

Supporting Information

Direct Synthesis of Secondary Benzylic Alcohols Enabled by Photoredox/Ni Dual-Catalyzed Cross-Coupling

Rauful Alam and Gary A Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,
231 South 34th Street, Philadelphia, Pennsylvania 19104-6323

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

Contents:

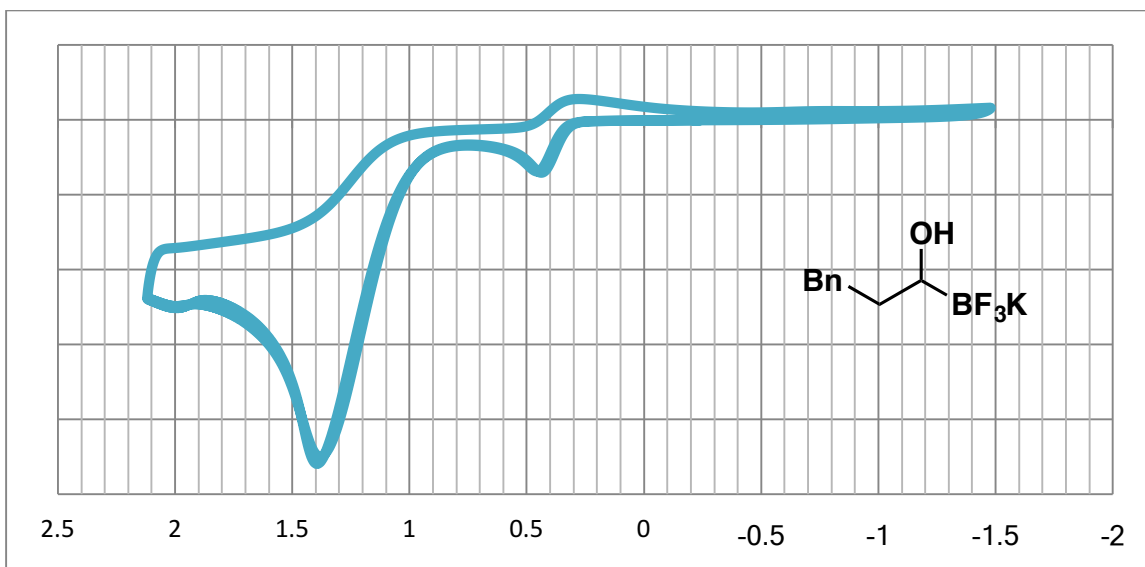
Experimental setup for gram scale reaction of 6a	S2
Cyclic Voltammogram of Compound 3a	S2
^1H , ^{13}C , ^{11}B , ^{19}F NMR Spectra	S3-S50

Gram scale reaction for the synthesis of 6a:

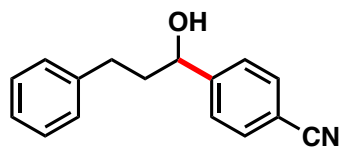


Figure A: 1. Reaction components were added to a Schlenk tube and then purged/evacuated with N_2 . **2.** Reaction mixture in dioxane. **3.** Schlenk tube was placed in blue LED chamber while a fan was placed at the top to keep the temperature nearly at $25\text{ }^\circ\text{C}$. **4.** Reaction mixture after 24 h. **5.** Isolated compound.

Cyclic Voltammogram of α -Hydroxyalkyltrifluoroborate 3a: Voltammetric measurements were recorded using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as an internal reference ($E_{1/2}^0 = +0.40\text{ V}$ vs SCE) and Bu_4NPF_6 as the electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.001 V at a scan rate of 0.5 V/s.



H NMR of compound **6a** (CDCl₃, 500 MHz)

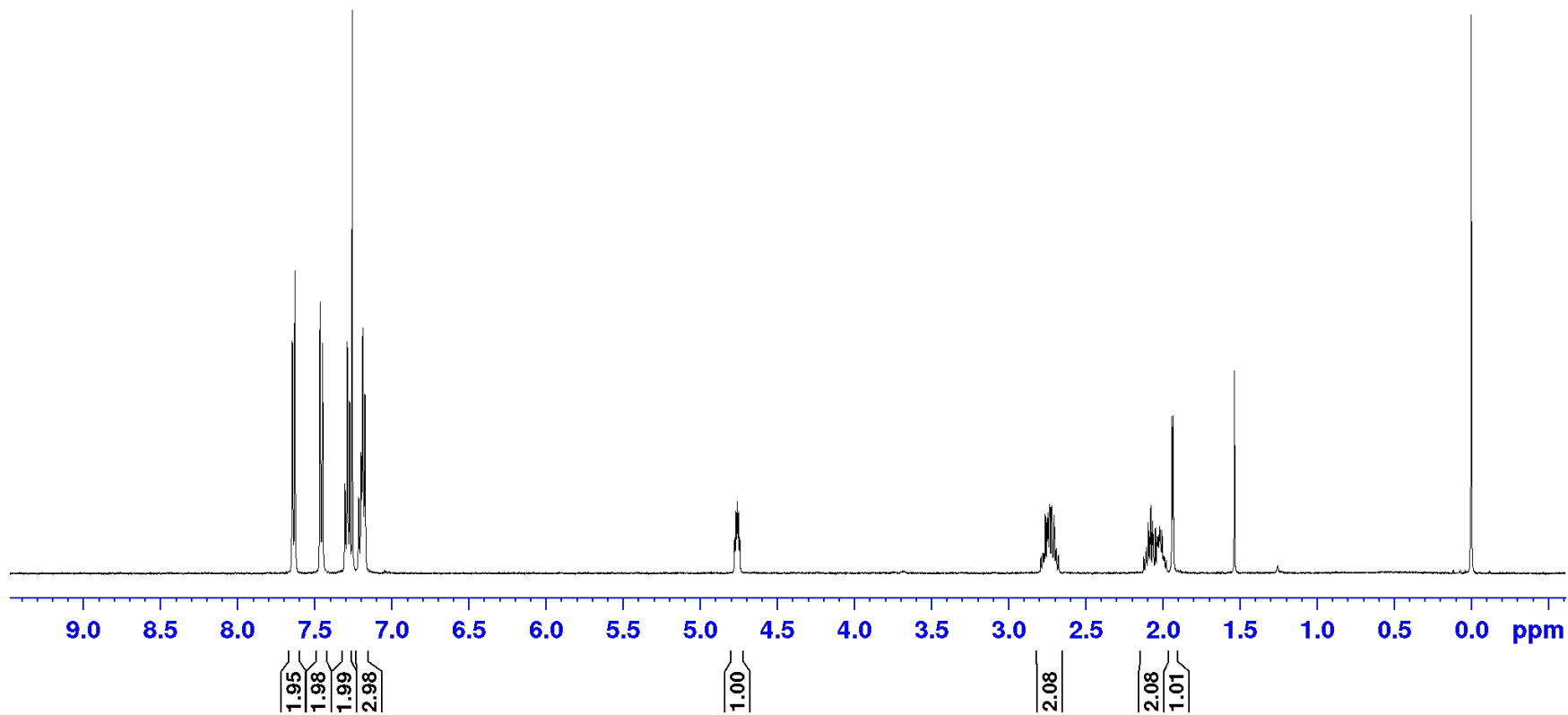


7.65
7.63
7.47
7.45
7.30
7.27
7.22
7.17

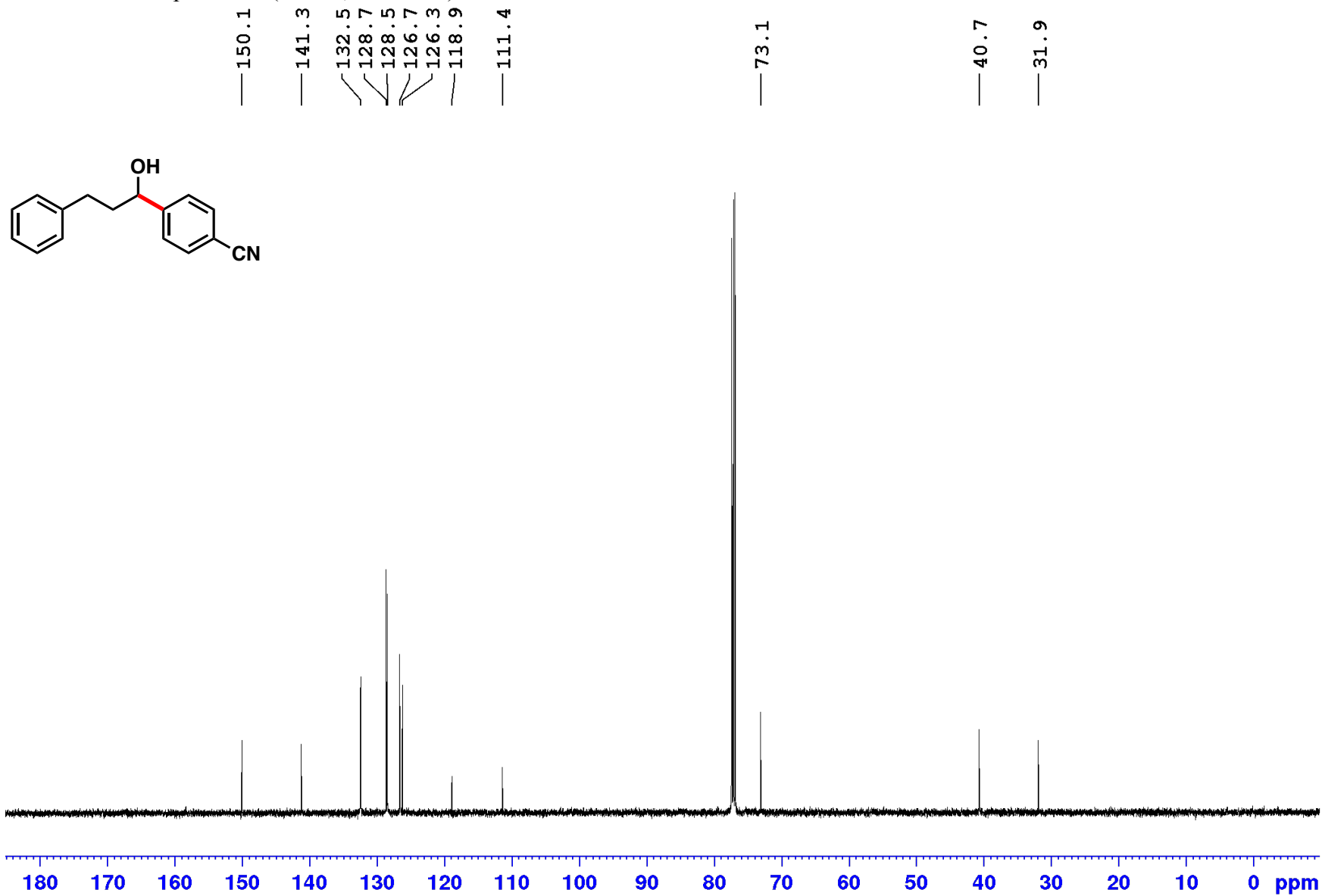
4.78
4.74

2.79
2.68

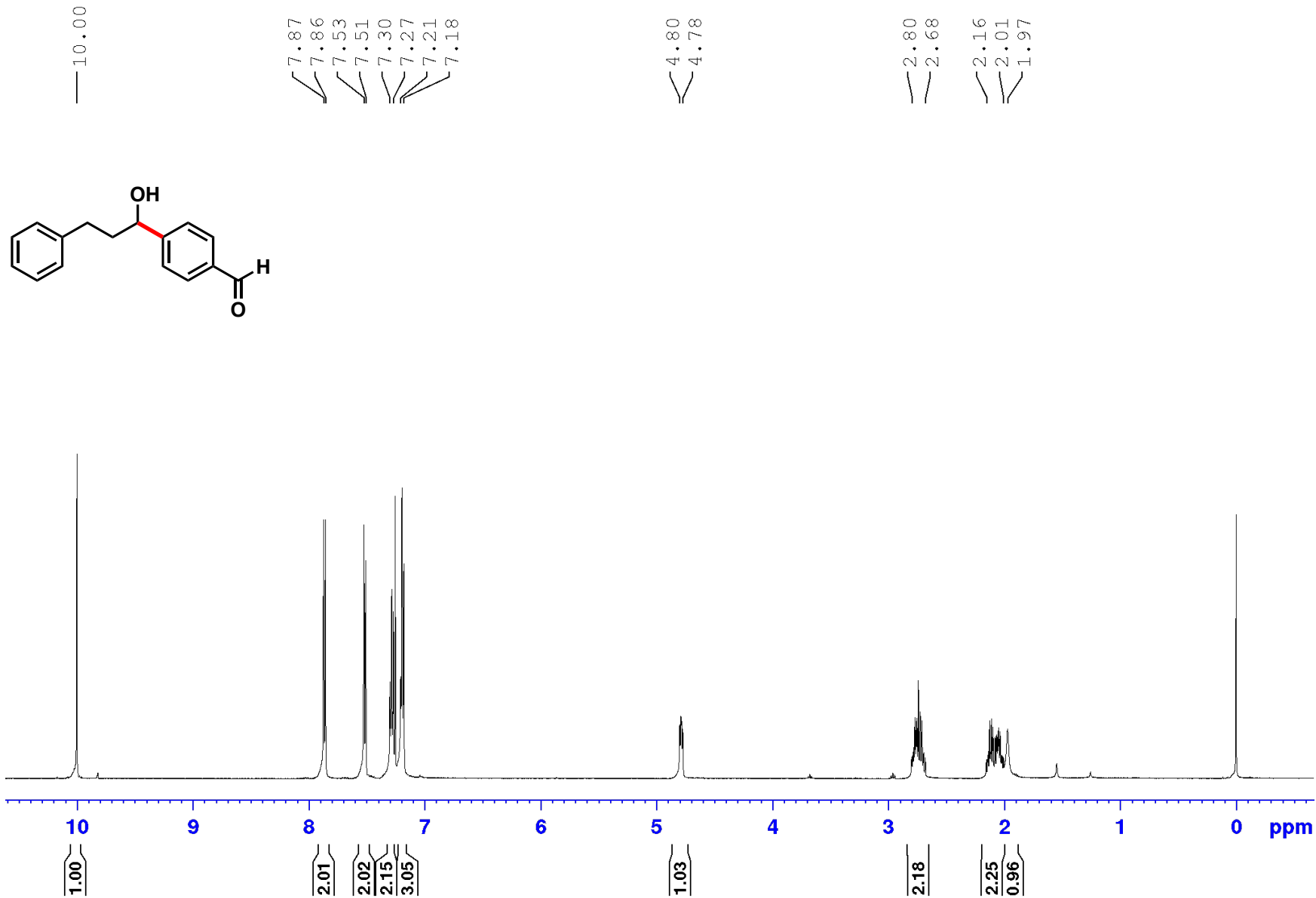
2.12
1.98
1.94
1.93



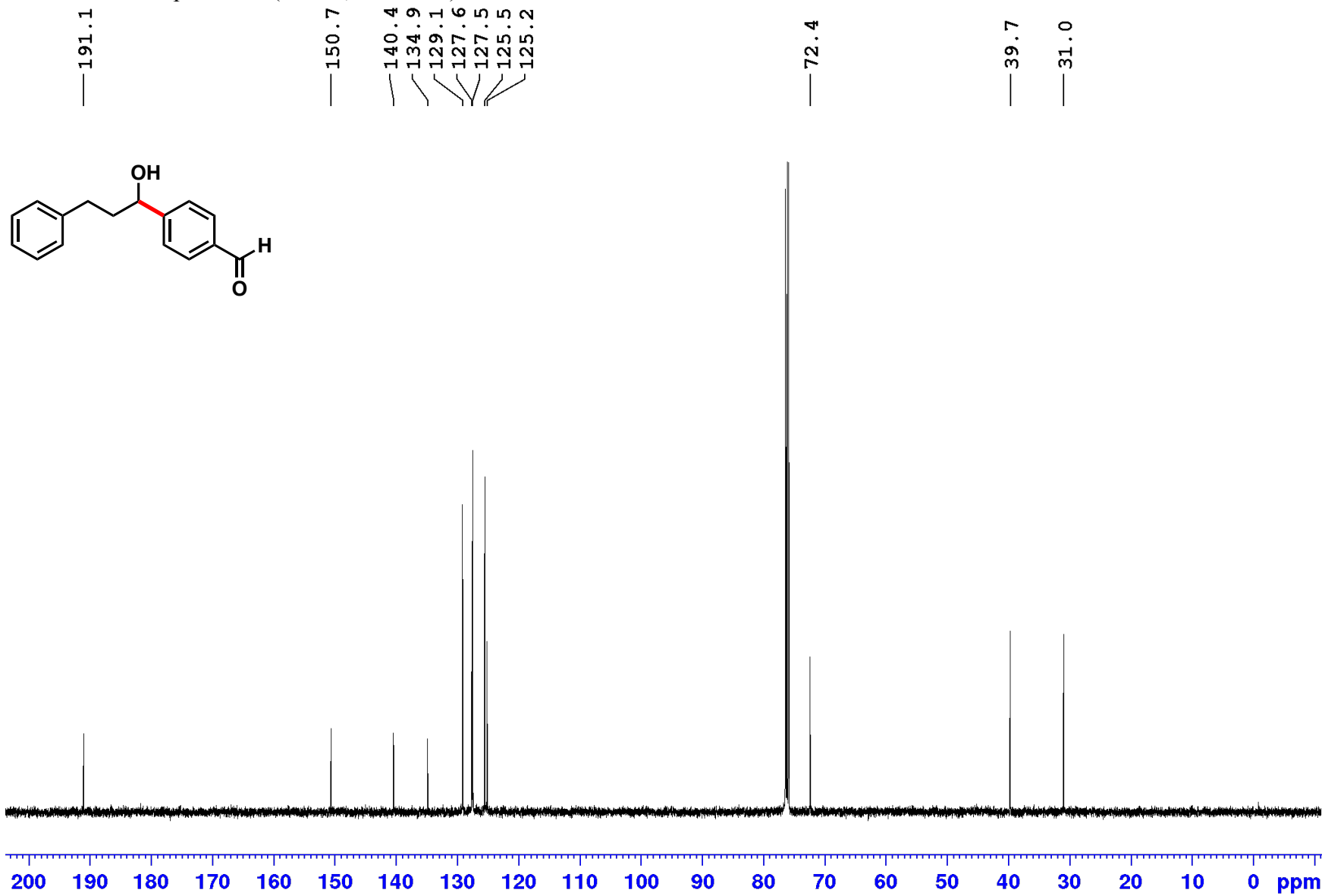
^{13}C NMR of compound **6a** (CDCl_3 , 125 MHz)



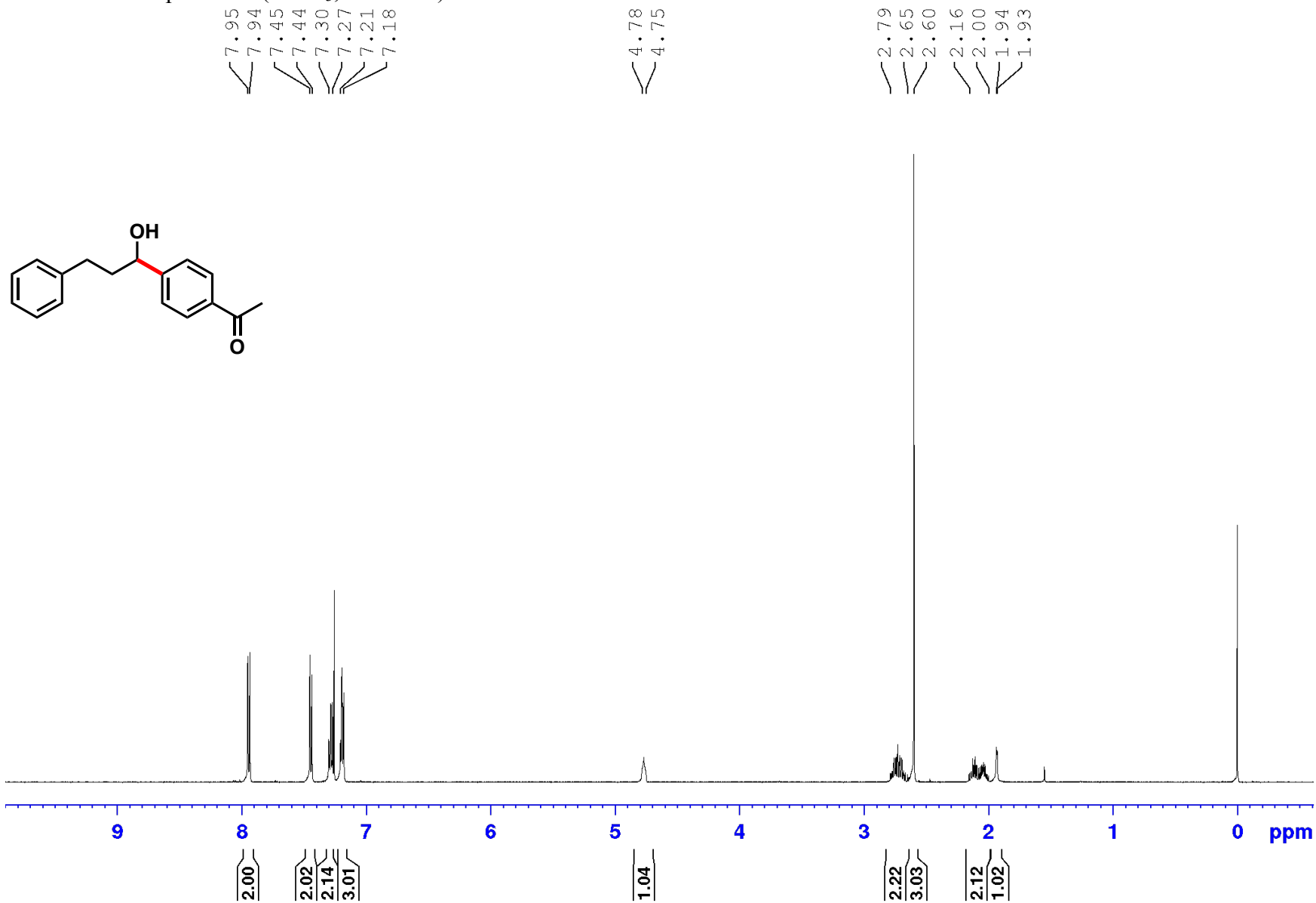
^1H NMR of compound **6b** (CDCl_3 , 500 MHz)



