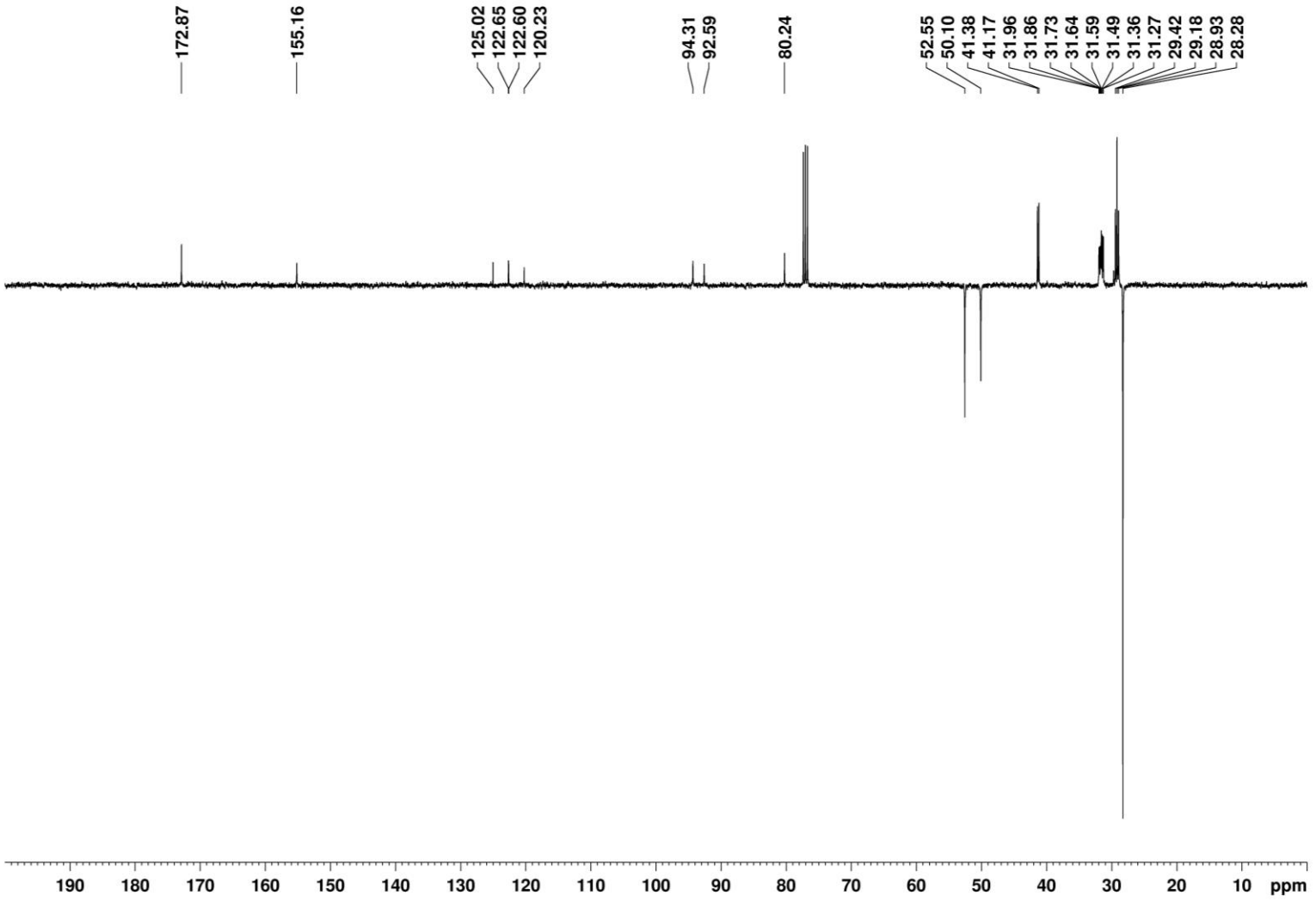
$CDCl_3$, 100 MHz

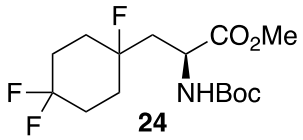

F
CO2Me
O
NHBoc
23
CDCl3, 377 MHz
-159.80
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm


F
CO2Me
O
NHBoc
23
CDCl3, {1H} 377 MHz
-159.80
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

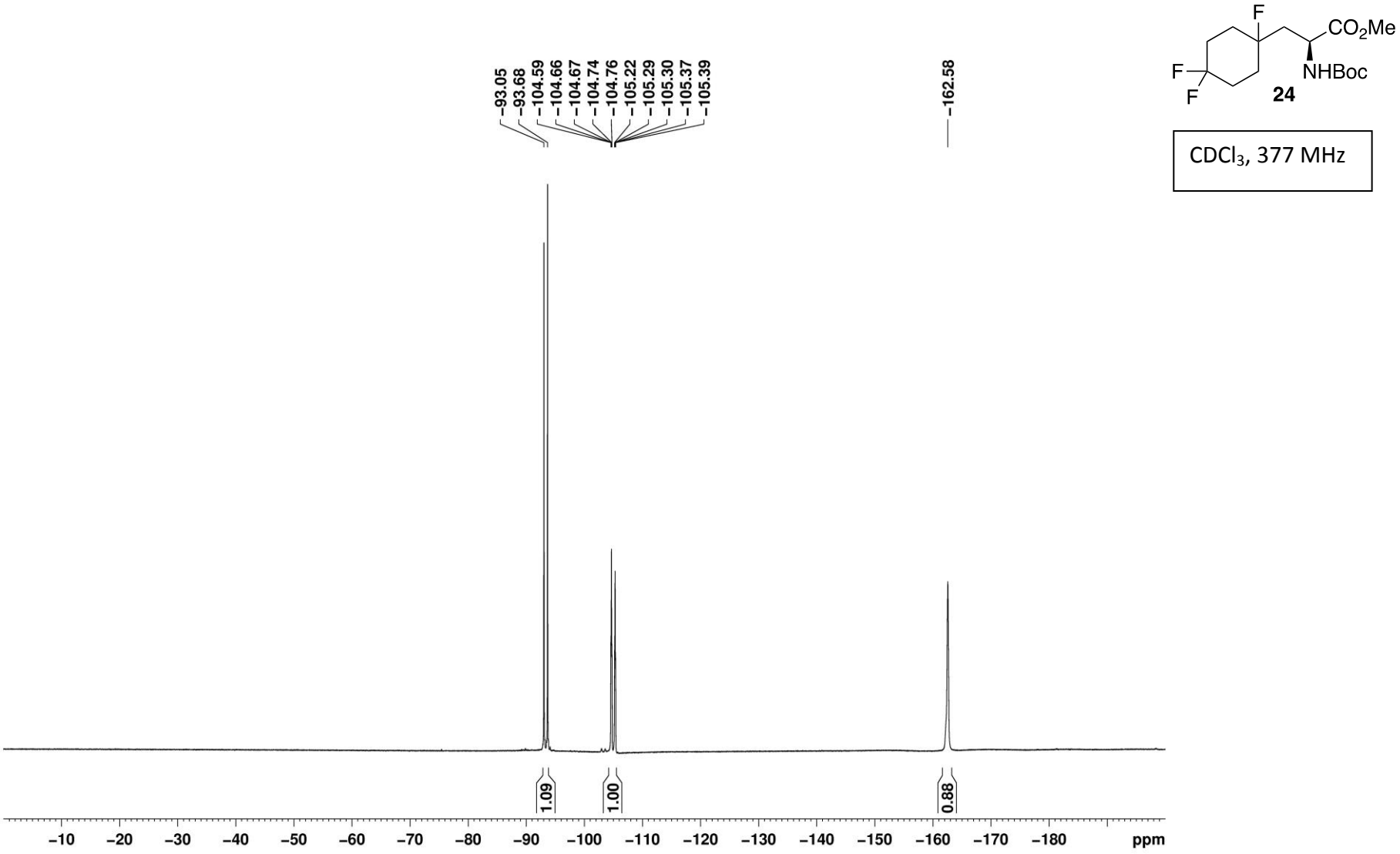


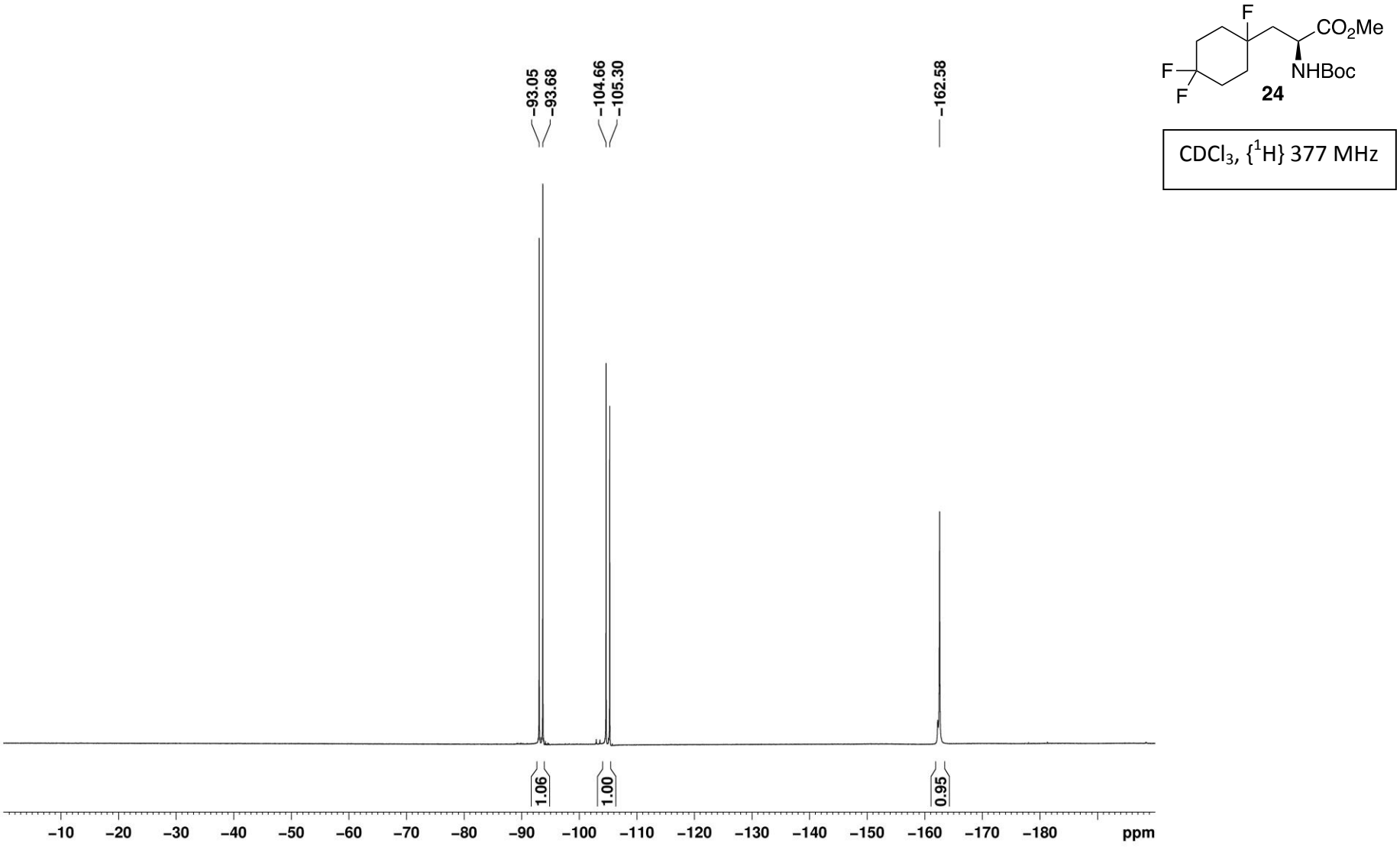
$CDCl_3$, 400 MHz

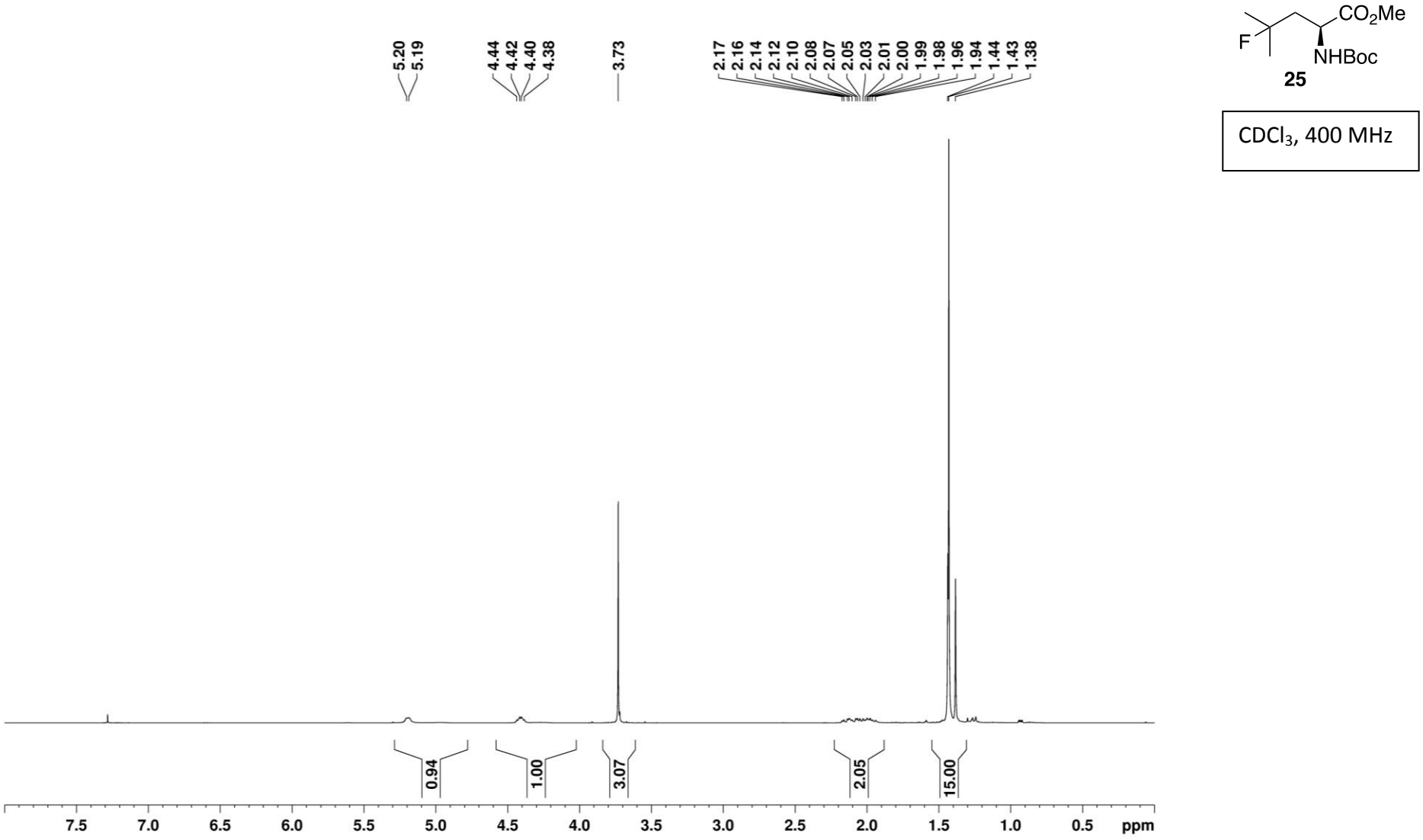




$CDCl_3$, 100 MHz

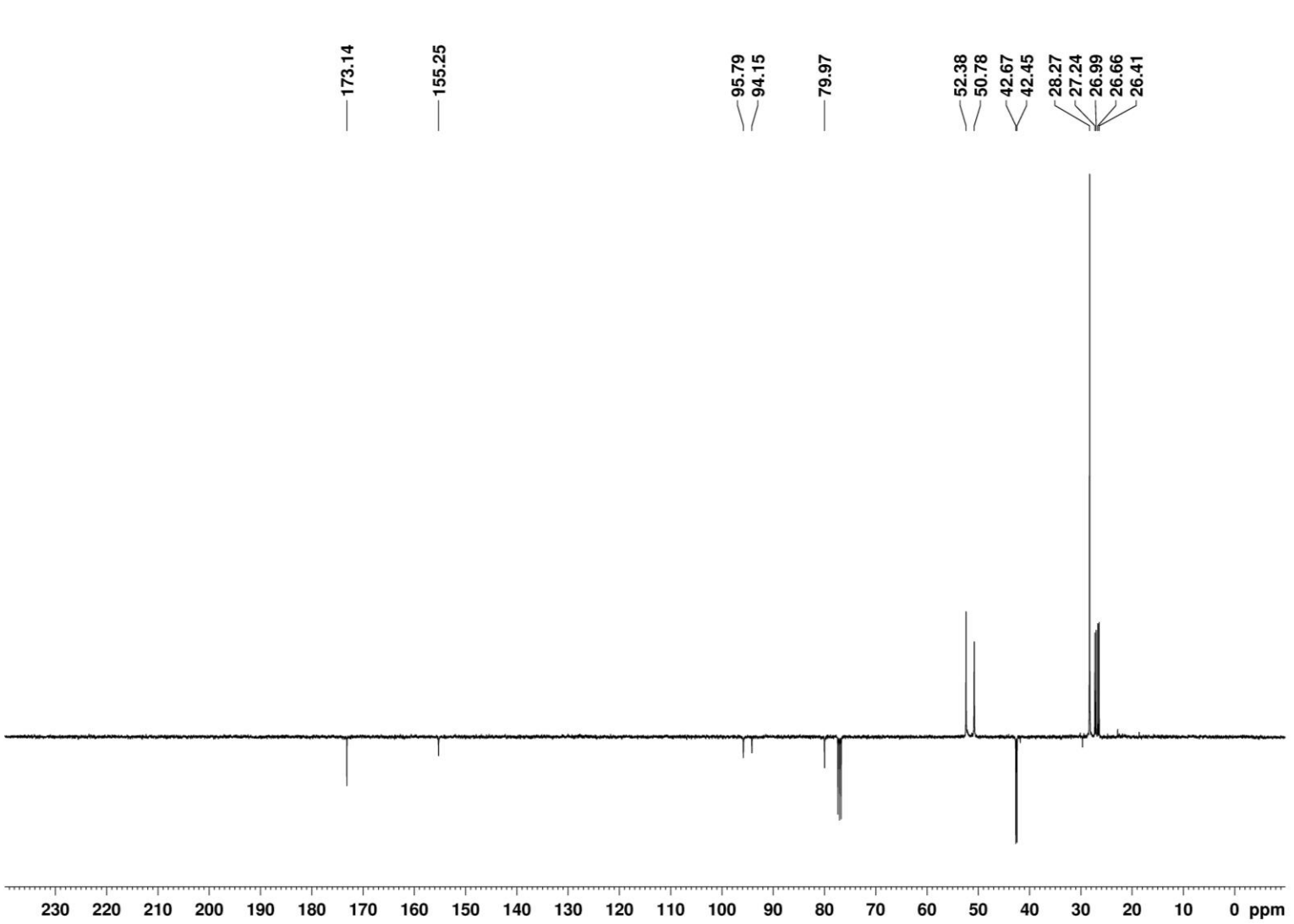

F
CO2Me
F
NHBoc
F
24
CDCl3, 377 MHz
-93.05
-93.68
-104.59
-104.66
-104.67
-104.74
-104.76
-105.22
-105.29
-105.30
-105.37
-105.39
-162.58
1.09
1.00
0.88
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm

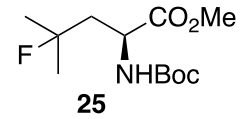

F
CO2Me
F
NHBoc
F
24
CDCl3, {1H} 377 MHz
-93.05
-93.68
-104.66
-105.30
-162.58
1.06
1.00
0.95
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm



25

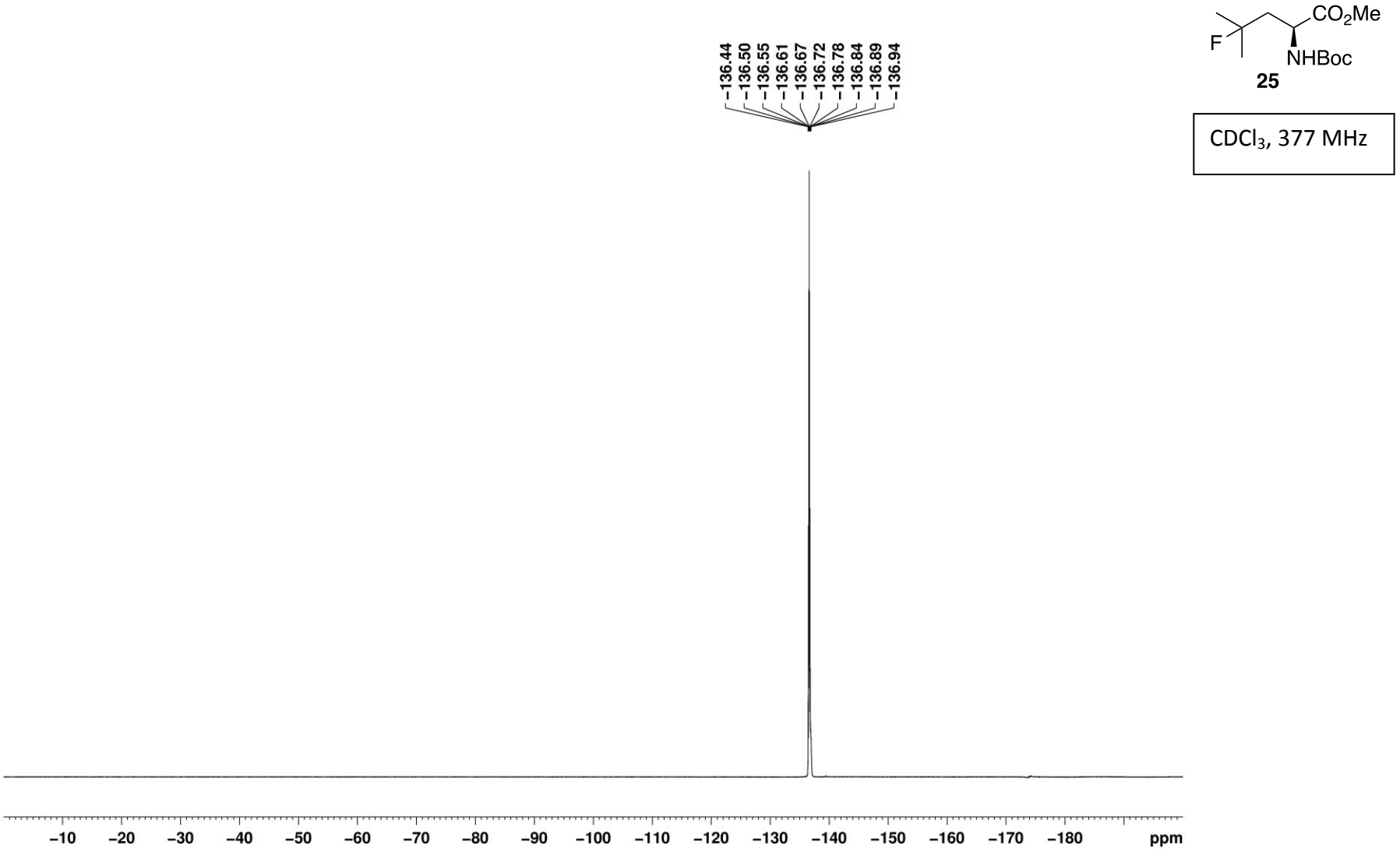
$CDCl_3$, 400 MHz

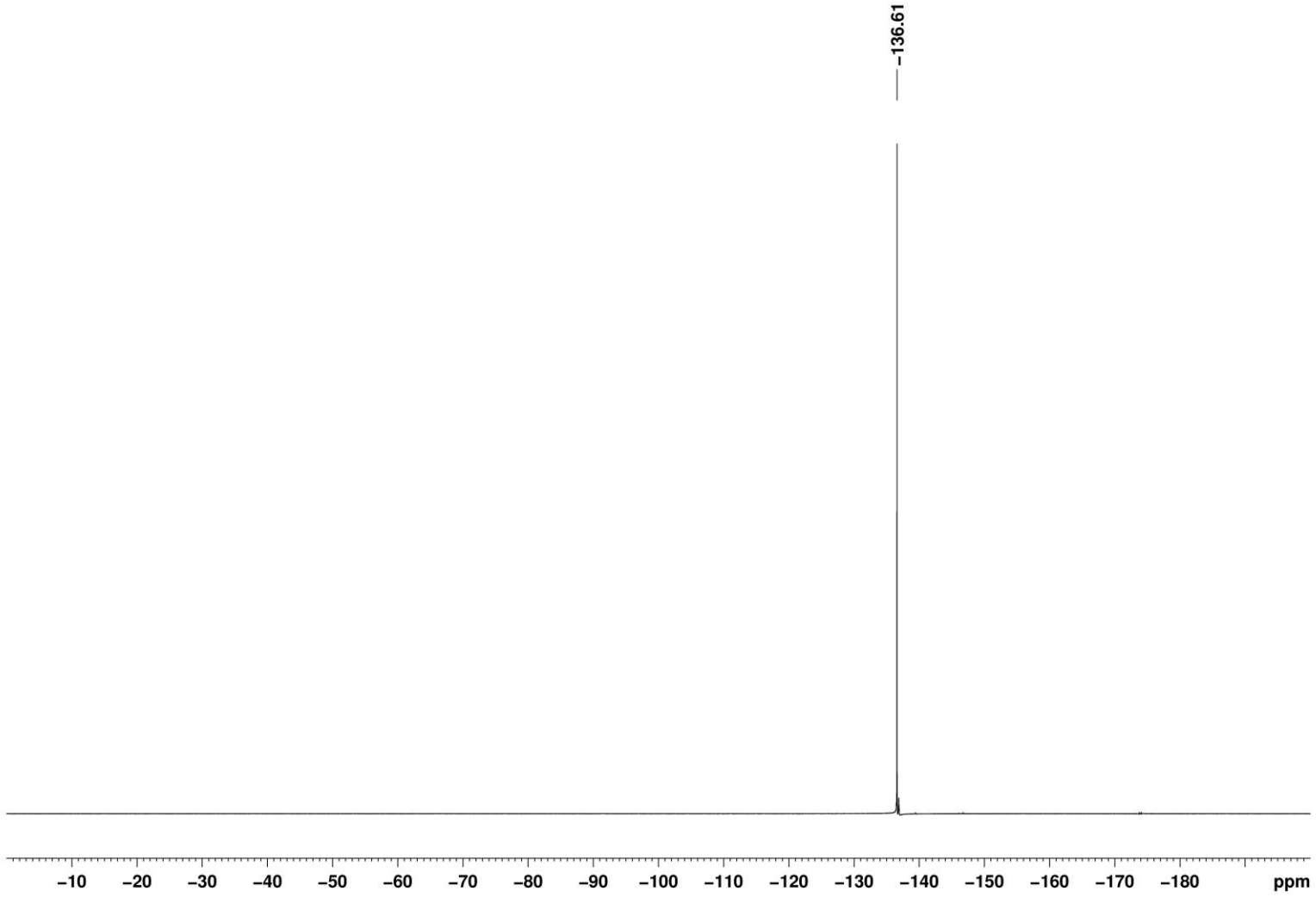


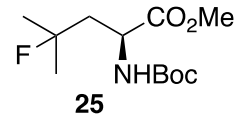


25

$CDCl_3$, 100 MHz

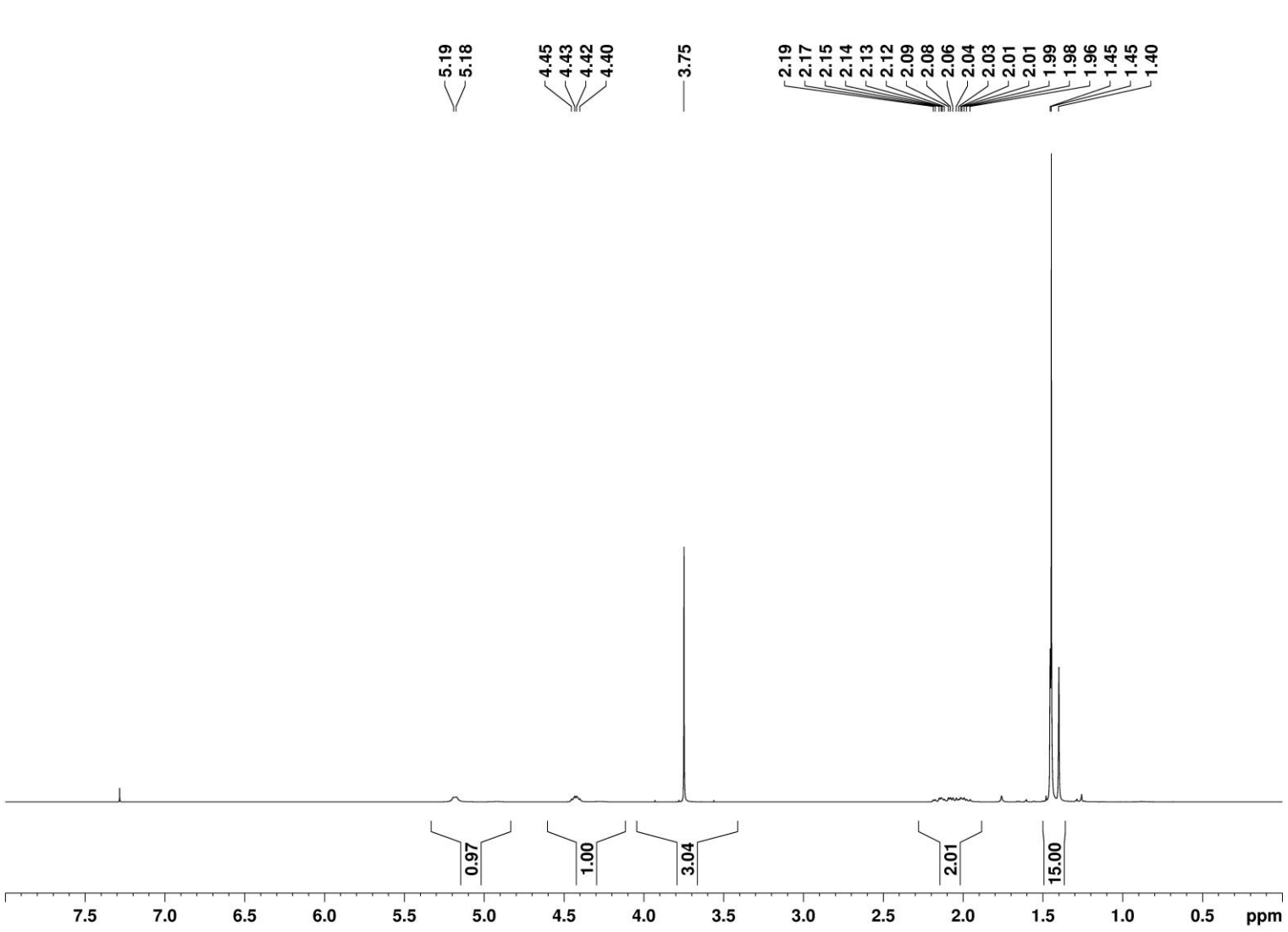

-136.44
-136.50
-136.55
-136.61
-136.67
-136.72
-136.78
-136.84
-136.89
-136.94
F
CO2Me
NHBoc
25
CDCl3, 377 MHz
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

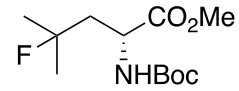




25

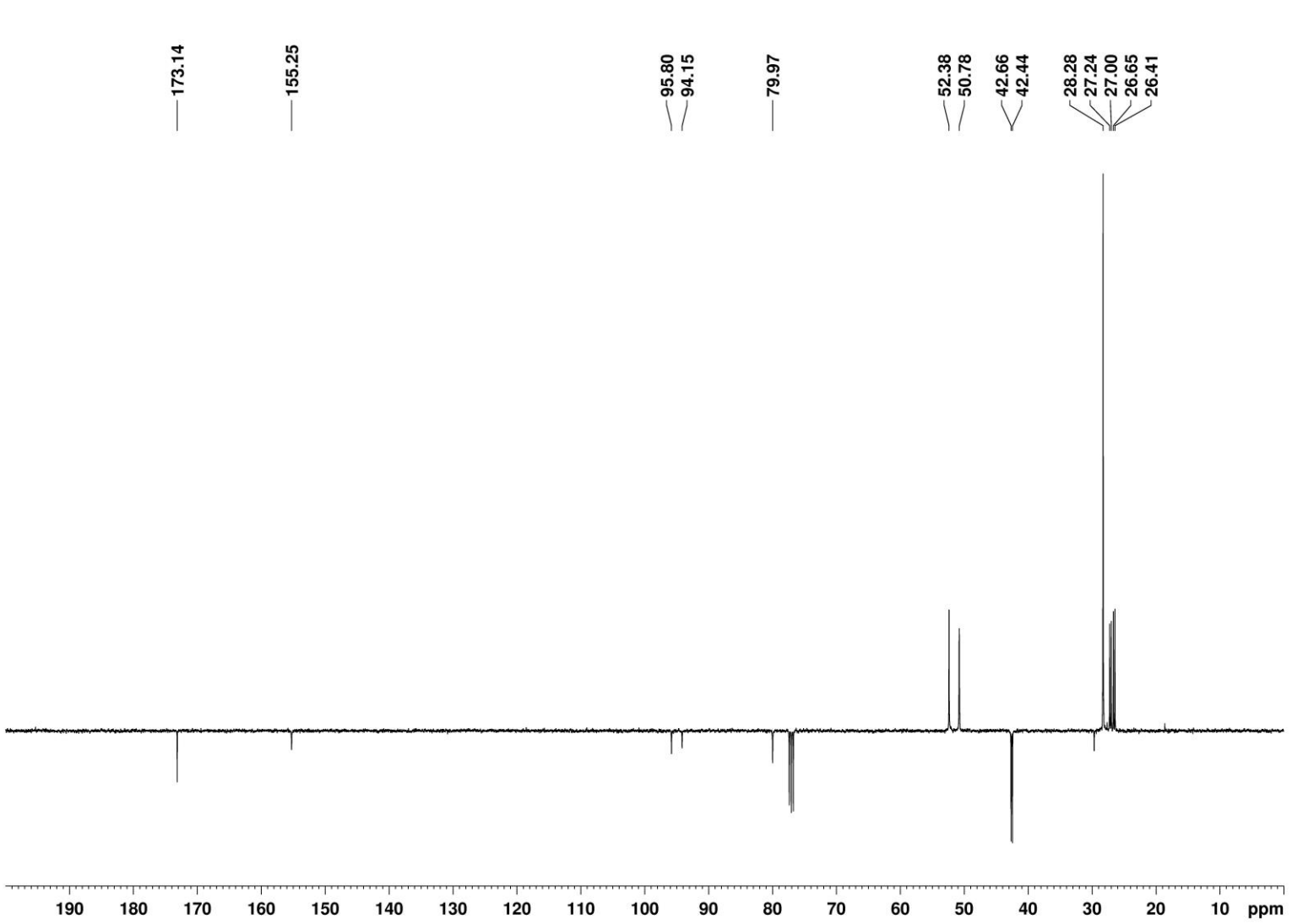
$CDCl_3$, {^{1}H} 377 MHz

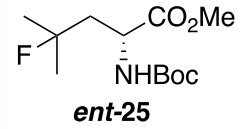




***ent*-25**

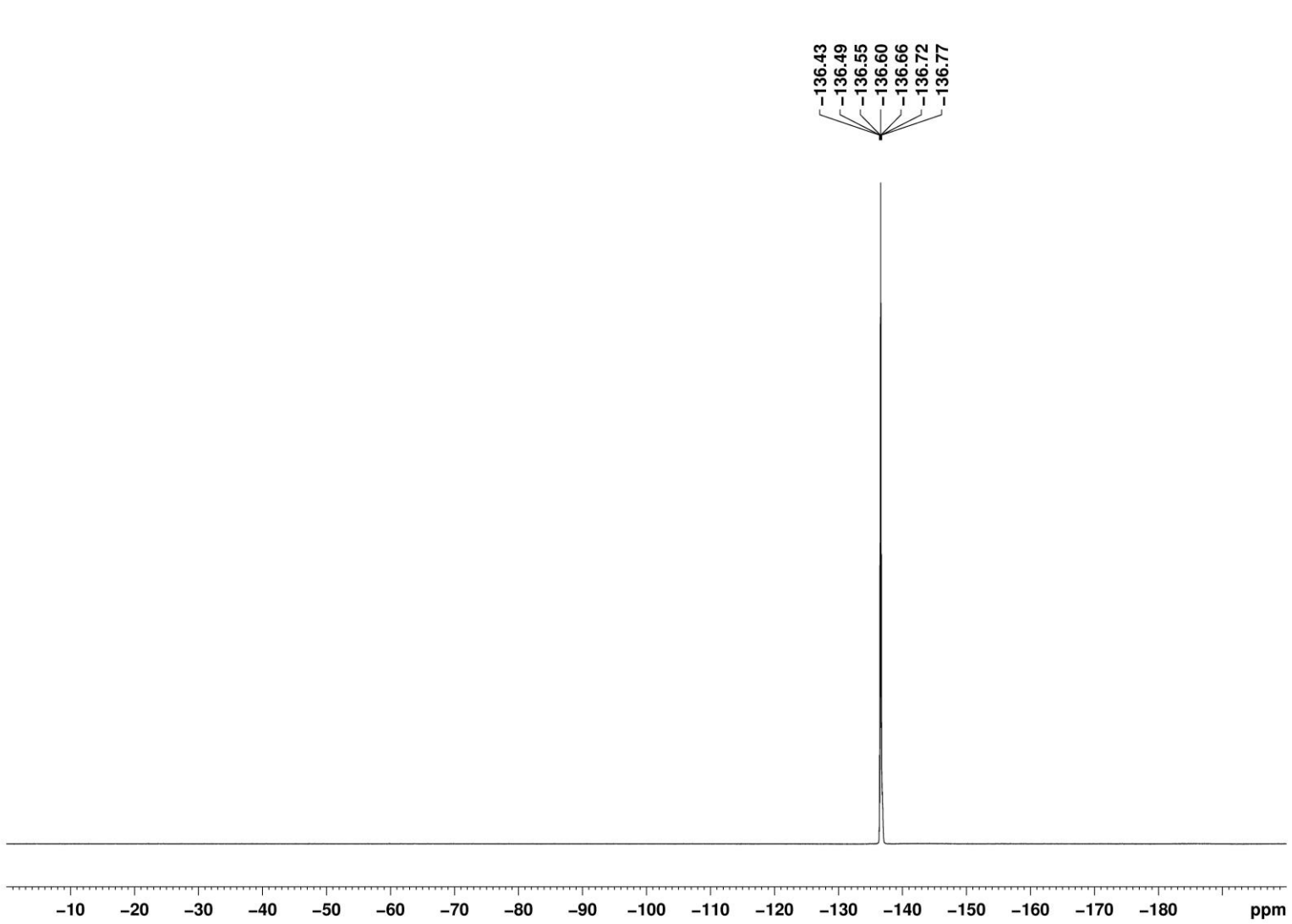
$CDCl_3$, 400 MHz

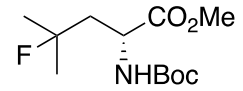




***ent*-25**

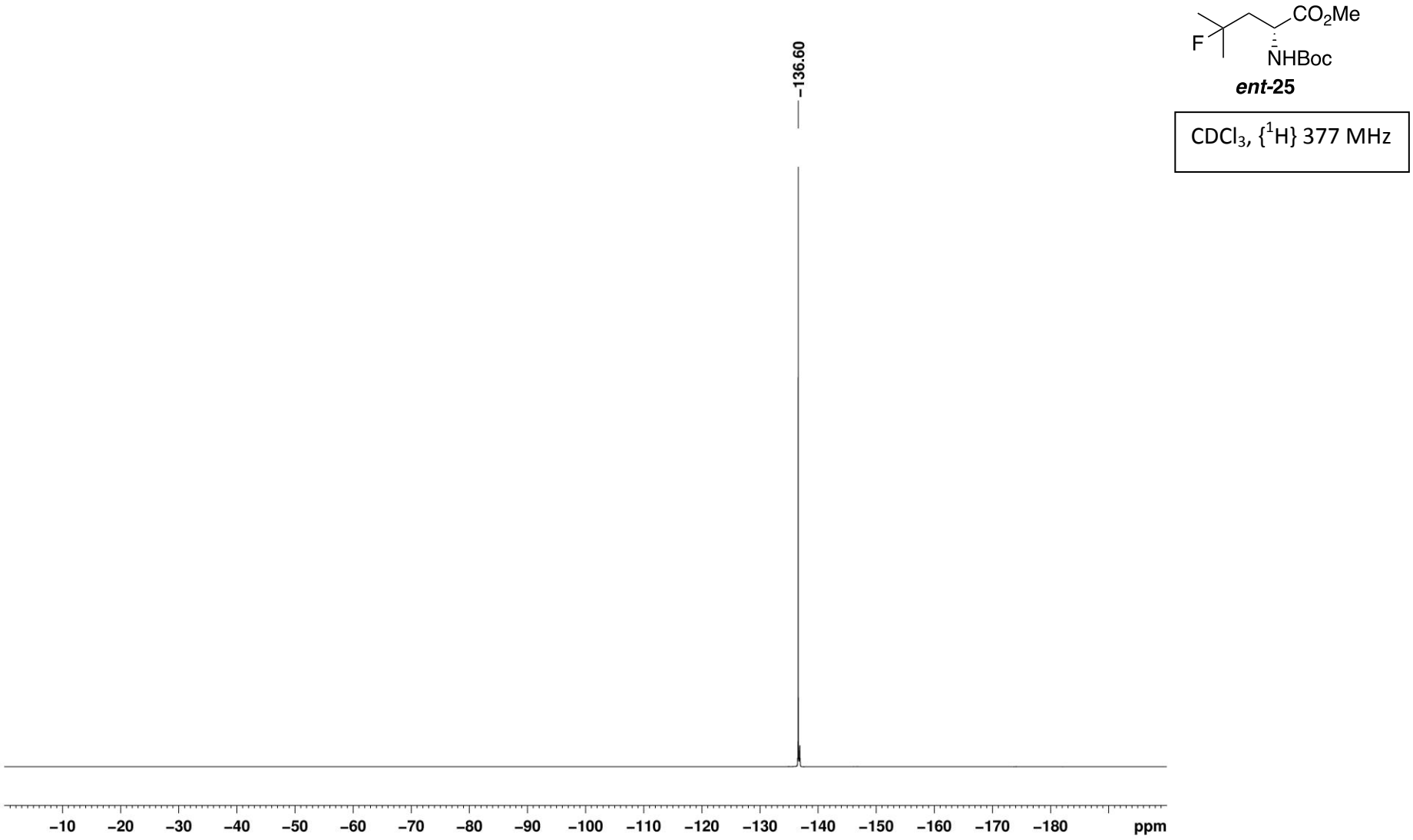
$CDCl_3$, 100 MHz

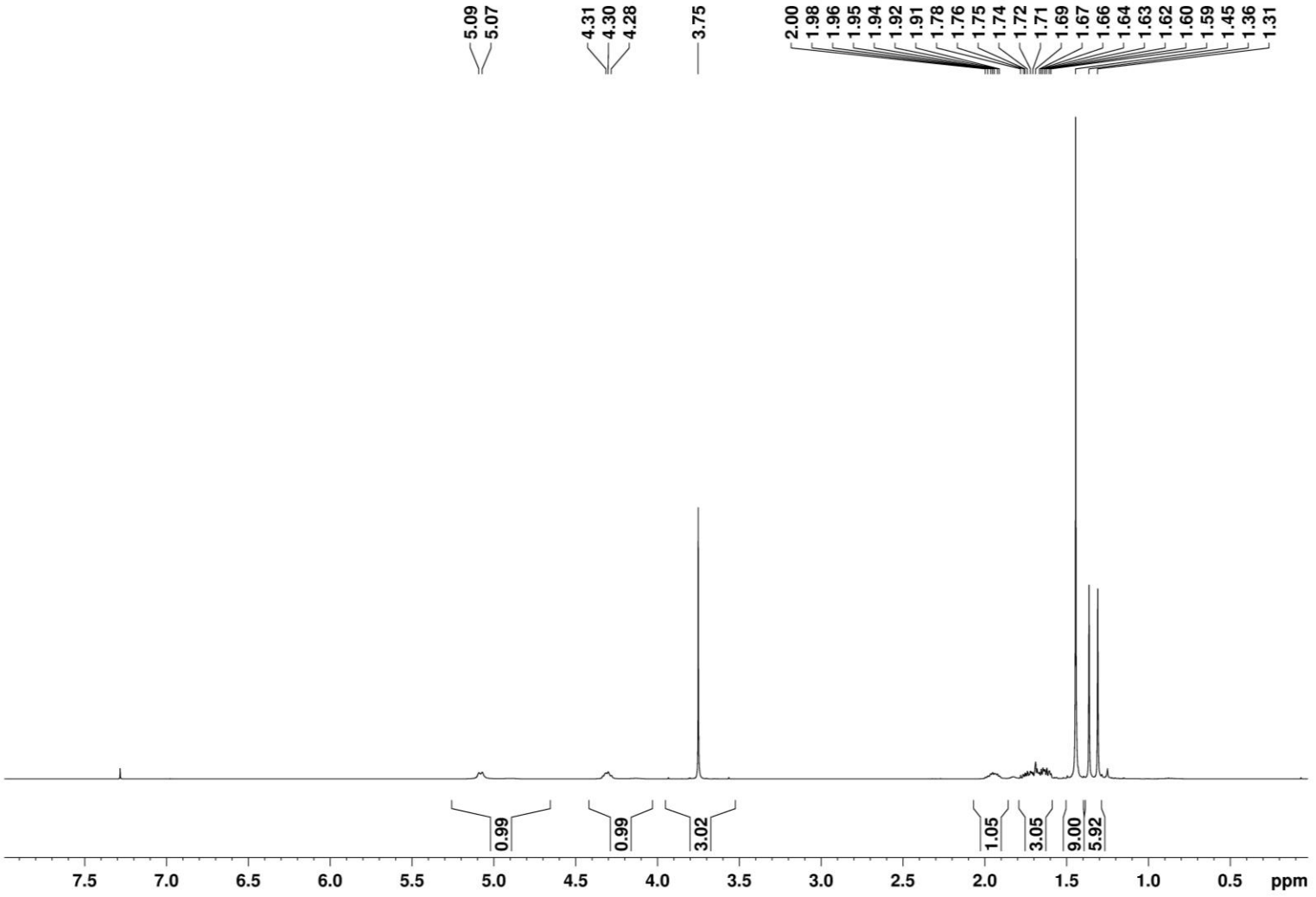


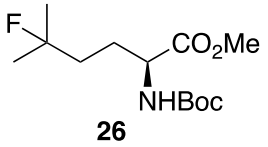


***ent*-25**

$CDCl_3$, 377 MHz

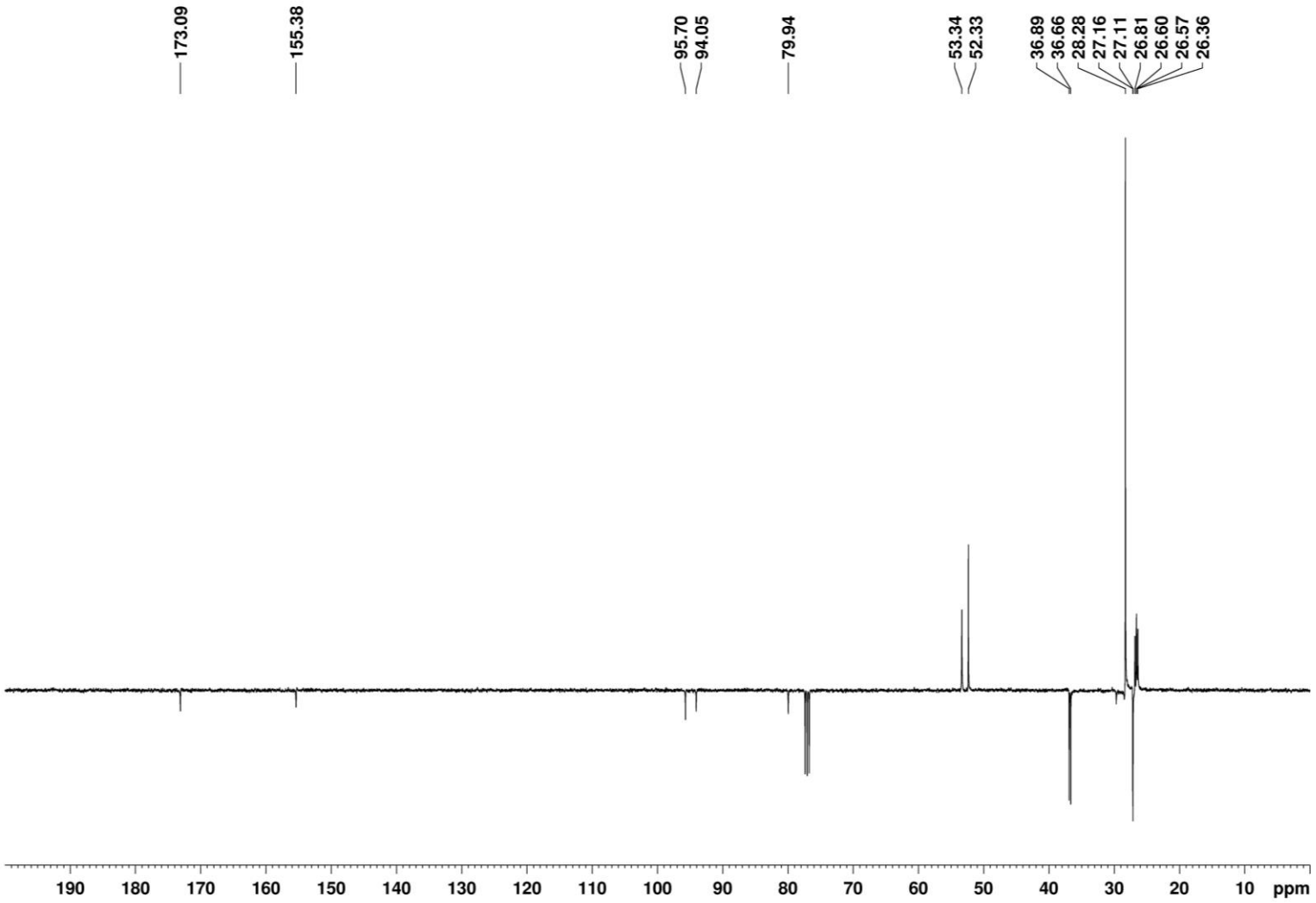

CO2Me
F
NHBoc
ent-25
CDCl3, {1H} 377 MHz
-136.60
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

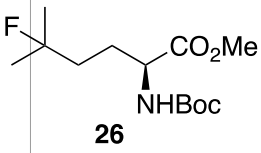




26

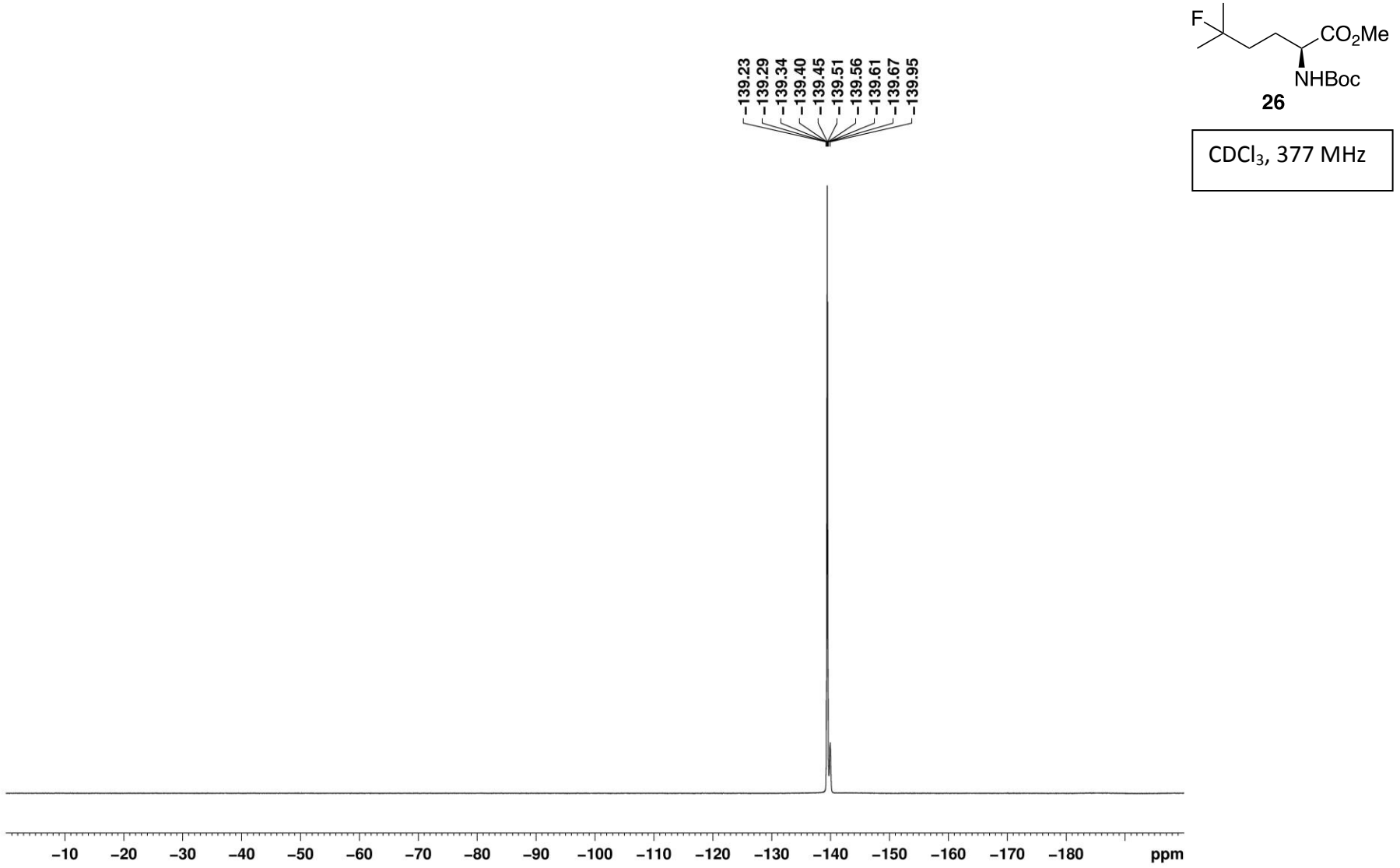
$CDCl_3$, 400 MHz

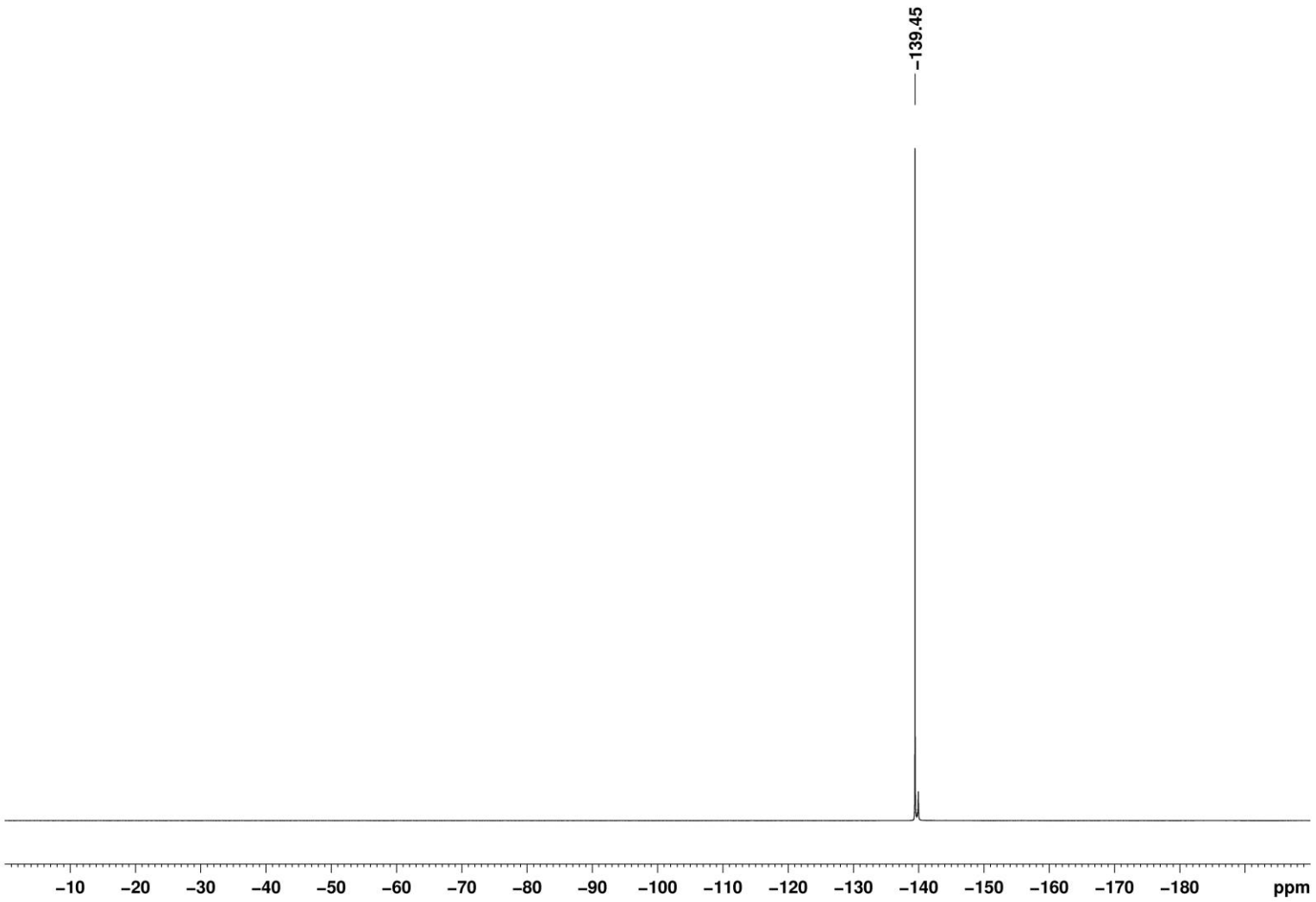


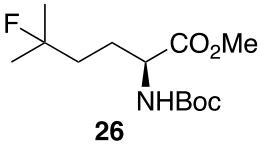


26

$CDCl_3$, 100 MHz

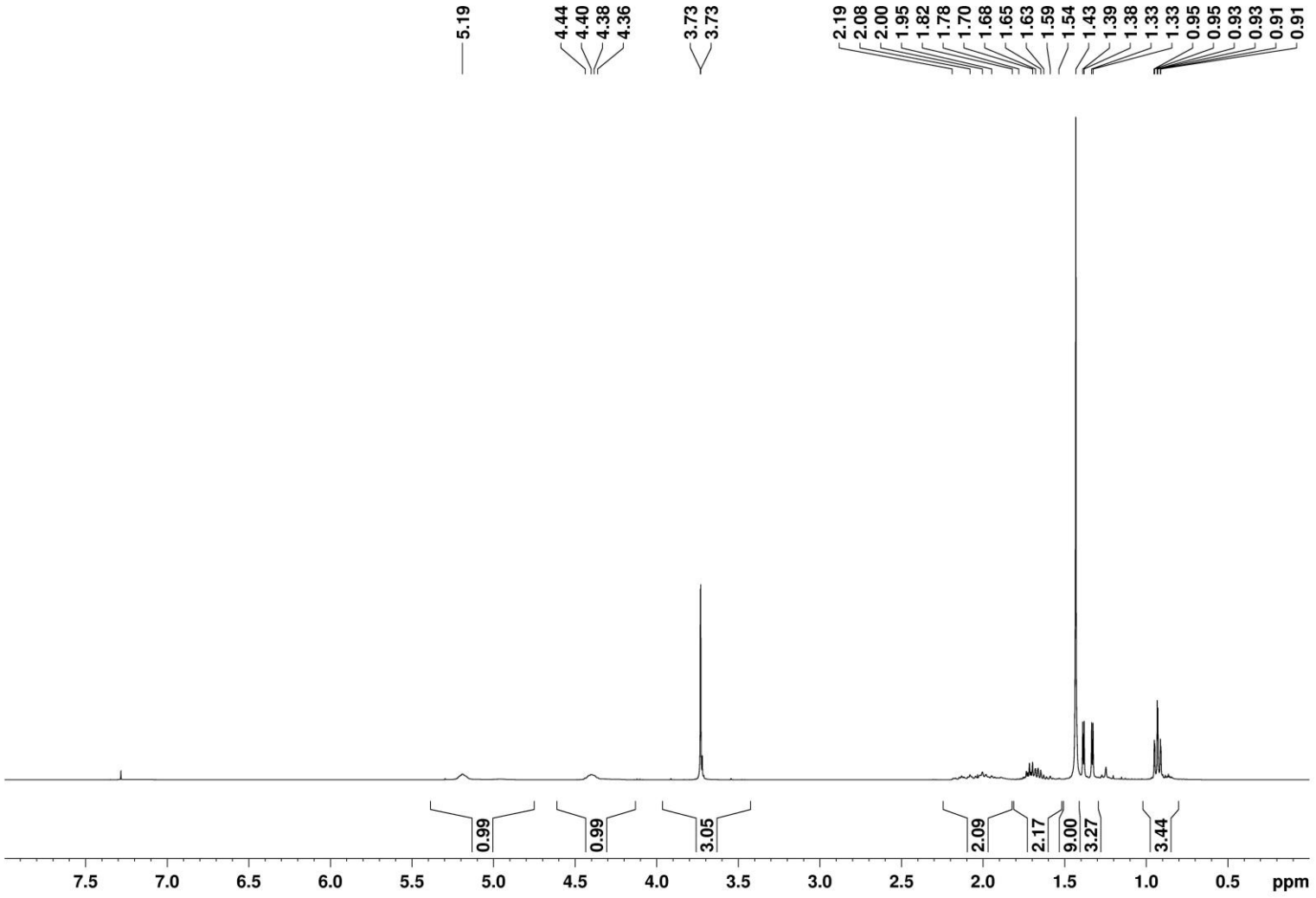

F
CO2Me
NHBoc
26
CDCl3, 377 MHz
-139.23
-139.29
-139.34
-139.40
-139.45
-139.51
-139.56
-139.61
-139.67
-139.95
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