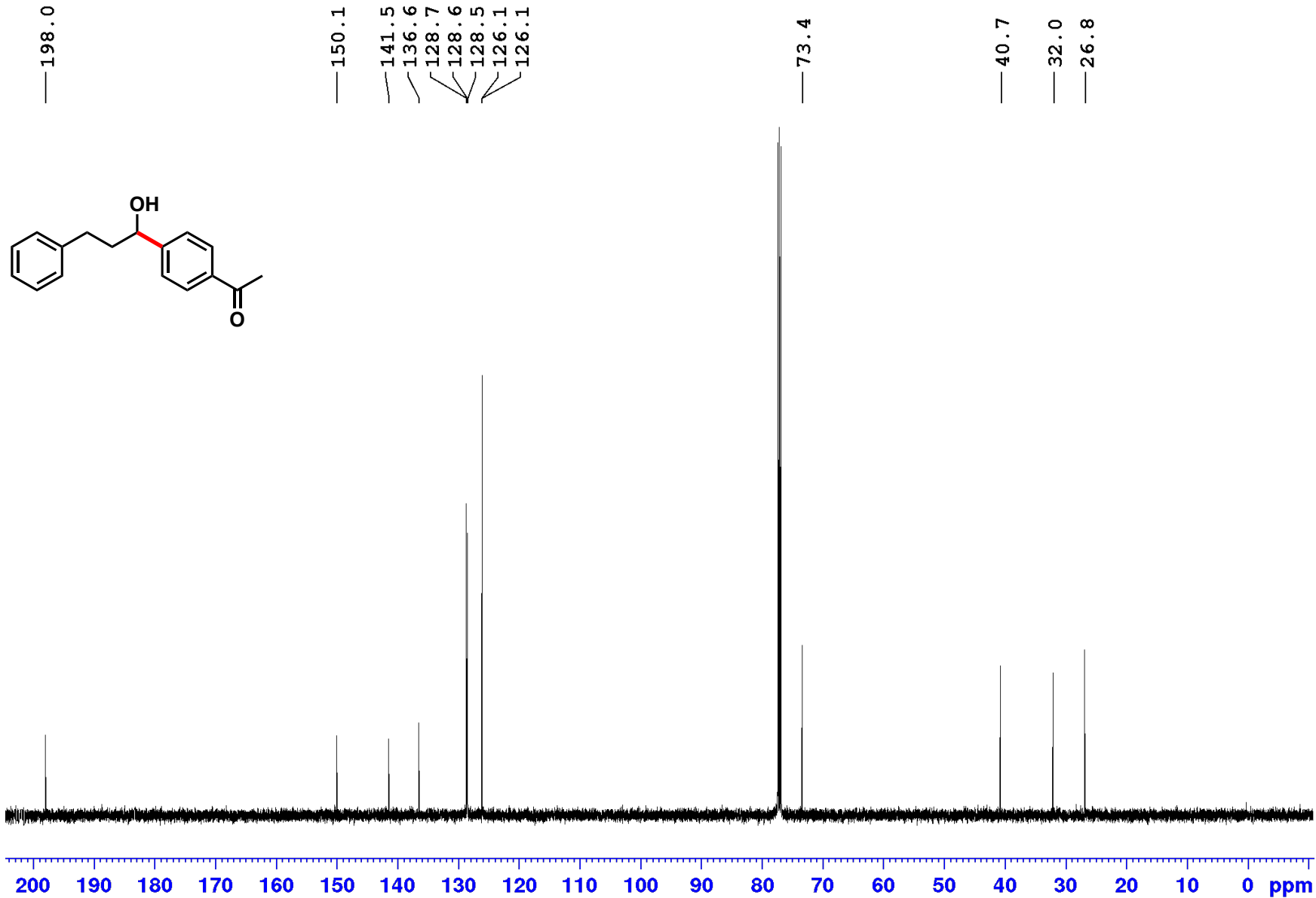
^{13}C NMR of compound **6b** (CDCl_3 , 125 MHz)



^1H NMR of compound **6c** (CDCl_3 , 500 MHz)



^{13}C NMR of compound **6c** (CDCl_3 , 125 MHz)



^1H NMR of compound **6d** (CDCl_3 , 500 MHz)

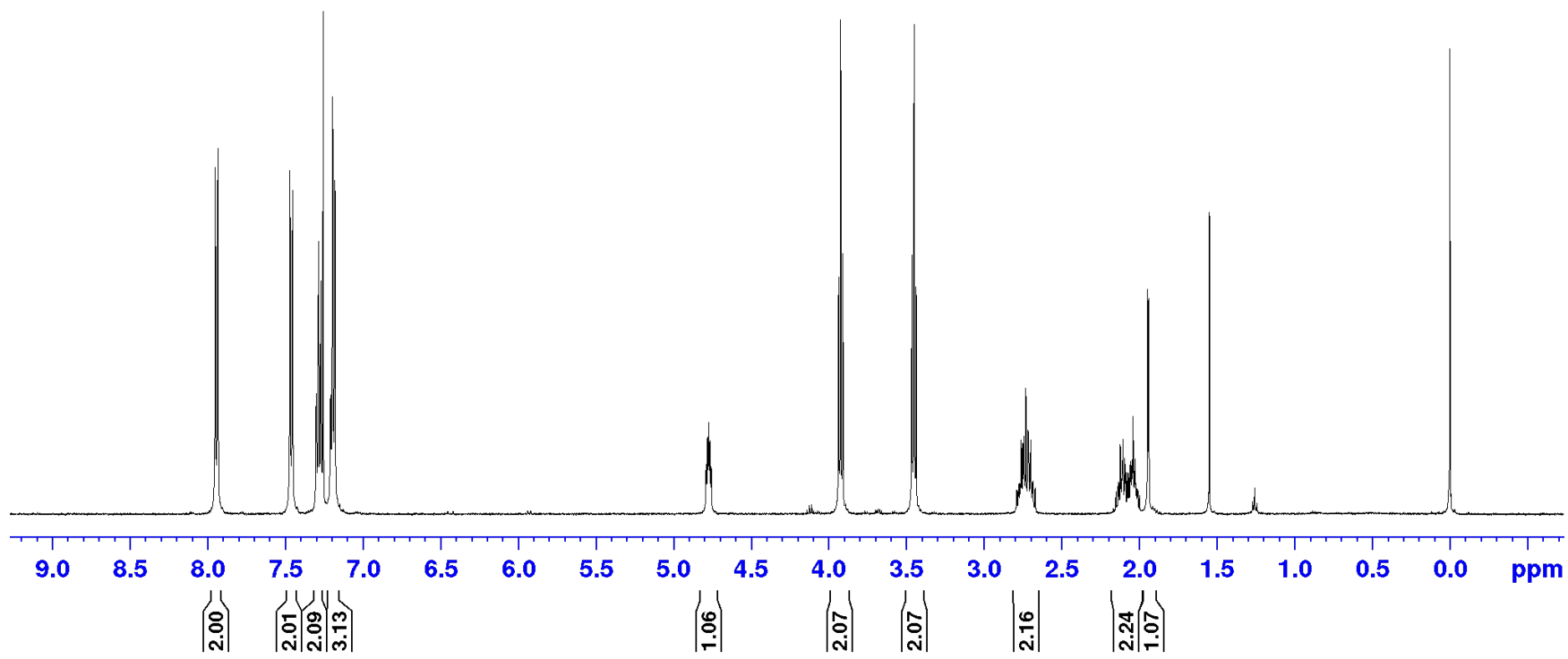
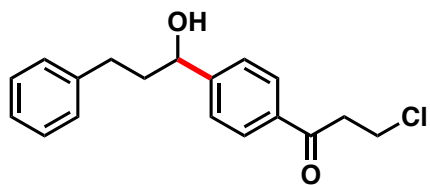
7.95
7.94
7.47
7.45
7.30
7.27
7.21
7.18

4.79
4.76

3.94
3.92
3.91
3.46
3.45
3.44

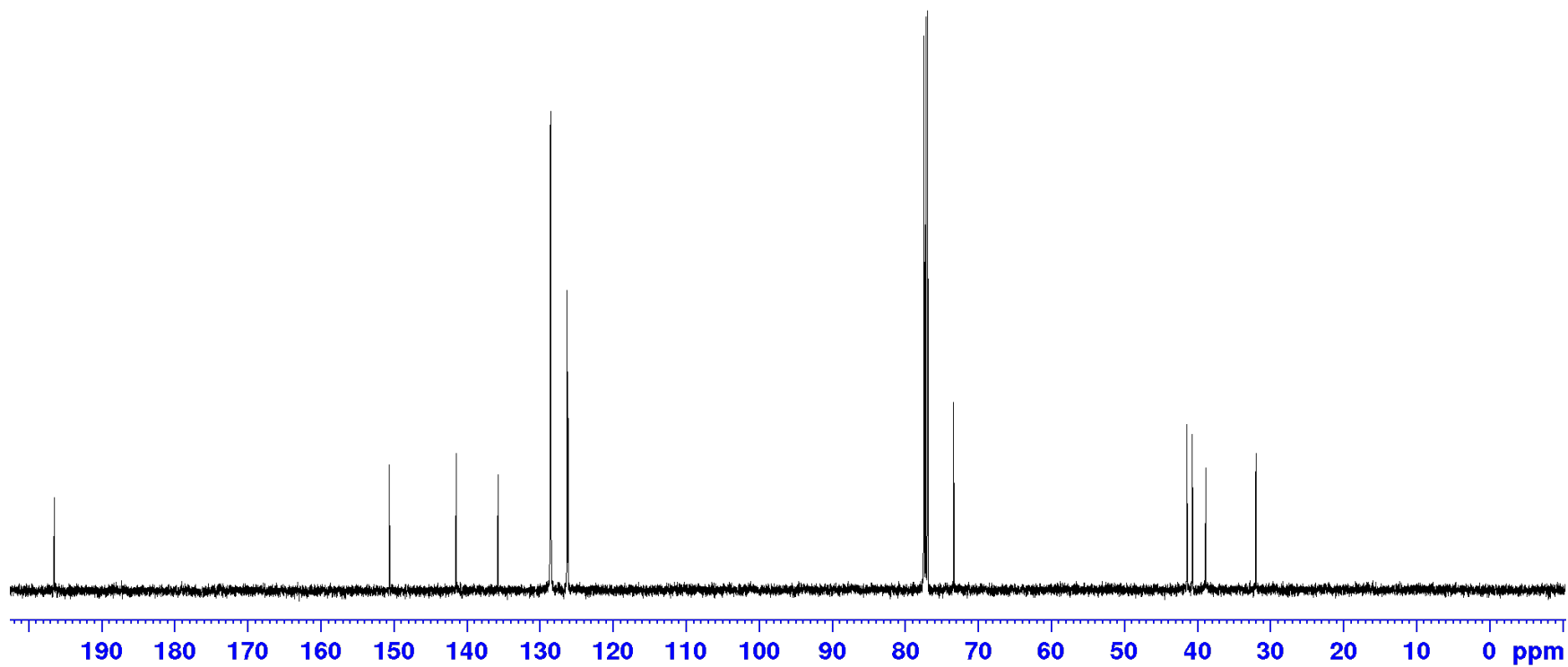
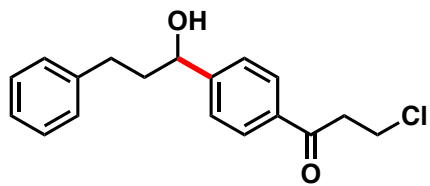
2.79
2.67

2.15
2.00
1.95
1.94

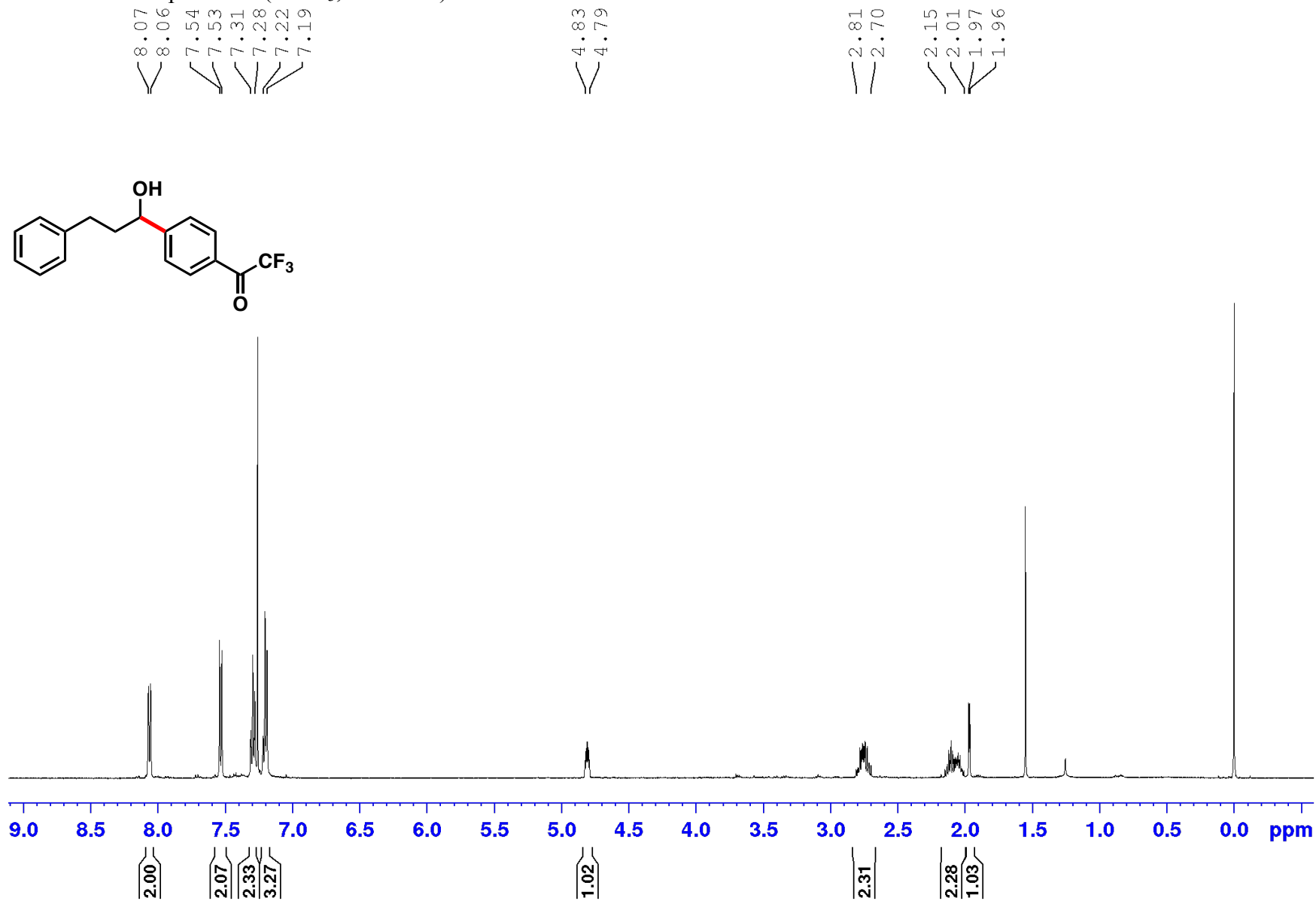


^{13}C NMR of compound **6d** (CDCl_3 , 125 MHz)

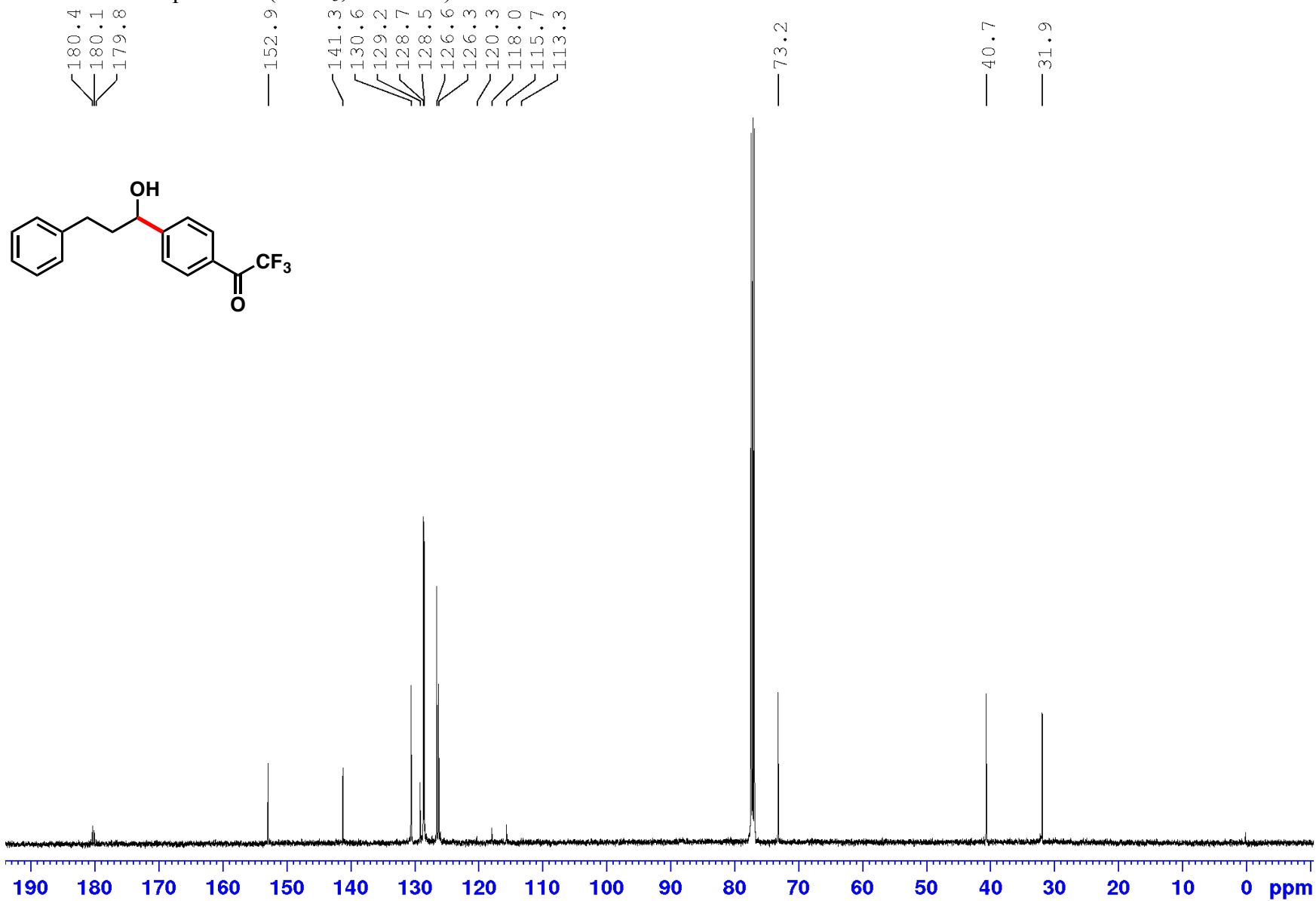
— 196.5
— 150.6
— 141.5
— 135.7
— 128.6
— 128.5
— 128.5
— 126.3
— 126.2
— 73.3
— 41.4
— 40.6
— 38.8
— 32.0



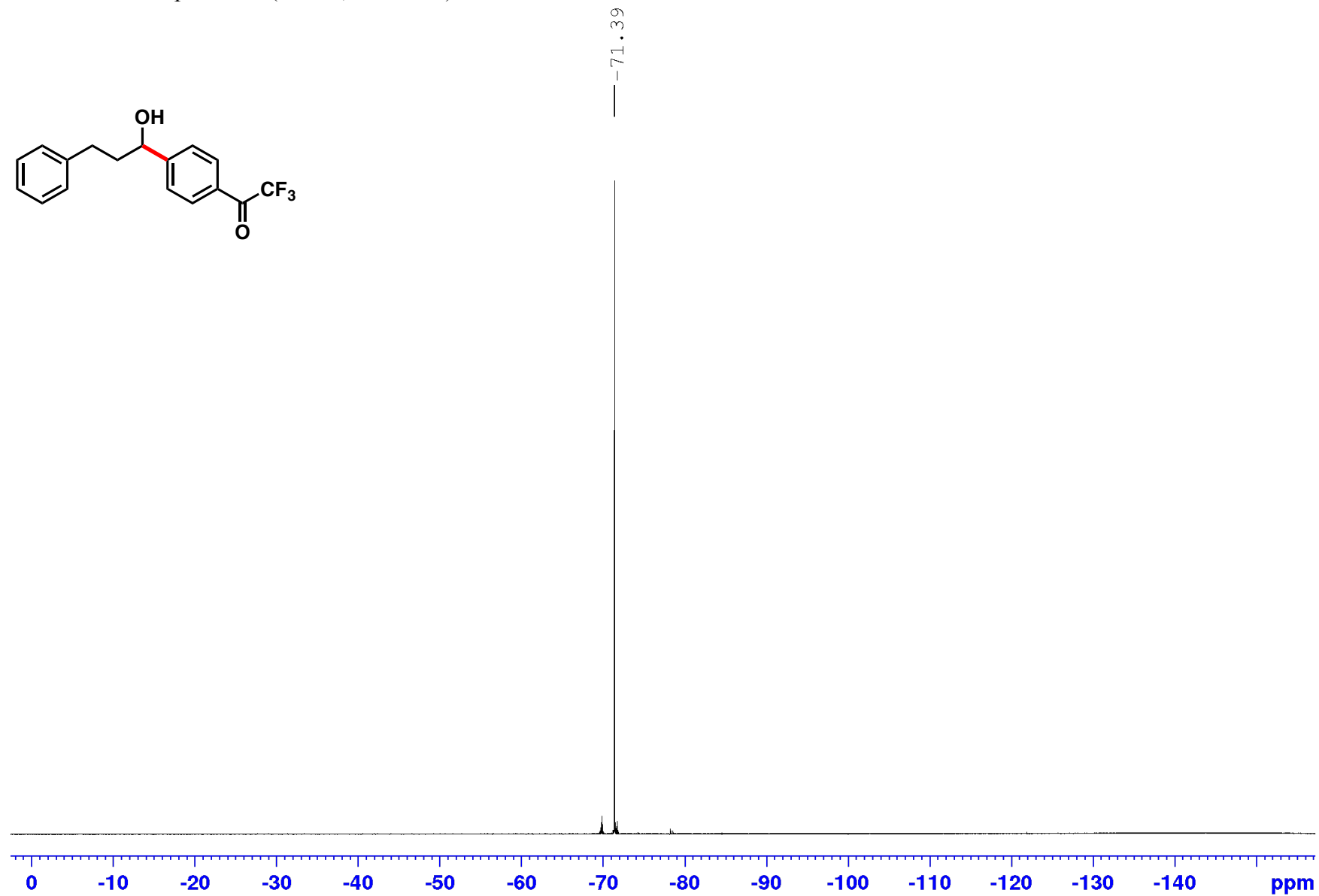
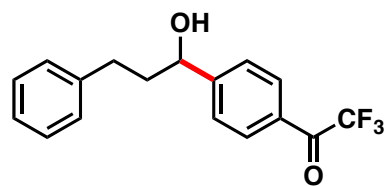
¹H NMR of compound **6e** (CDCl₃, 500 MHz)



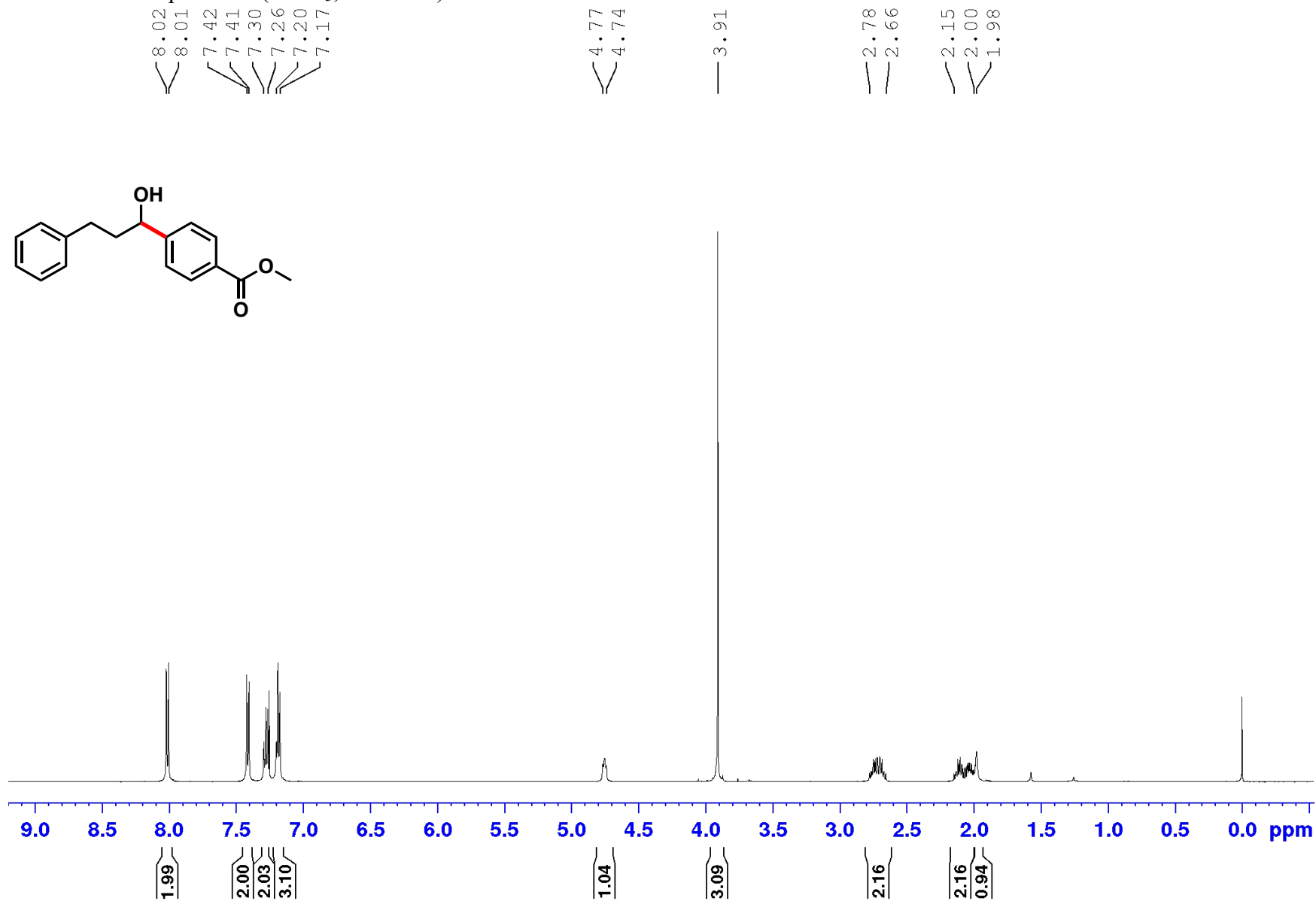
¹³C NMR of compound **6e** (CDCl₃, 125 MHz)



^{19}F NMR of compound **6e** (CDCl_3 , 471 MHz)



^1H NMR of compound **6f** (CDCl_3 , 500 MHz)

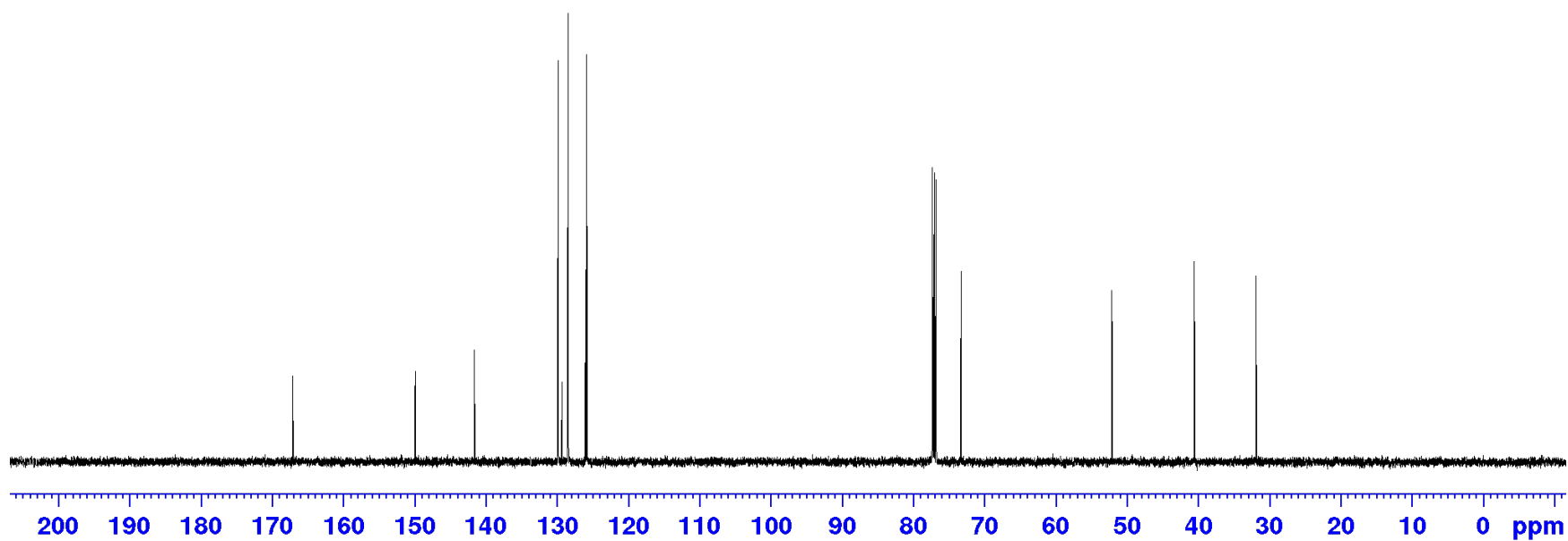
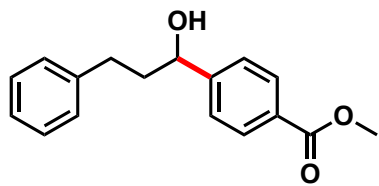


^{13}C NMR of compound **6f** (CDCl_3 , 125 MHz)

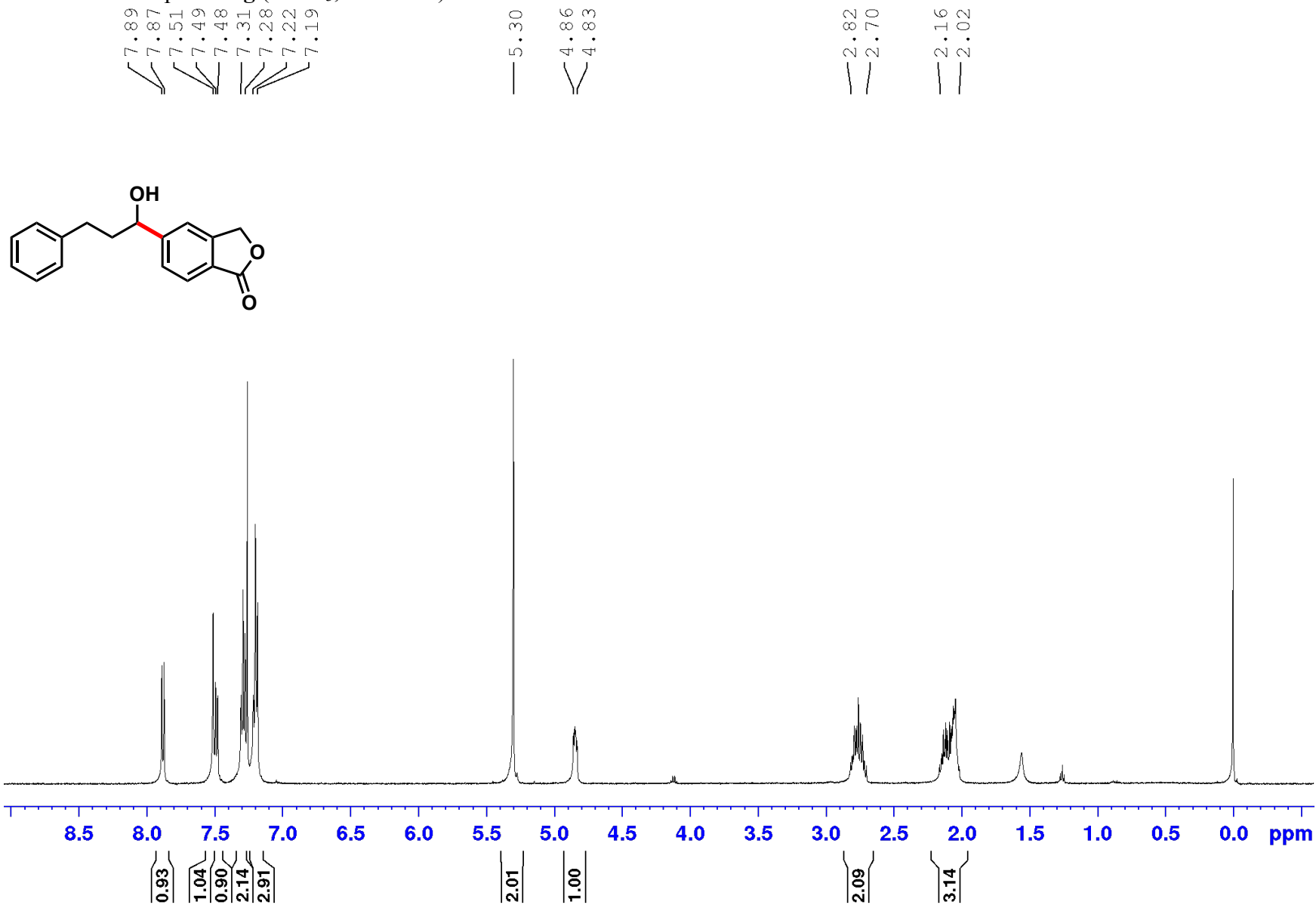
— 167.1
— 149.9
— 141.6
— 129.9
— 129.4
— 128.6
— 128.5
— 126.1
— 125.9

— 73.4

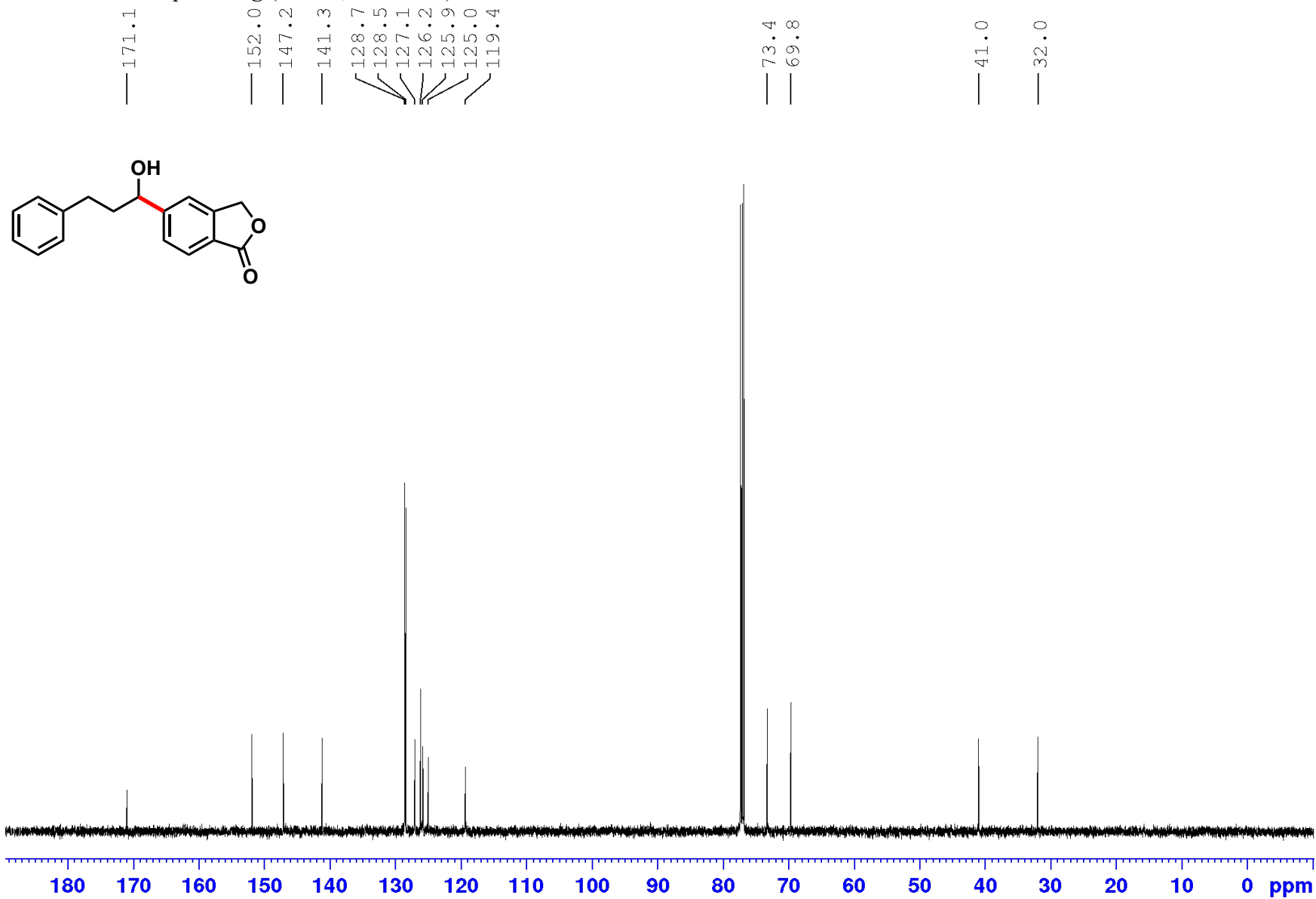
— 52.2
— 40.6
— 32.0



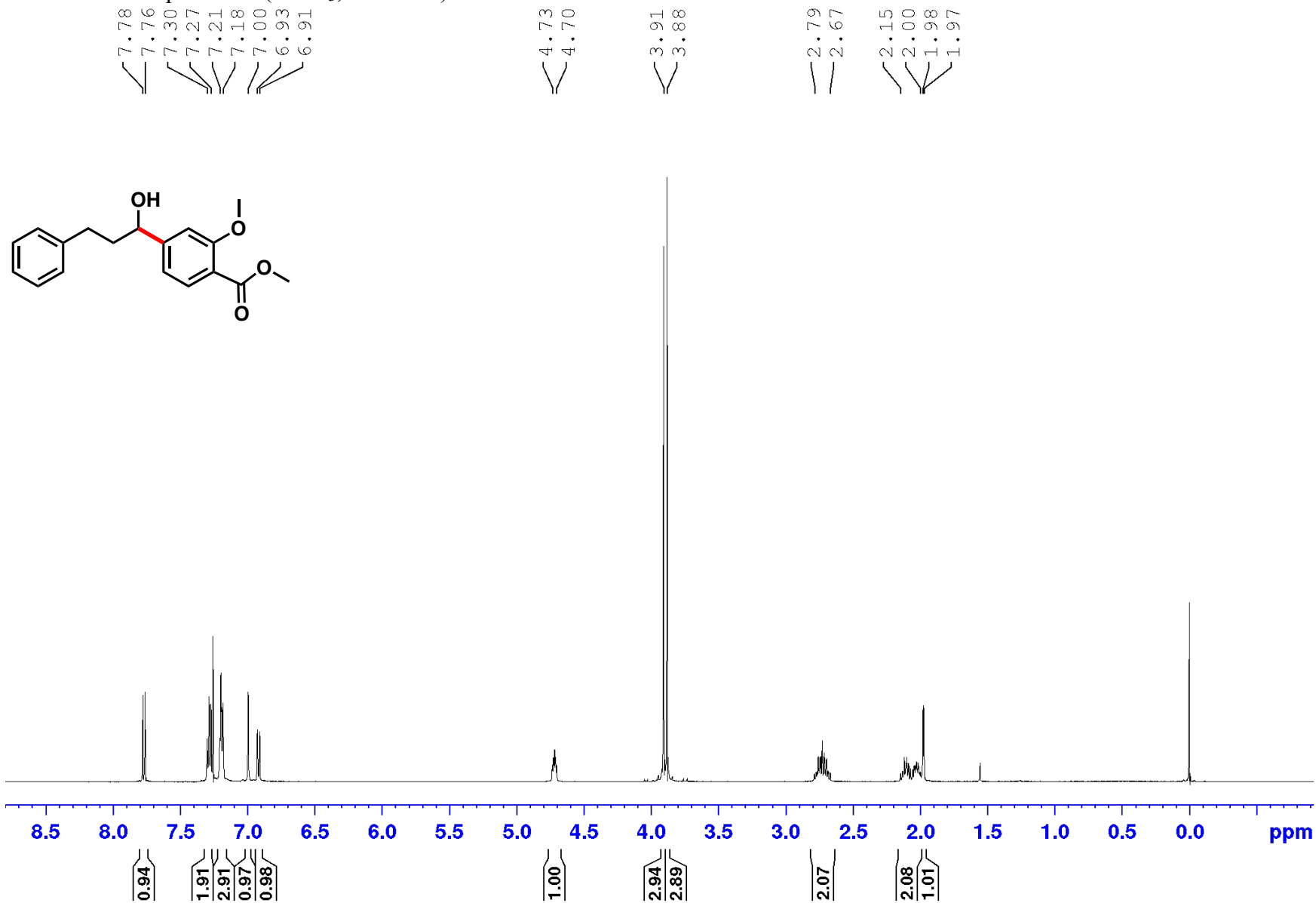
¹H NMR of compound **6g** (CDCl₃, 500 MHz)



^{13}C NMR of compound **6g** (CDCl_3 , 125 MHz)



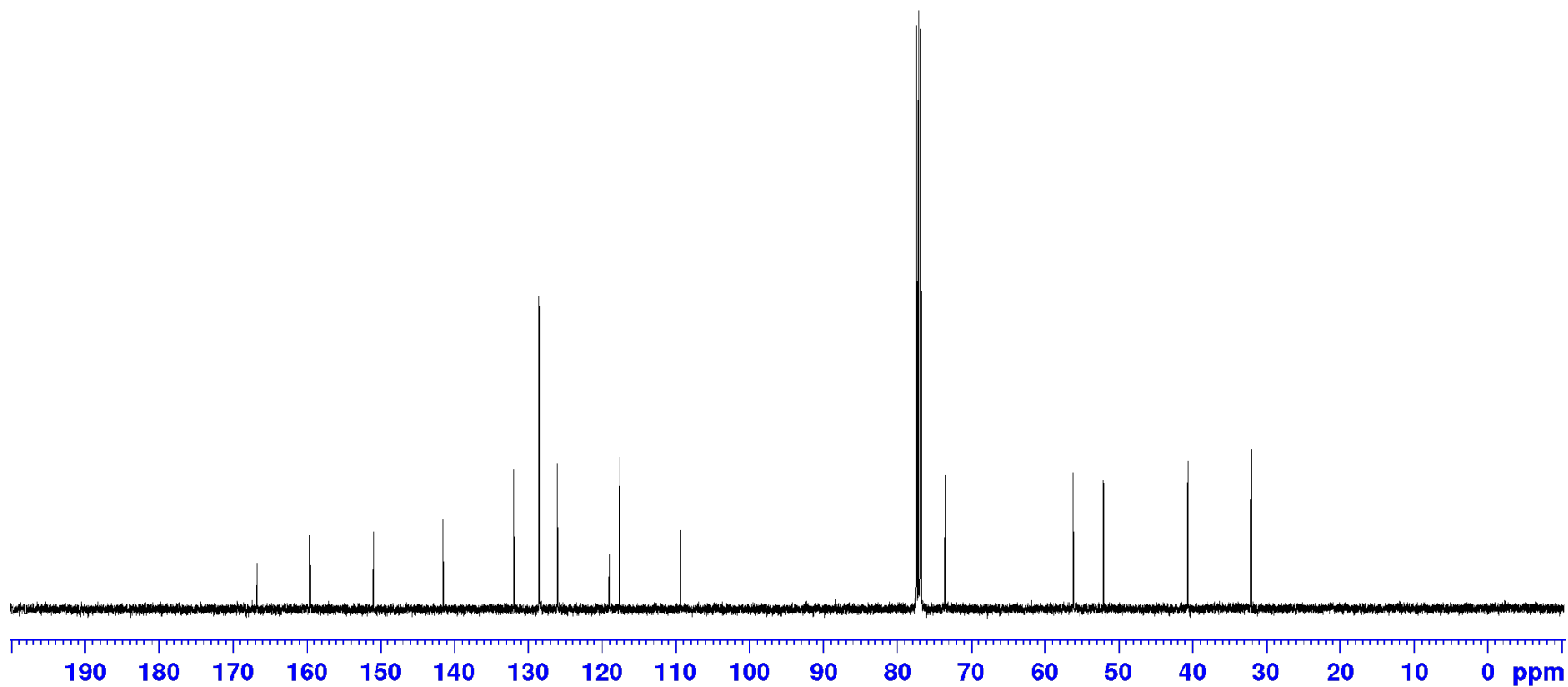
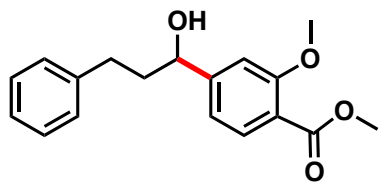
¹H NMR of compound **6h** (CDCl₃, 500 MHz)