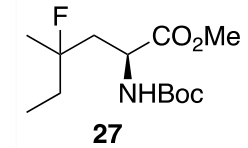




26

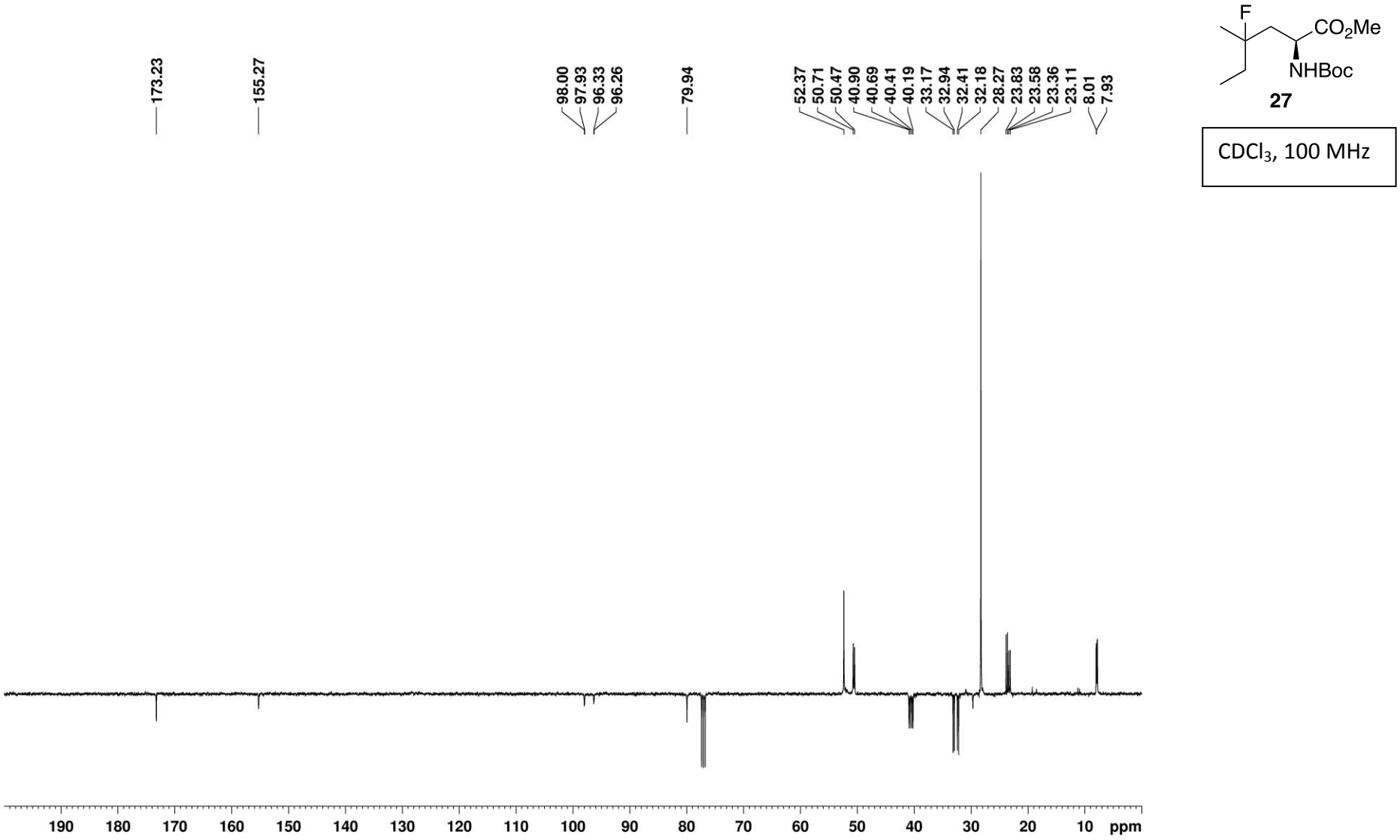
$CDCl_3$, {^{1}H} 377 MHz





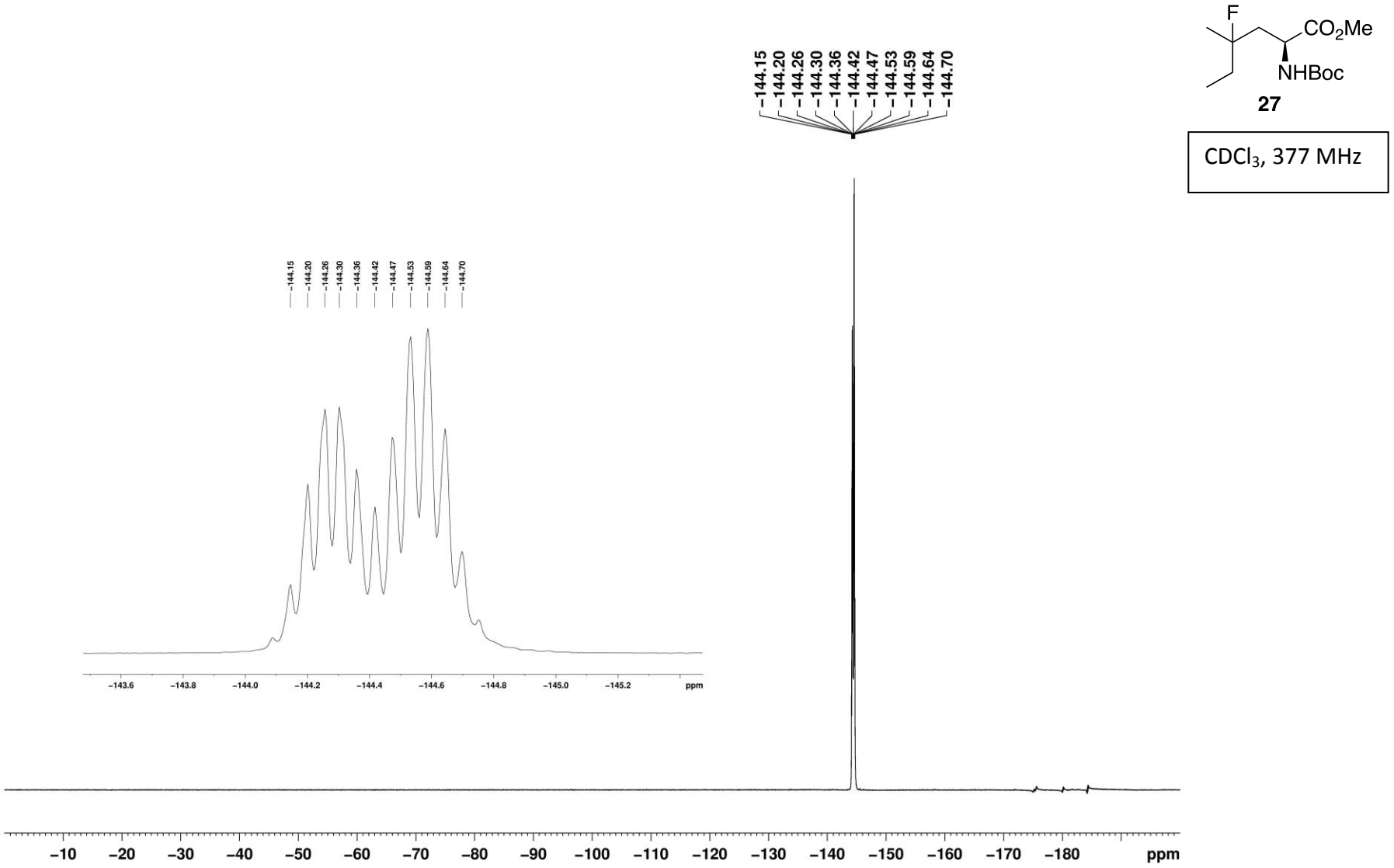
27

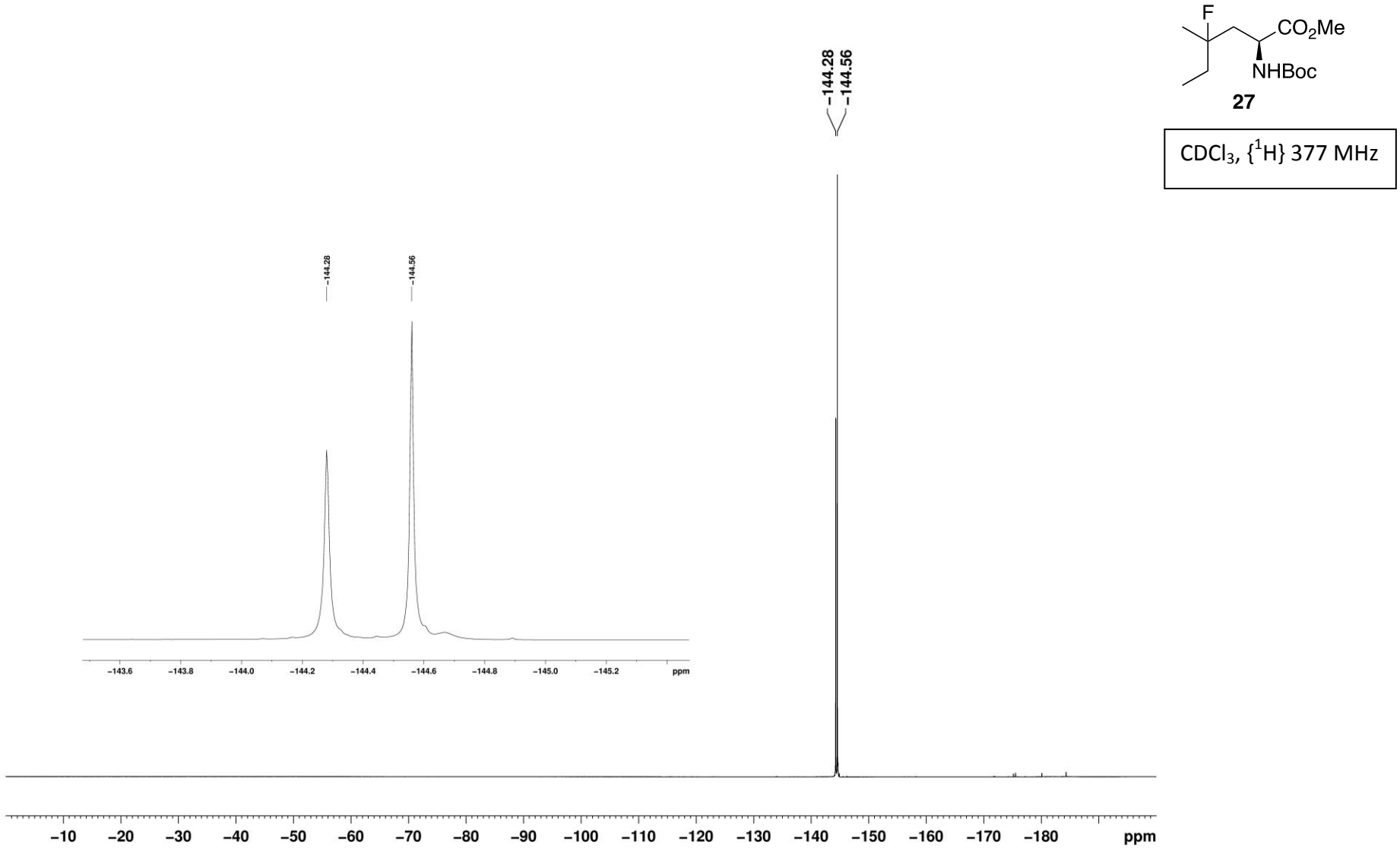
$CDCl_3$, 400 MHz

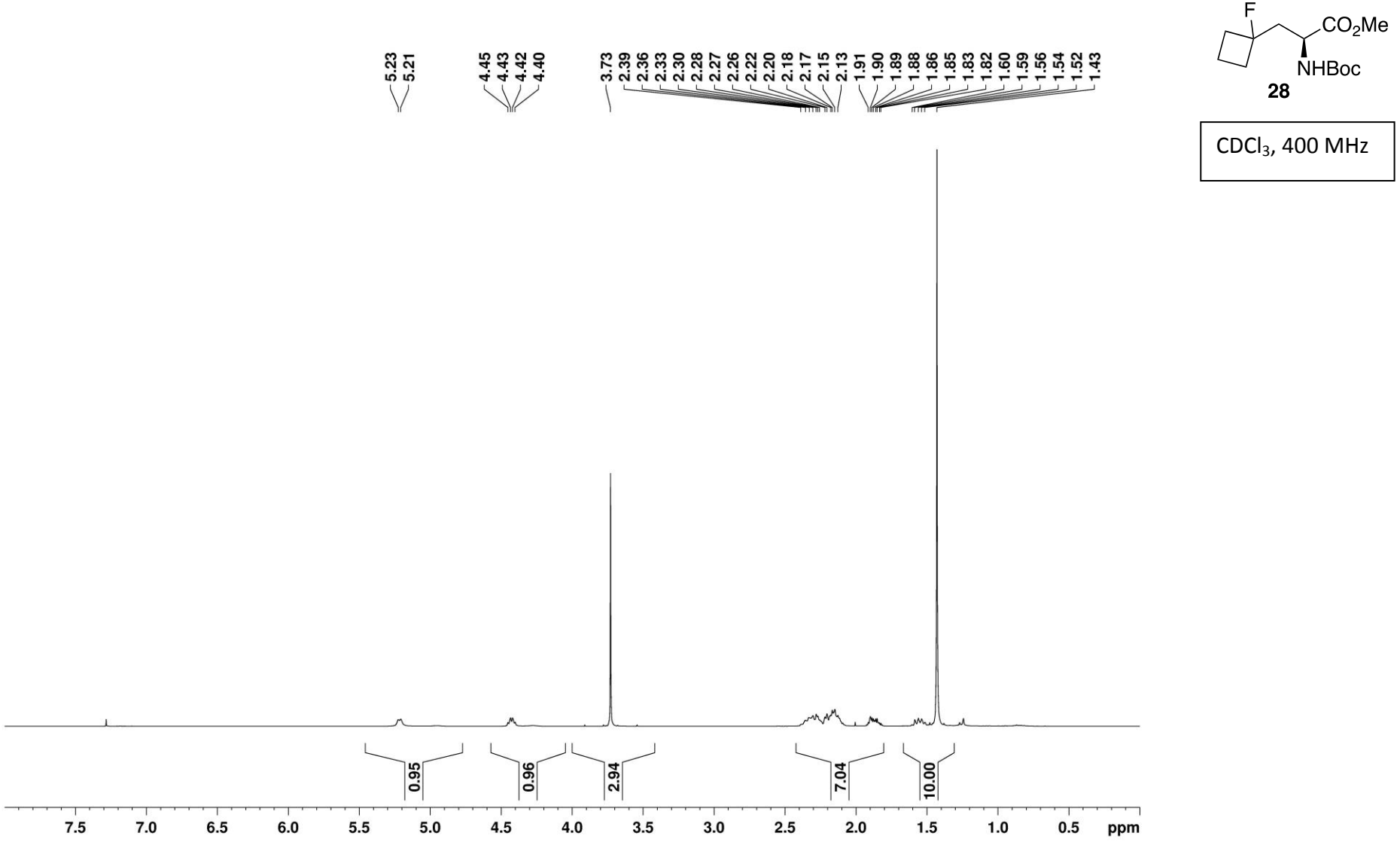


27

$CDCl_3$, 100 MHz

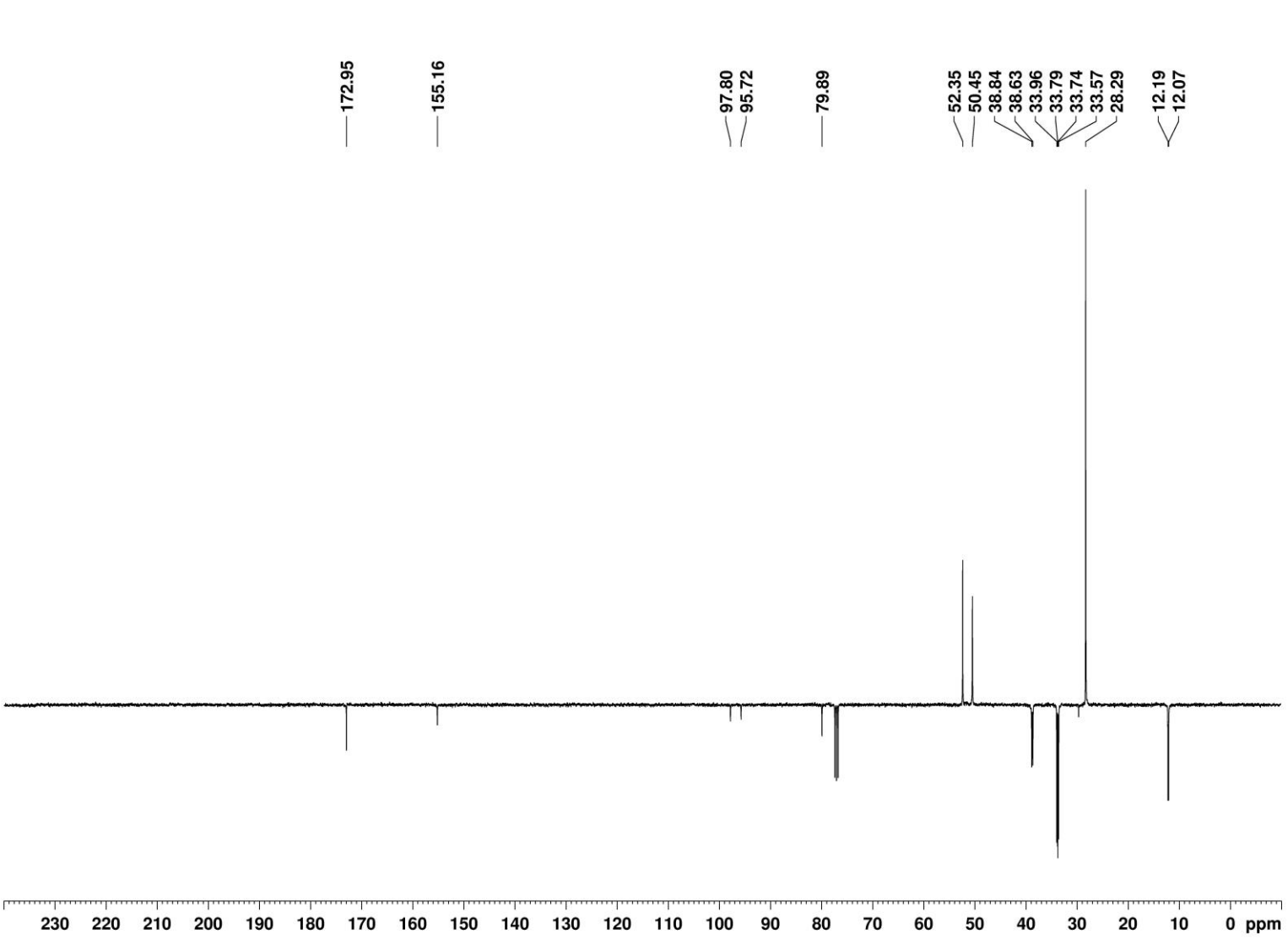

F
CO2Me
NHBoc
27
CDCl3, 377 MHz
−144.15
−144.20
−144.26
−144.30
−144.36
−144.42
−144.47
−144.53
−144.59
−144.64
−144.70
−143.6
−143.8
−144.0
−144.2
−144.4
−144.6
−144.8
−145.0
−145.2
ppm
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
ppm

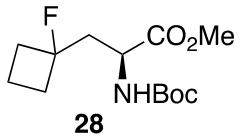

F
CO2Me
NHBoc
27
CDCl3, {1H} 377 MHz
-144.28
-144.56
-143.6
-143.8
-144.0
-144.2
-144.4
-144.6
-144.8
-145.0
-145.2
ppm
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm