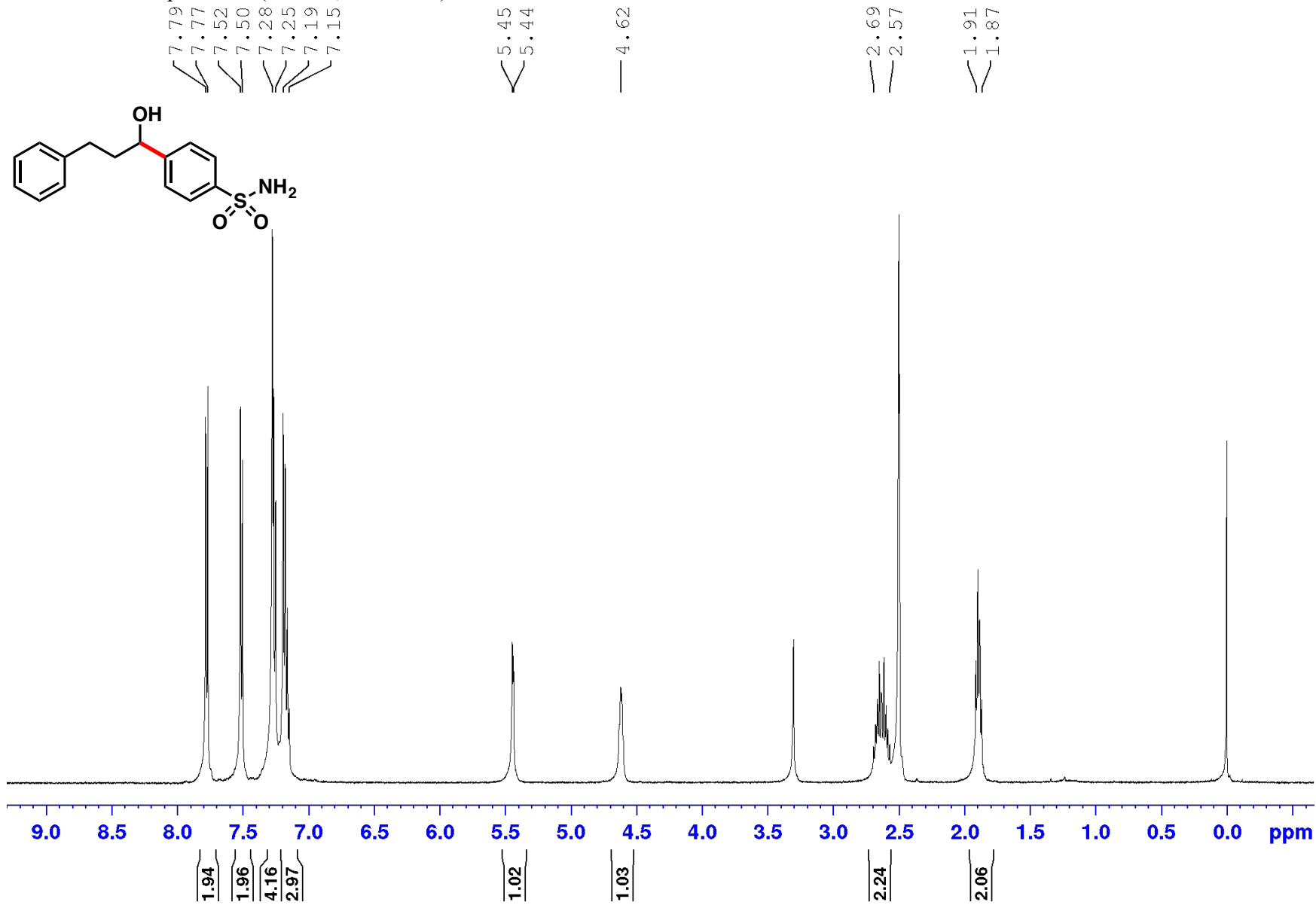
¹³C NMR of compound **6h** (CDCl₃, 125 MHz)

— 166.6
— 159.6
— 151.0
— 141.6
— 132.0
— 128.6
— 128.6
— 126.1
— 119.1
— 117.7
— 109.5

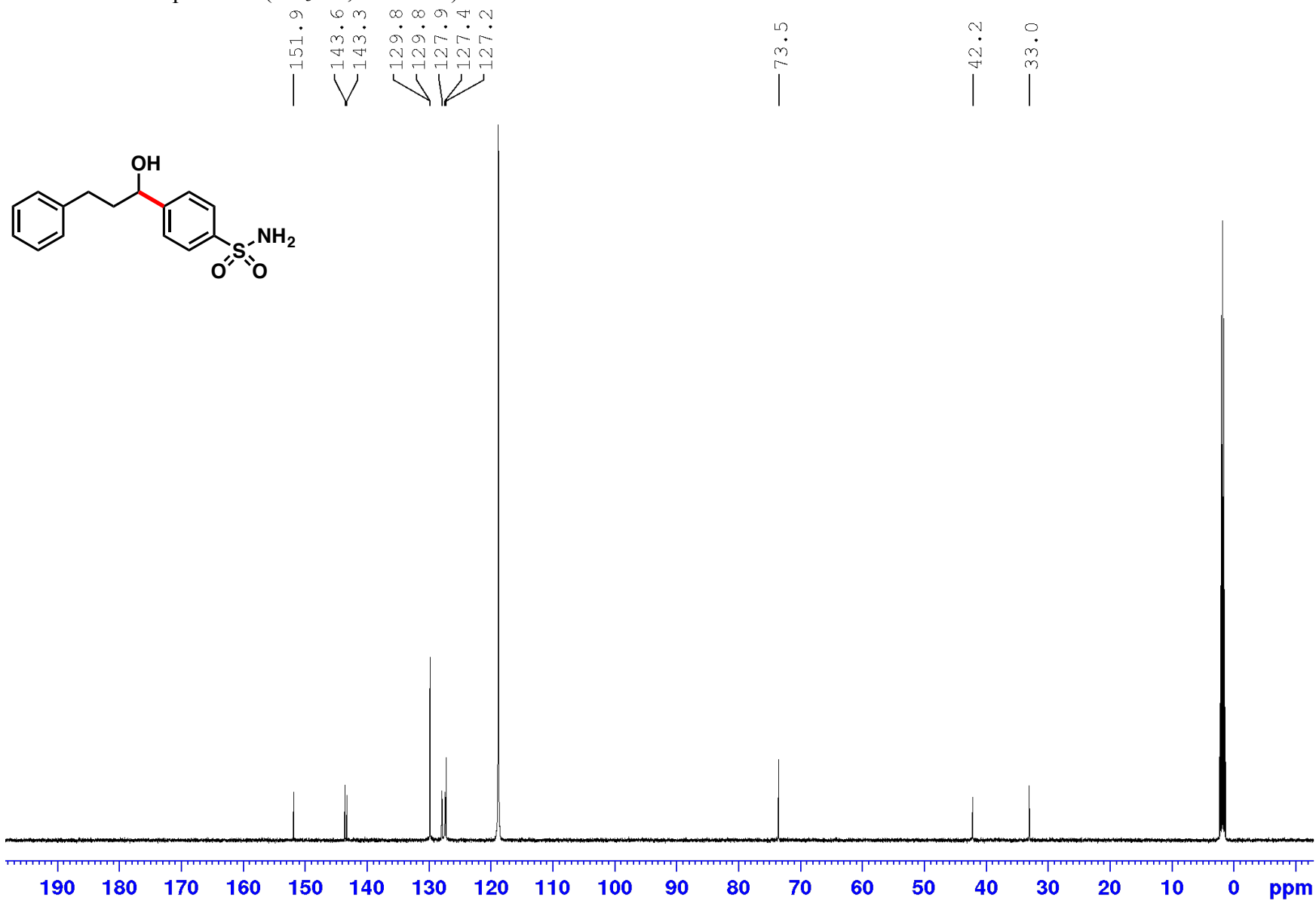
— 73.5
— 56.2
— 52.1
— 40.6
— 32.0



¹H NMR of compound **6i** (DMSO, 500 MHz)



^{13}C NMR of compound **6i** (CD_3CN , 125 MHz)



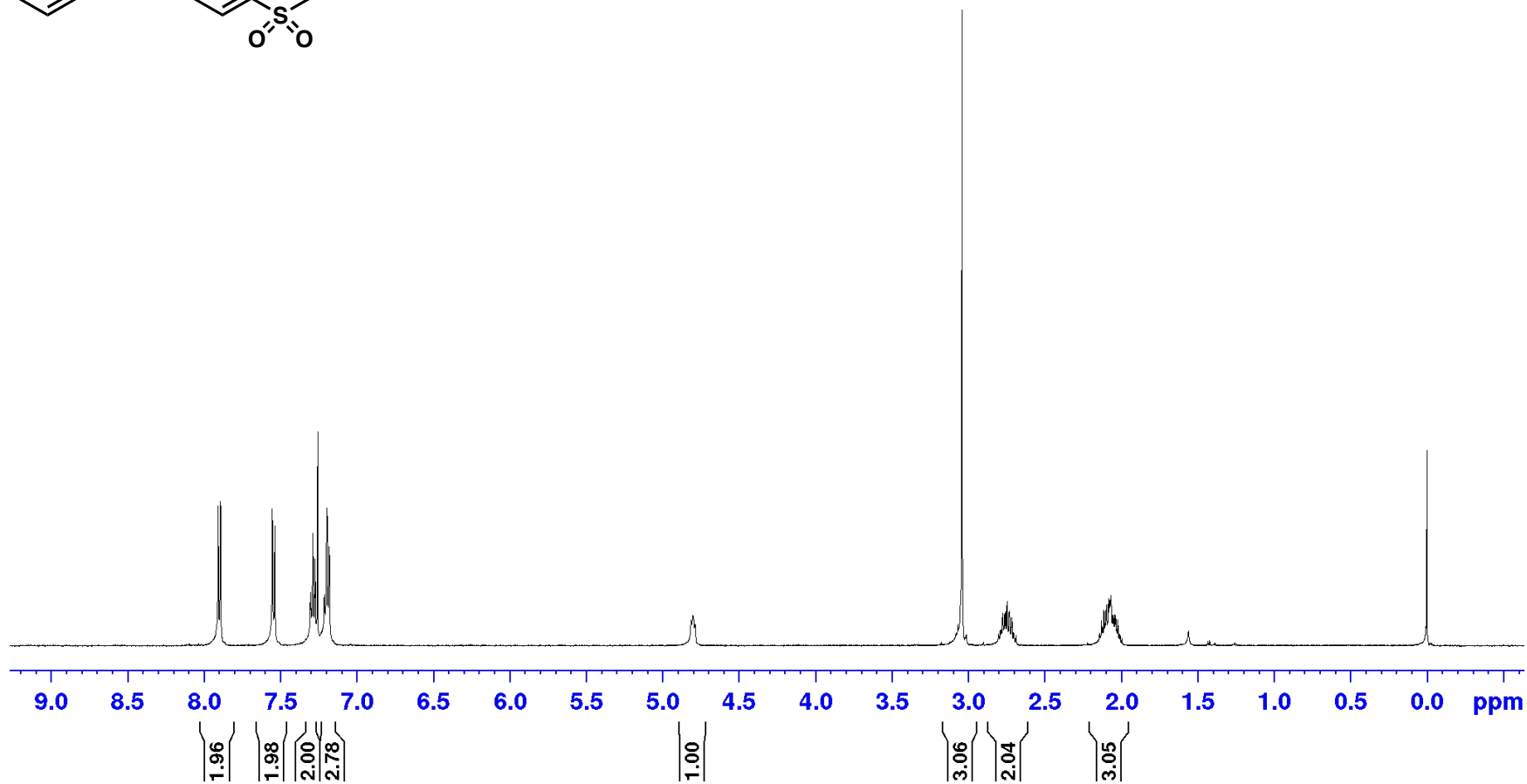
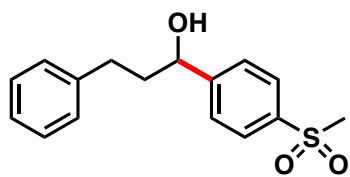
¹H NMR of compound **6j** (CDCl₃, 500 MHz)

7.91
7.89
7.55
7.54
7.30
7.27
7.21
7.18

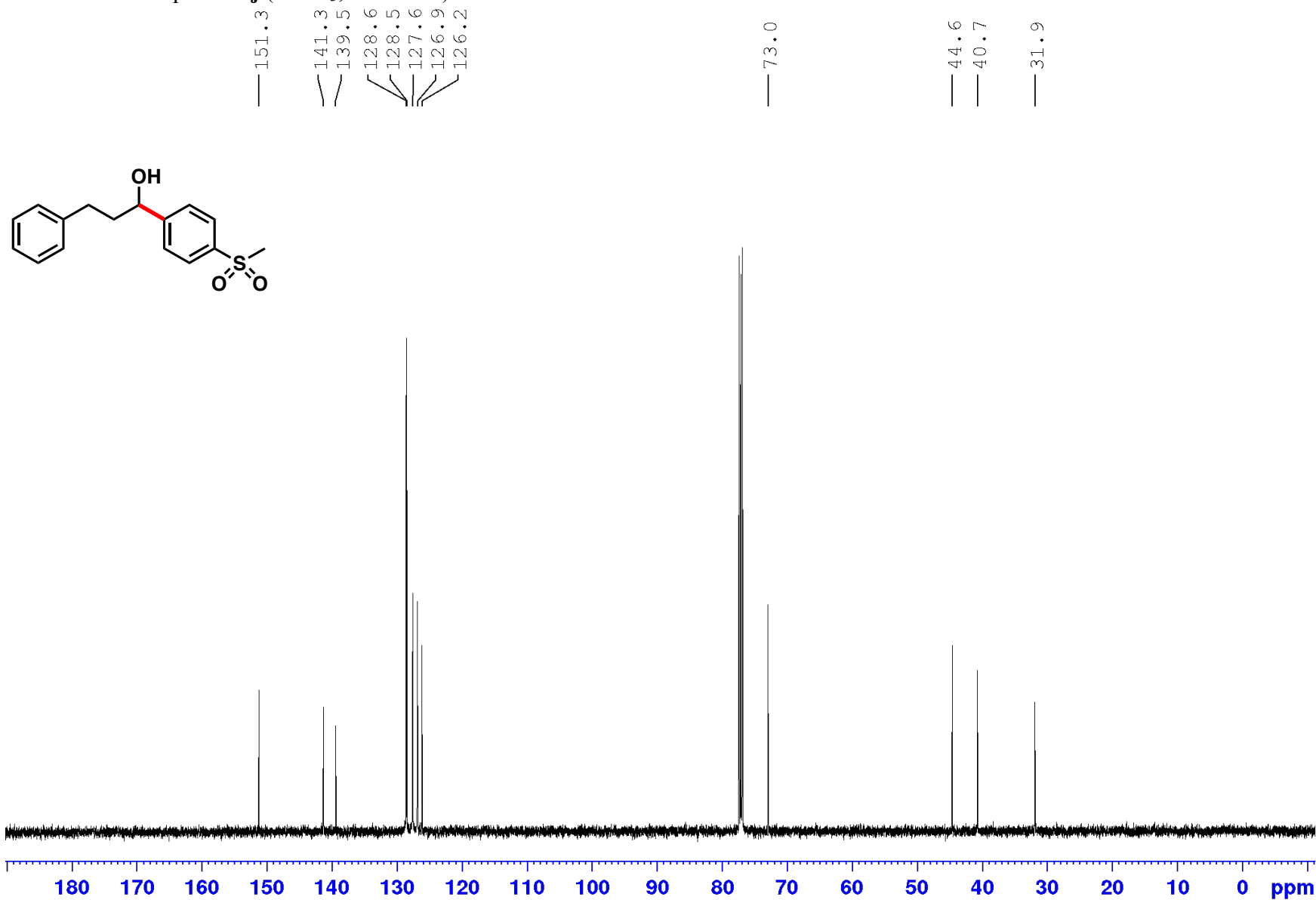
4.81
4.79

3.04
2.80
2.69

2.14
2.00



^{13}C NMR of compound **6j** (CDCl_3 , 125 MHz)



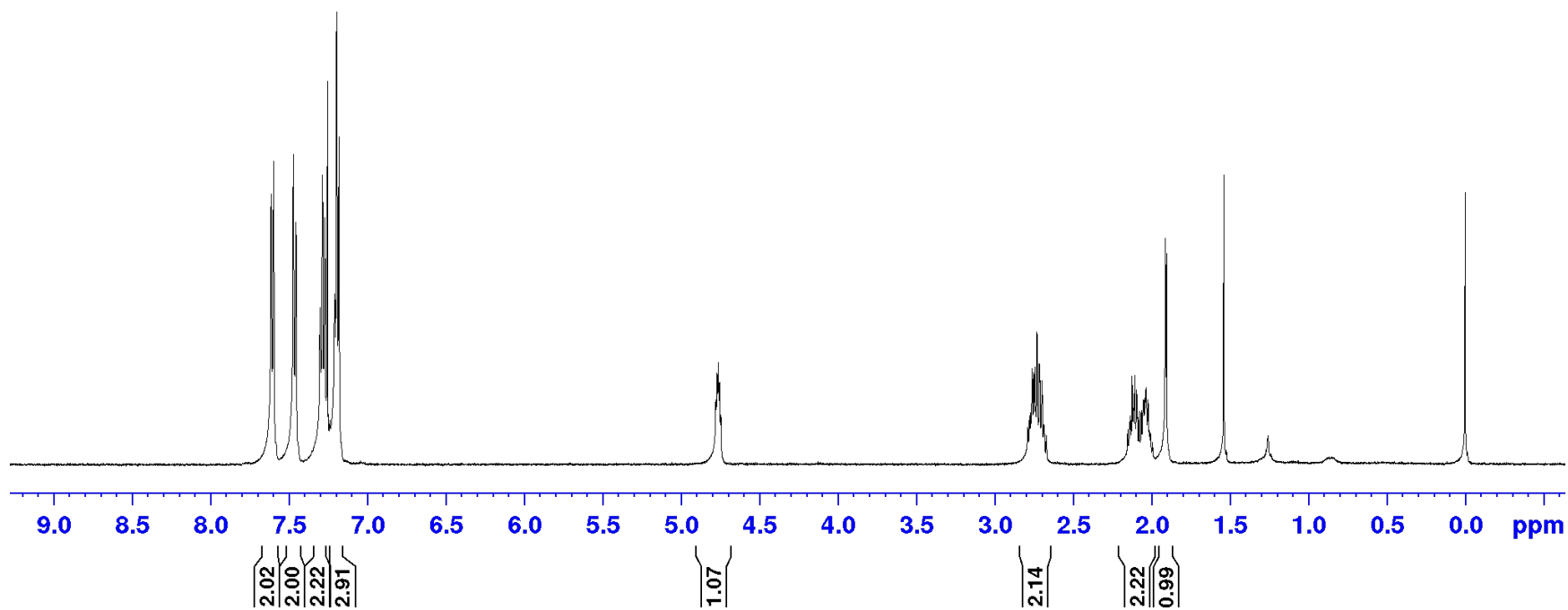
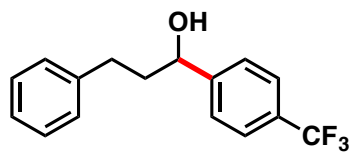
¹H NMR of compound **6k** (CDCl₃, 500 MHz)

7.61
7.60
7.47
7.46
7.30
7.27
7.21
7.18

4.78
4.75

2.79
2.67

2.15
1.99
1.91
1.90



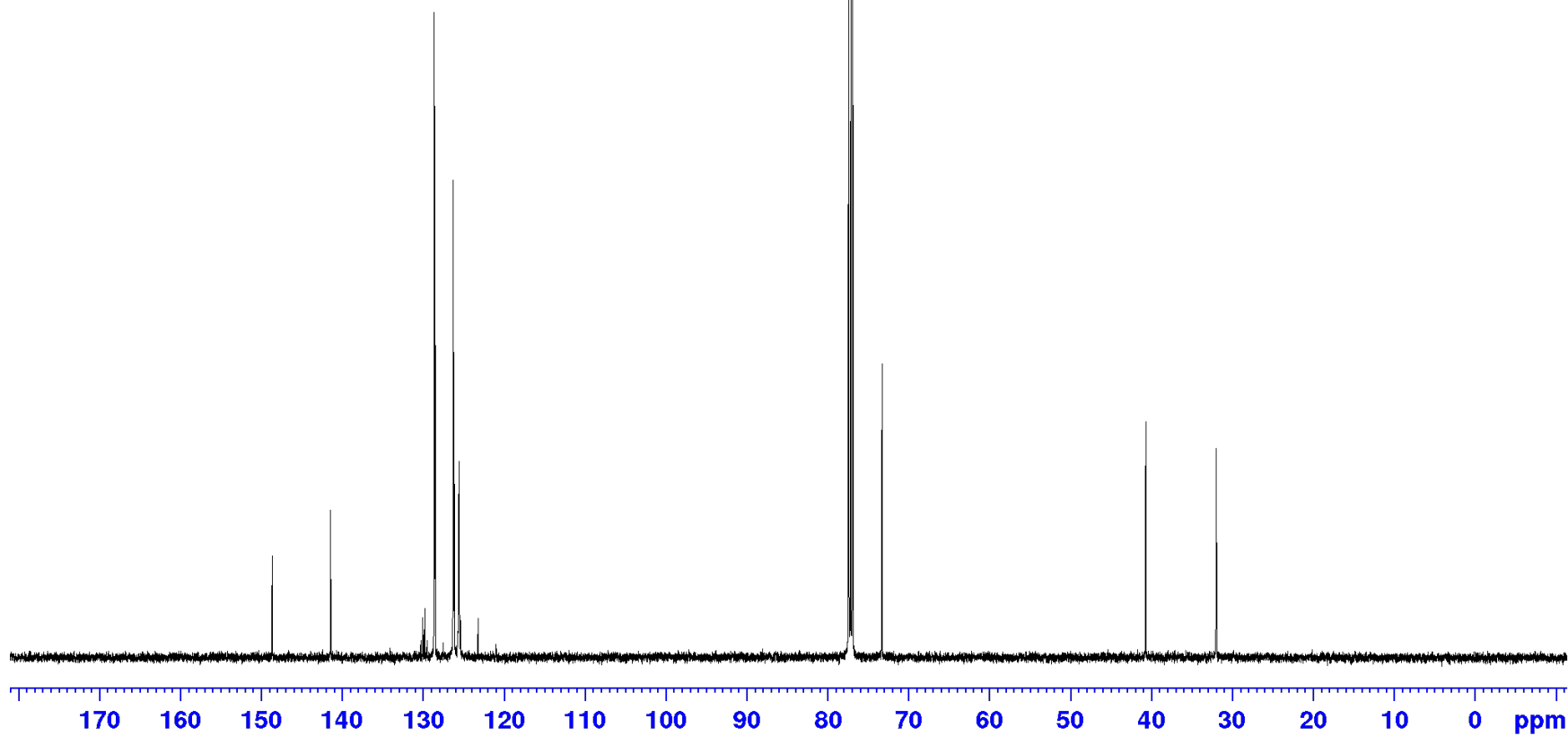
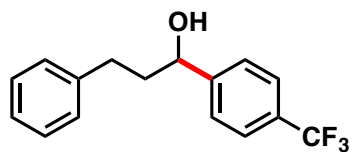
¹³C NMR of compound **6k** (CDCl₃, 125 MHz)

— 148.7
— 141.5
129.8
128.6
128.5
126.3
126.2
125.6
123.2

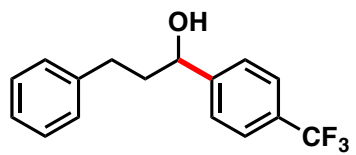
— 73.3

— 40.7

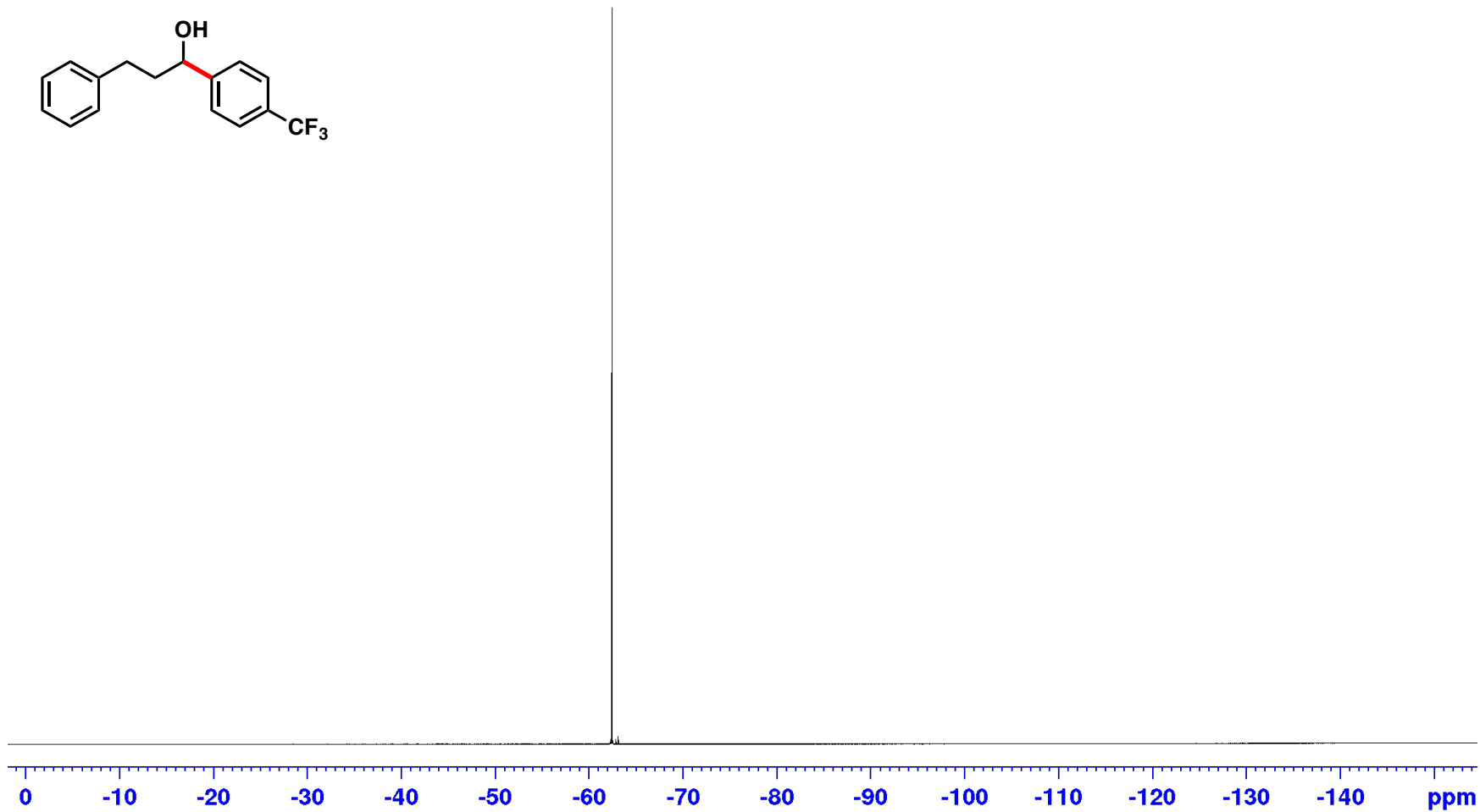
— 32.0



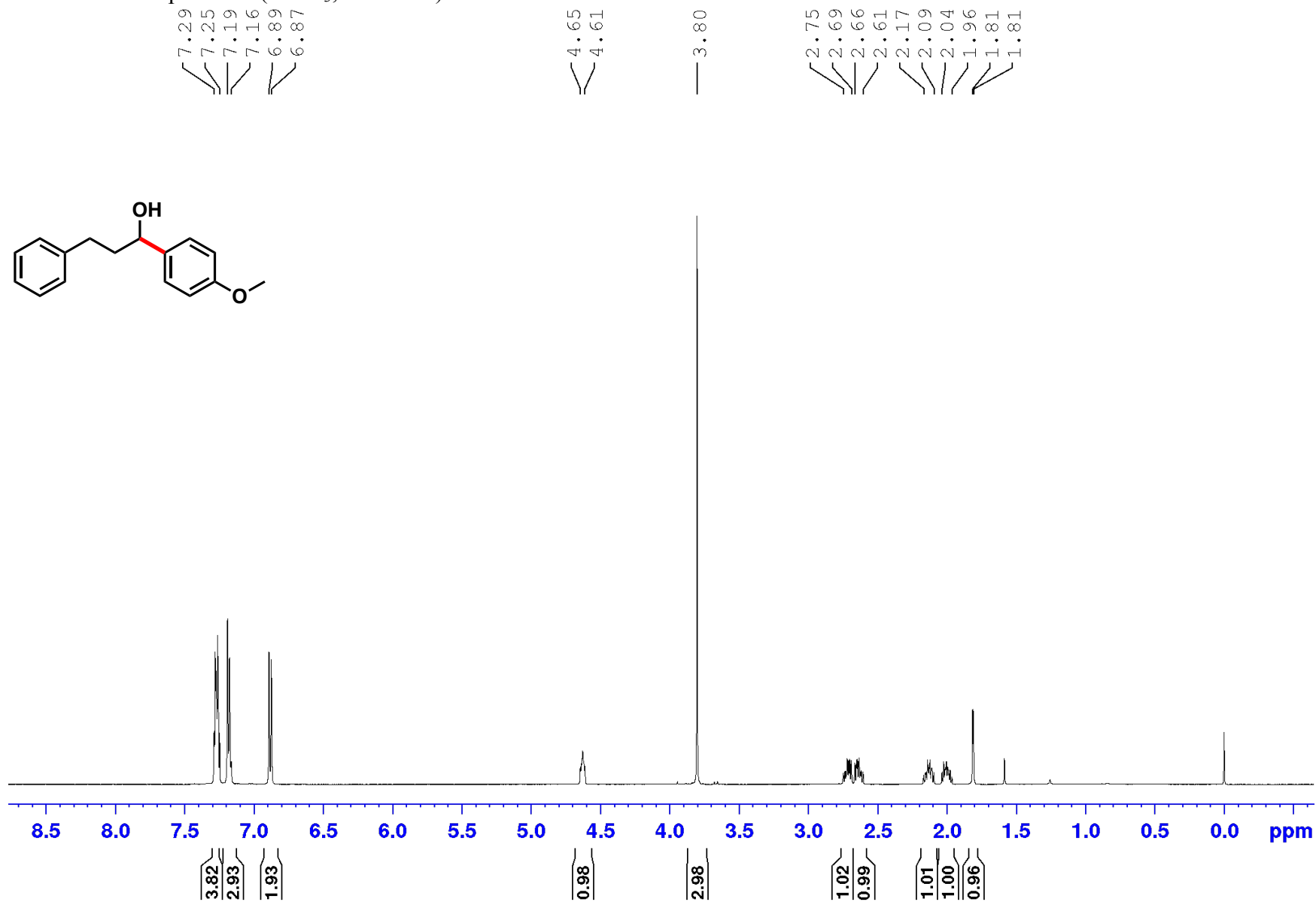
^{19}F NMR of compound **6k** (CDCl_3 , 470 MHz)



— -62.46



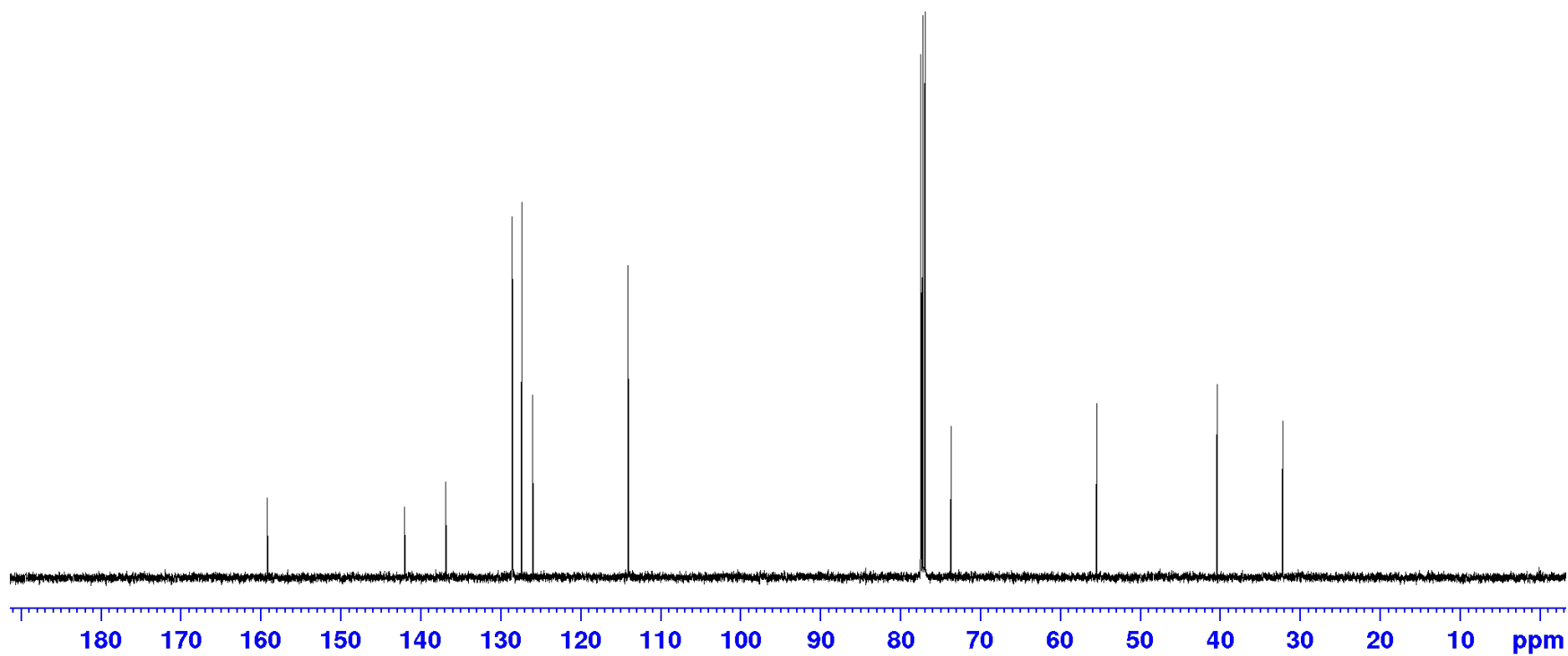
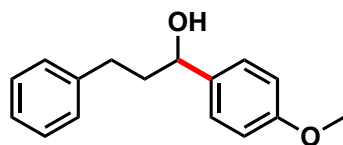
^1H NMR of compound **61** (CDCl_3 , 500 MHz)



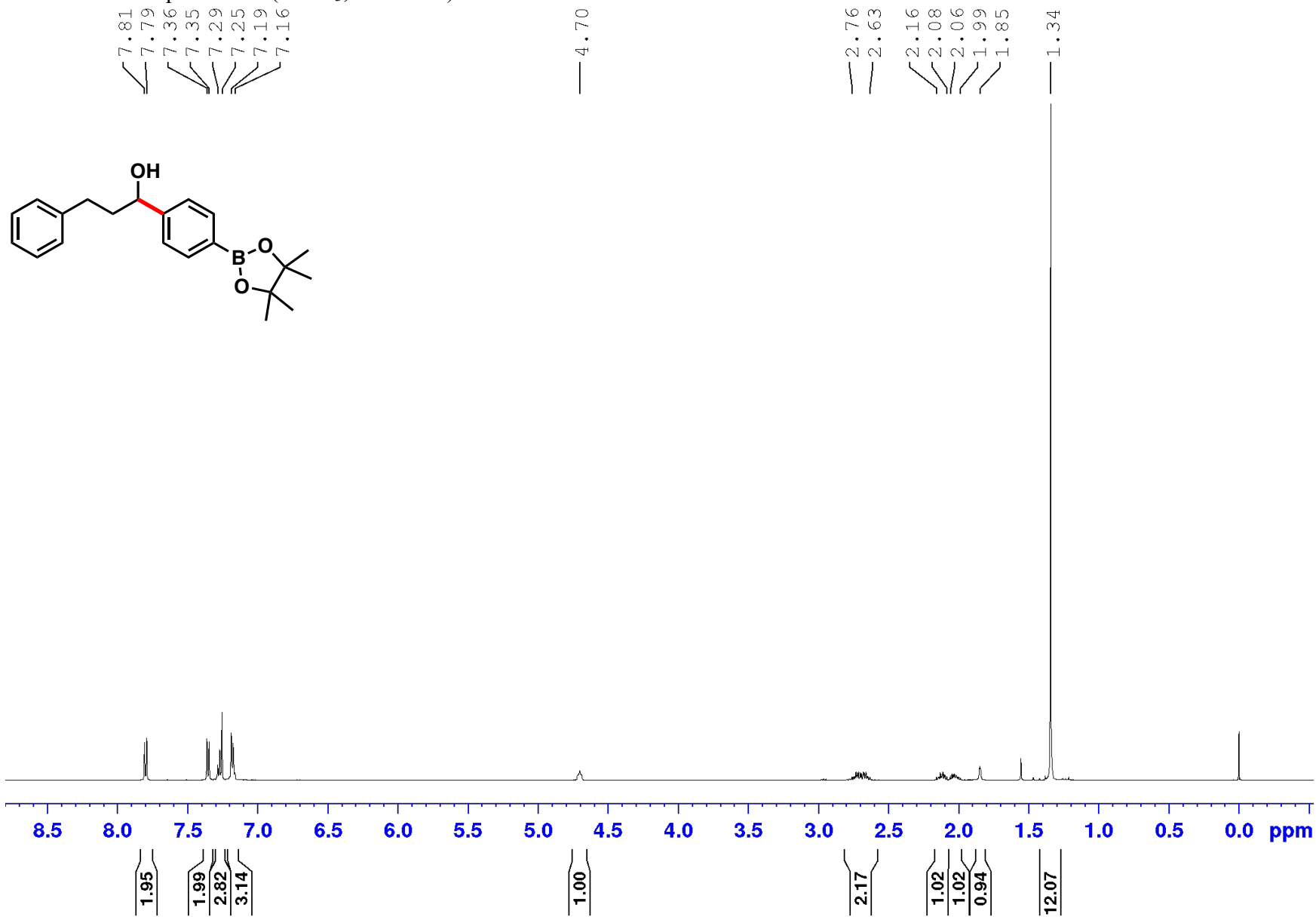
^{13}C NMR of compound **6I** (CDCl_3 , 125 MHz)

— 159.2
— 142.0
— 136.8
128.6
128.5
127.3
126.0
— 114.0

— 73.6
— 55.4
— 40.5
— 32.3



¹H NMR of compound **6m** (CDCl₃, 500 MHz)

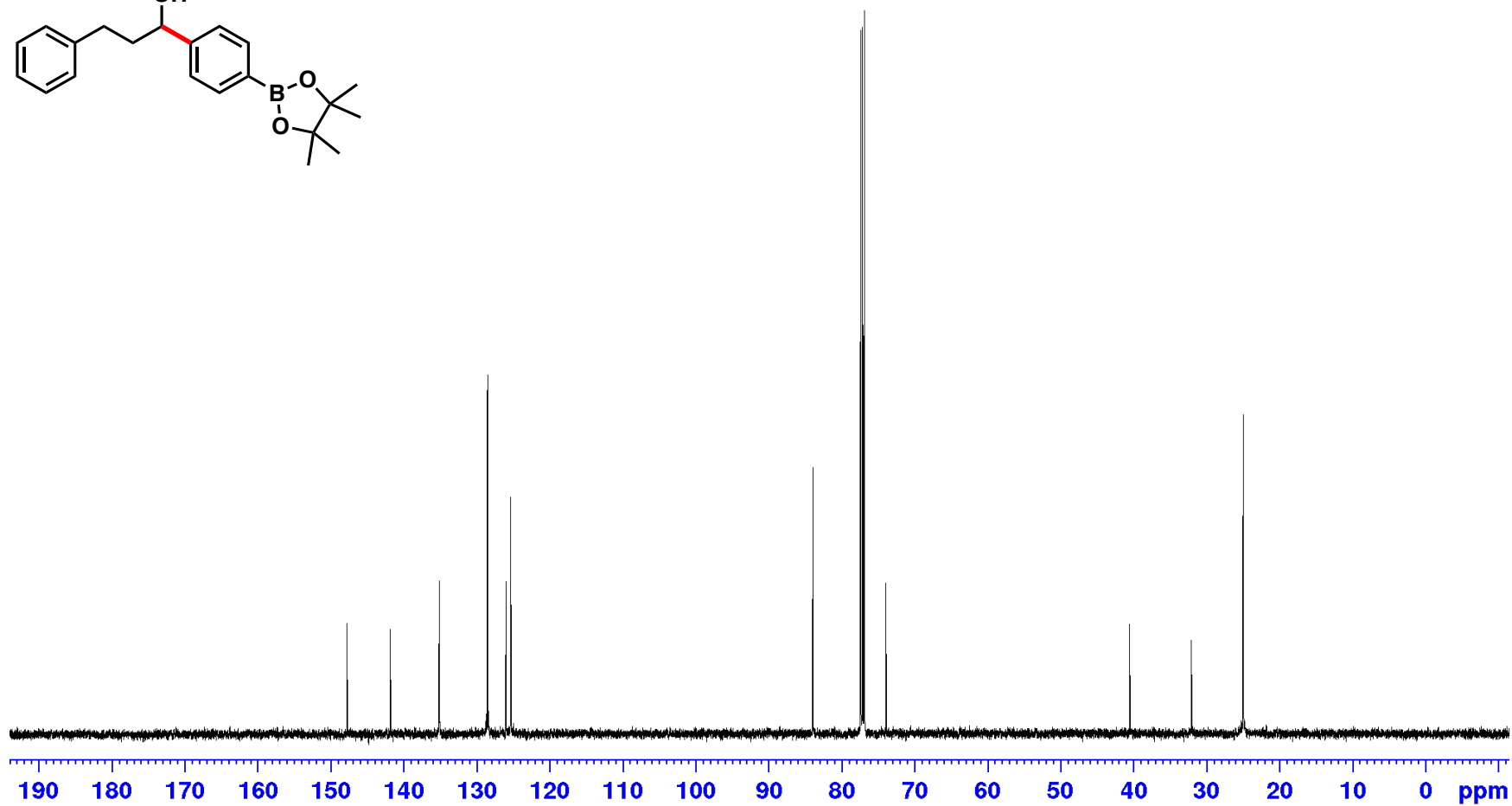
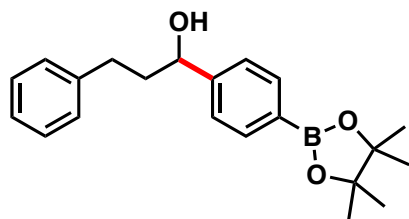


¹³C NMR of compound **6m** (CDCl₃, 125 MHz)