28

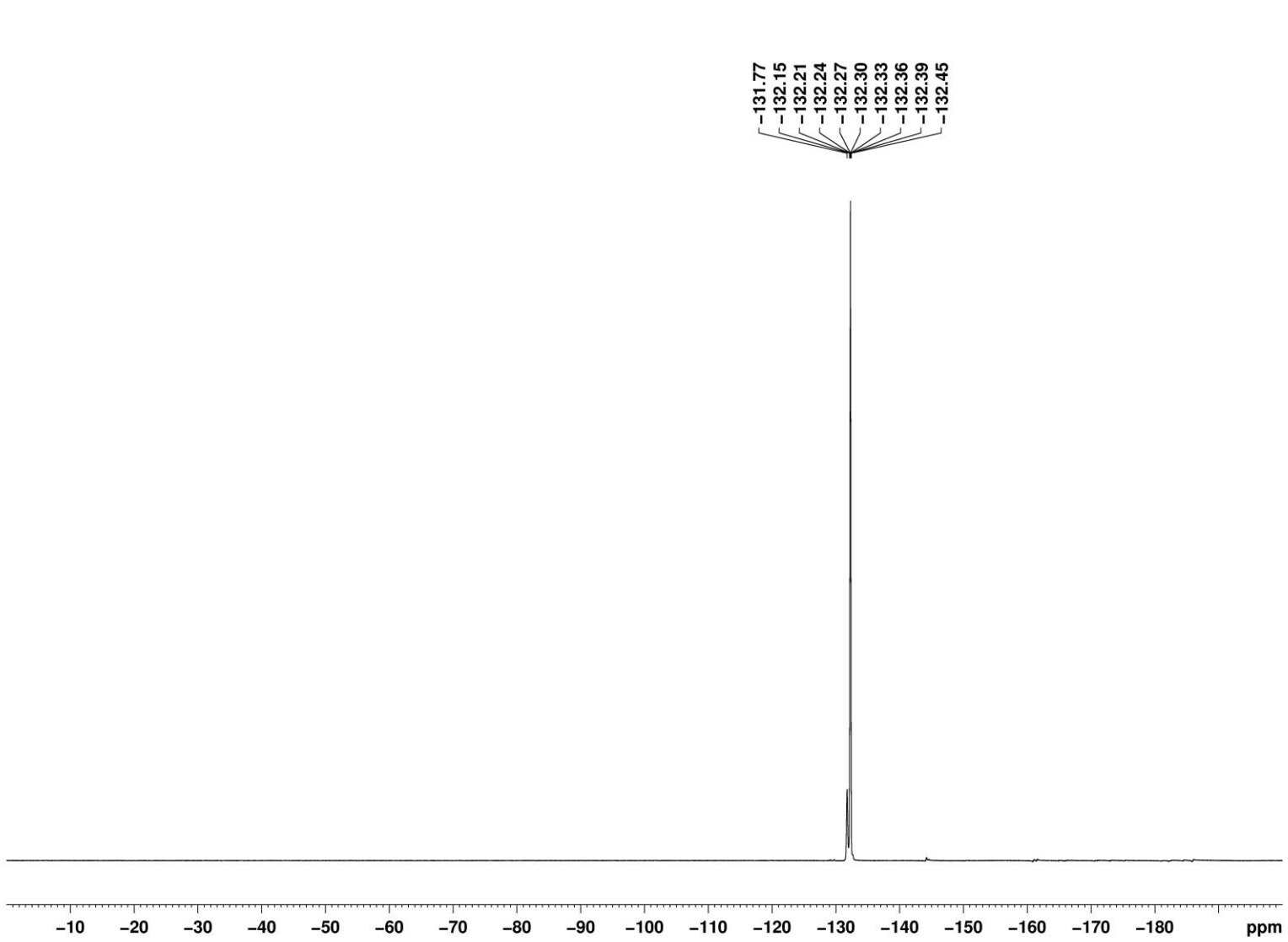
$CDCl_3$, 400 MHz

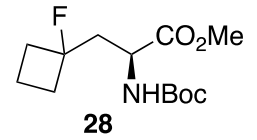




28

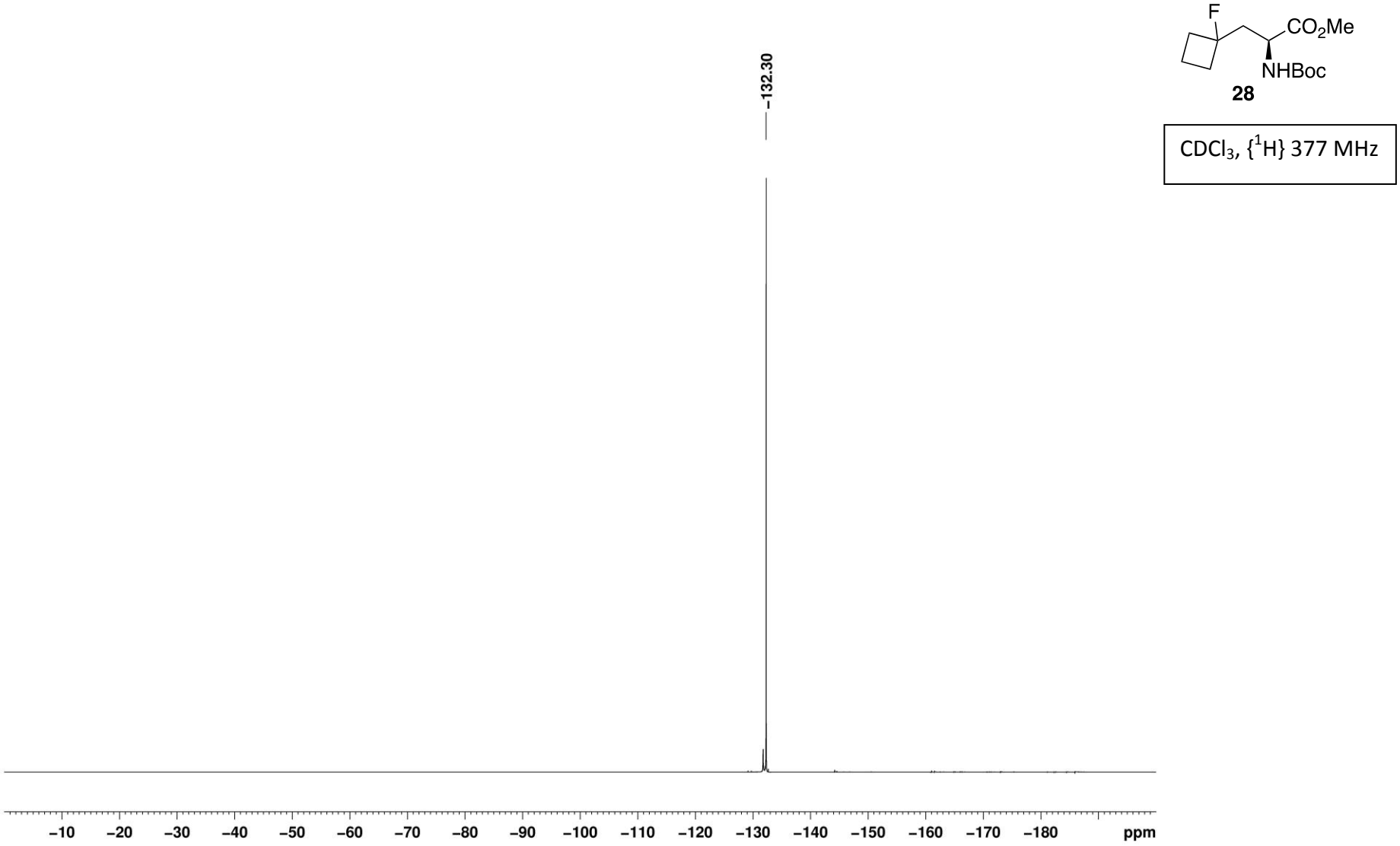
$CDCl_3$, 100 MHz

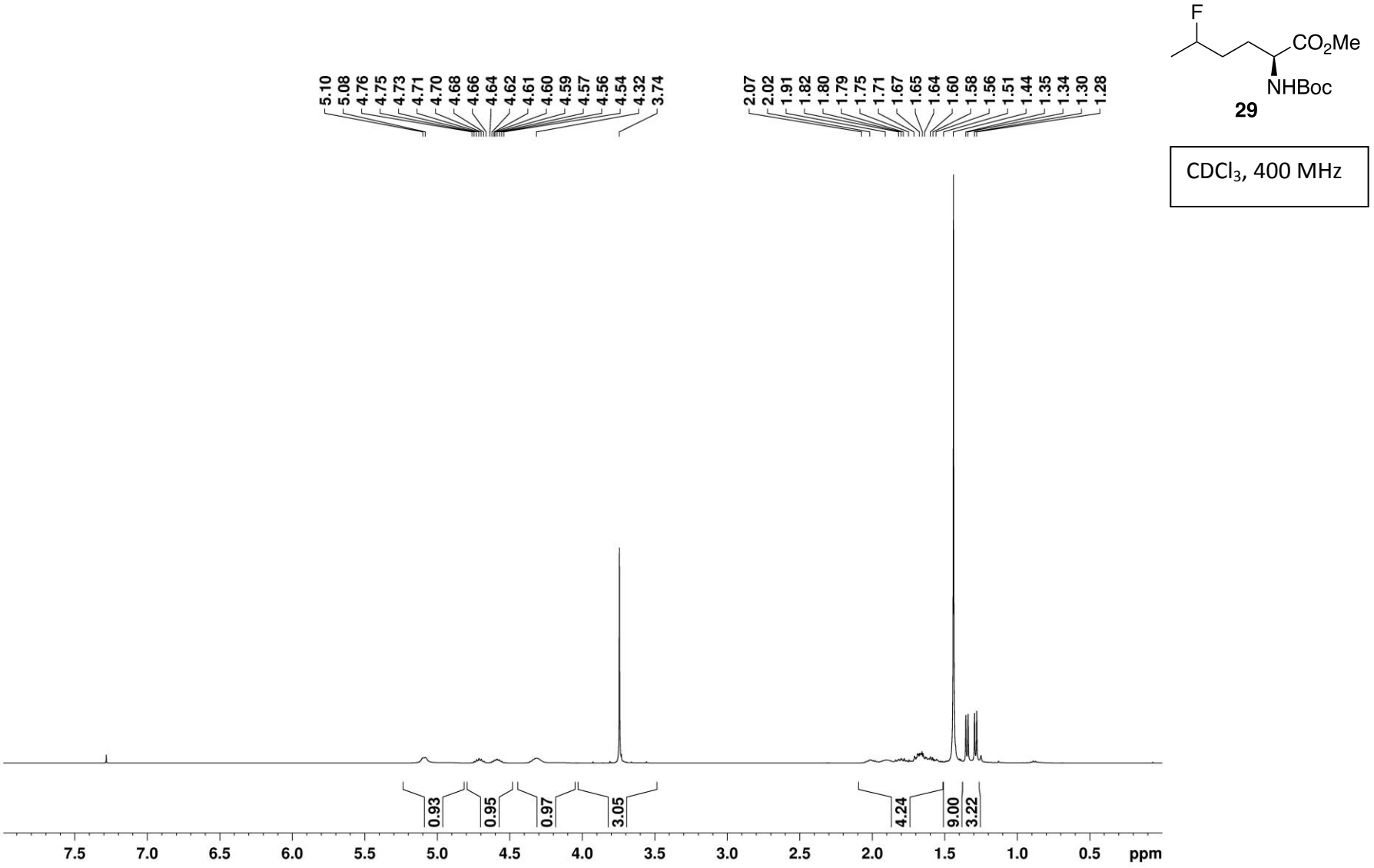




28

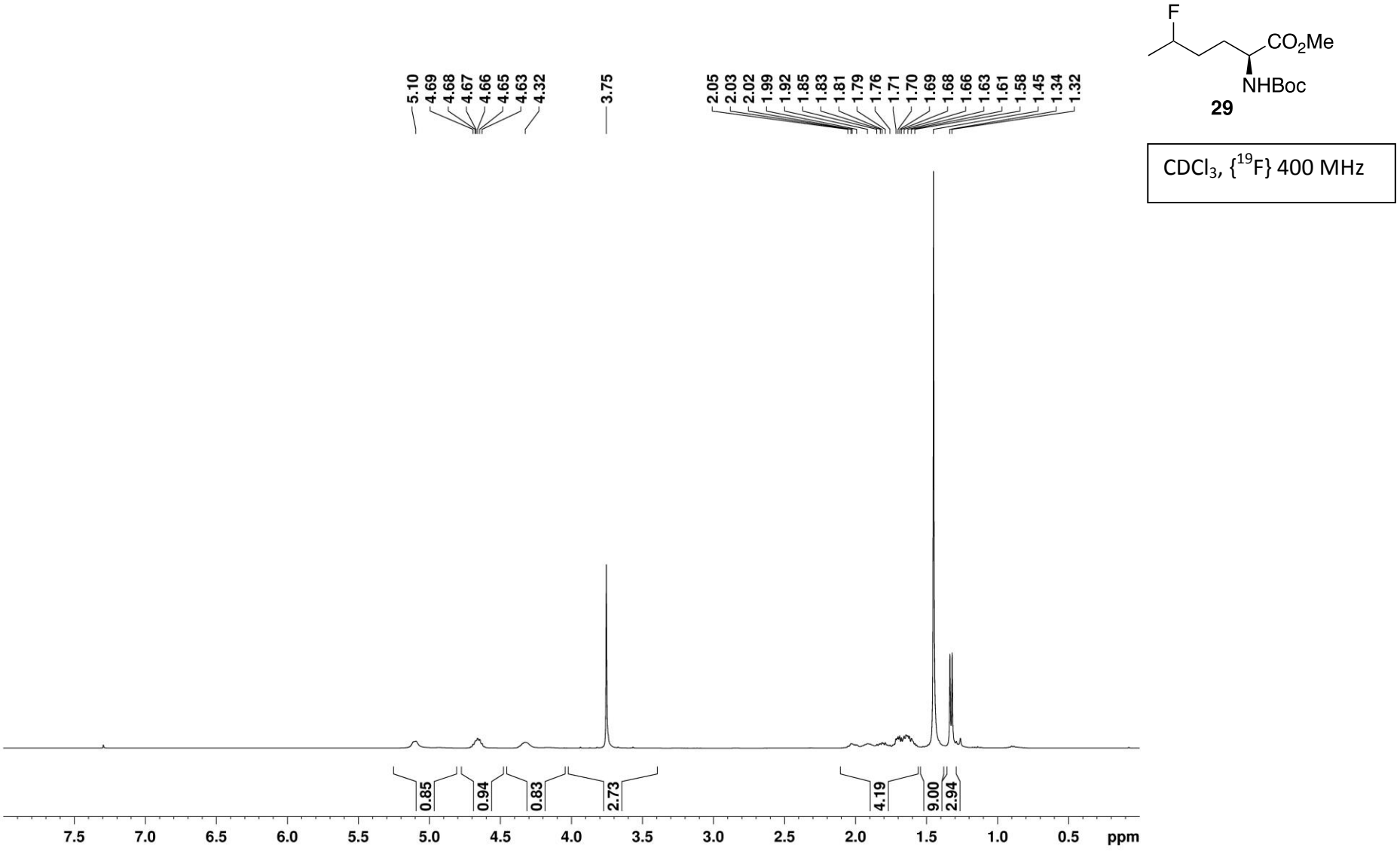
$CDCl_3$, 377 MHz

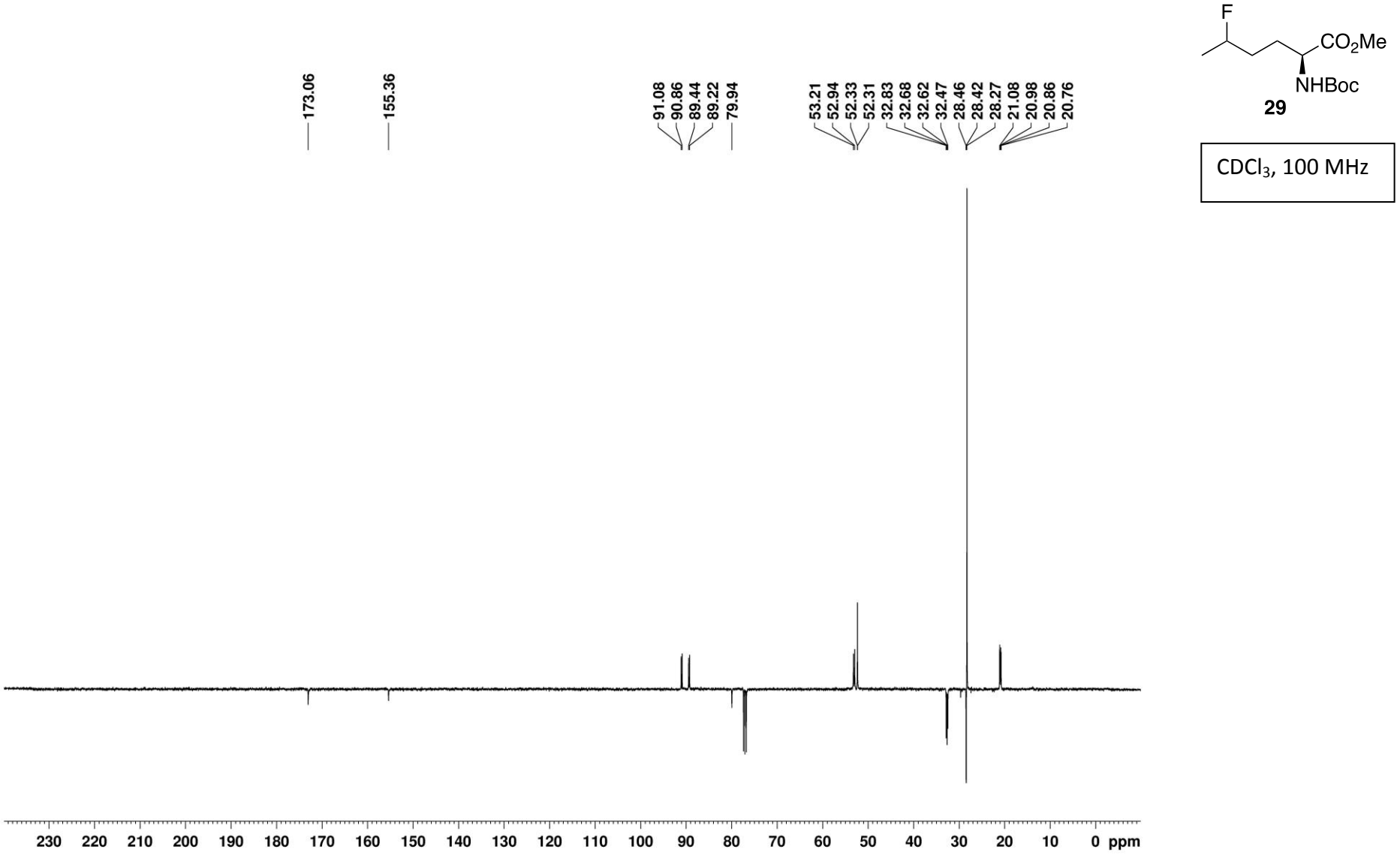

F
CO2Me
NHBoc
28
CDCl3, {1H} 377 MHz
-132.30
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

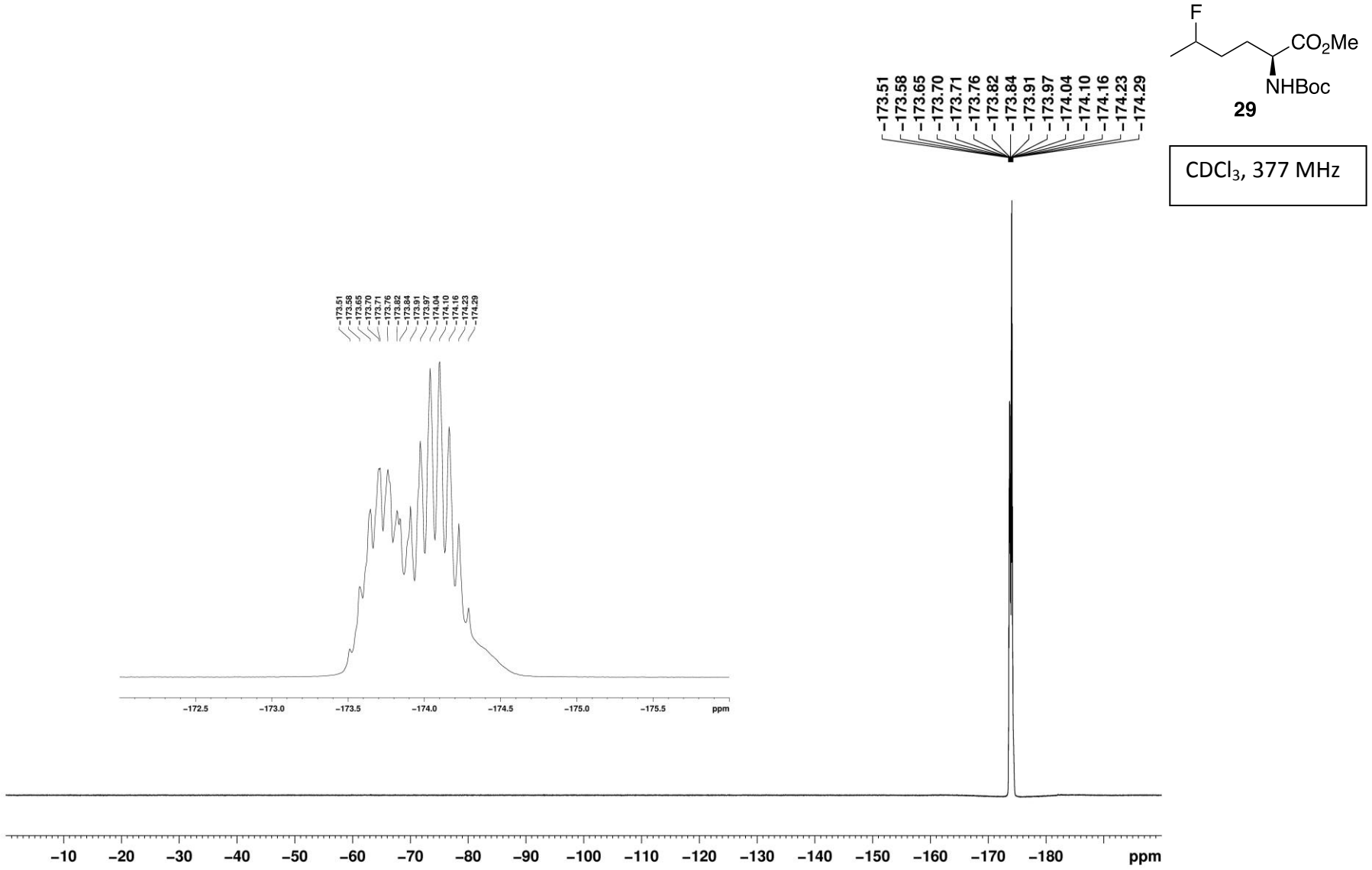


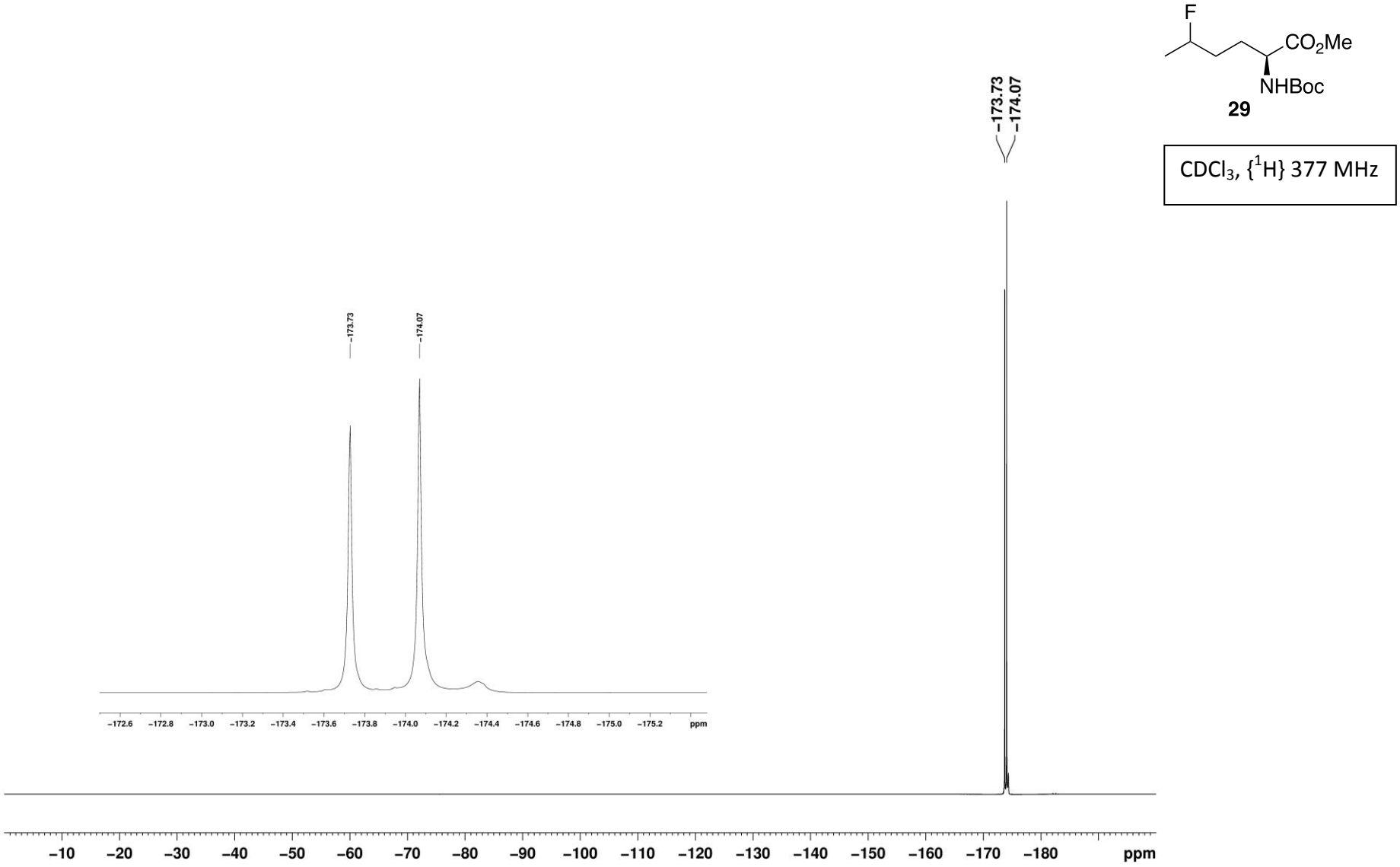
29

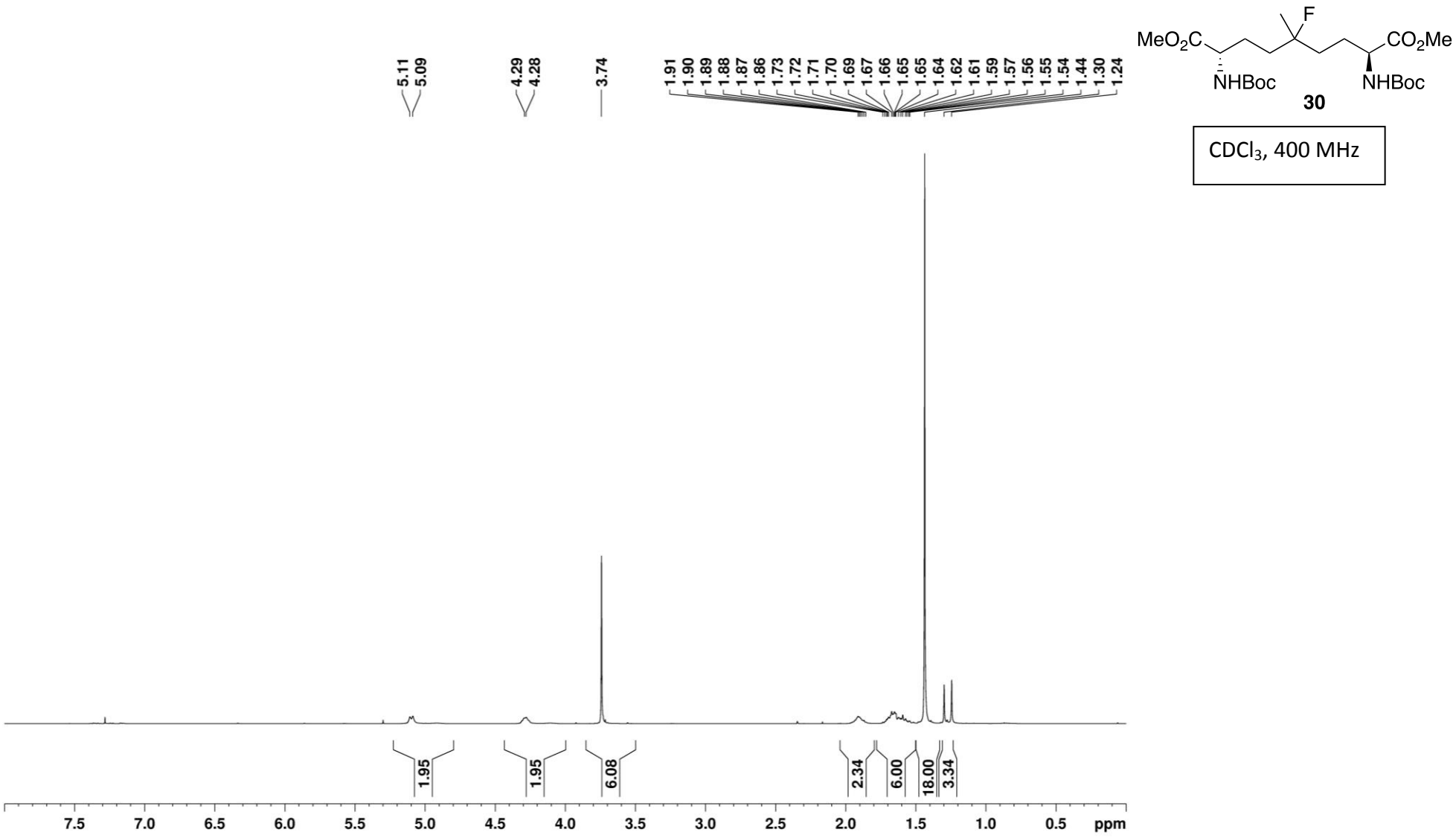
$CDCl_3$, 400 MHz

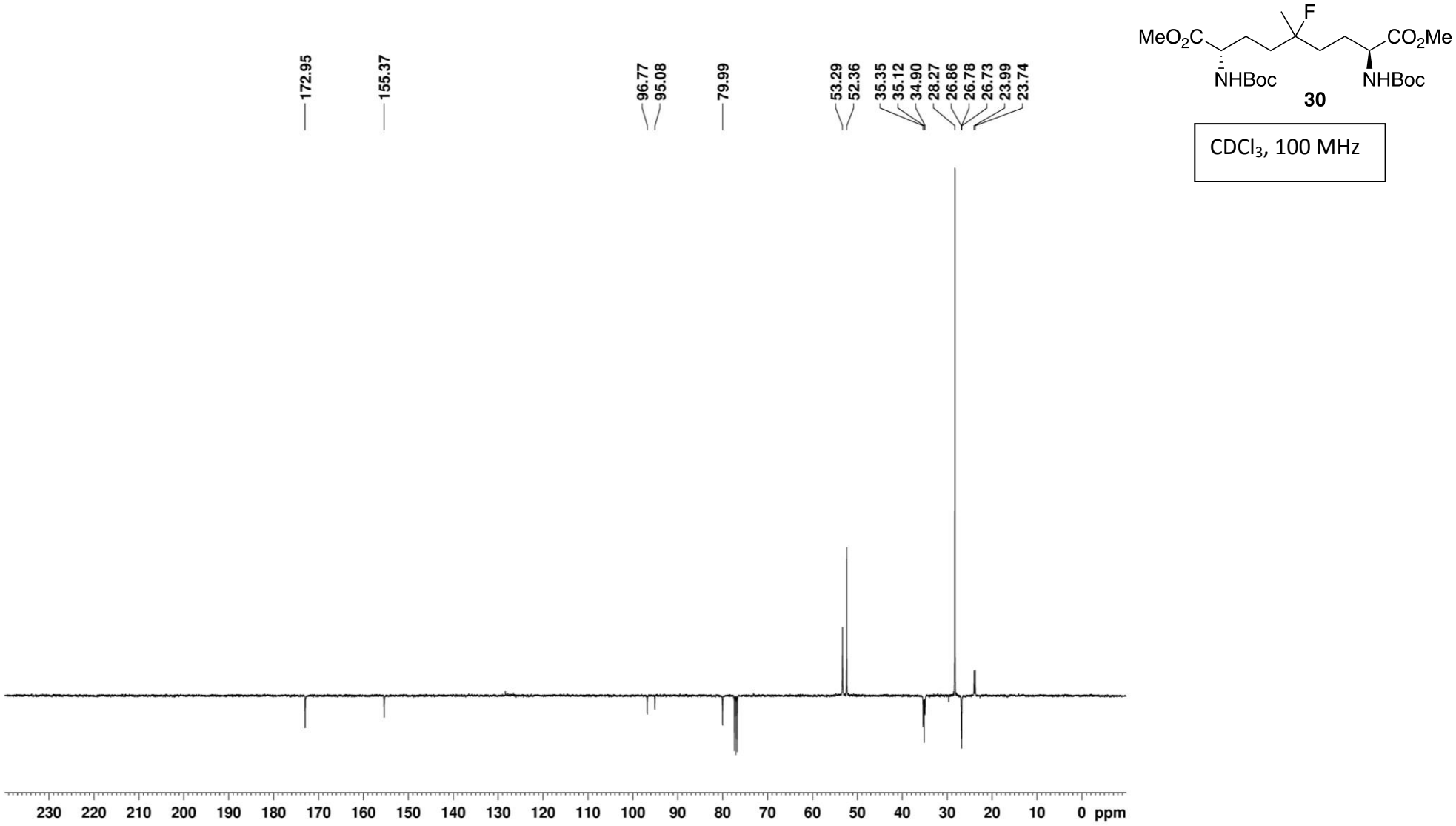

F
CO2Me
NHBoc
29
CDCl3, {19F} 400 MHz
5.10
4.69
4.68
4.67
4.66
4.65
4.63
4.32
3.75
2.05
2.03
2.02
1.99
1.92
1.85
1.83
1.81
1.79
1.76
1.71
1.70
1.69
1.68
1.66
1.63
1.61
1.58
1.45
1.34
1.32
0.85
0.94
0.83
2.73
4.19
9.00
2.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


F
CO2Me
NHBoc
29
CDCl3, 100 MHz
173.06
155.36
91.08
90.86
89.44
89.22
79.94
53.21
52.94
52.33
52.31
32.83
32.68
32.62
32.47
28.46
28.42
28.27
21.08
20.98
20.86
20.76
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F
CO2Me
NHBoc
29
CDCl3, 377 MHz
−173.51
−173.58
−173.65
−173.70
−173.71
−173.76
−173.82
−173.84
−173.91
−173.97
−174.04
−174.10
−174.16
−174.23
−174.29
−172.5
−173.0
−173.5
−174.0
−174.5
−175.0
−175.5
ppm
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
ppm

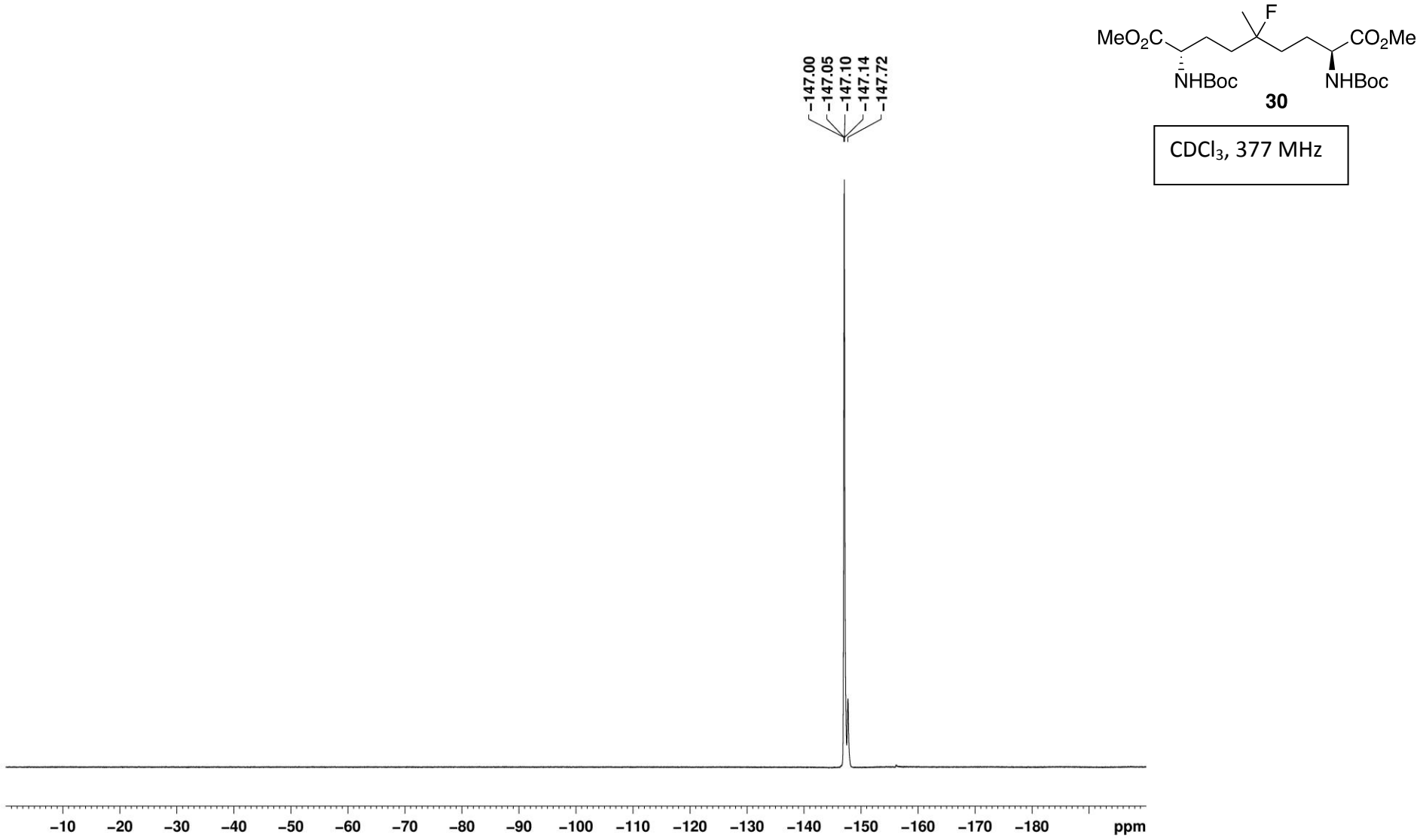

F
CO2Me
NHBoc
29
CDCl3, {1H} 377 MHz
-173.73
-174.07
-173.73
-174.07
-172.6 -172.8 -173.0 -173.2 -173.4 -173.6 -173.8 -174.0 -174.2 -174.4 -174.6 -174.8 -175.0 -175.2 ppm
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 ppm