— 147.8
— 141.9
— 135.2
— 128.6
— 128.5
— 126.0
— 125.4

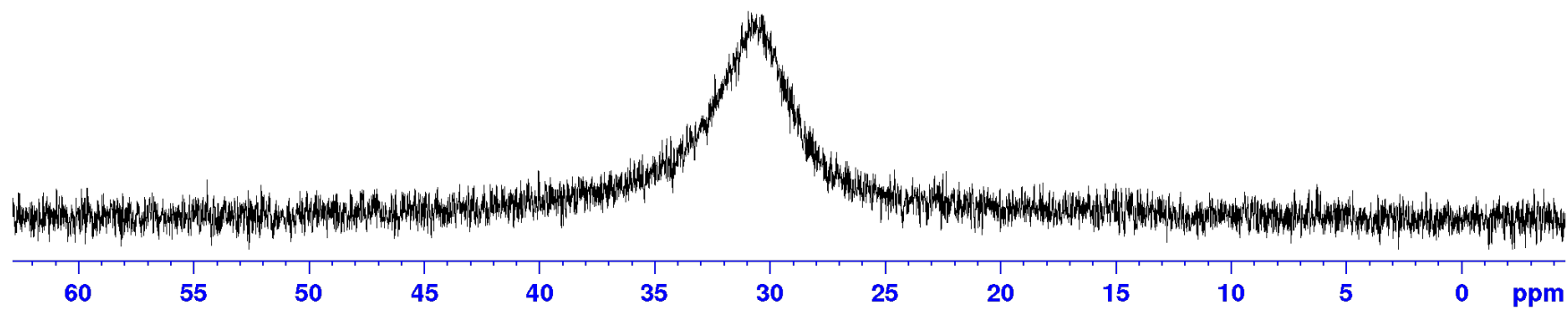
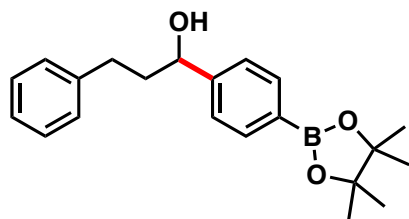
— 83.9
— 73.9

— 40.5
— 32.1
— 25.0



^{11}B NMR of compound **6m** (CDCl_3 , 160 MHz)

— 30.94



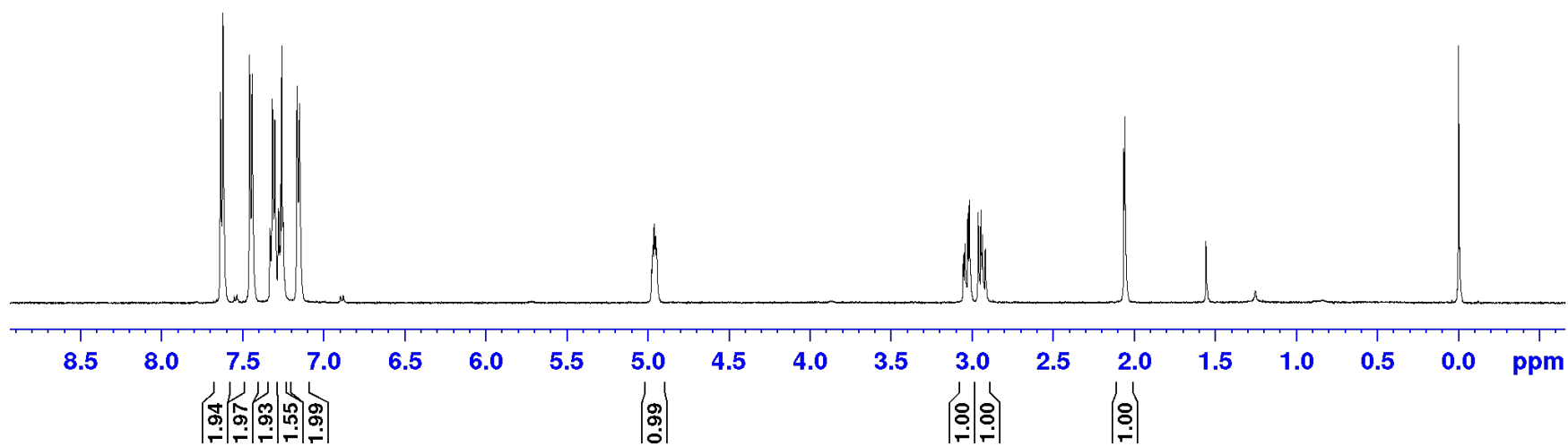
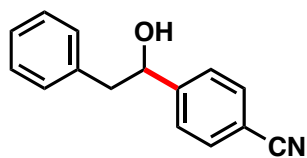
S31

^1H NMR of compound **6p** (CDCl_3 , 500 MHz)

7.64
7.62
7.46
7.44
7.33
7.30
7.28
7.25
7.16
7.15

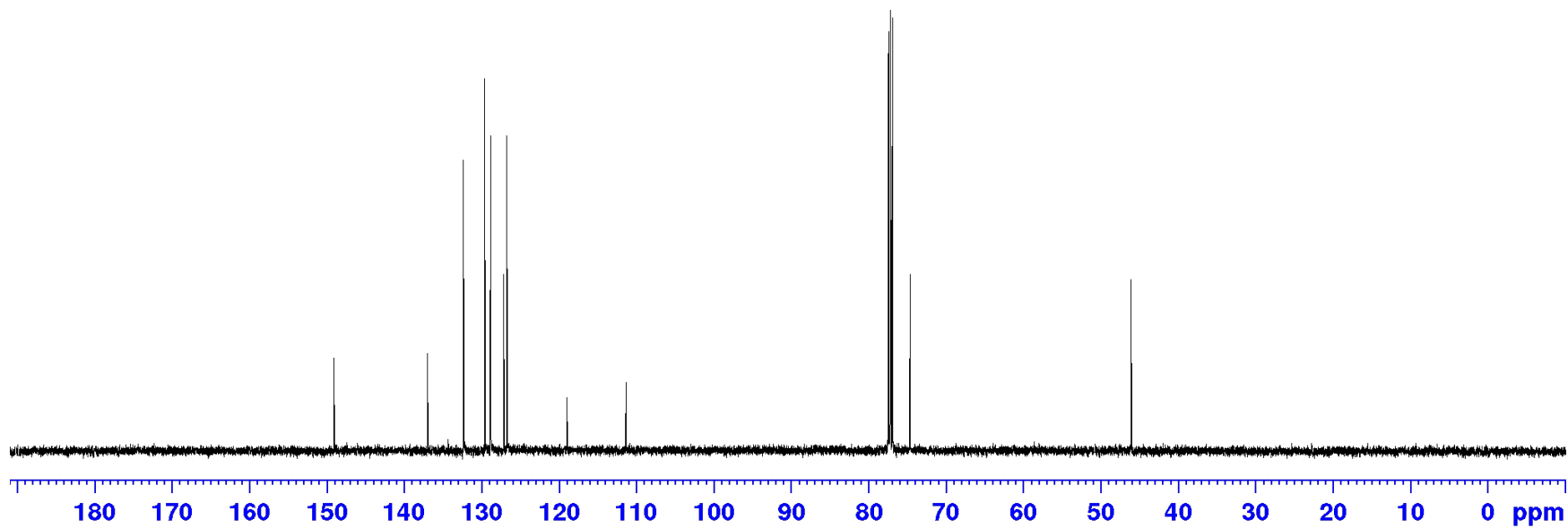
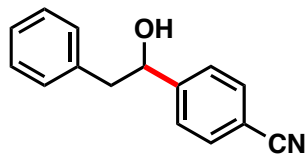
4.98
4.95

3.05
3.04
3.03
3.02
2.96
2.95
2.94
2.92
2.06
2.06

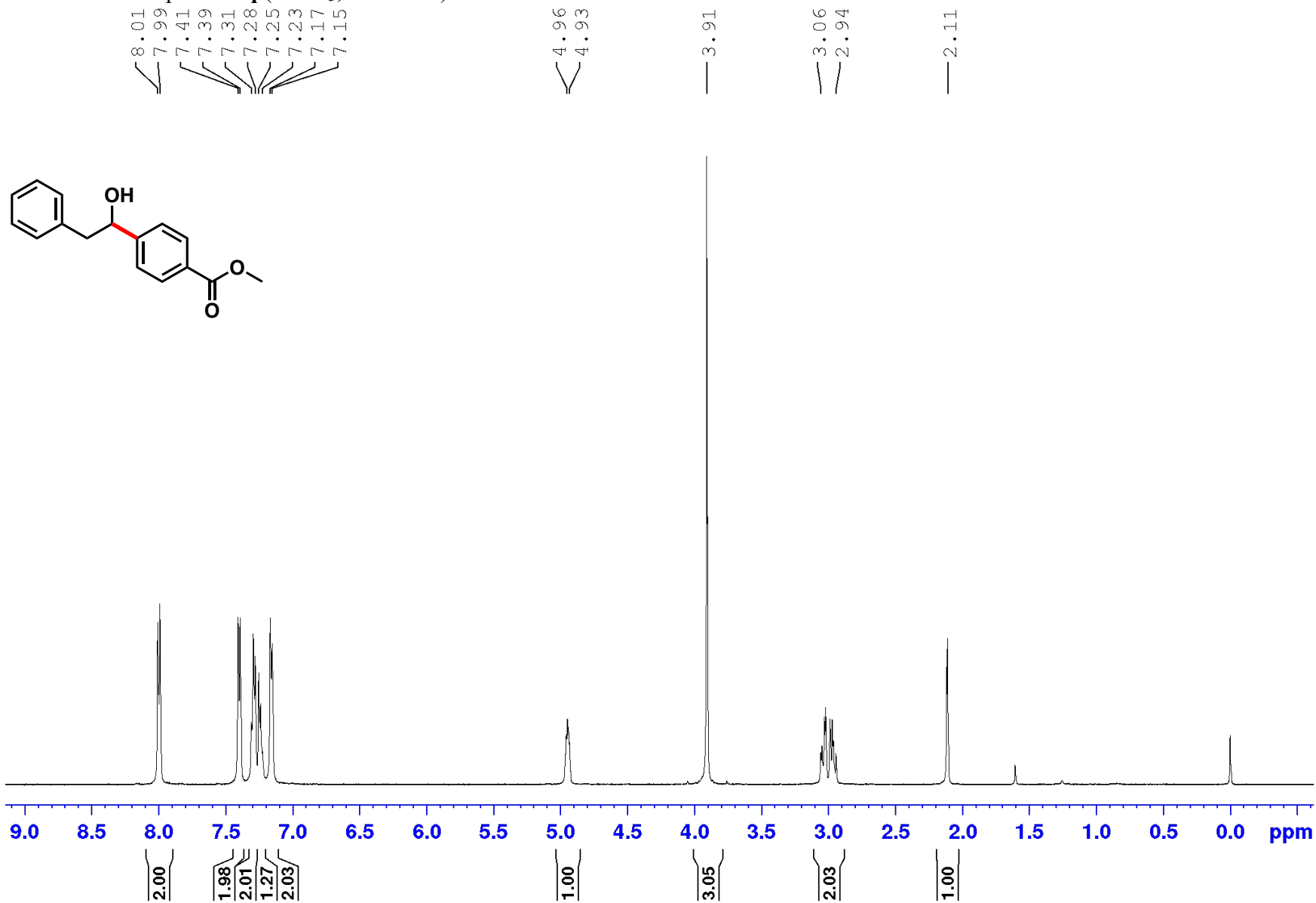


^{13}C NMR of compound **6p** (CDCl_3 , 125 MHz)

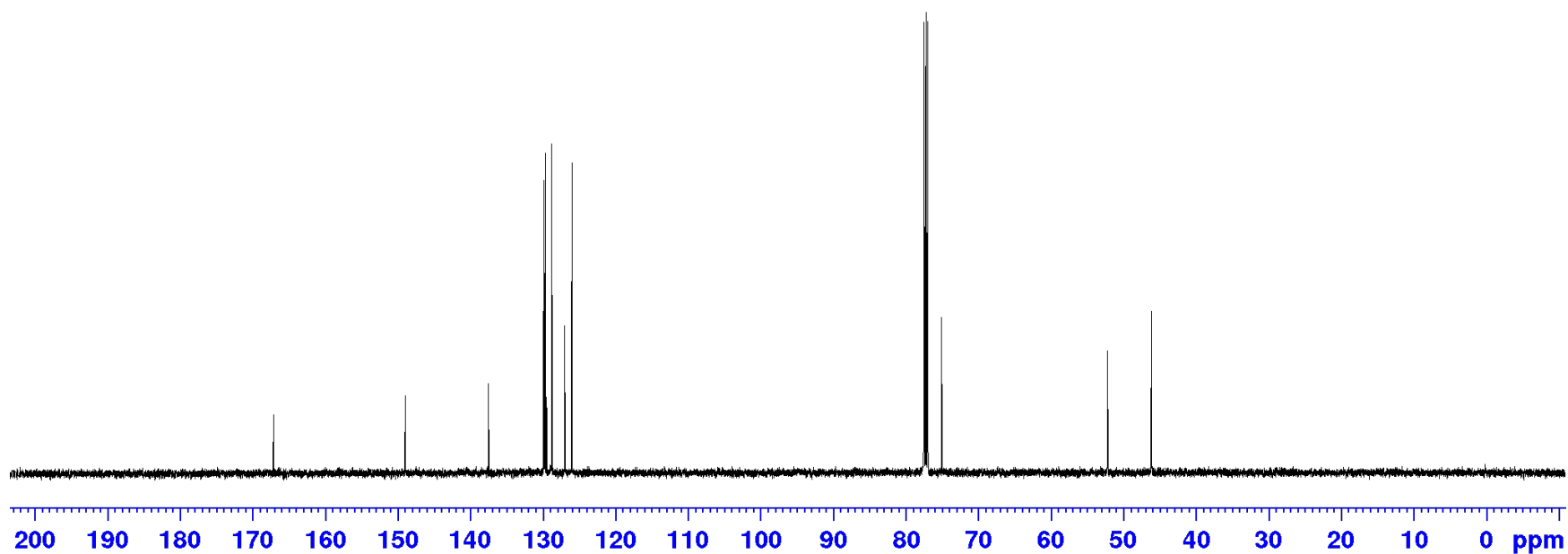
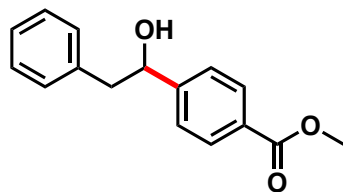
— 149.1
— 137.0
— 132.3
— 129.6
— 128.8
— 127.1
— 126.7
— 119.0
— 111.3
— 74.6
— 46.2



^1H NMR of compound **6q** (CDCl_3 , 500 MHz)



^{13}C NMR of compound **6q** (CDCl_3 , 125 MHz)



^1H NMR of compound **6r** (CDCl_3 , 500 MHz)

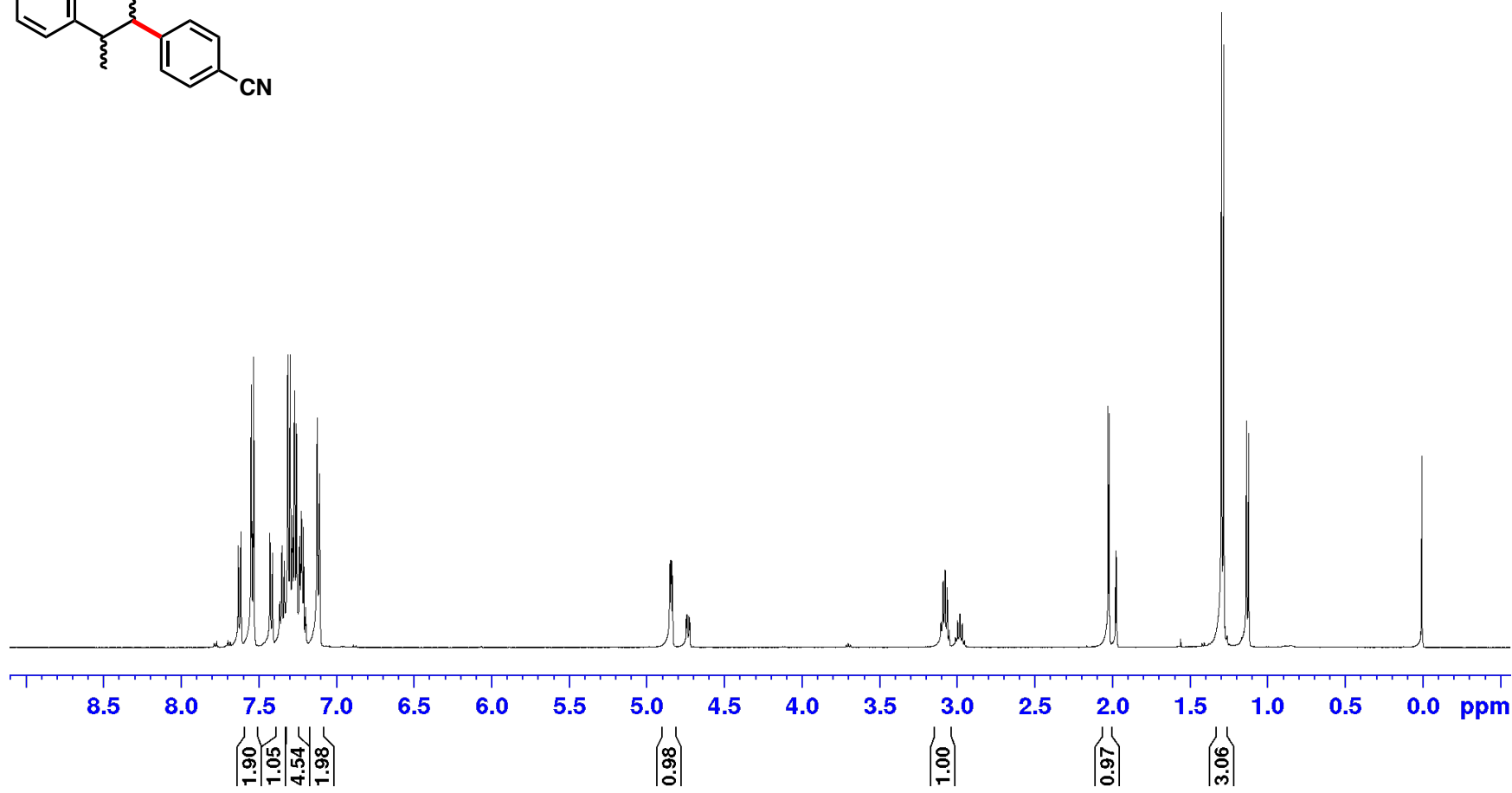
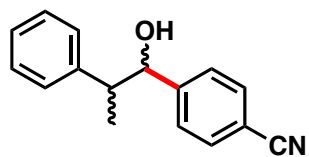
7.63
7.62
7.55
7.53
7.43
7.41
7.37
7.34
7.31
7.26
7.13
7.11

4.85
4.83
4.74
4.74
4.73
4.72

3.10
3.05
3.01
2.95

2.03
2.02
1.98
1.97

1.30
1.28
1.14
1.12



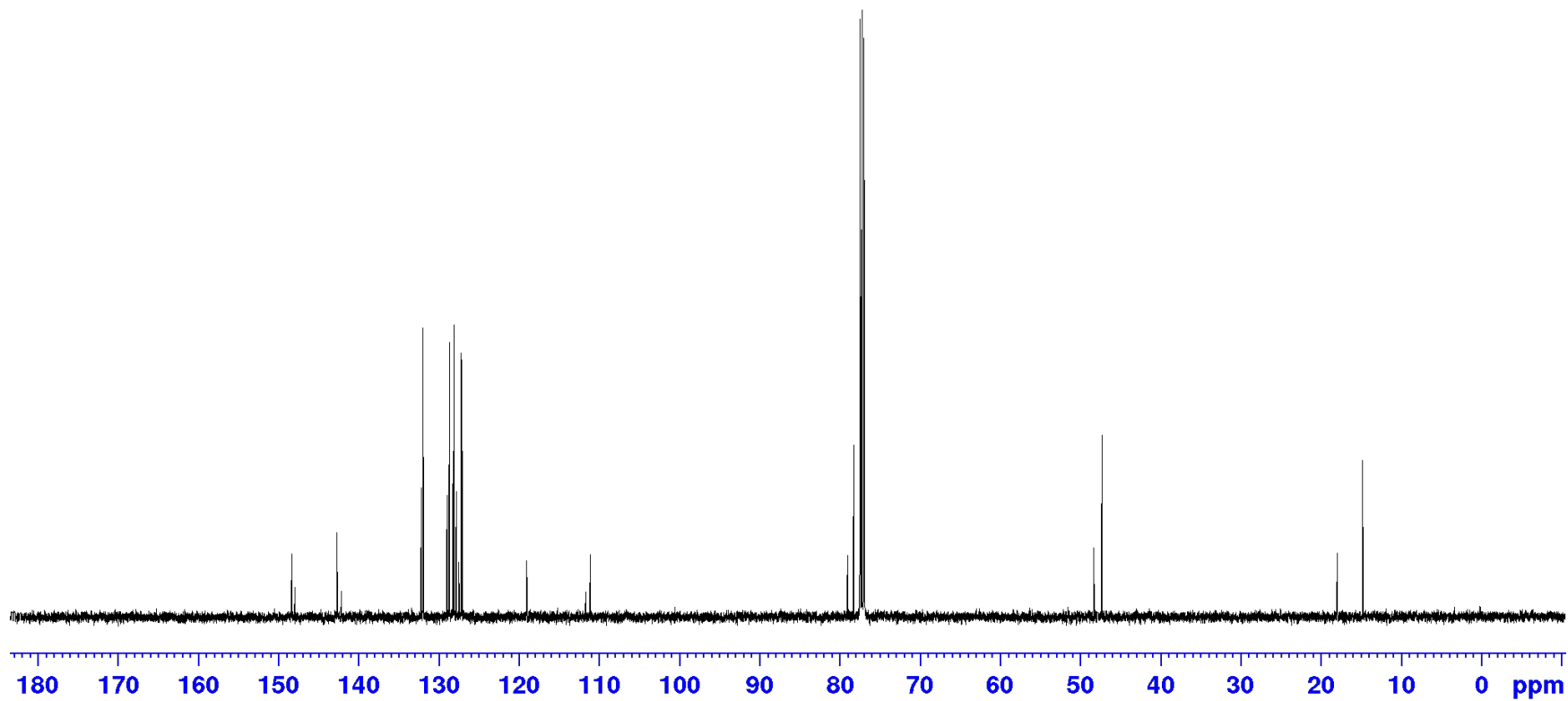
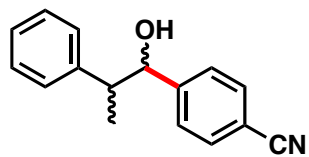
¹³C NMR of compound **6r** (CDCl₃, 125 MHz)

148.3
147.9
142.7
142.1
132.1
131.9
128.9
128.6
128.2
128.1
127.8
127.4
127.1
127.0
119.0
119.0
111.6
111.1

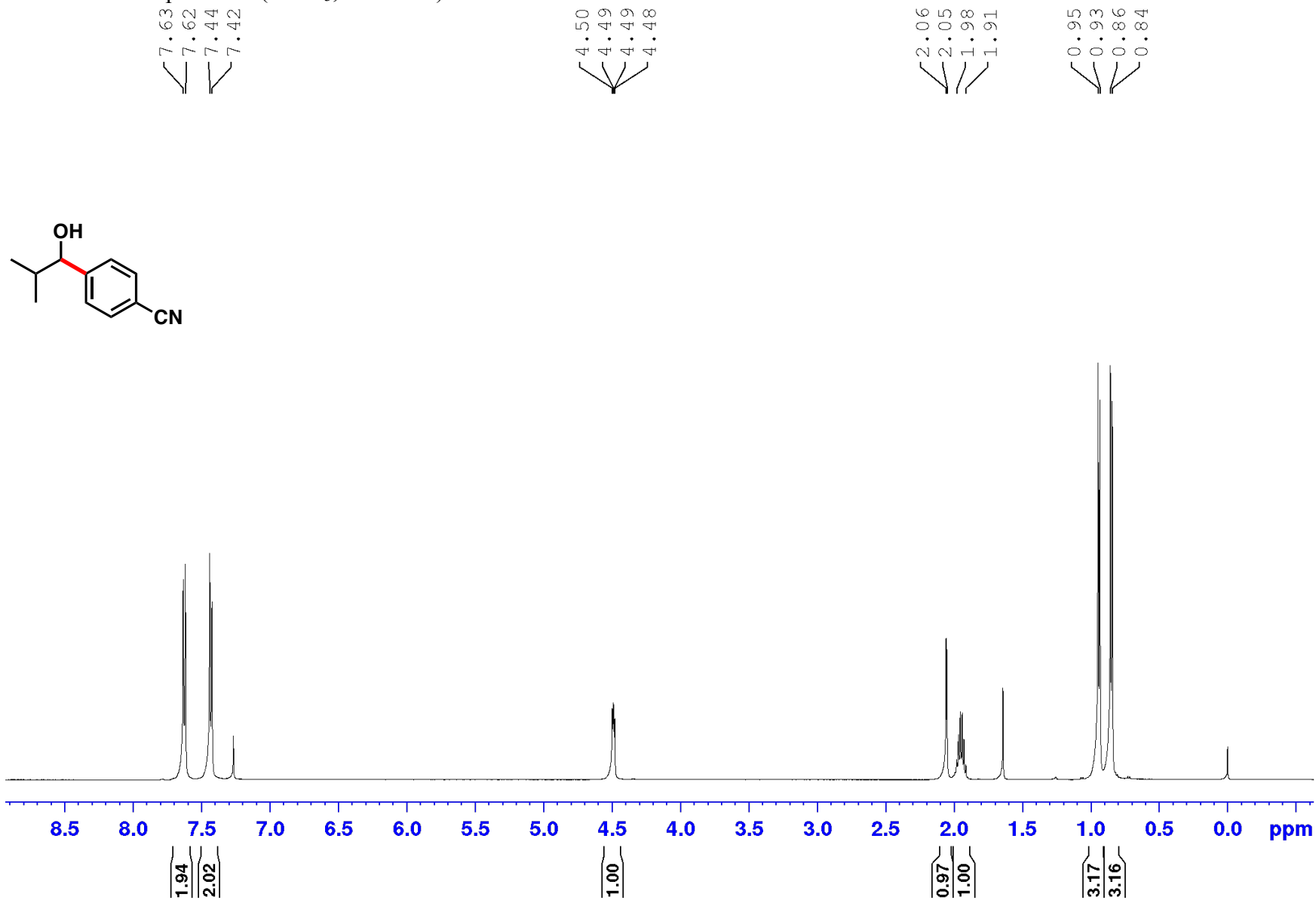
79.0
78.2

48.2
47.3

18.0
14.8



^1H NMR of compound **6s** (CDCl_3 , 500 MHz)



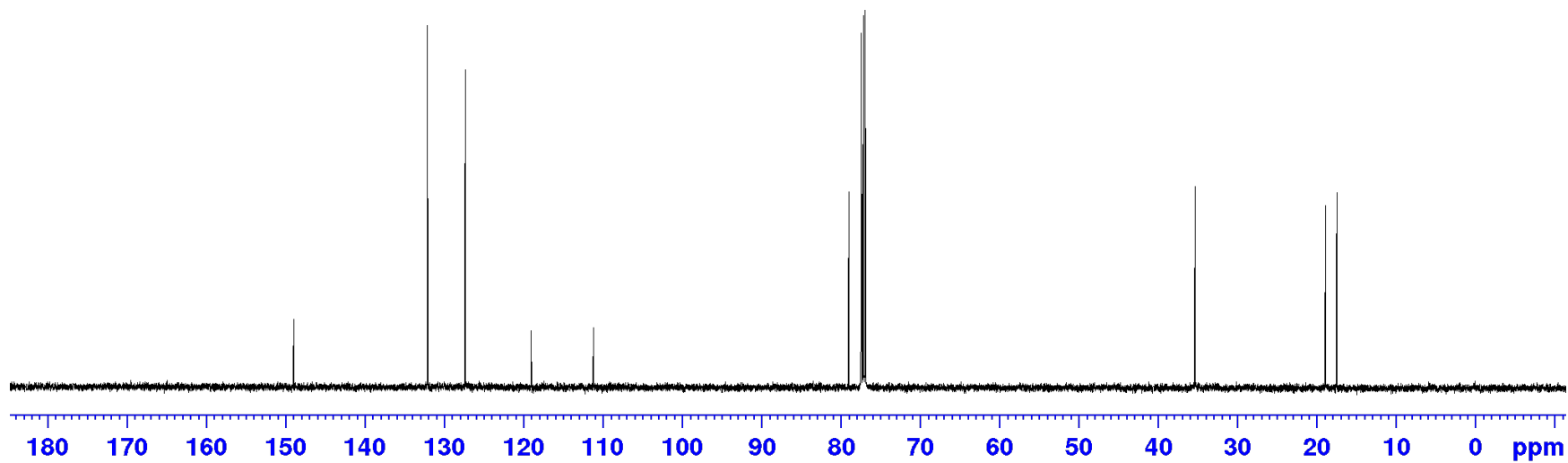
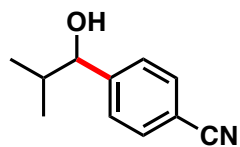
^{13}C NMR of compound **6s** (CDCl_3 , 125 MHz)

— 149.1
— 132.1
— 127.3
— 119.0
— 111.2

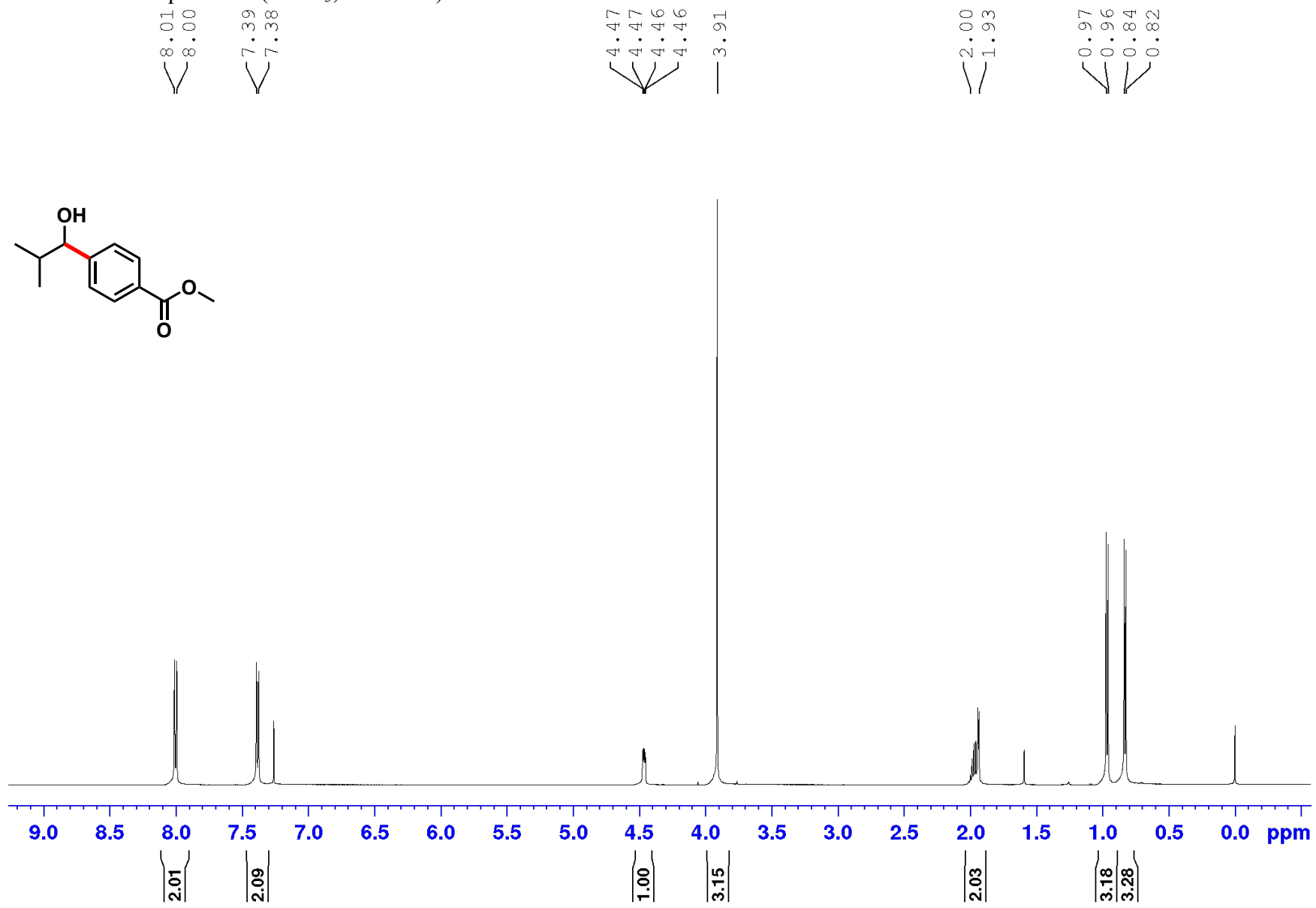
— 79.0

— 35.4

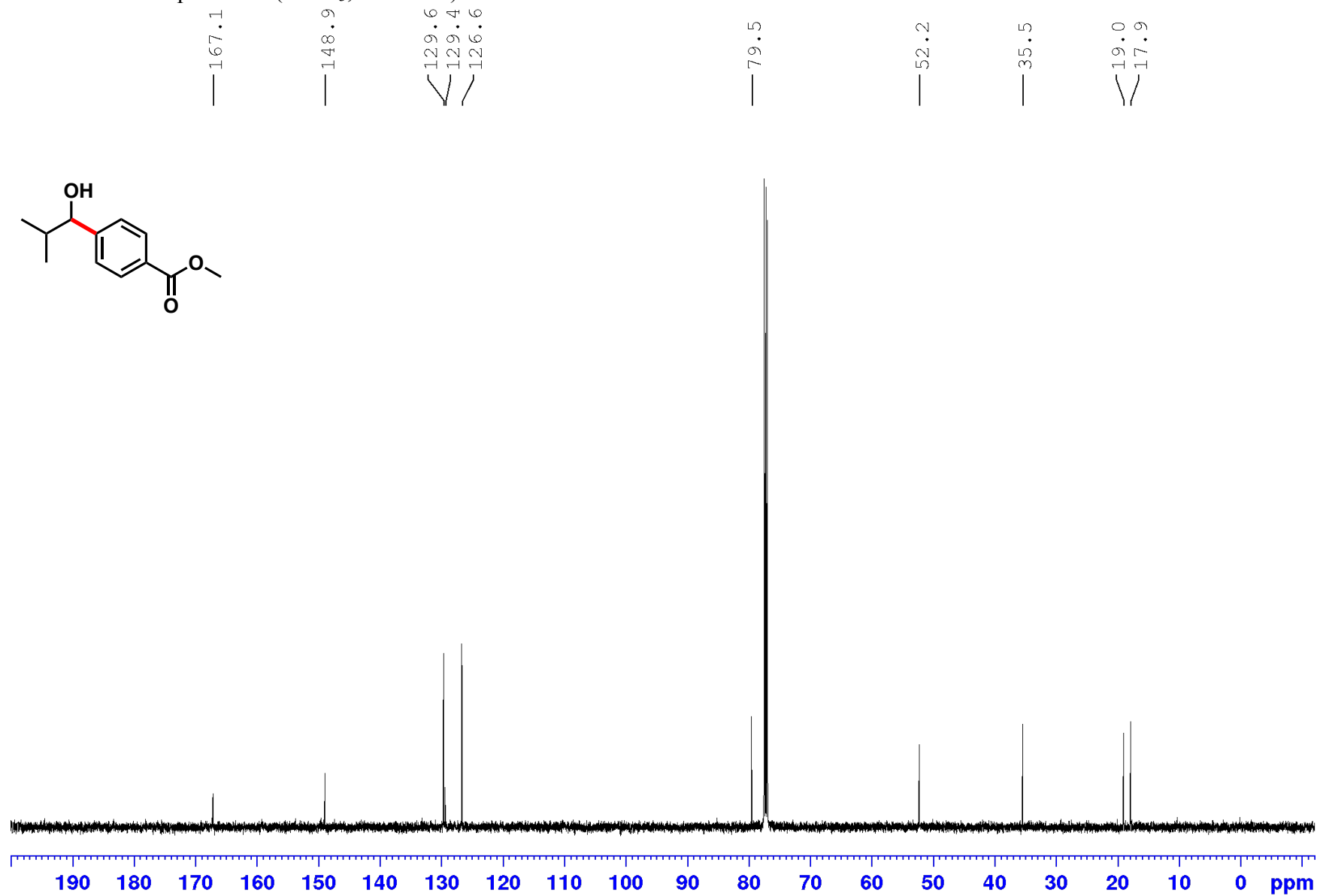
— 19.0
— 17.6



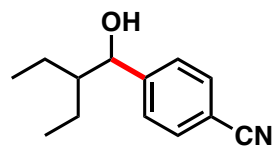
¹H NMR of compound **6t** (CDCl₃, 500 MHz)



^{13}C NMR of compound **6t** (CDCl_3 , 125 MHz)



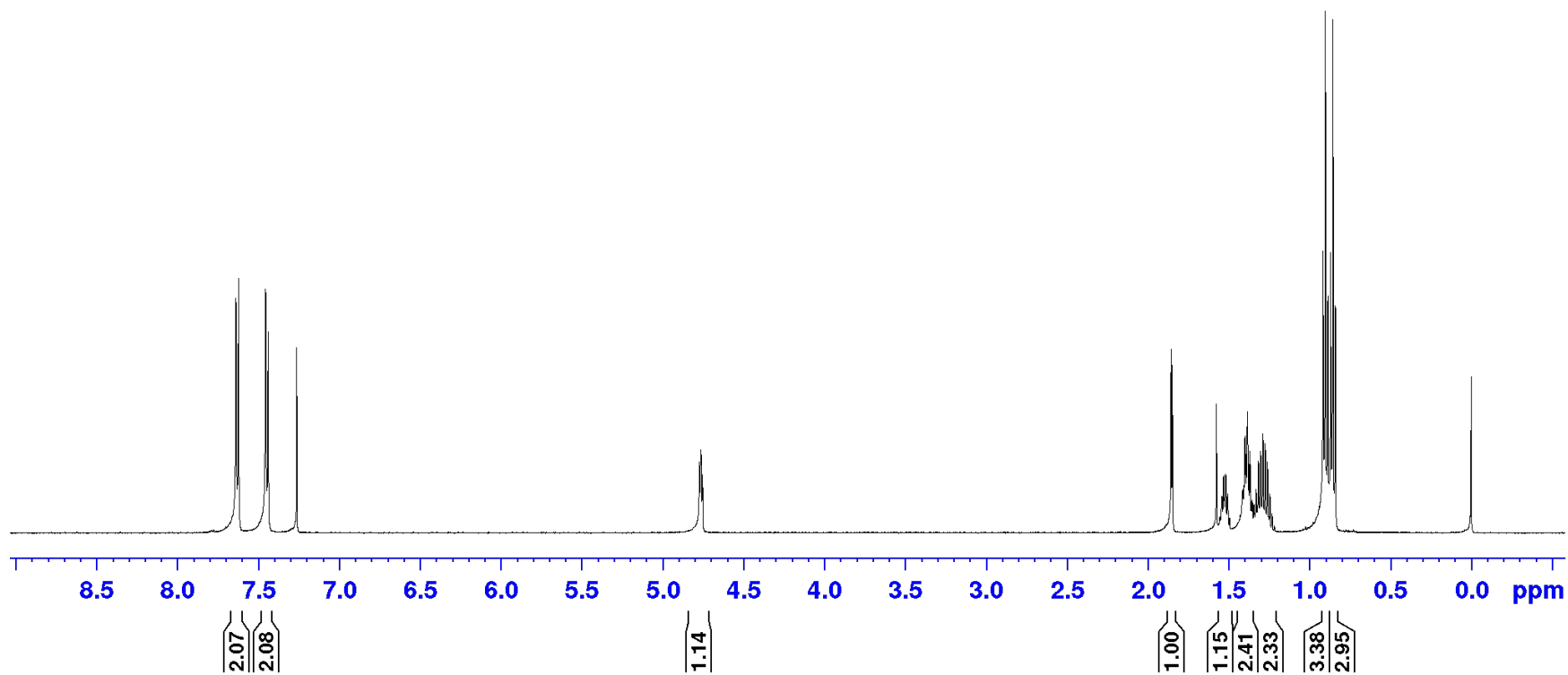
^1H NMR of compound **6u** (CDCl_3 , 500 MHz)



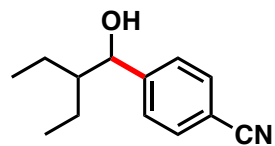
7.64
7.62
7.46
7.44

4.77
4.75

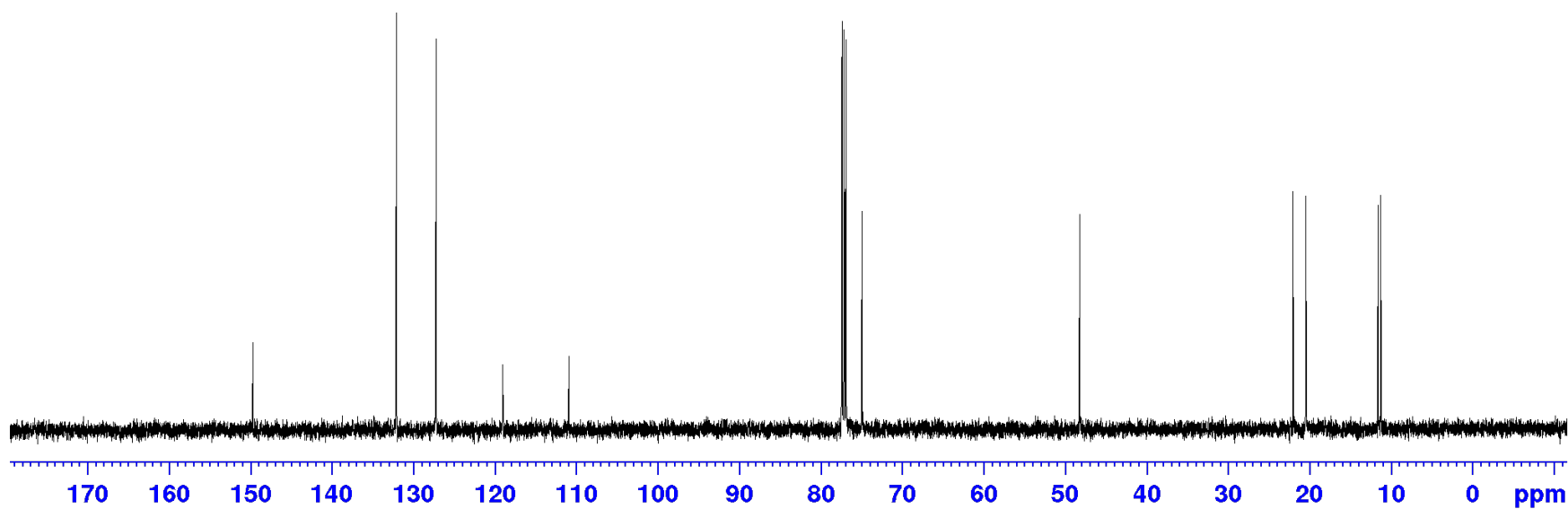
1.86
1.85
1.56
1.49
1.42
1.35
1.34
1.22
0.92
0.90
0.89
0.87
0.86
0.84