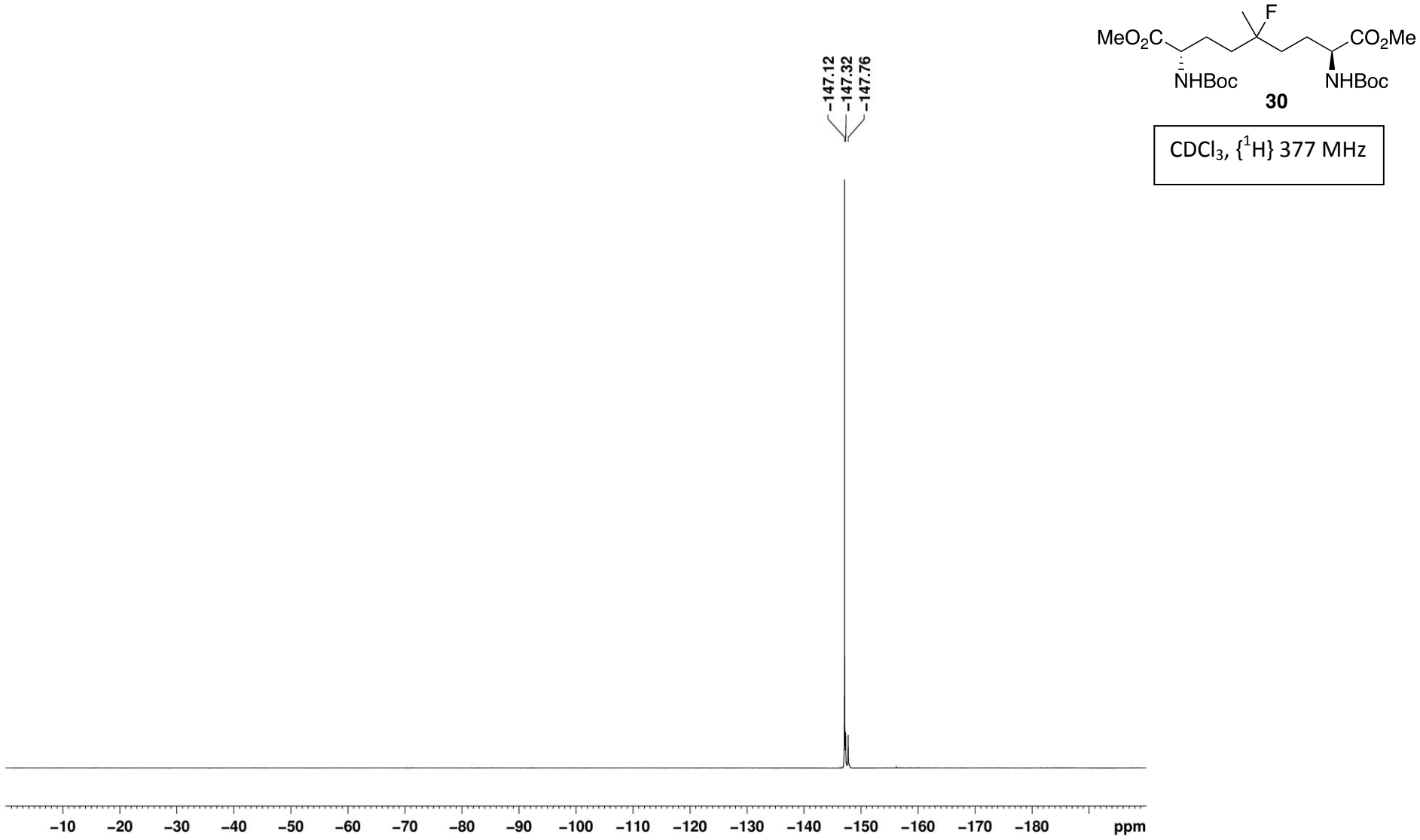

MeO2C
F
CO2Me
NHBoc
NHBoc
30
CDCl3, 400 MHz
5.11
5.09
4.29
4.28
3.74
1.91
1.90
1.89
1.88
1.87
1.86
1.73
1.72
1.71
1.70
1.69
1.67
1.66
1.65
1.65
1.64
1.62
1.61
1.59
1.57
1.56
1.55
1.54
1.44
1.30
1.24
1.95
1.95
6.08
2.34
6.00
18.00
3.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

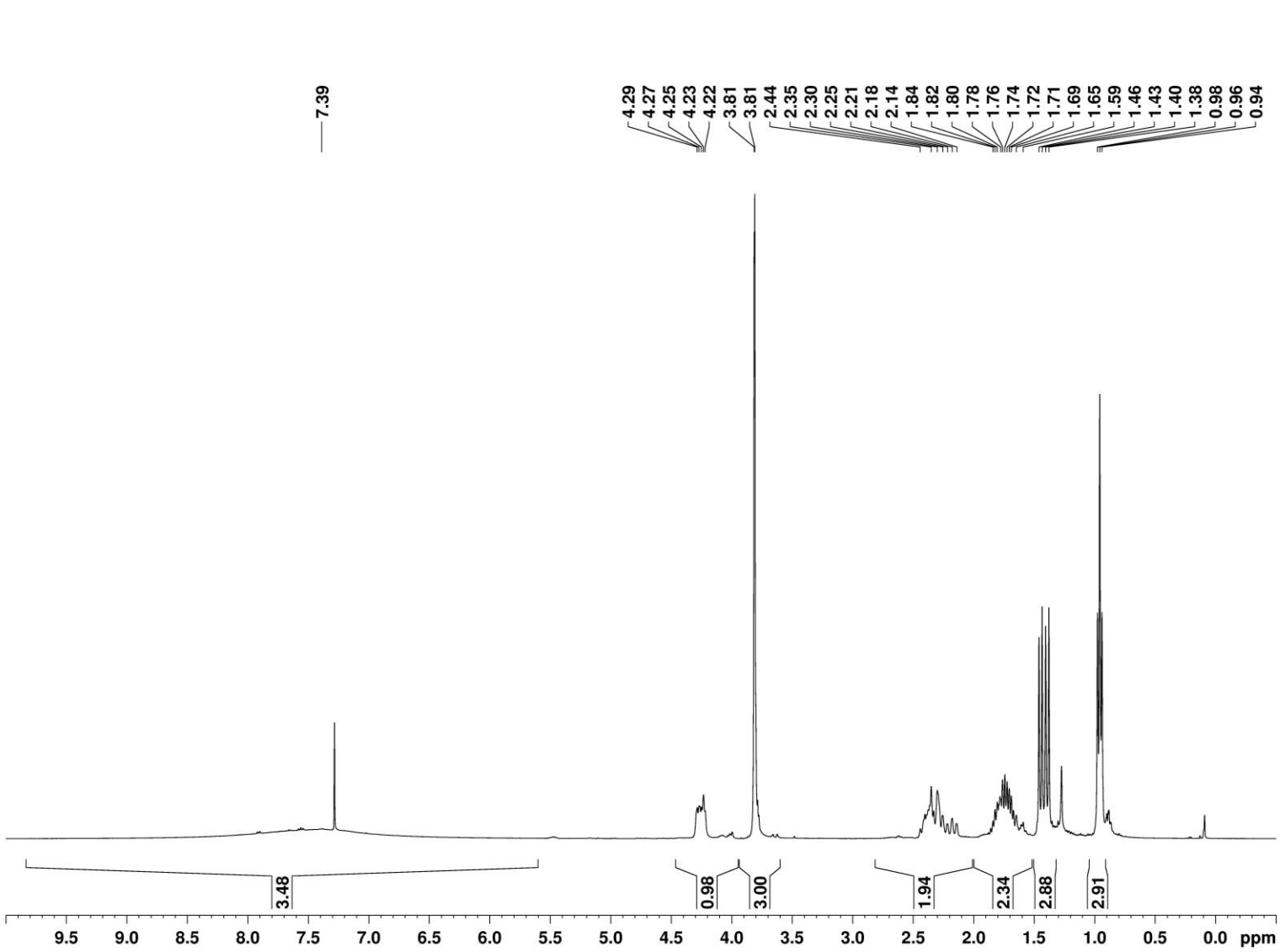


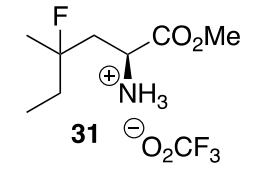
30

$CDCl_3$, 100 MHz

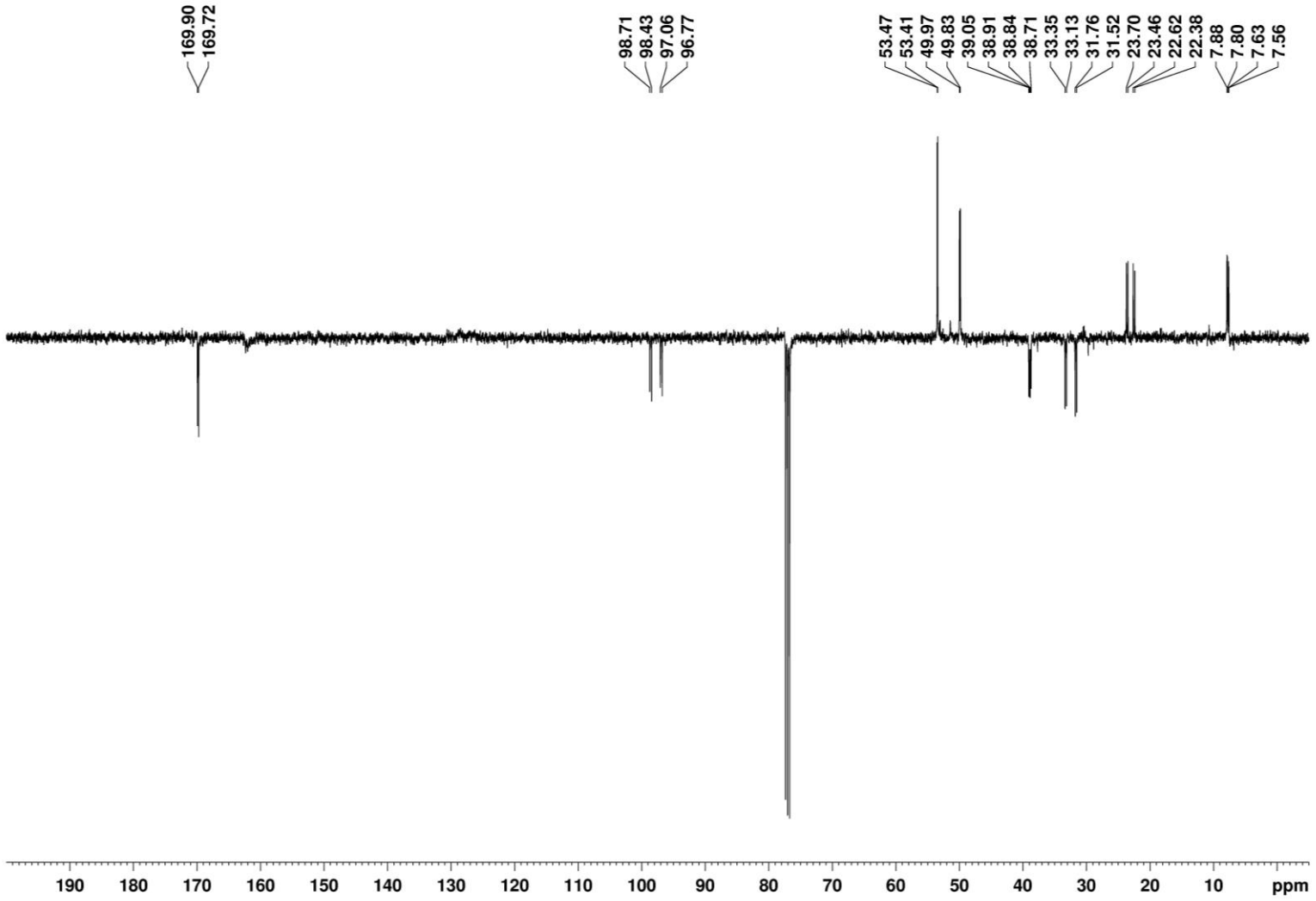

MeO2C
F
CO2Me
NHBoc
NHBoc
30
CDCl3, 377 MHz
-147.00
-147.05
-147.10
-147.14
-147.72
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

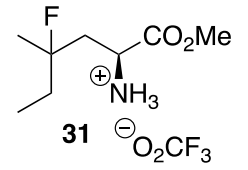

MeO2C
F
CO2Me
NHBoc
NHBoc
30
CDCl3, {1H} 377 MHz
-147.12
-147.32
-147.76
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm



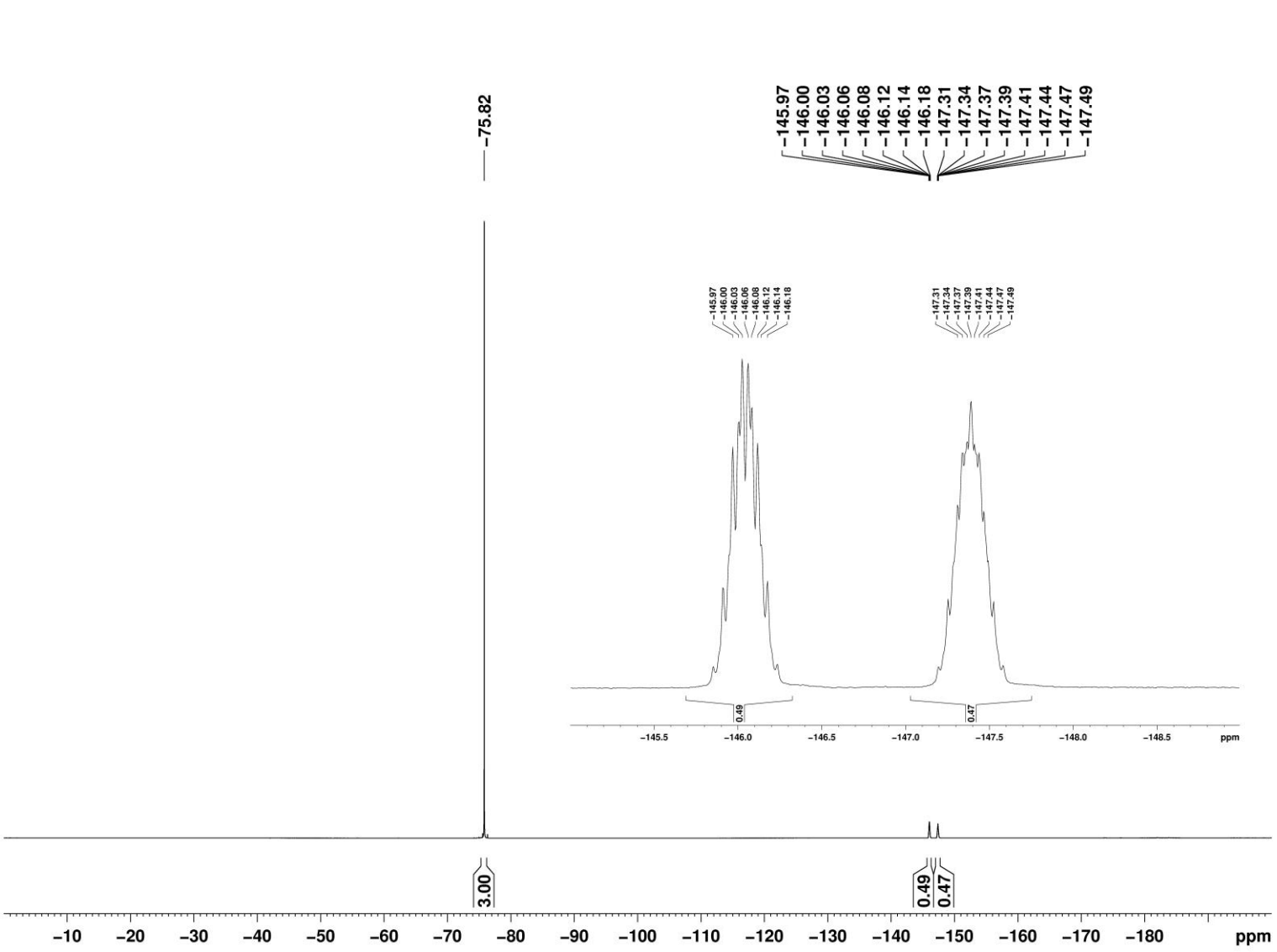


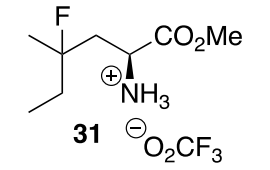
$CDCl_3$, 400 MHz



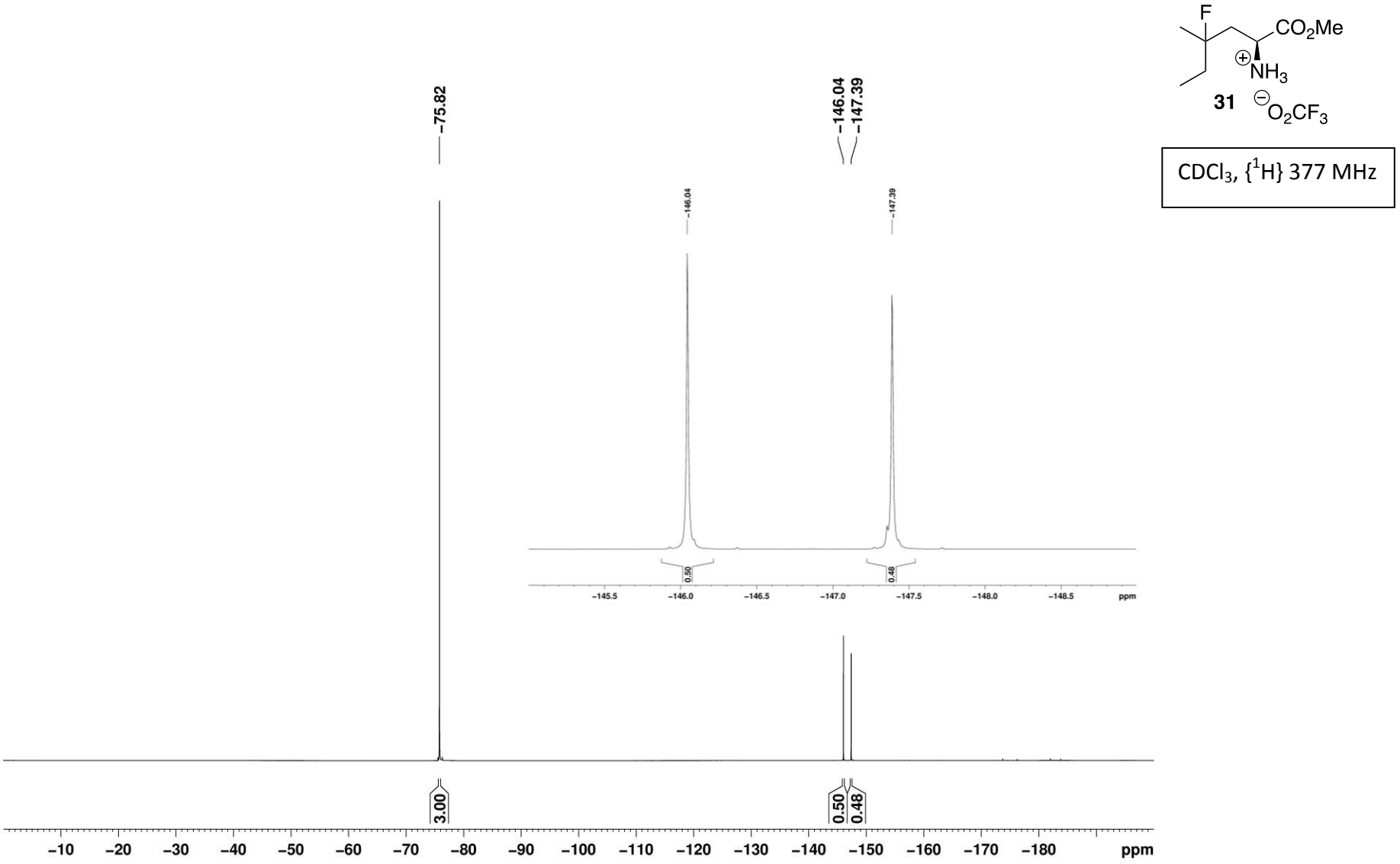


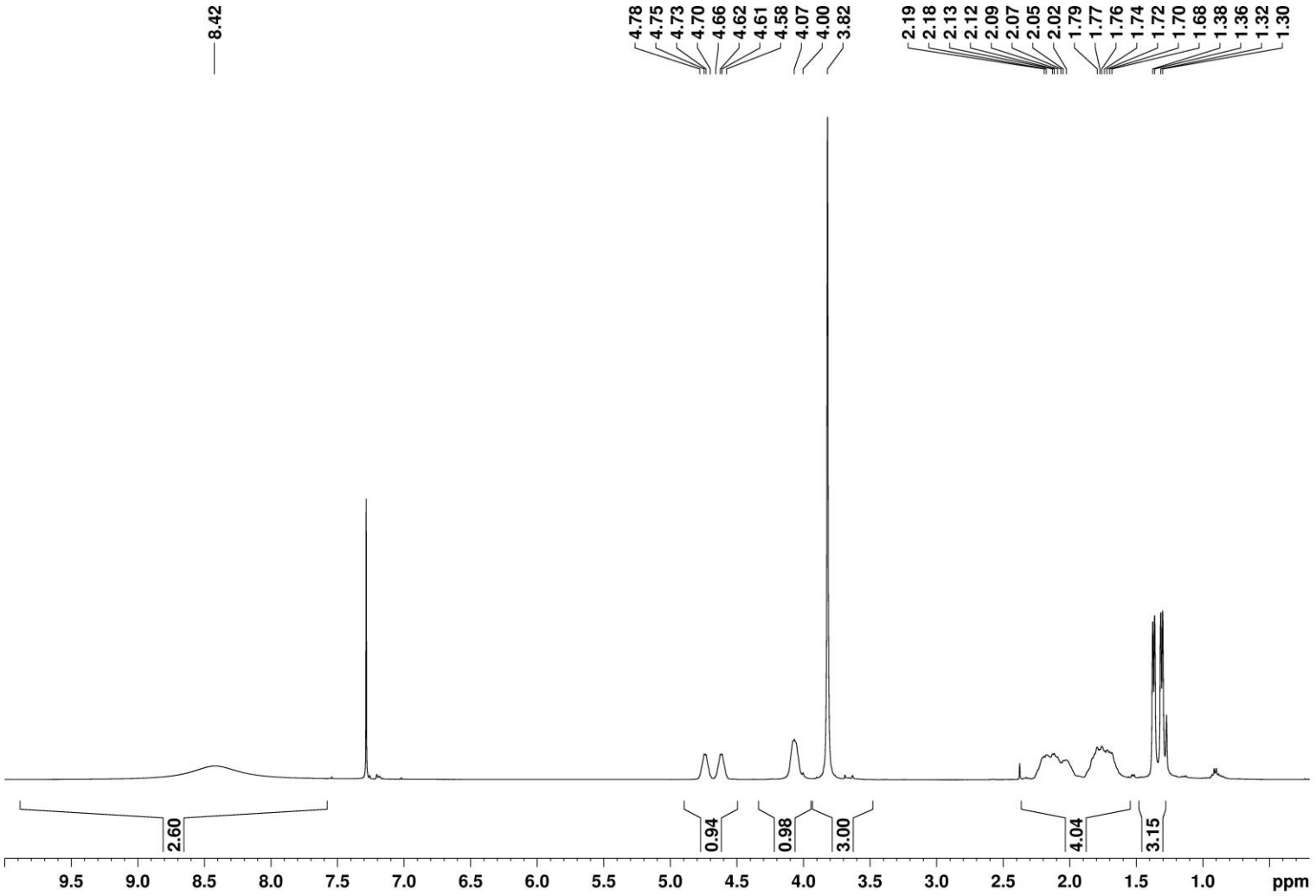
$CDCl_3$, 100 MHz

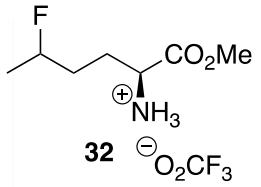




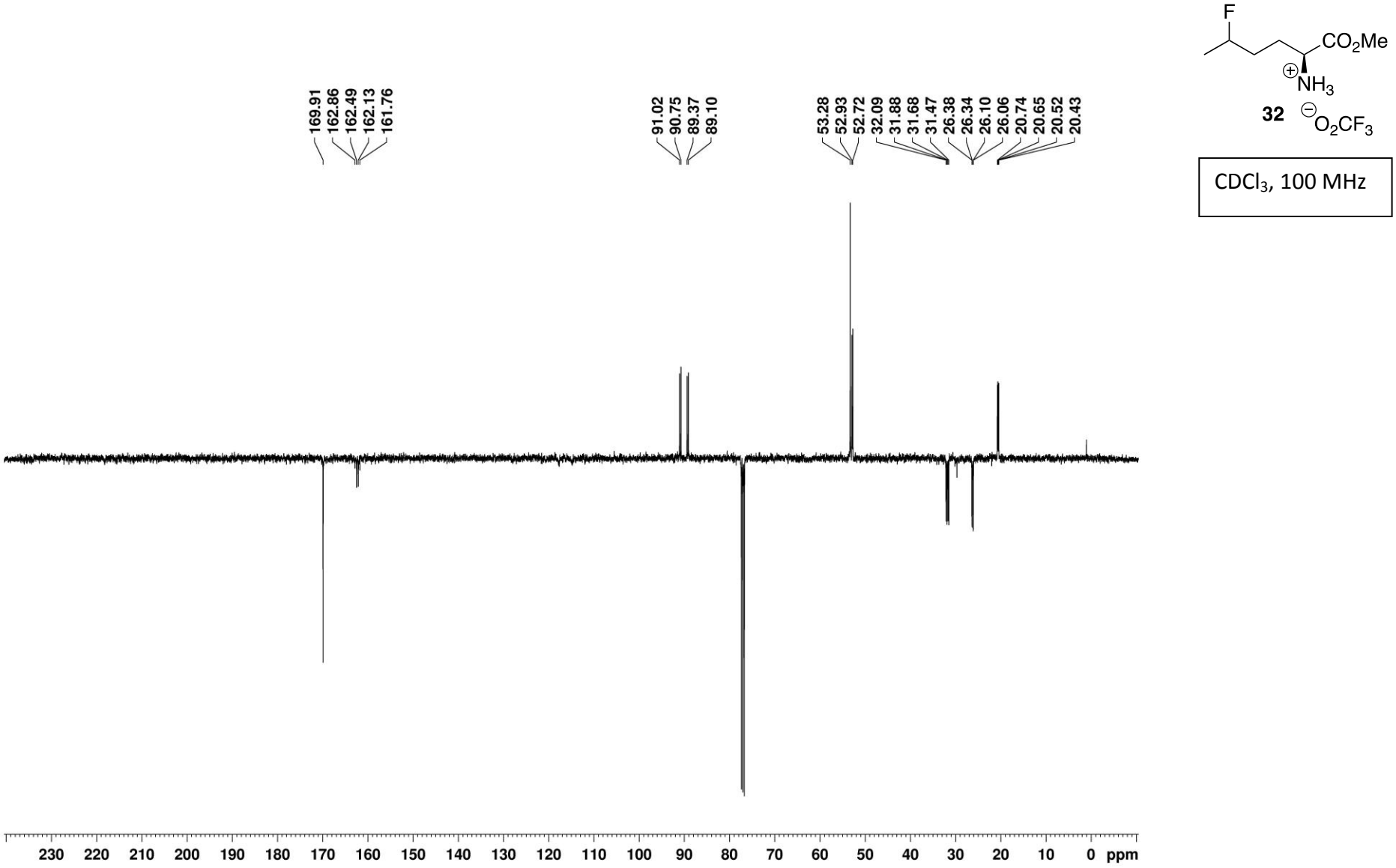
$CDCl_3$, 377 MHz


F
CO2Me
NH3
31
O2CF3
CDCl3, {1H} 377 MHz
-75.82
-146.04
-147.39
3.00
0.50
0.48
ppm