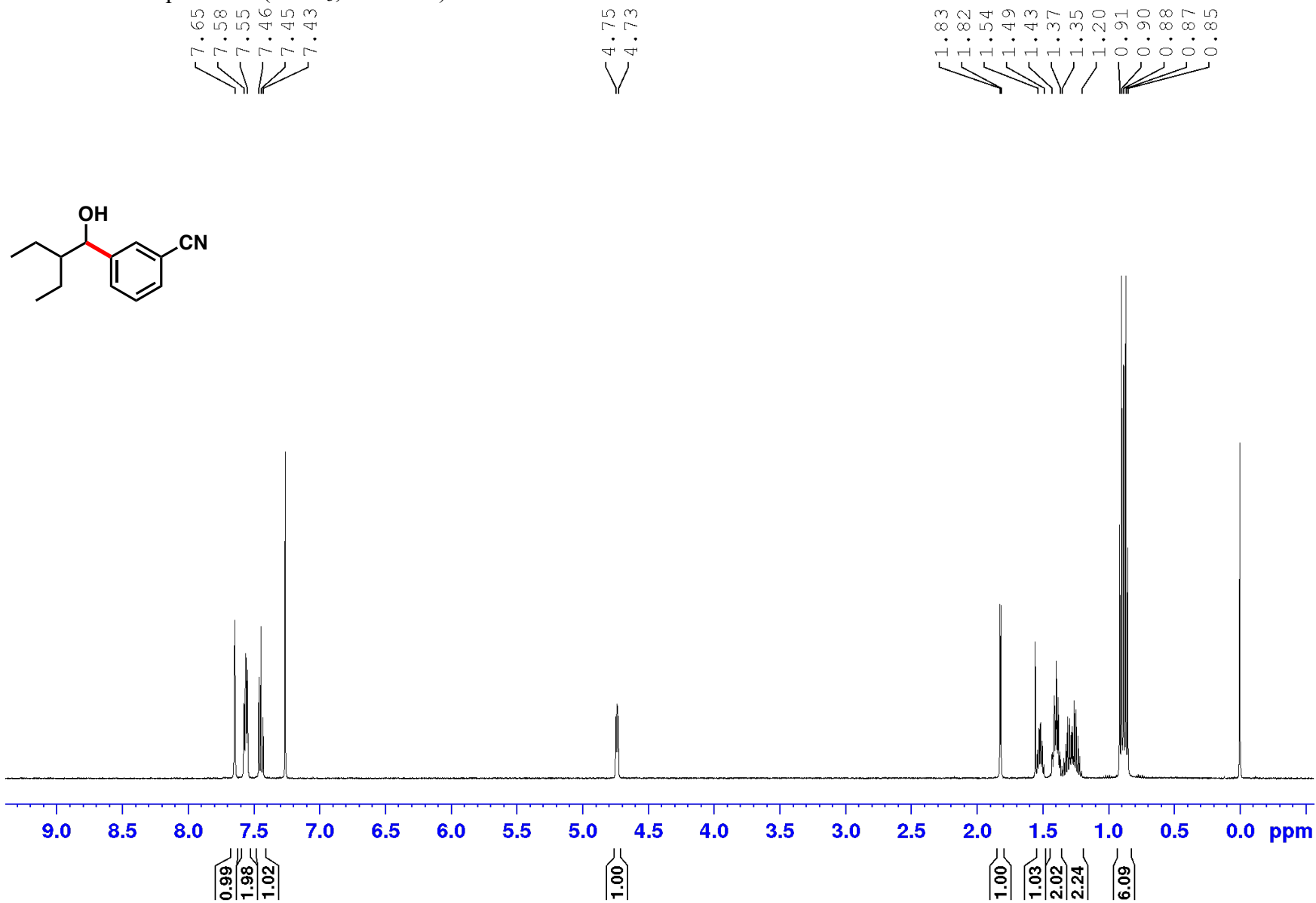
^{13}C NMR of compound **6u** (CDCl_3 , 125 MHz)



—149.7
—132.1
—127.2
—119.1
—110.9
—74.9
—48.2
—22.0
—20.5
—11.6
—11.3

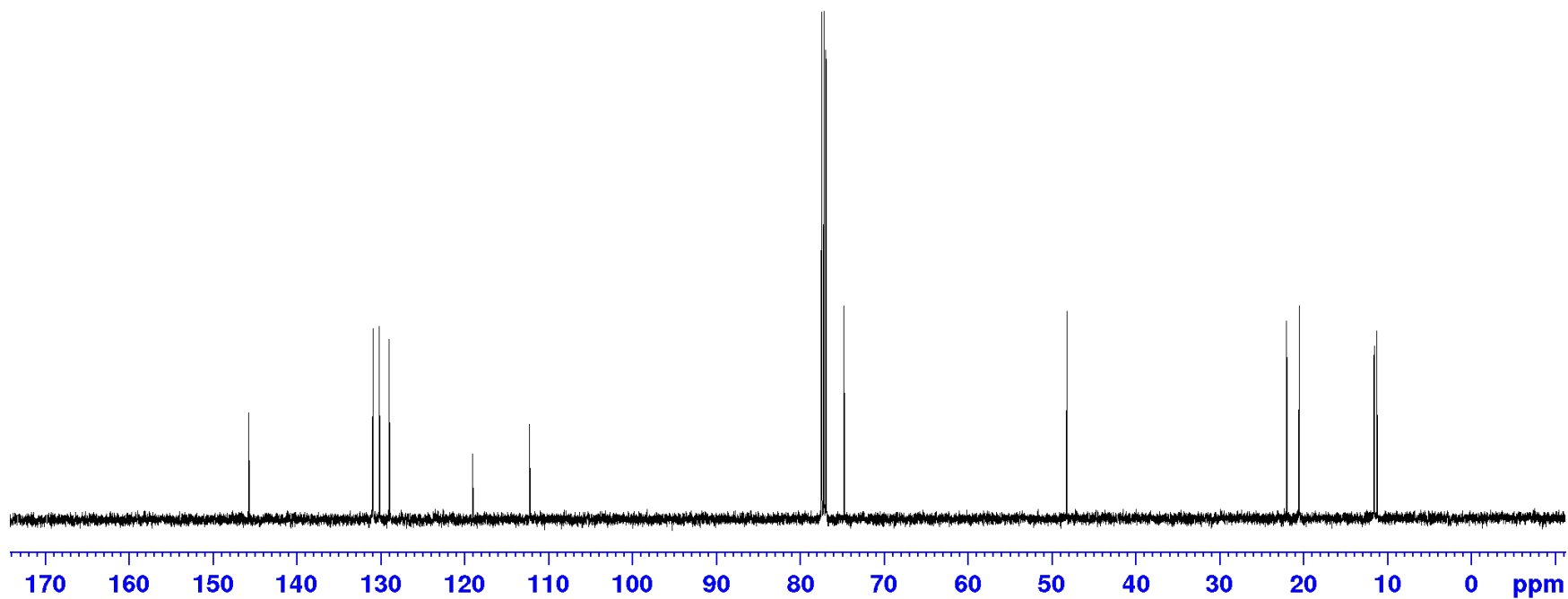
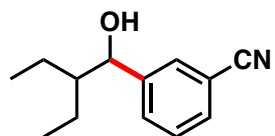


^1H NMR of compound **6v** (CDCl_3 , 500 MHz)

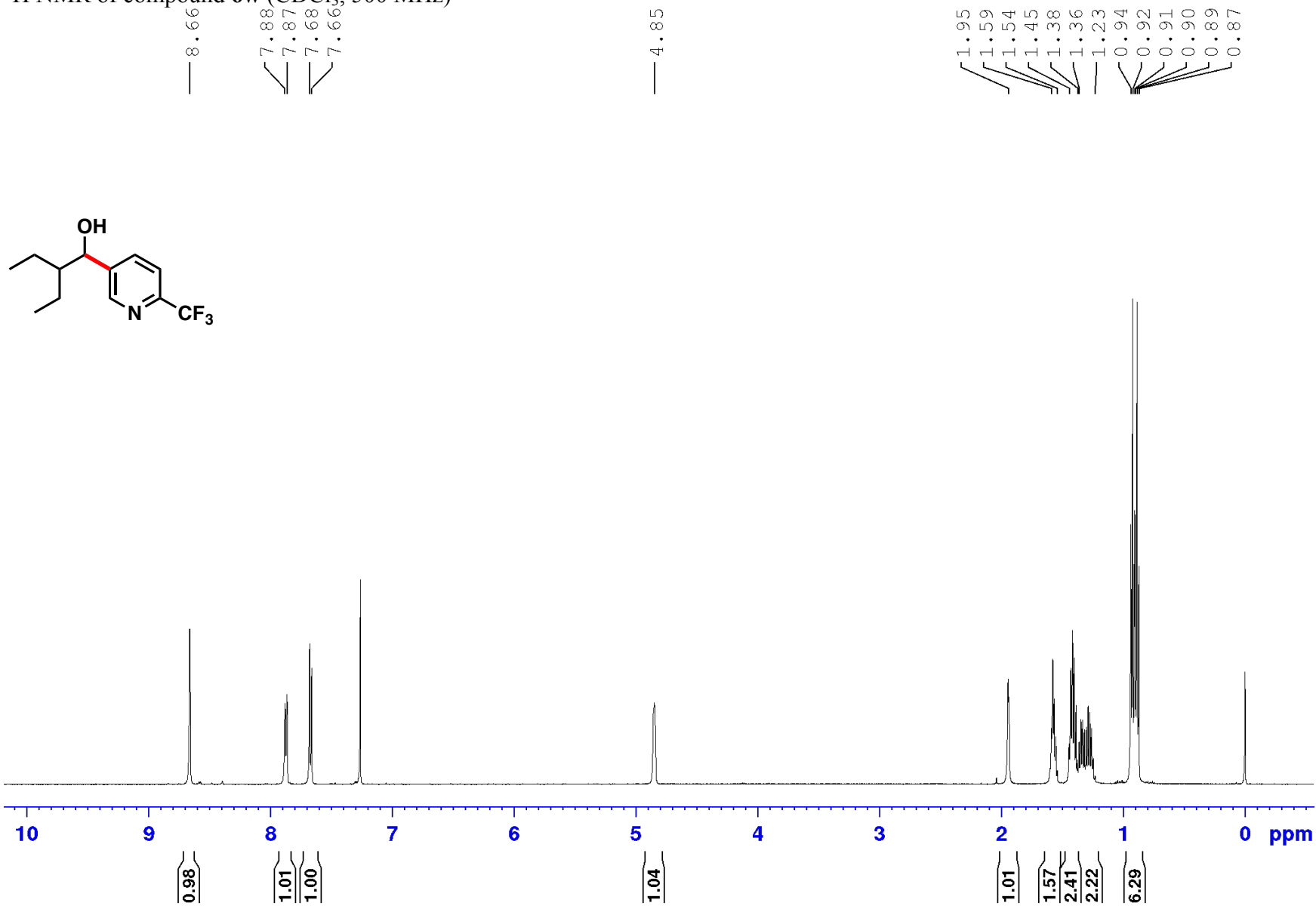


^{13}C NMR of compound **6v** (CDCl_3 , 125 MHz)

— 145.7
— 131.0
— 131.0
— 130.2
— 129.1
— 119.1
— 112.3
— 74.7
— 48.2
— 22.0
— 20.5
— 11.6
— 11.2



¹H NMR of compound **6w** (CDCl₃, 500 MHz)



¹³C NMR of compound **6w** (CDCl₃, 125 MHz)

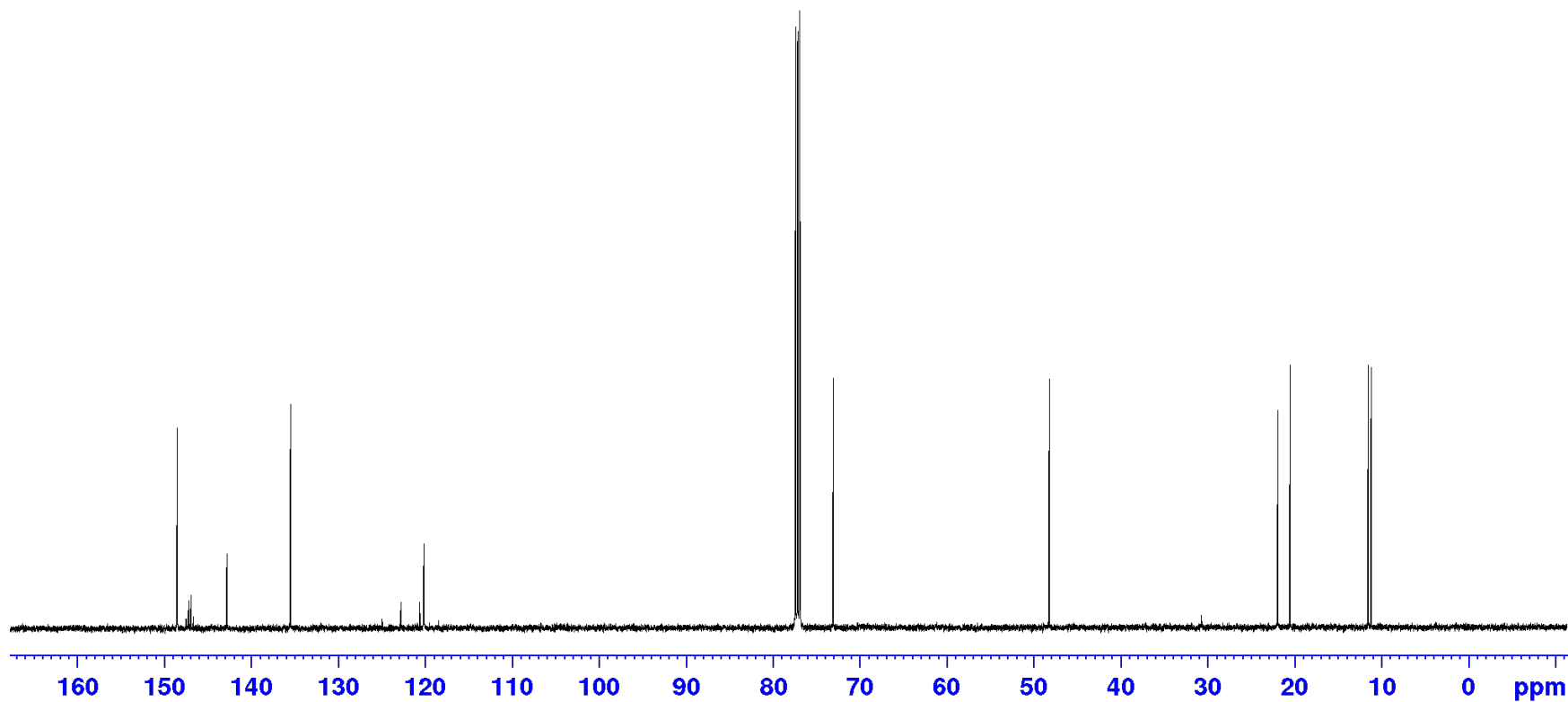
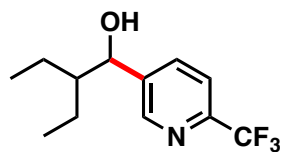
148.5
147.5
147.2
147.0
146.7
142.8
135.5
125.0
122.8
120.6
120.2
118.5

73.1

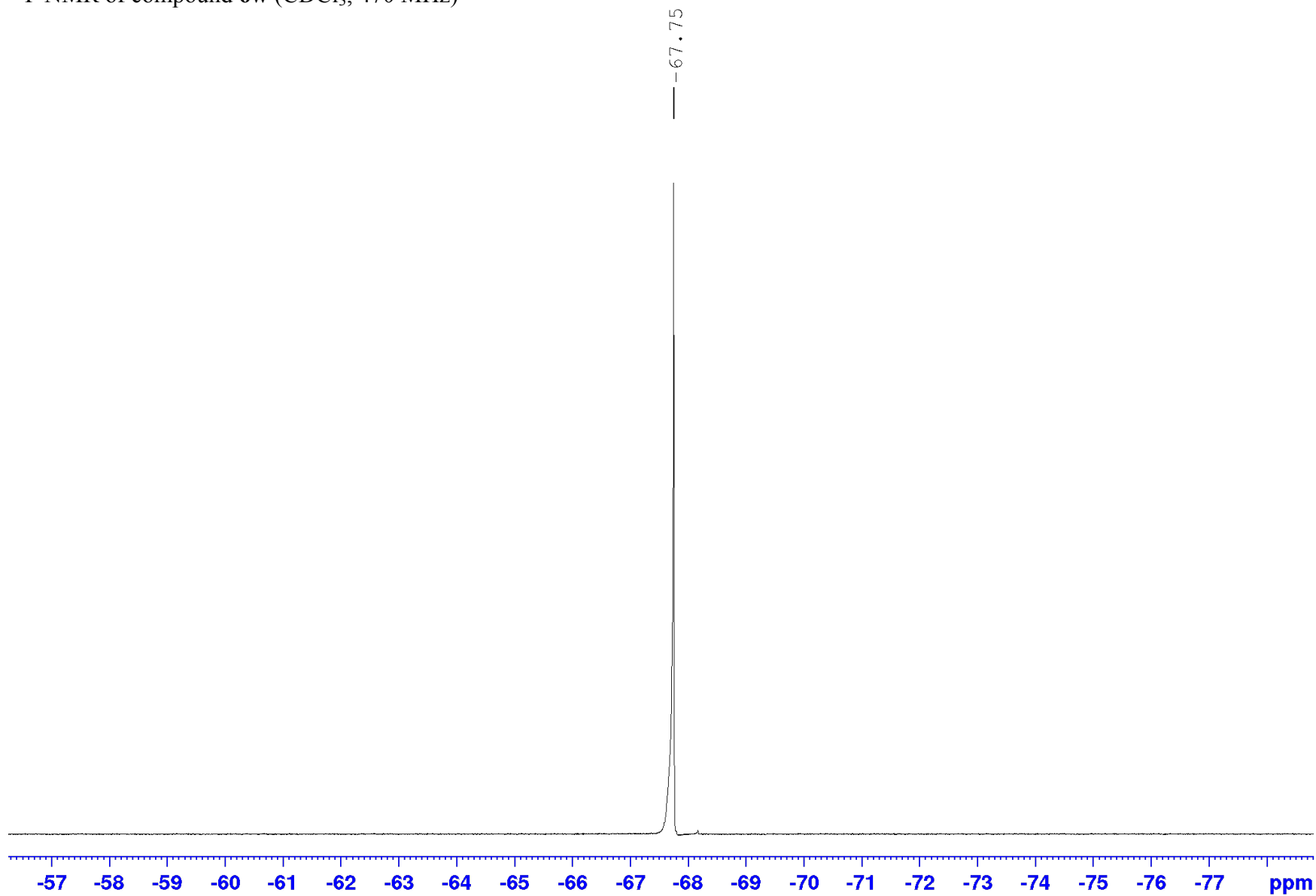
48.2

21.9
20.5

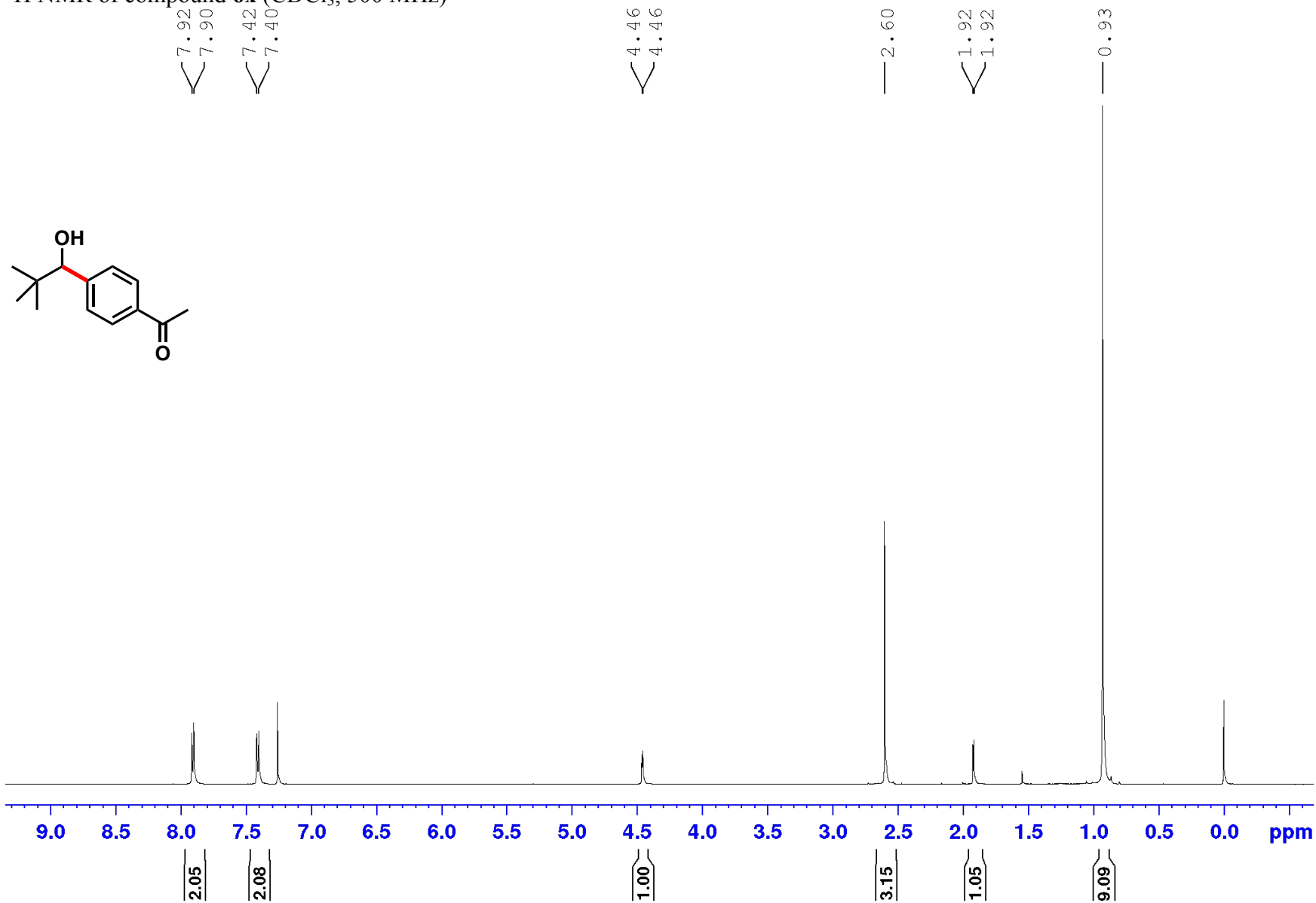
11.5
11.2



^{19}F NMR of compound **6w** (CDCl_3 , 470 MHz)



^1H NMR of compound **6x** (CDCl_3 , 500 MHz)



¹³C NMR of compound **6x** (CDCl₃, 125 MHz)

— 198.1

— 147.7

— 136.4

< 128.0
127.8

— 82.1

— 35.9

< 26.7
26.0