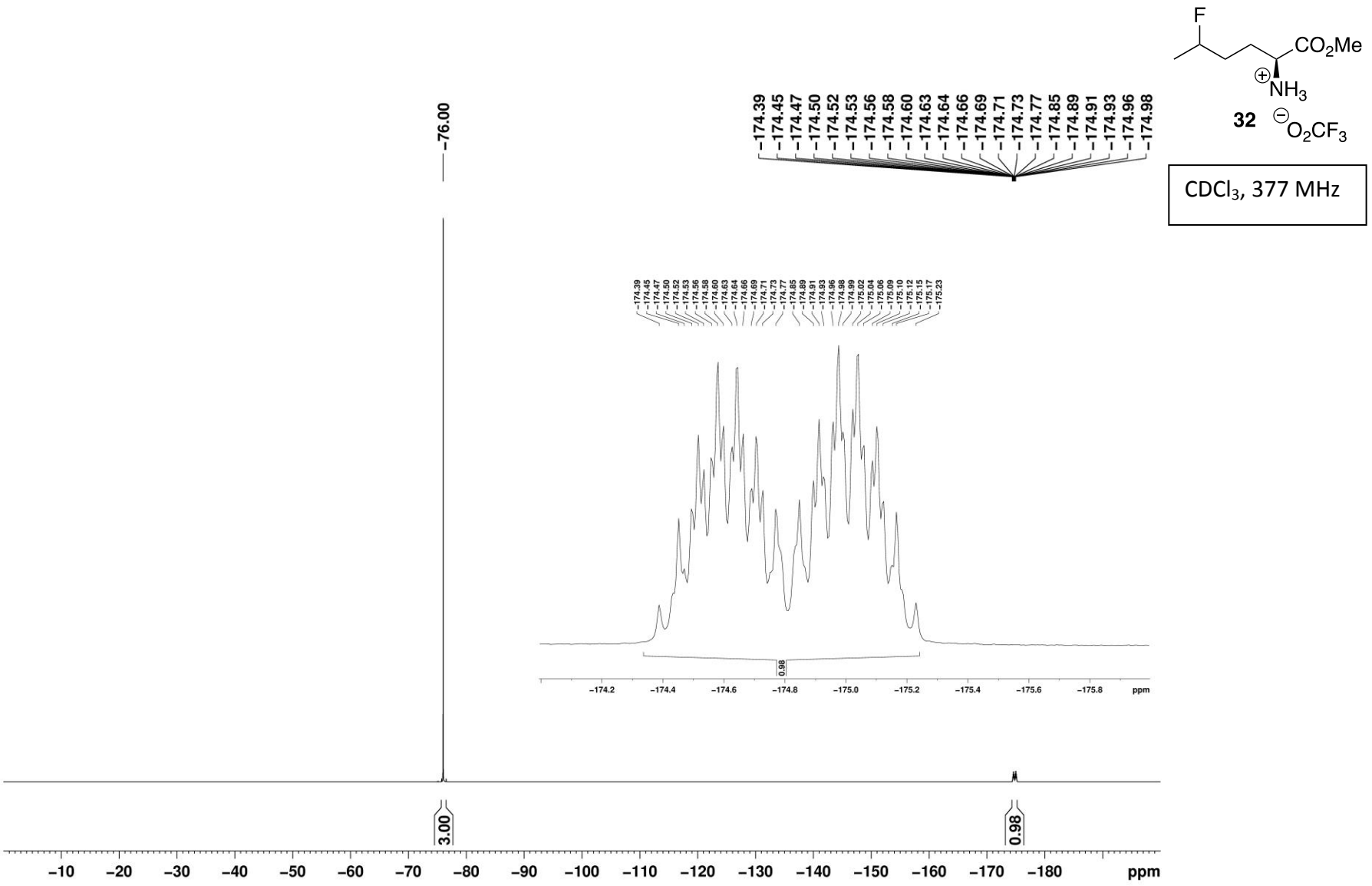


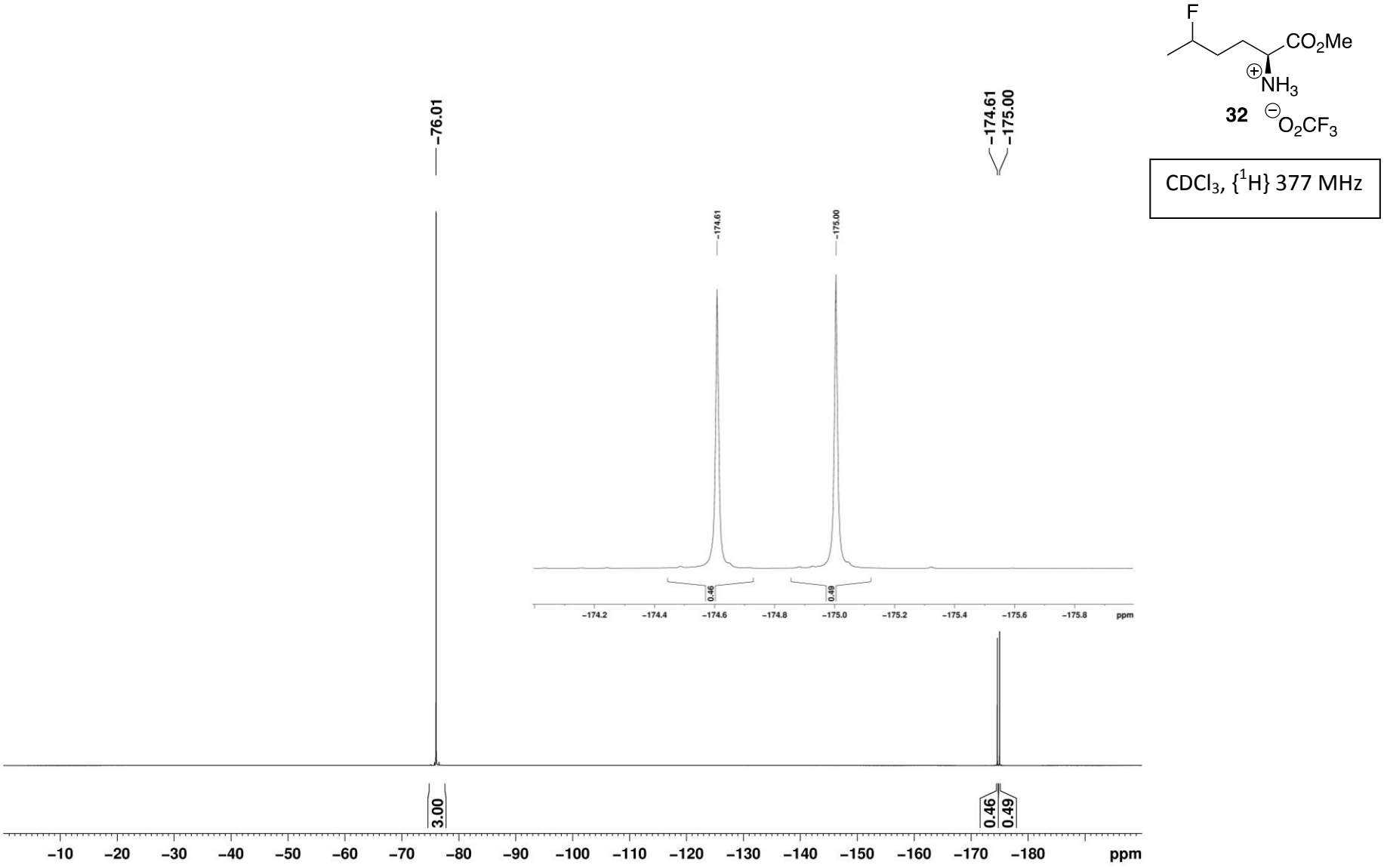


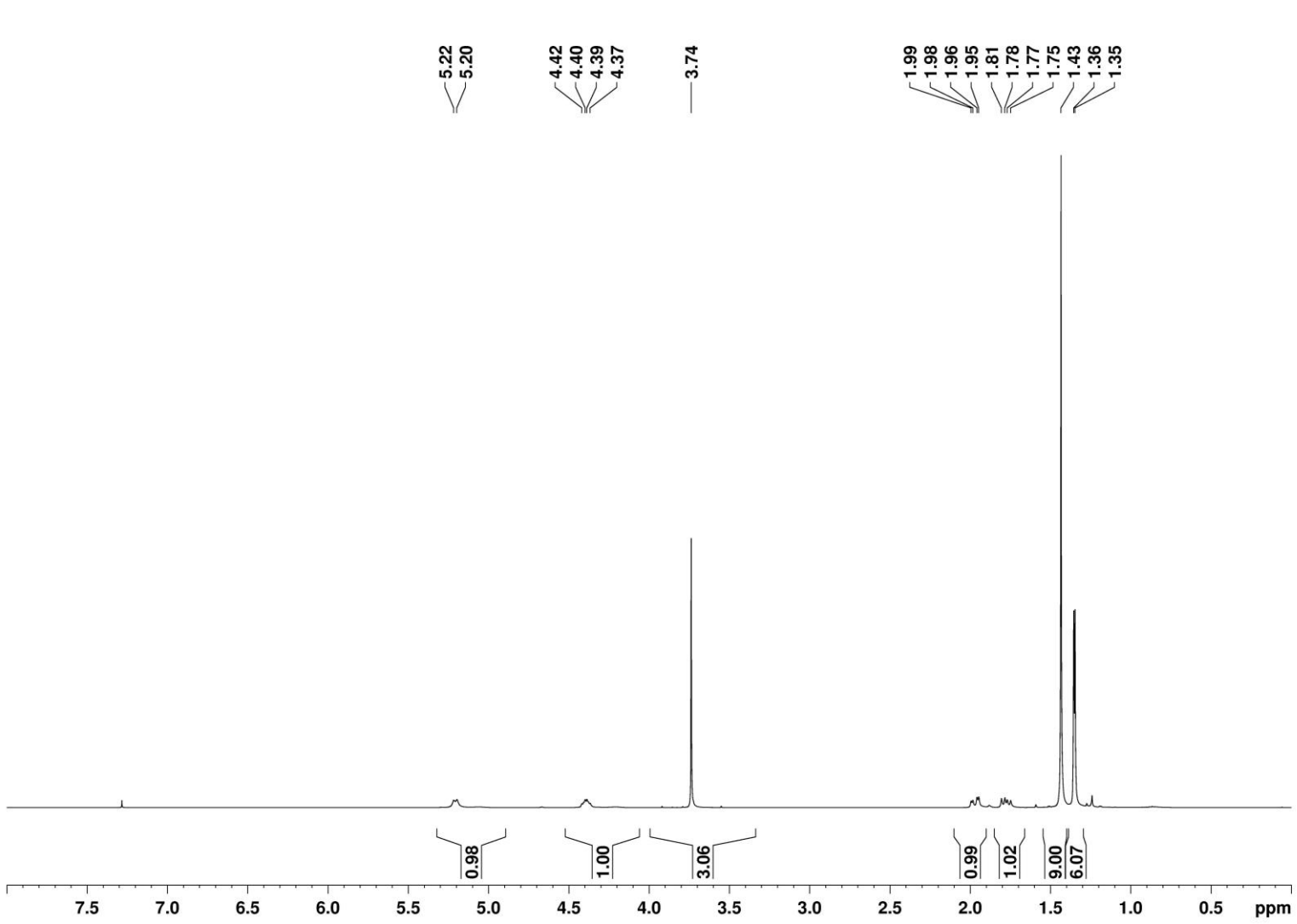
$CDCl_3$, 400 MHz

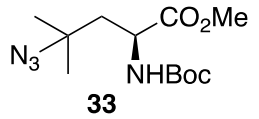


$CDCl_3$, 100 MHz


F
CO2Me
NH3
32
O2CF3
CDCl3, 377 MHz
-76.00
-174.39
-174.45
-174.47
-174.50
-174.52
-174.53
-174.56
-174.58
-174.60
-174.63
-174.64
-174.66
-174.69
-174.71
-174.73
-174.77
-174.85
-174.89
-174.91
-174.93
-174.96
-174.98
0.98
-174.2
-174.4
-174.6
-174.8
-175.0
-175.2
-175.4
-175.6
-175.8
ppm
3.00
0.98
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
ppm

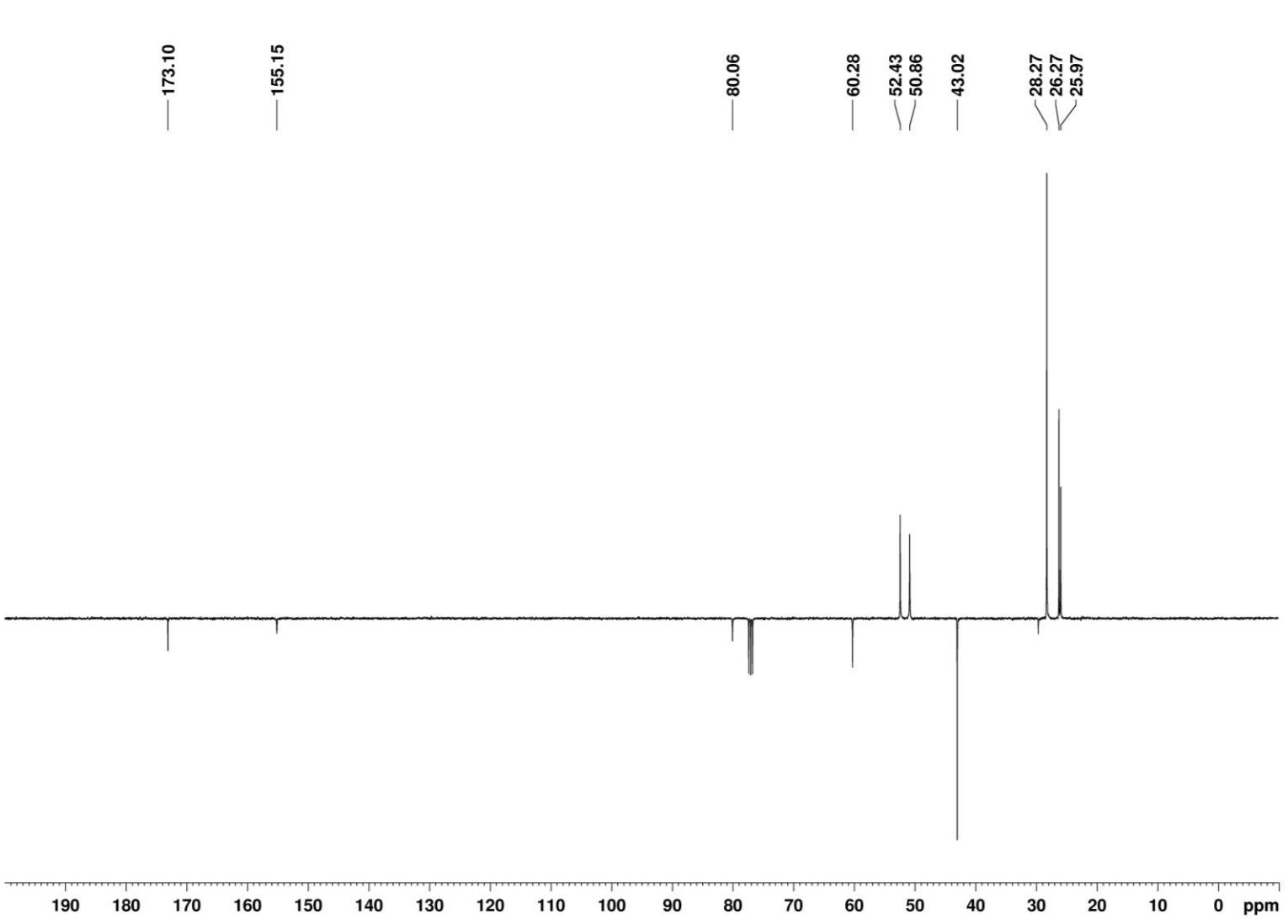

F
CO2Me
NH3
32
O2CF3
CDCl3, {1H} 377 MHz
-76.01
-174.61
-175.00
3.00
0.46
0.49
ppm

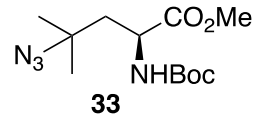




33

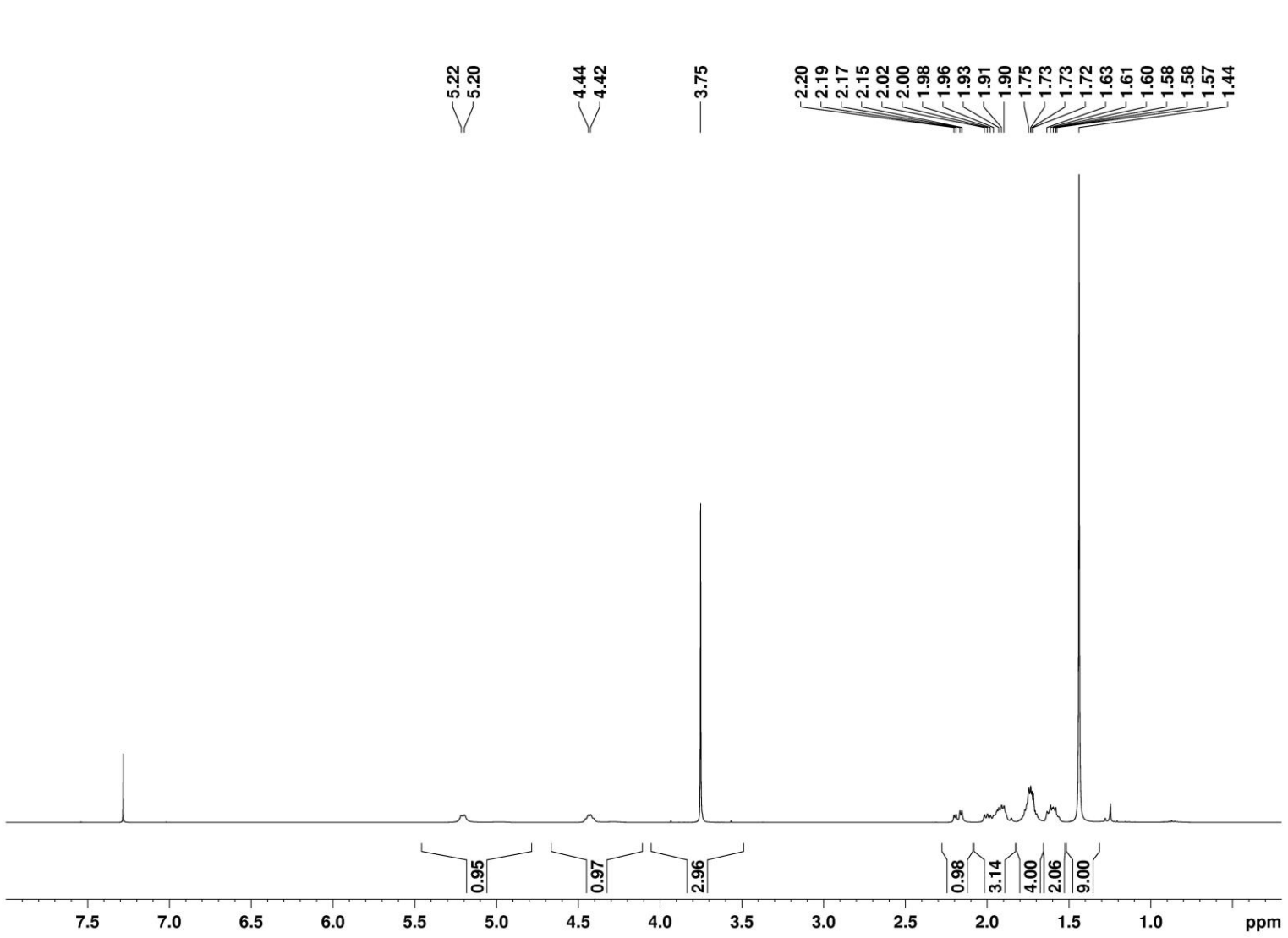
$CDCl_3$, 400 MHz

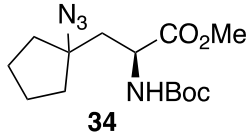




33

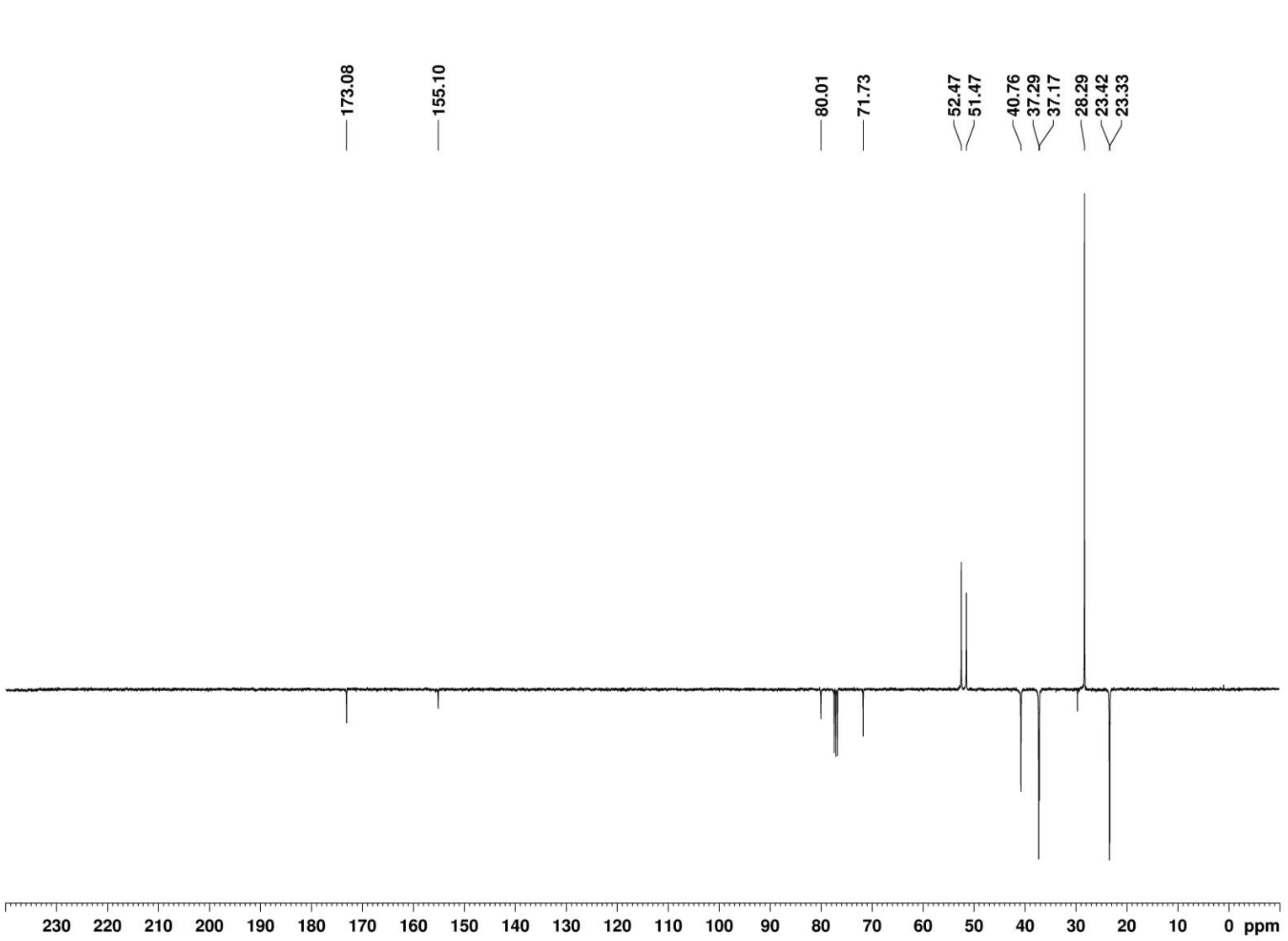
$CDCl_3$, 100 MHz

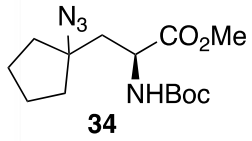




34

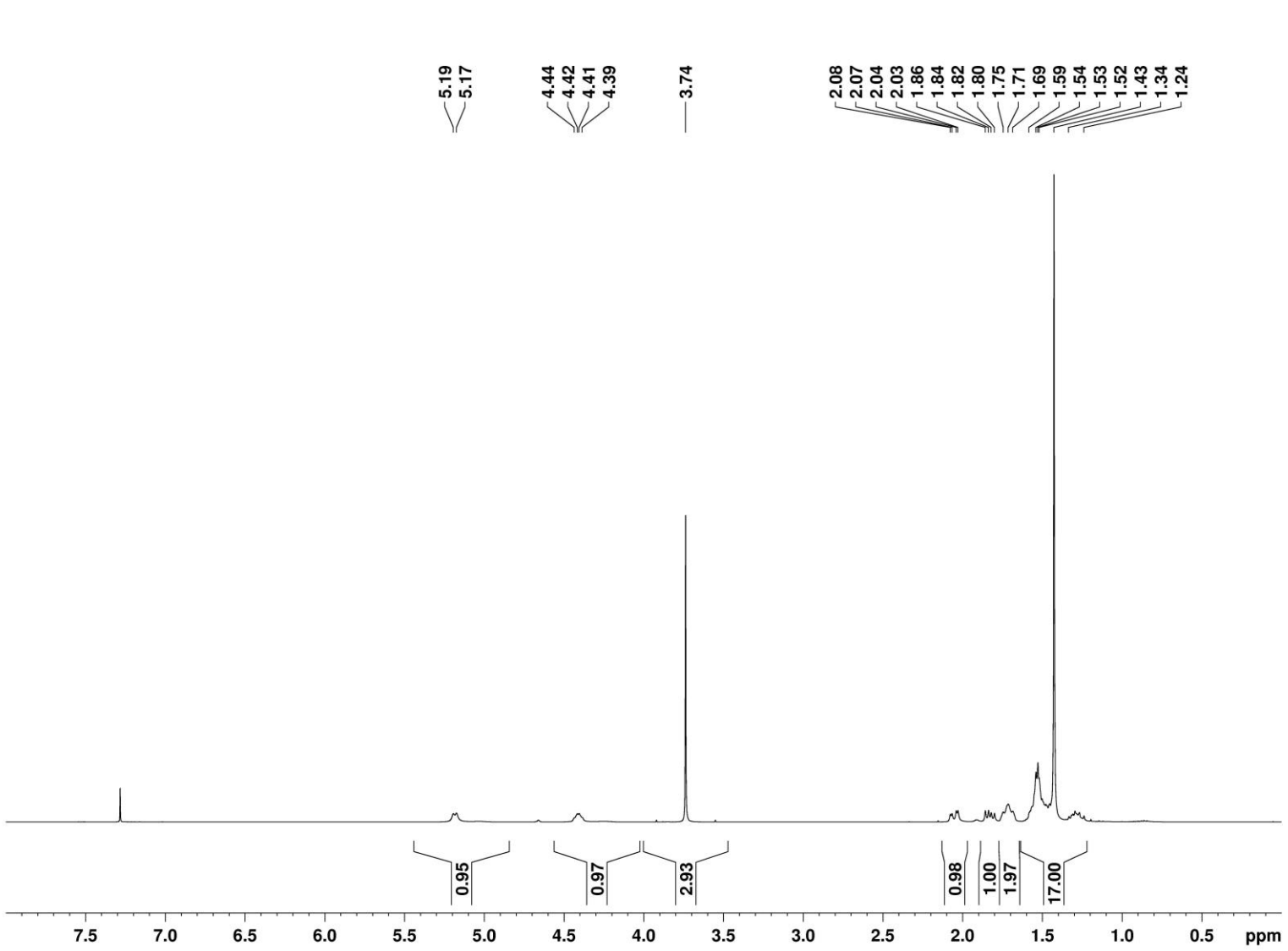
$CDCl_3$, 400 MHz

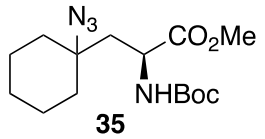




34

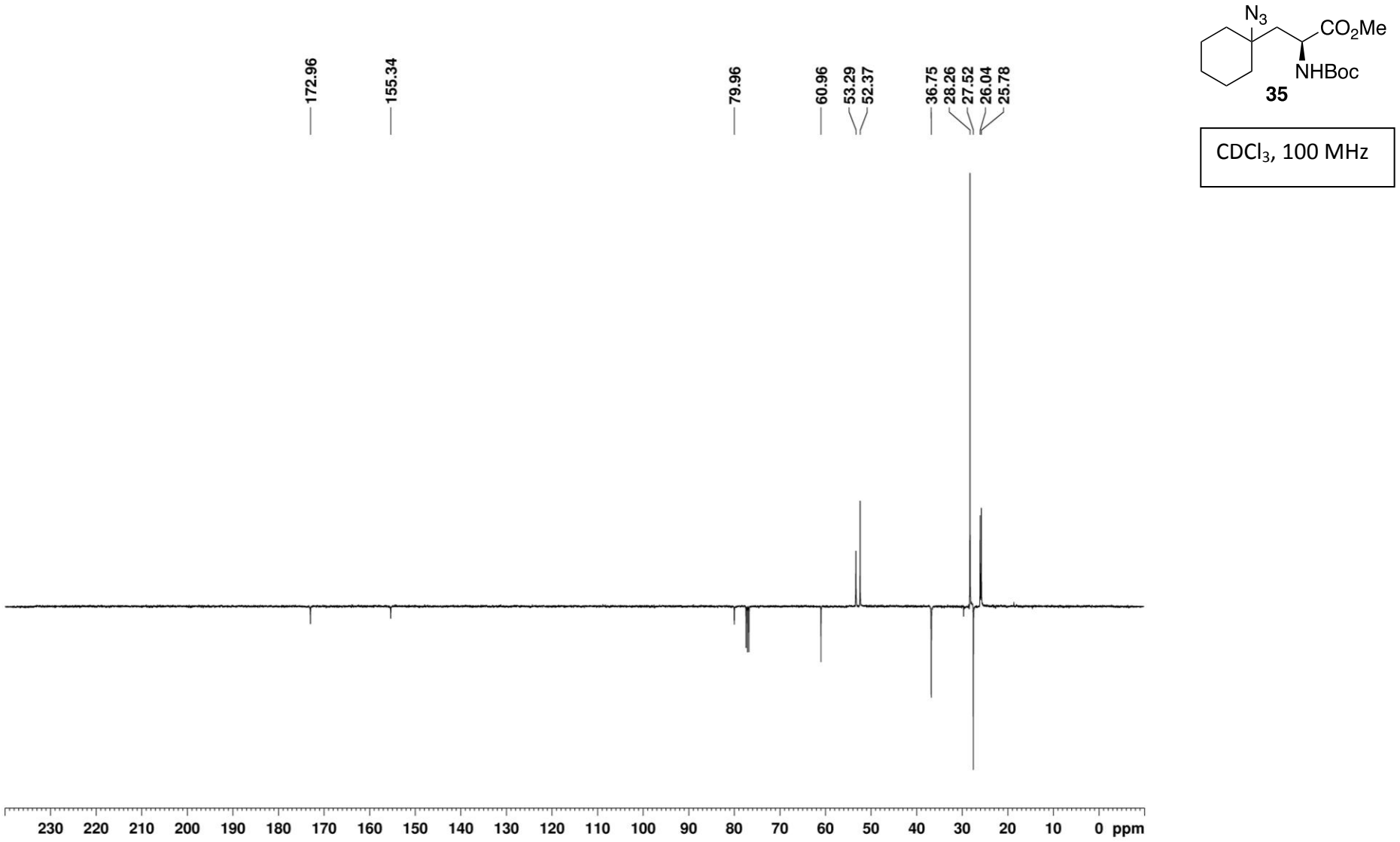
$CDCl_3$, 100 MHz





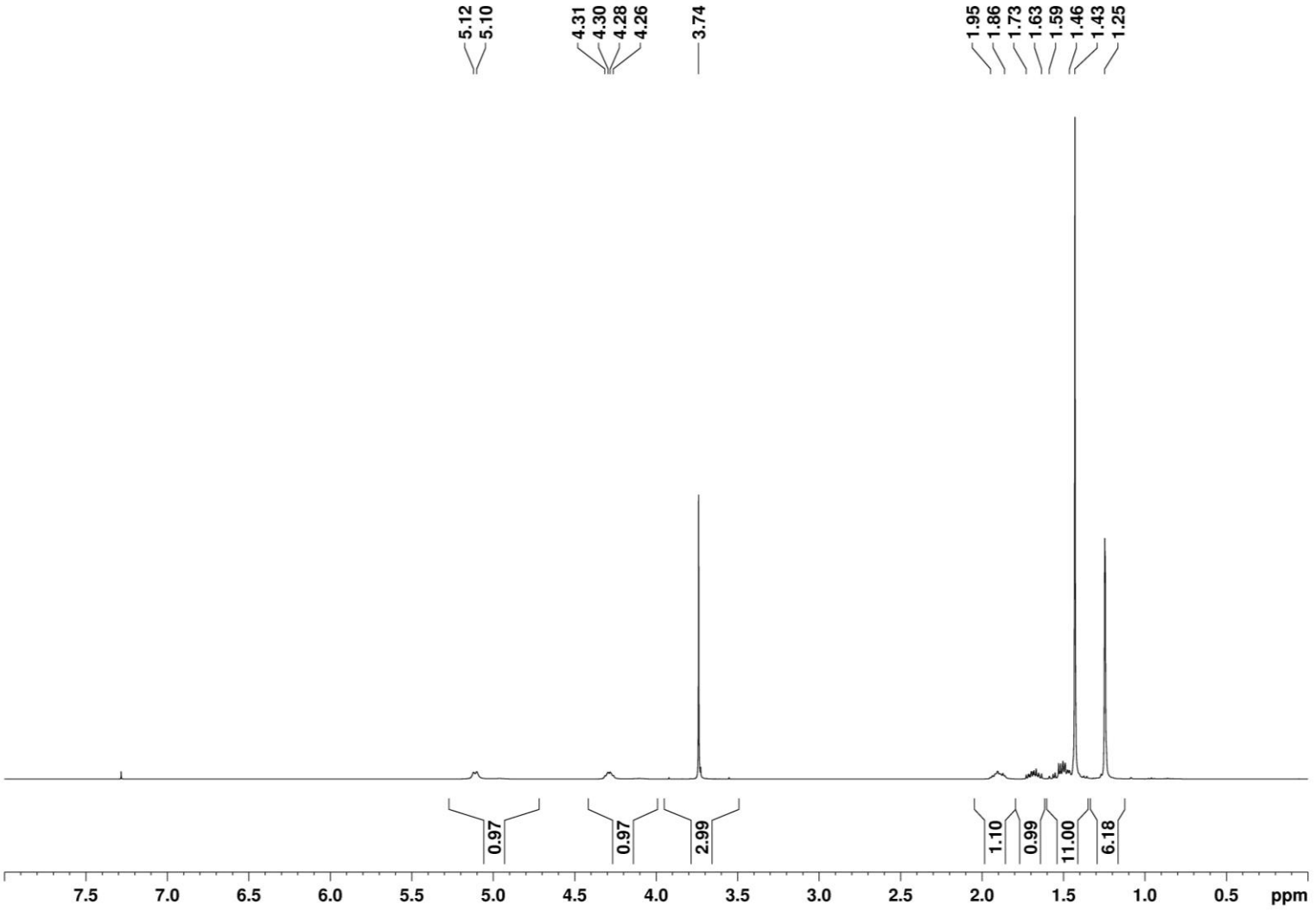
35

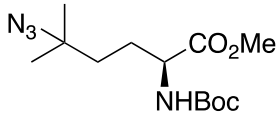
$CDCl_3$, 400 MHz



35

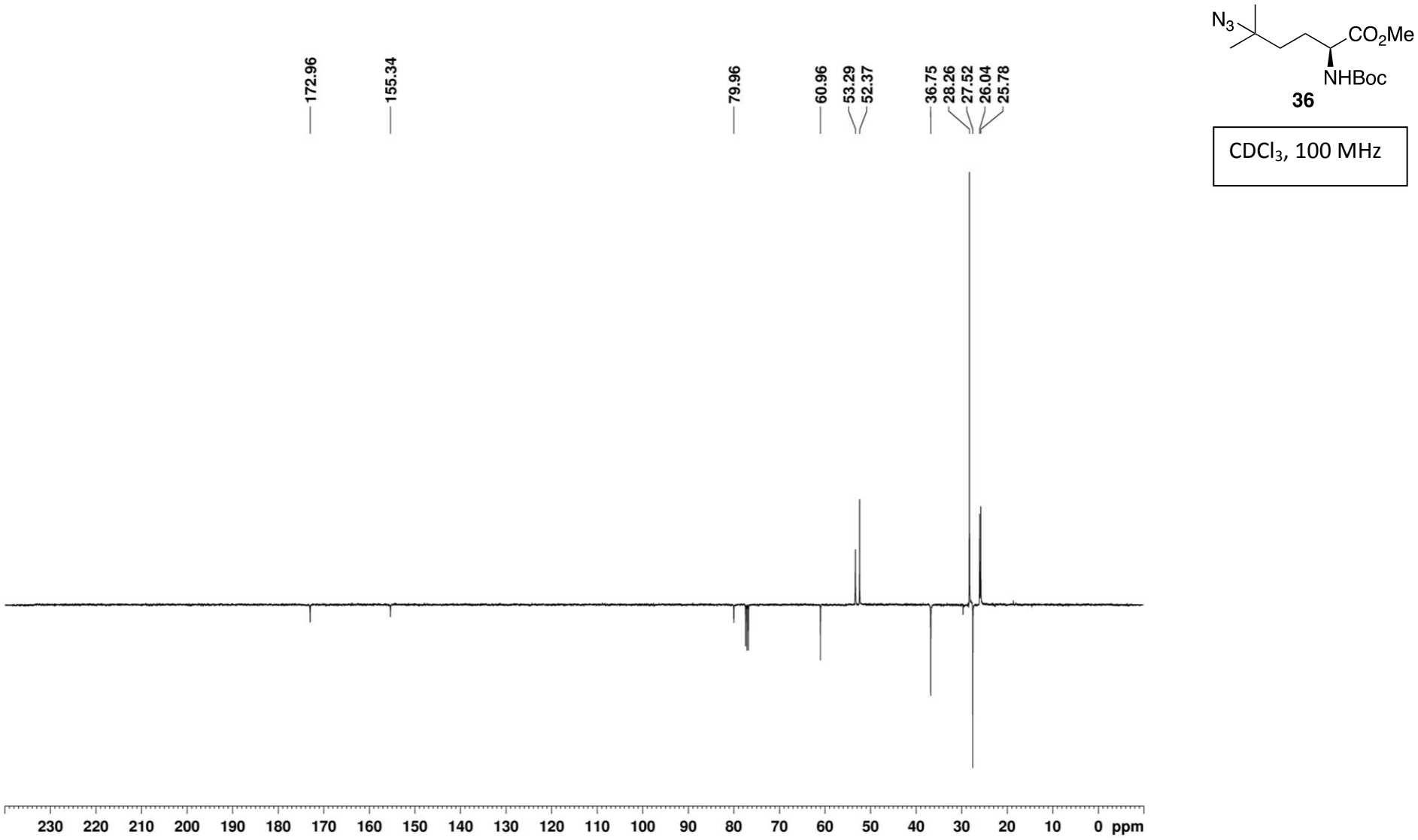
$CDCl_3$, 100 MHz





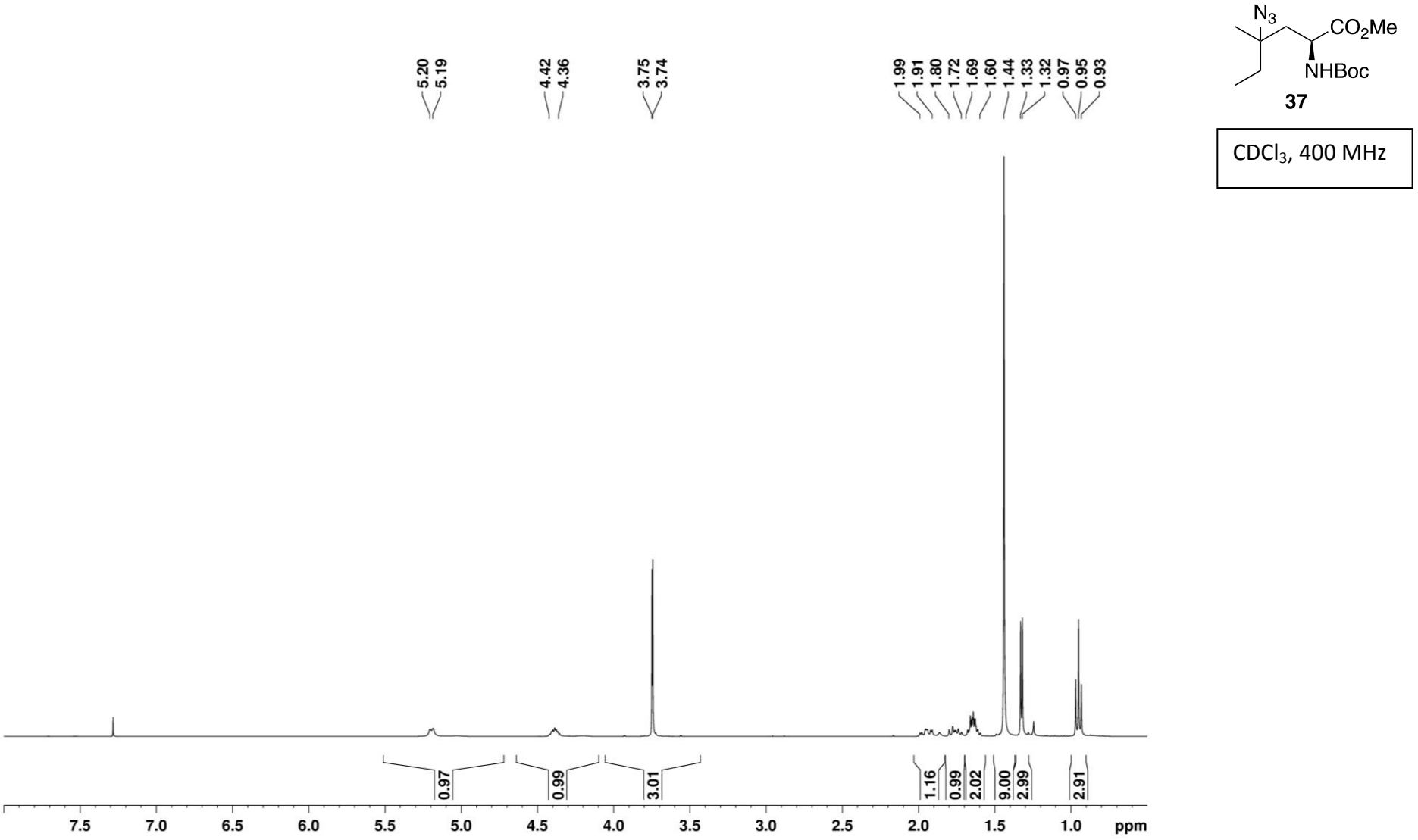
36

$CDCl_3$, 400 MHz



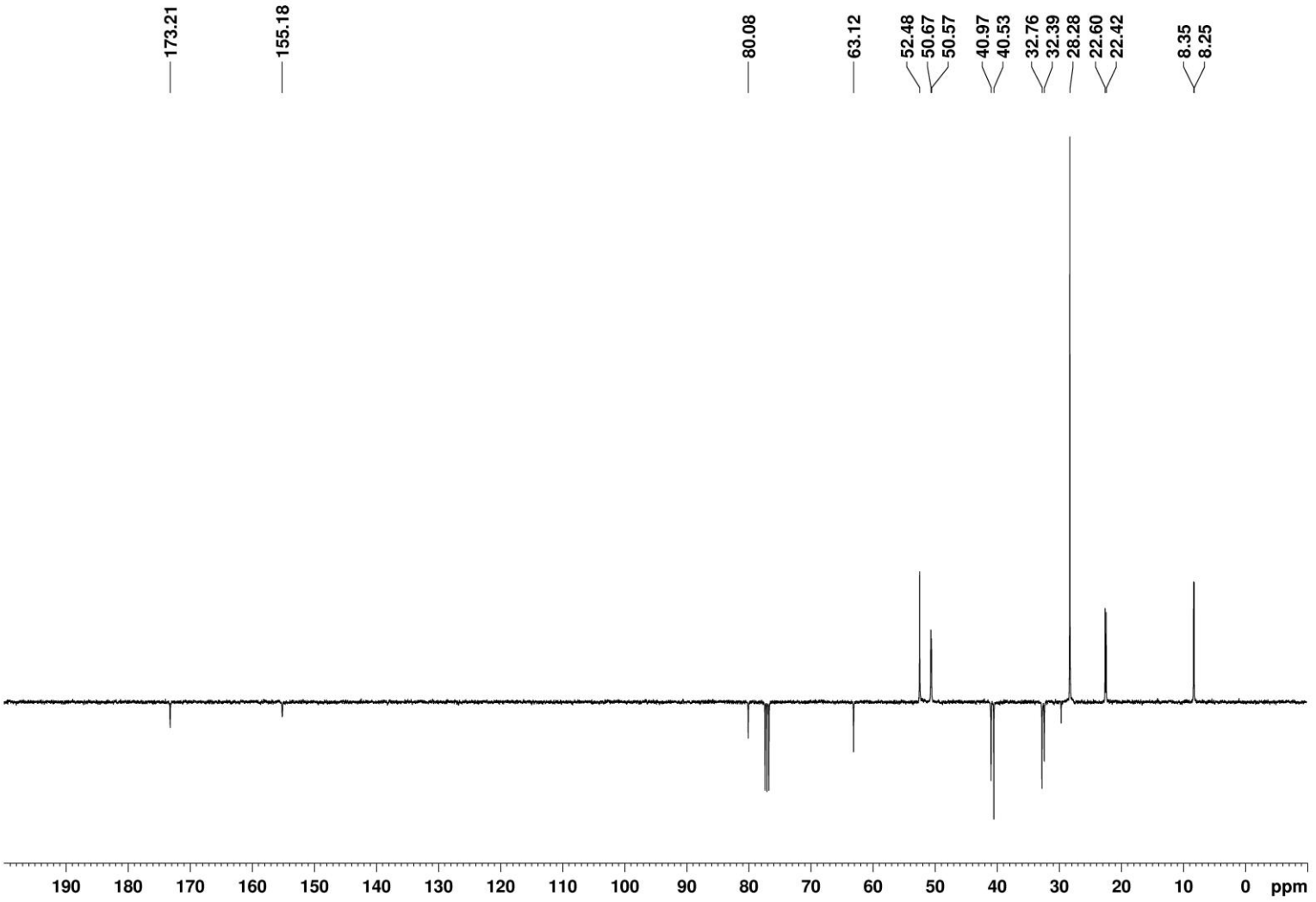
36

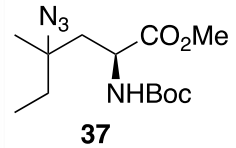
$CDCl_3$, 100 MHz



37

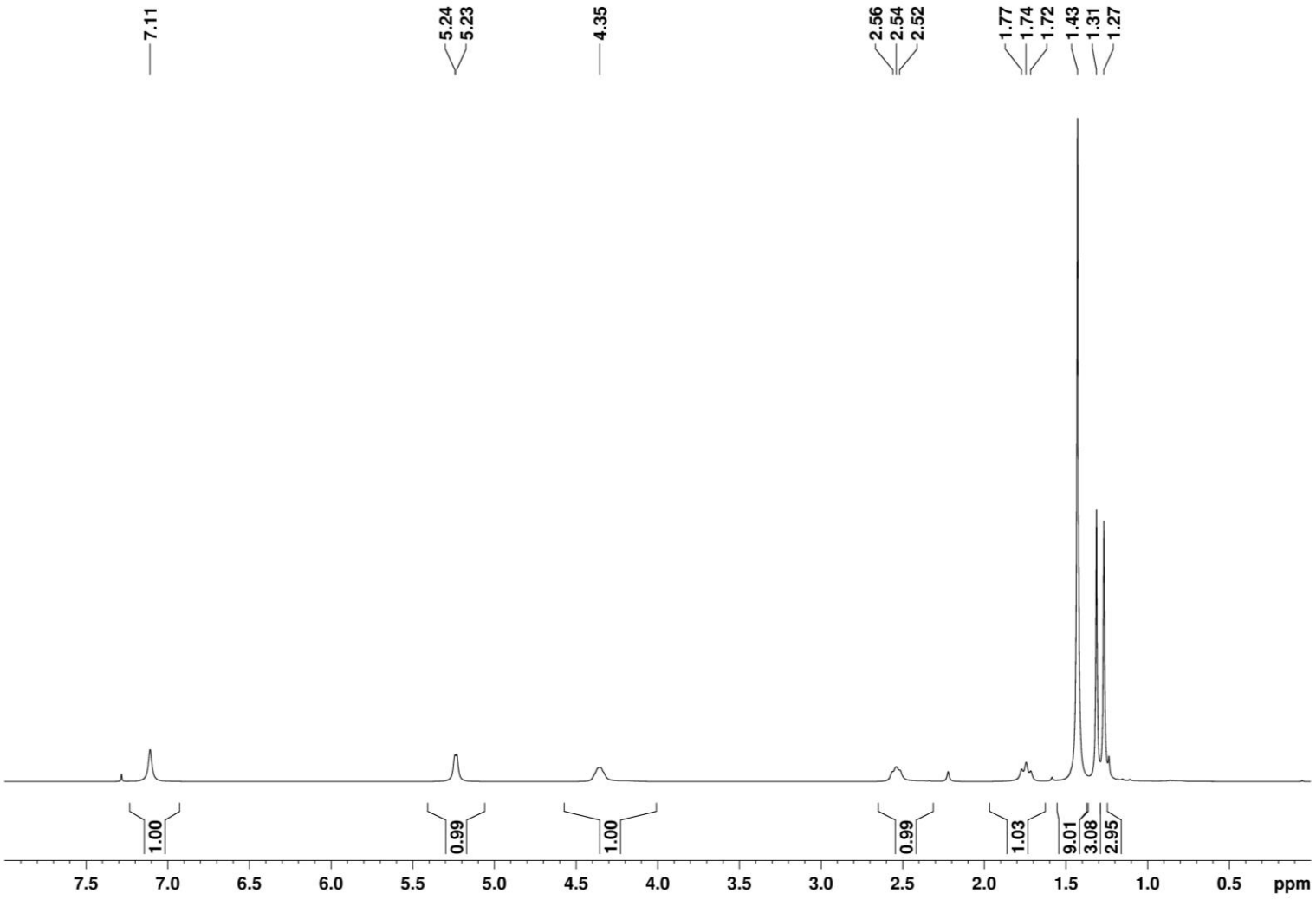
$CDCl_3$, 400 MHz

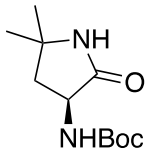




37

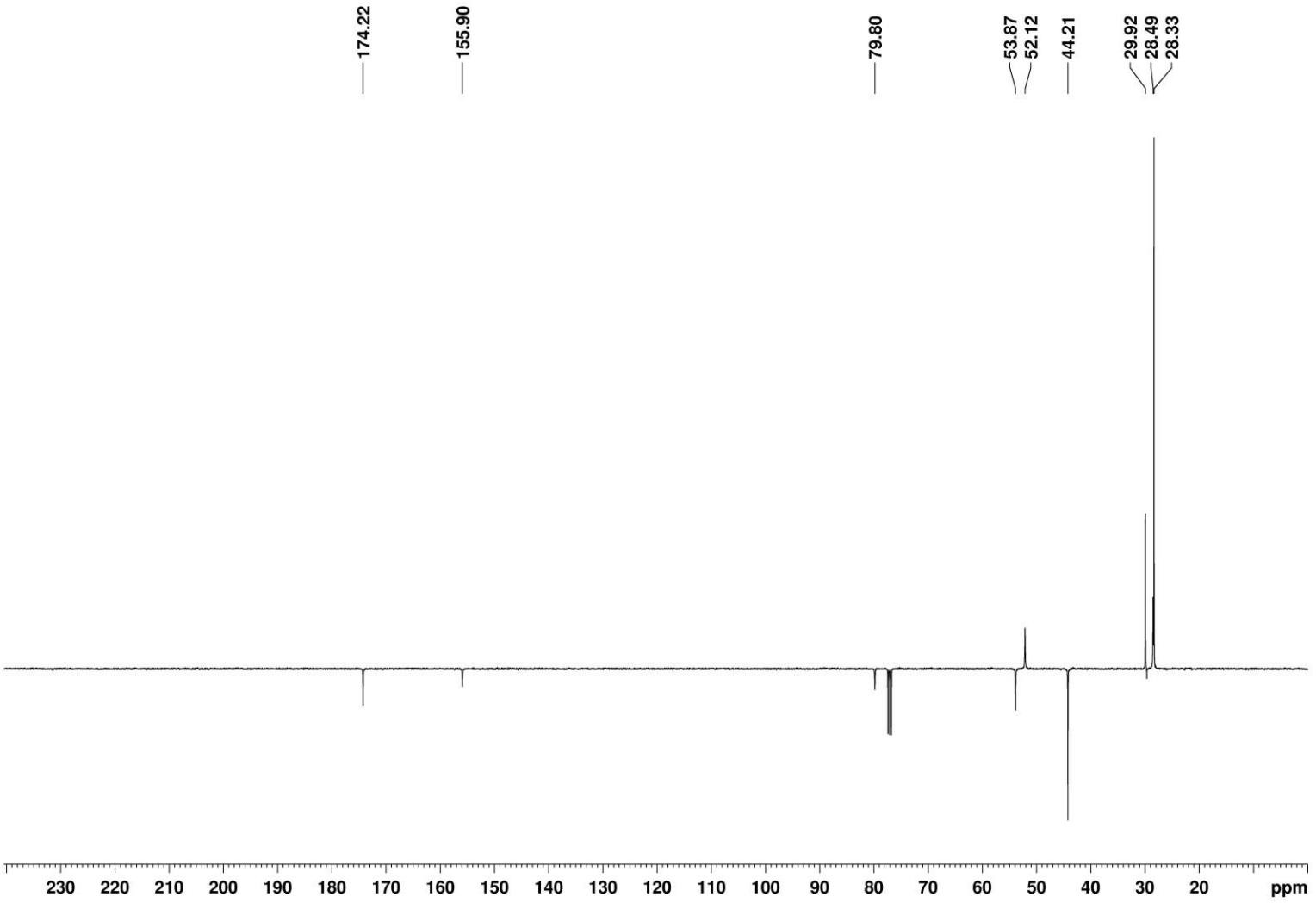
$CDCl_3$, 100 MHz

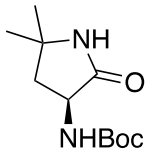




38

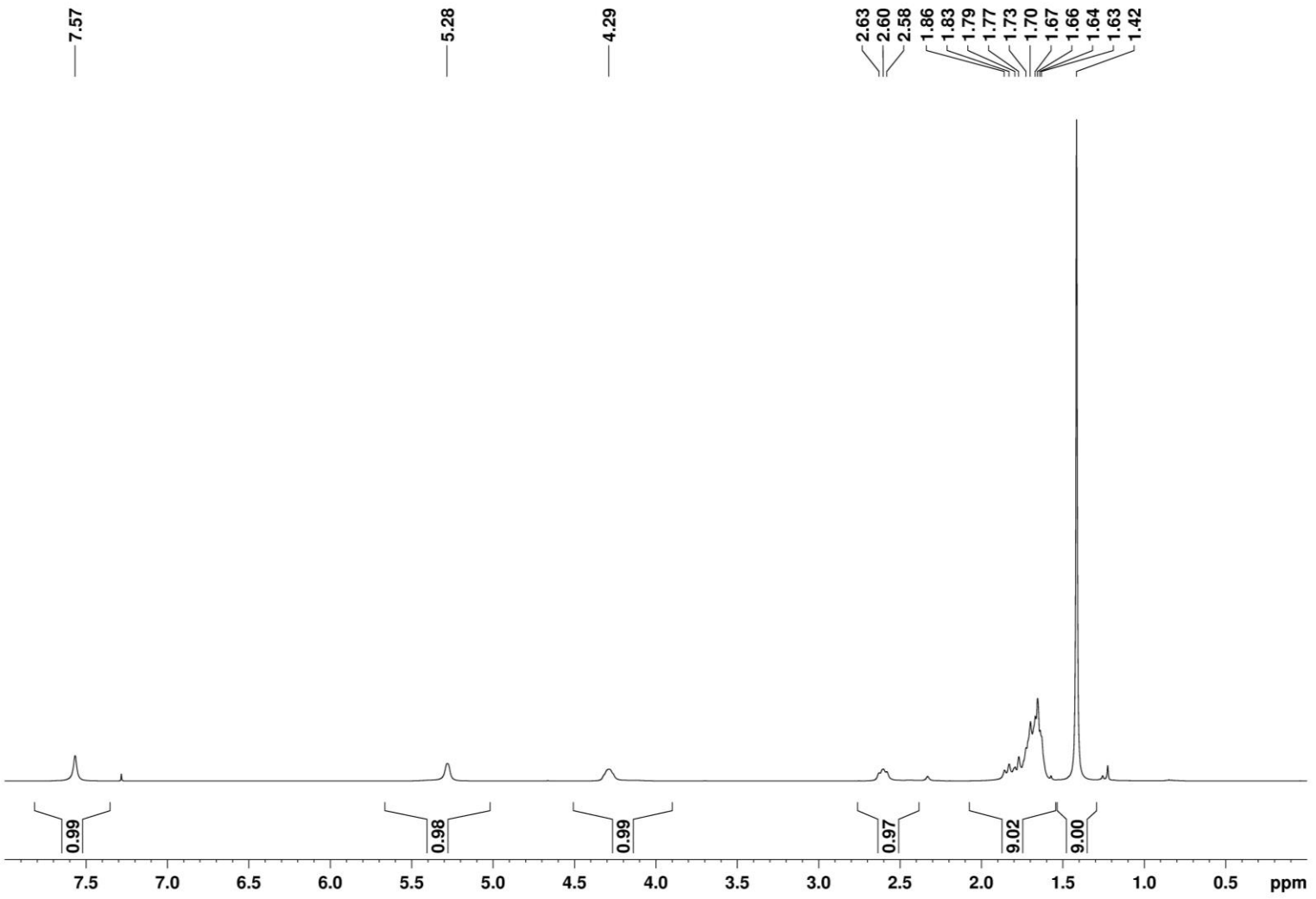
$CDCl_3$, 400 MHz

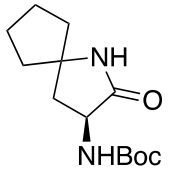




38

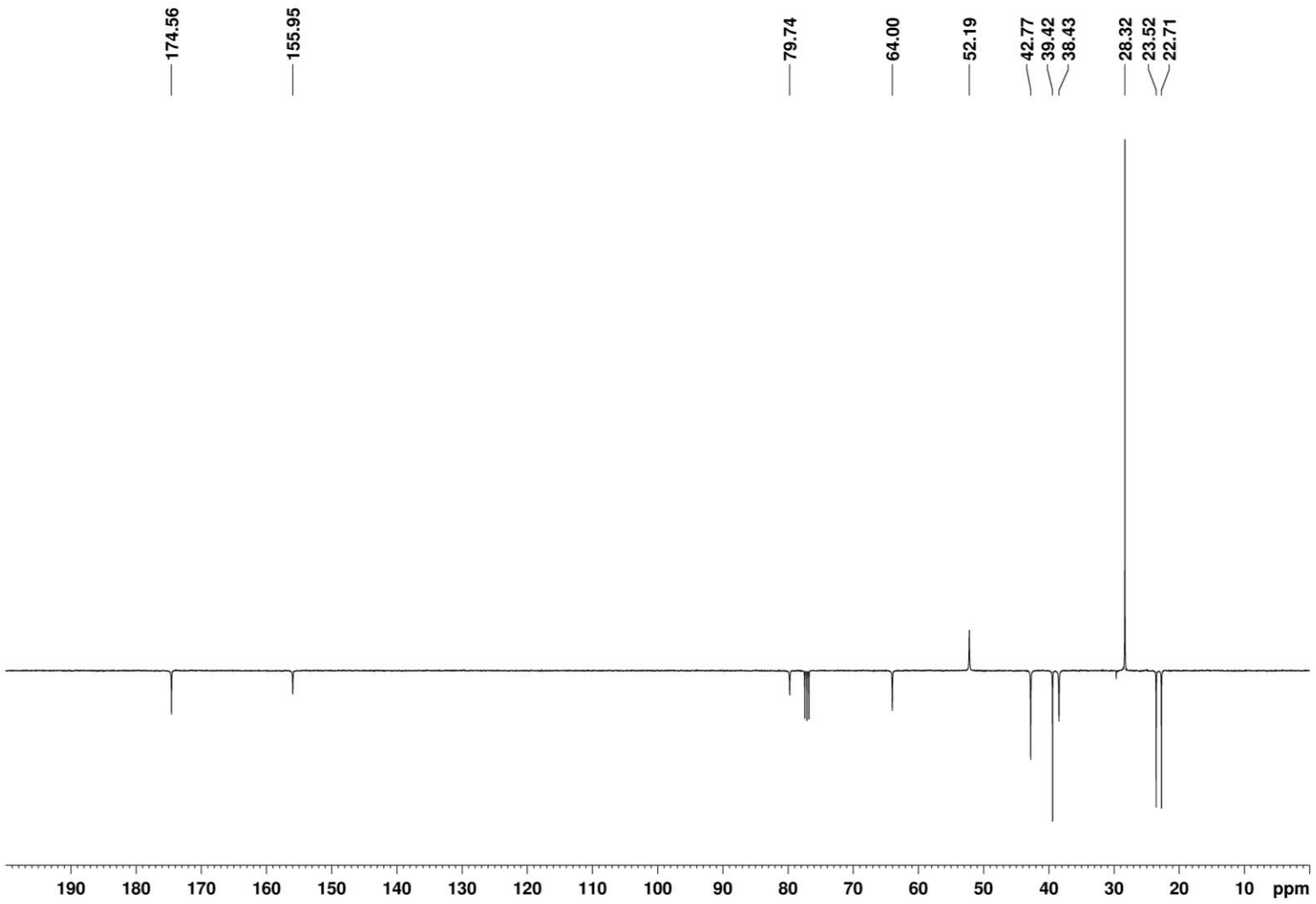
$CDCl_3$, 100 MHz

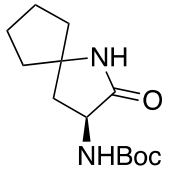




39

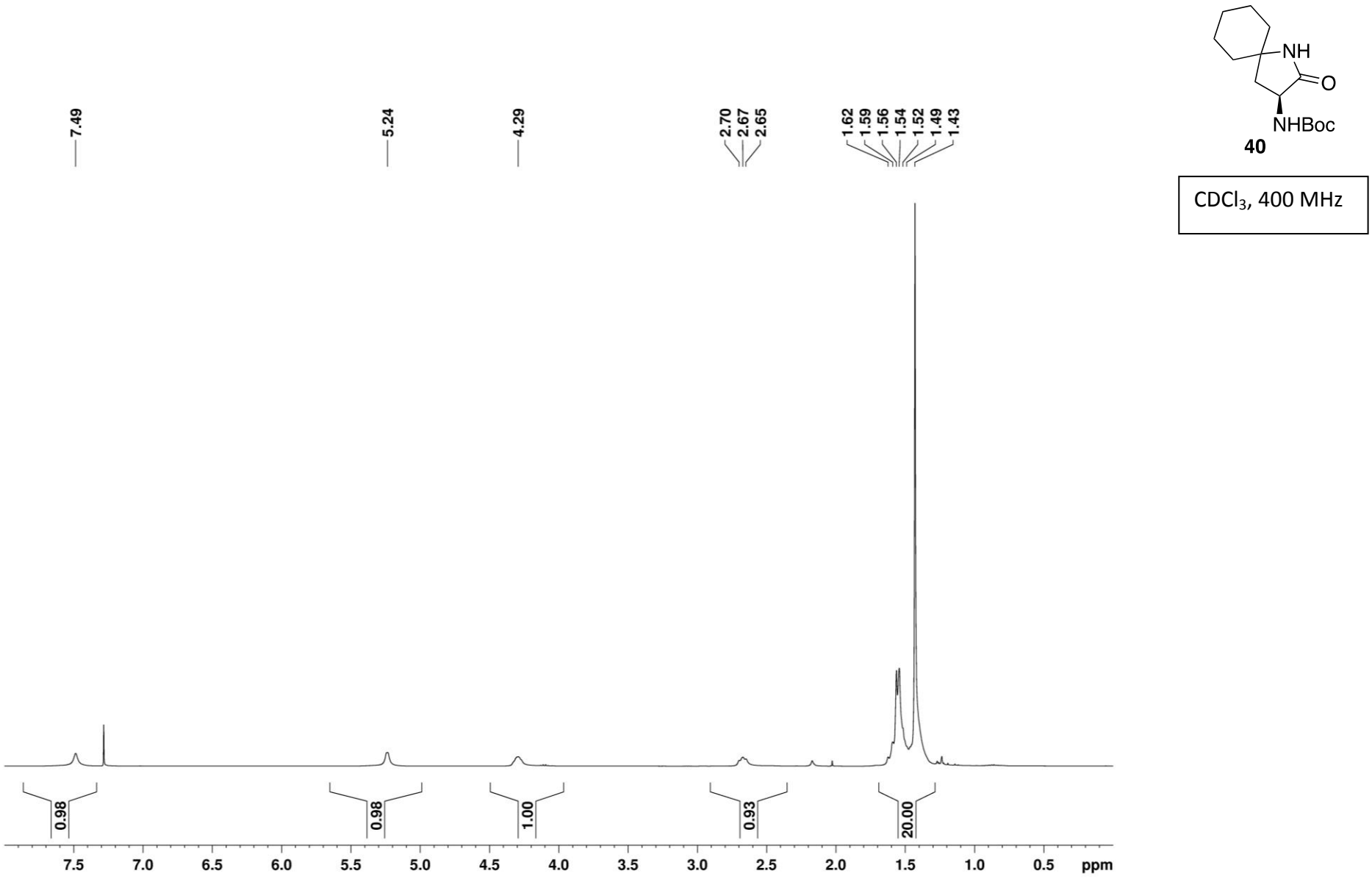
$CDCl_3$, 400 MHz





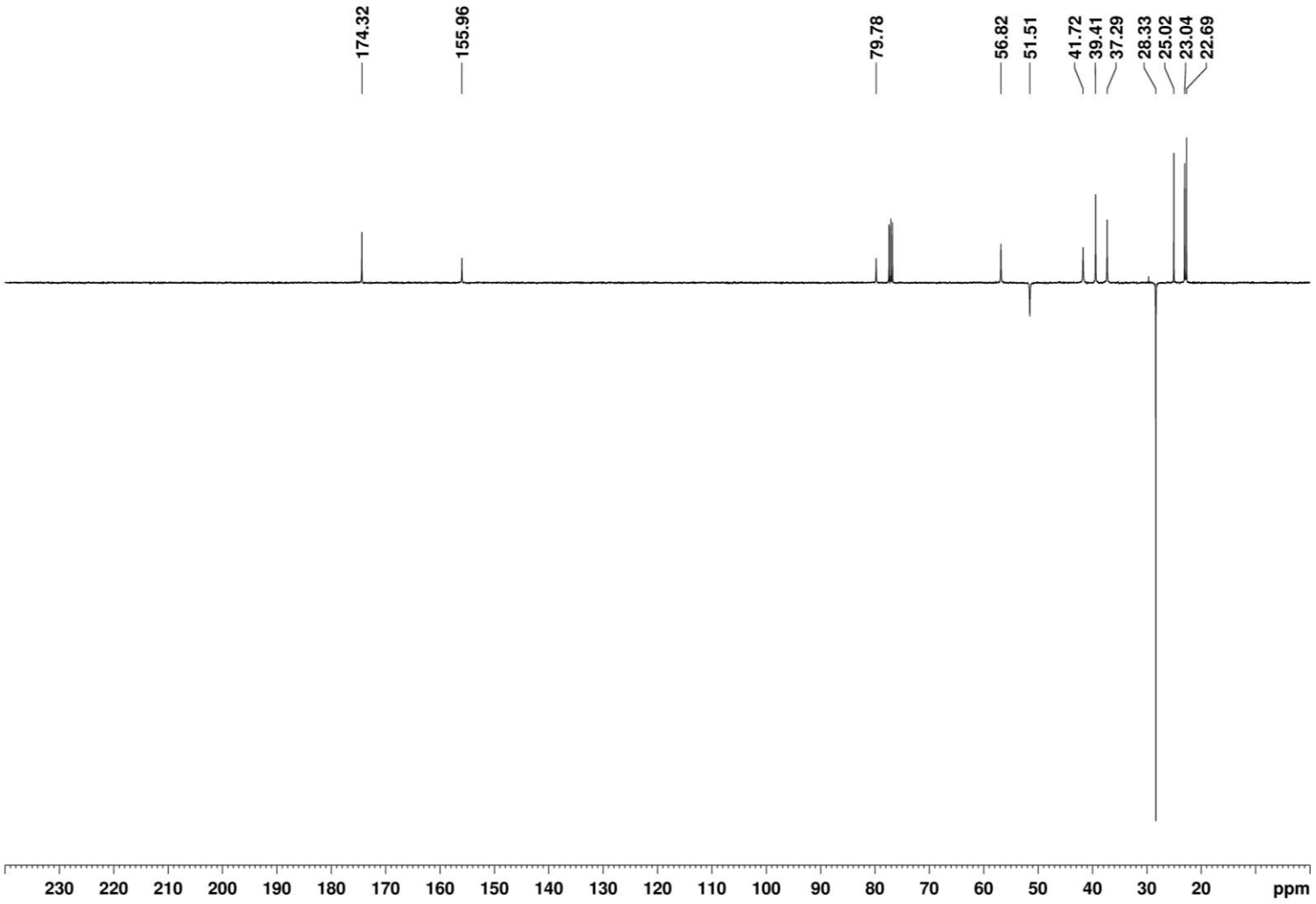
39

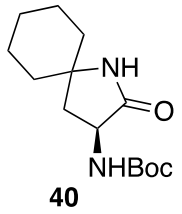
$CDCl_3$, 100 MHz



40

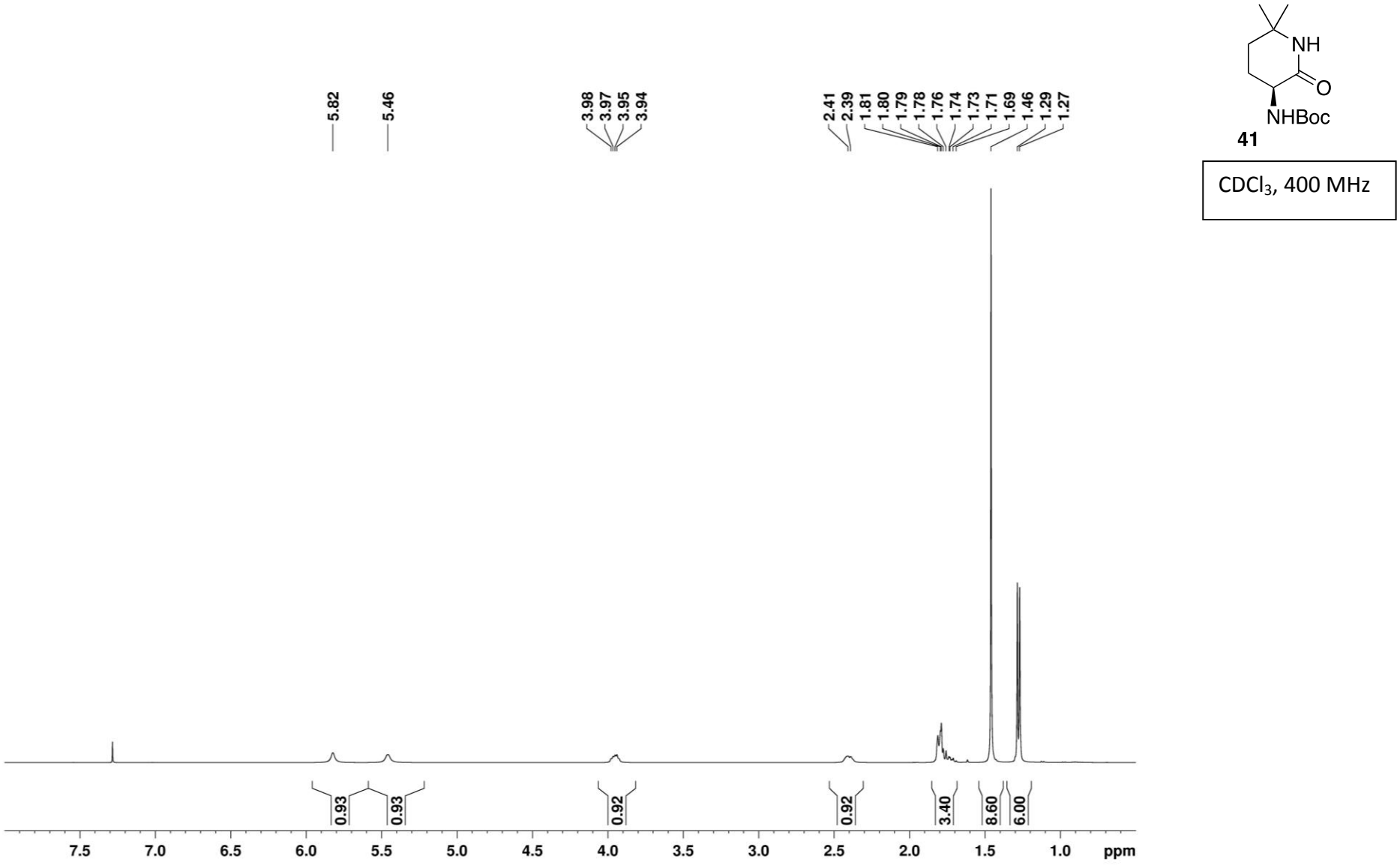
$CDCl_3$, 400 MHz





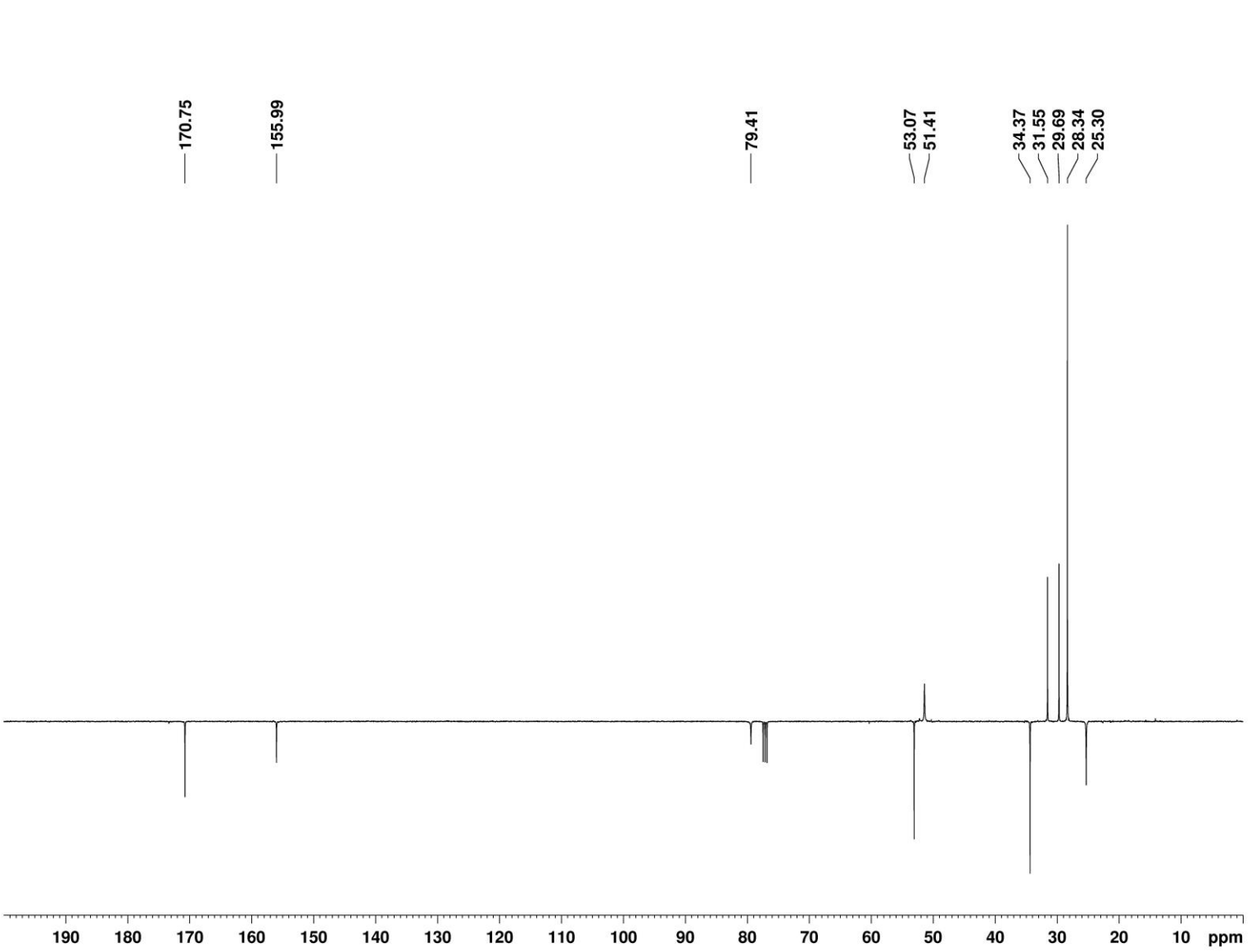
40

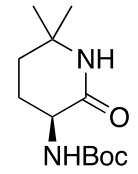
$CDCl_3$, 100 MHz



41

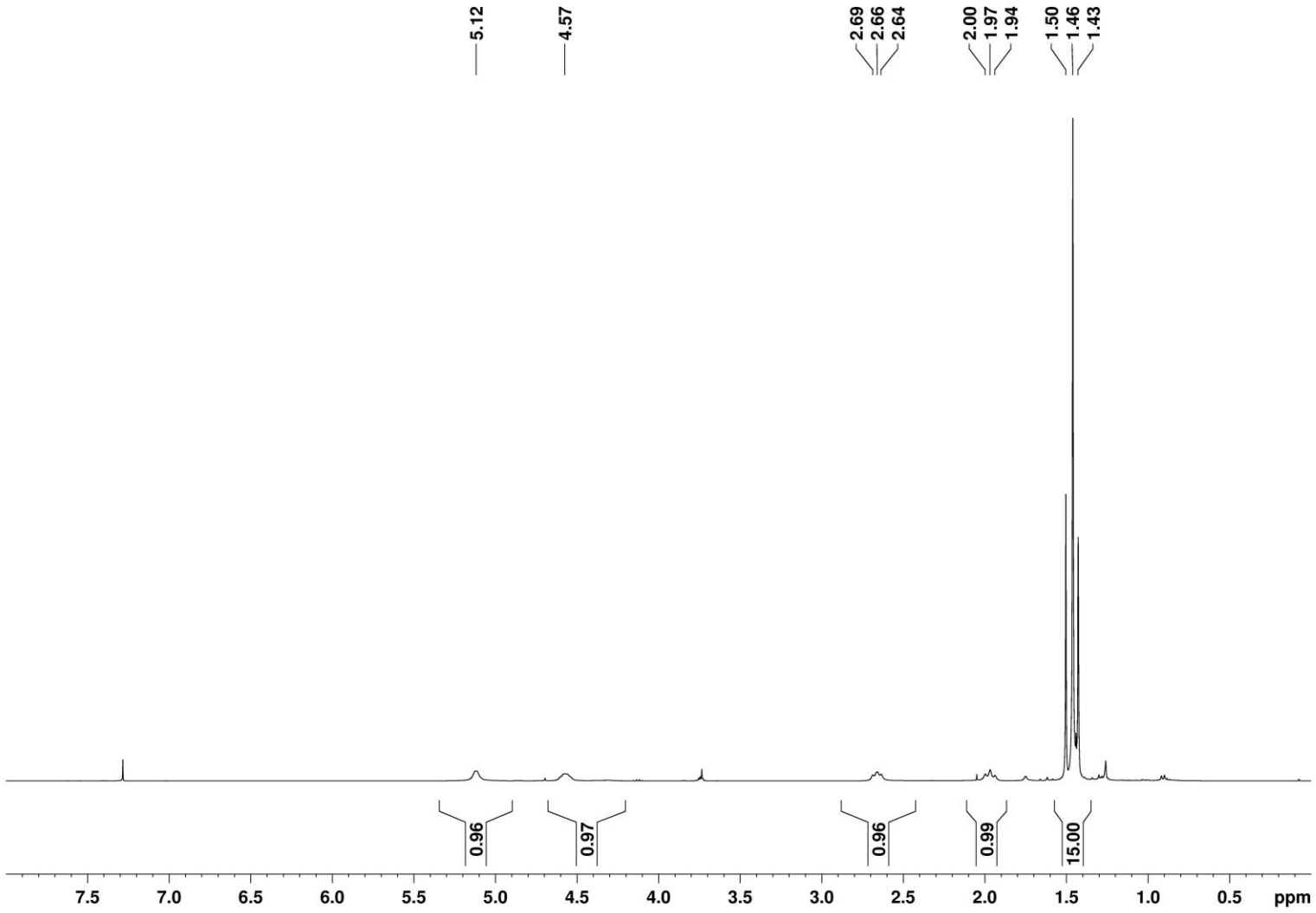
$CDCl_3$, 400 MHz

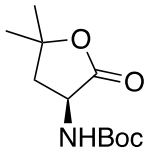




41

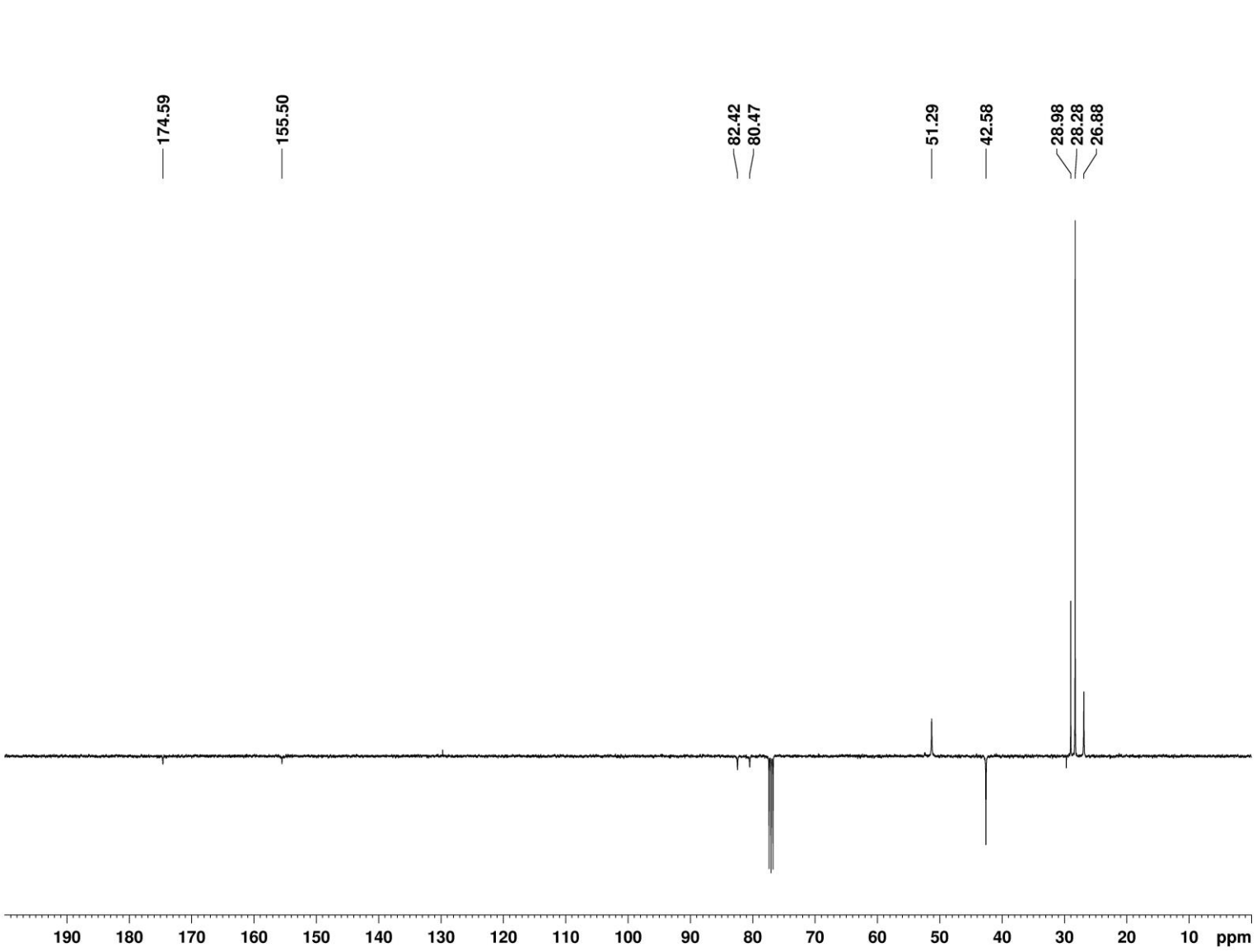
$CDCl_3$, 100 MHz

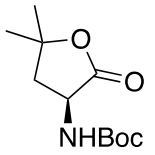




42

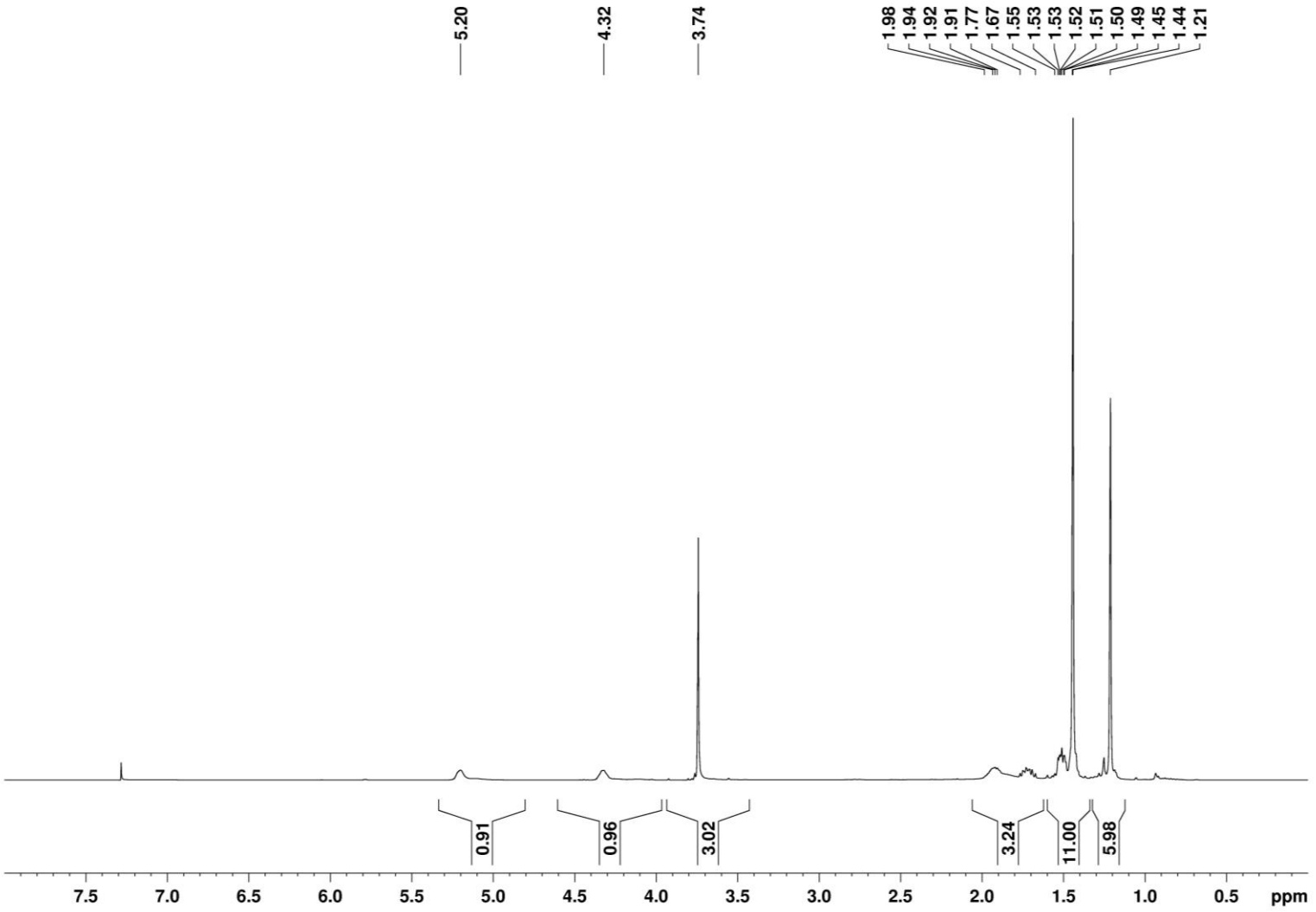
$CDCl_3$, 400 MHz

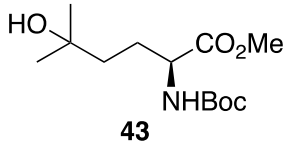




42

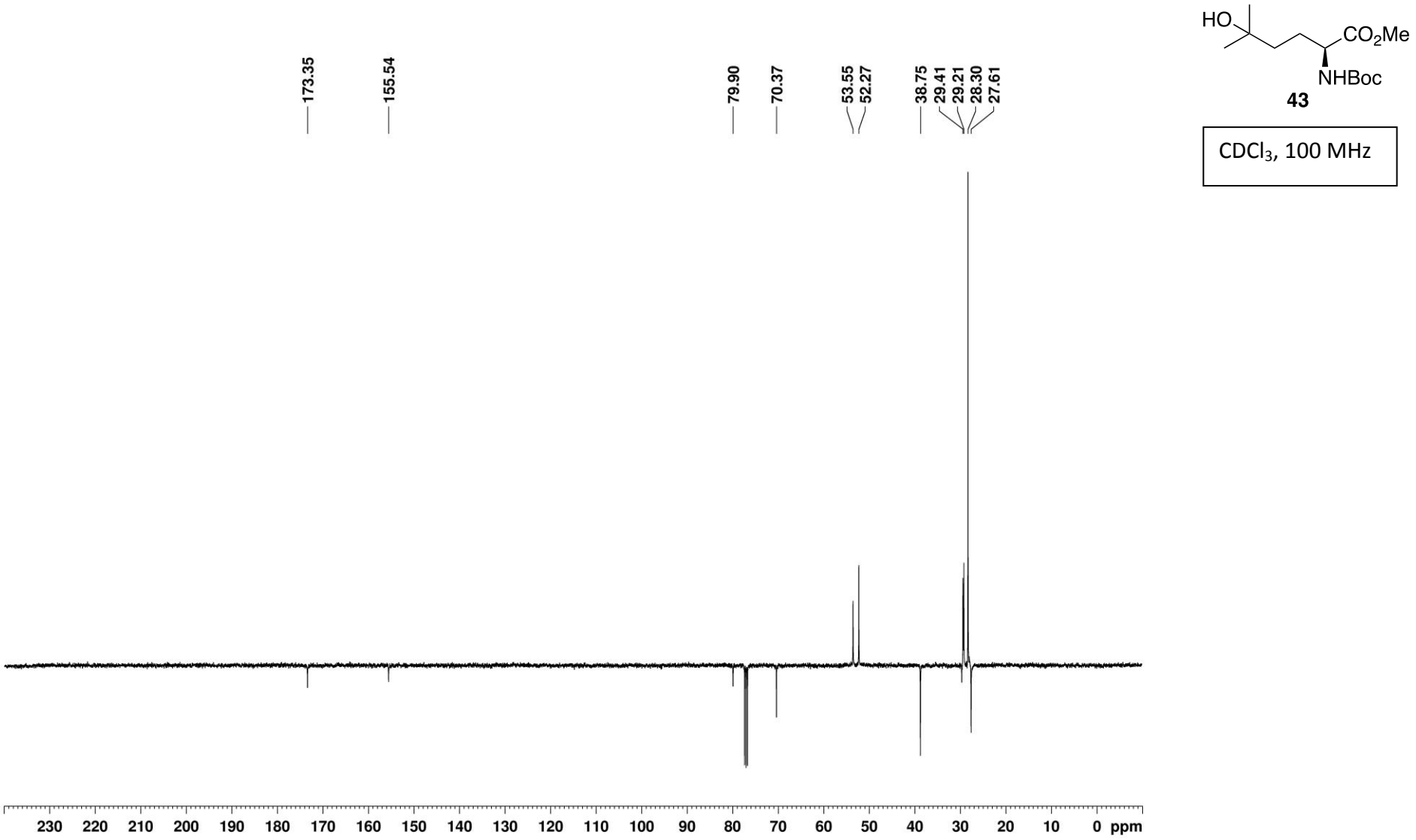
$CDCl_3$, 100 MHz





43

$CDCl_3$, 400 MHz

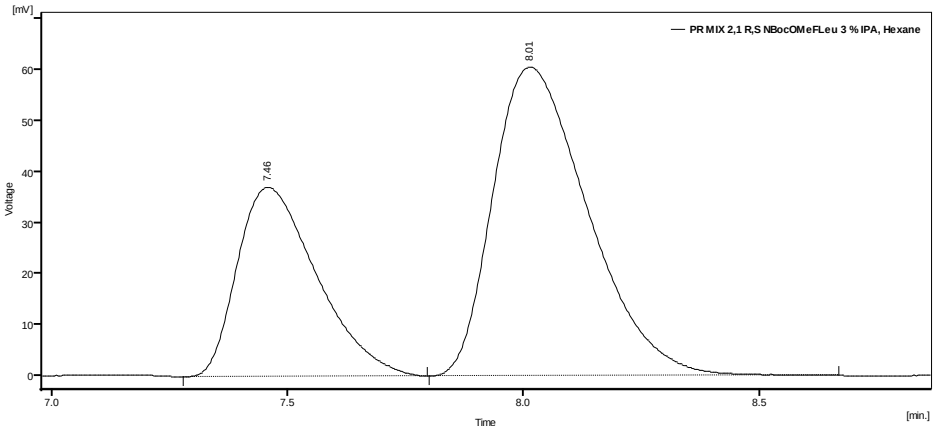


43

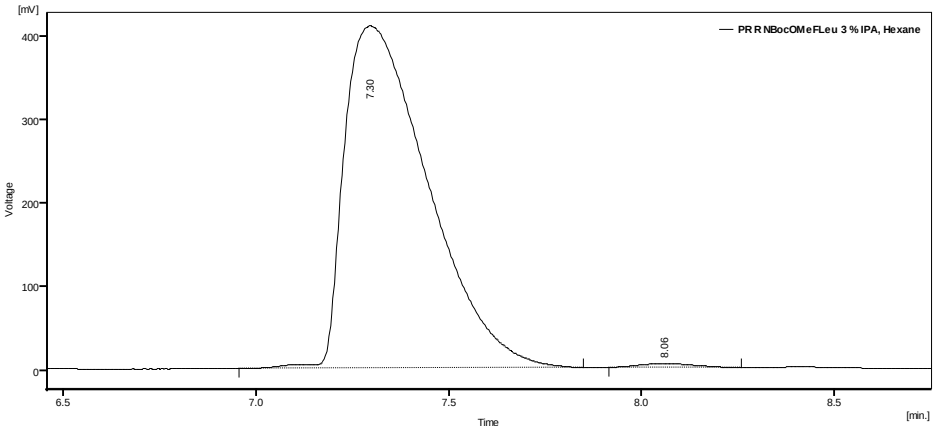
$CDCl_3$, 100 MHz

Chiral HPLC was carried out using a Lux-3u Cellulose-1 250 x 4.6 mm column at room temperature in 3 % isopropanol in hexane with a flow rate of 1 mL min^{-1}. The traces for the 1 : 2 mixture of ***ent*-25** : **25** (Plot 1), enantiomerically pure ***ent*-25** (Plot 2) and enantiomerically pure **25** (Plot 3) are shown.

Plot 1. HPLC trace for a 1 : 2 mixture of ***ent*-25** : **25**.



Plot 2. Chiral HPLC trace for ***ent*-25**.



Plot 3. Chiral HPLC trace for **25**.