

Supporting information

Suzuki-Miyaura Coupling of Halophenols and Phenol boronic Acids: Systematic Investigation of Positional Isomer-Effects and Conclusions for the Synthesis of Phytoalexins from *Pyrrinae*

Bernd Schmidt and Martin Riemer*

Universitaet Potsdam, Institut fuer Chemie, Organische Synthesechemie, Karl-Liebknecht-Strasse

24-25, D-14476 Golm, Germany

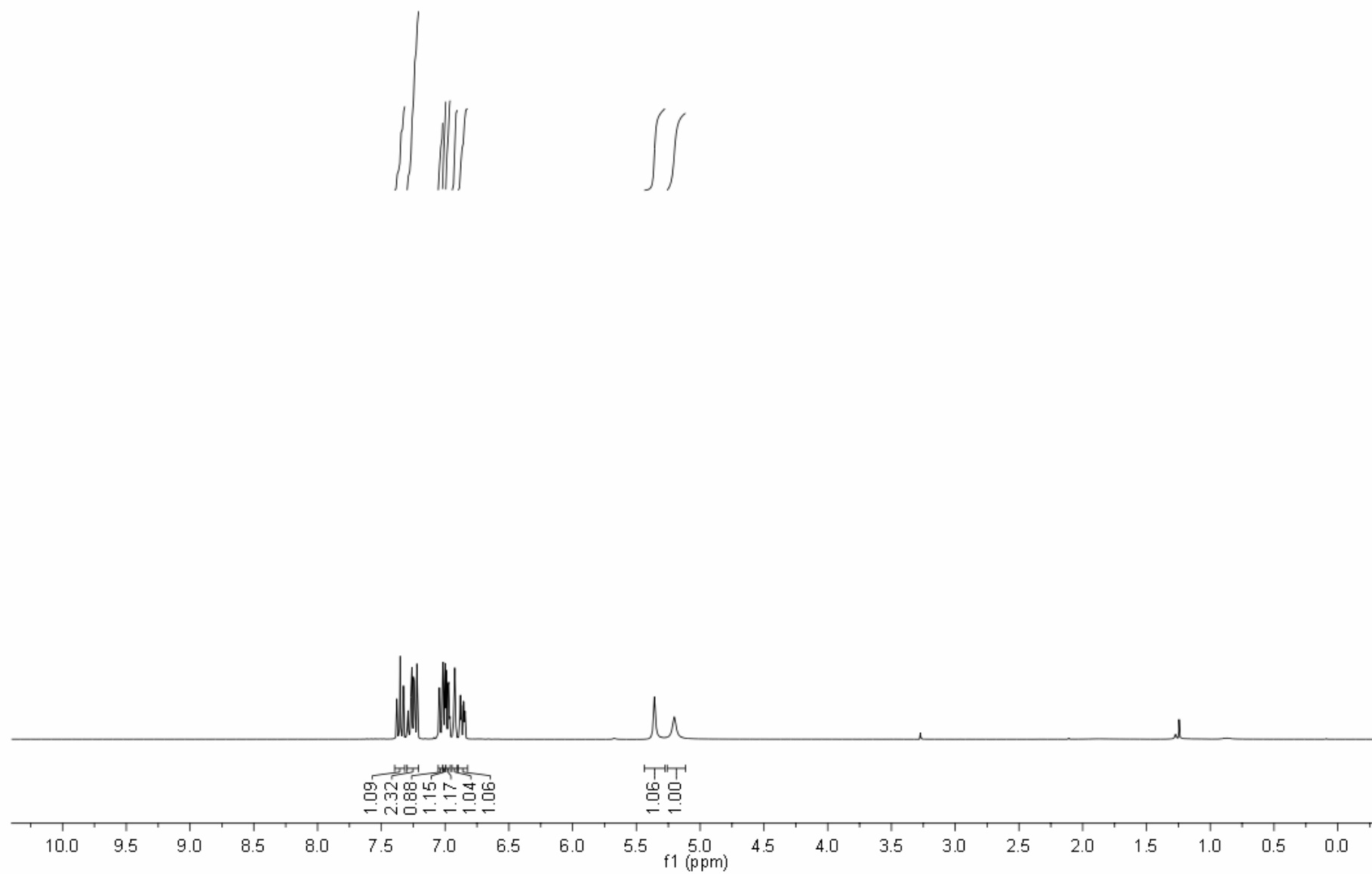
bernd.schmidt@uni-potsdam.de

Table of contents: copies of NMR-spectra

Biphenyl-2,3'-diol (10b).	S3
Biphenyl-2,4'-diol (10c)	S5
Biphenyl-3,3'-diol (10d)	S7
Biphenyl-3,4'-diol (10e)	S9
Biphenyl-4,4'-diol (10f)	S11
Biphenyl-3-ol (<i>m</i> - 12)	S13
Biphenyl-3-ol (<i>p</i> - 12)	S15
2'-Methoxybiphenyl-2-ol (17a)	S17
3'-Methoxybiphenyl-2-ol (17b)	S19
	S1

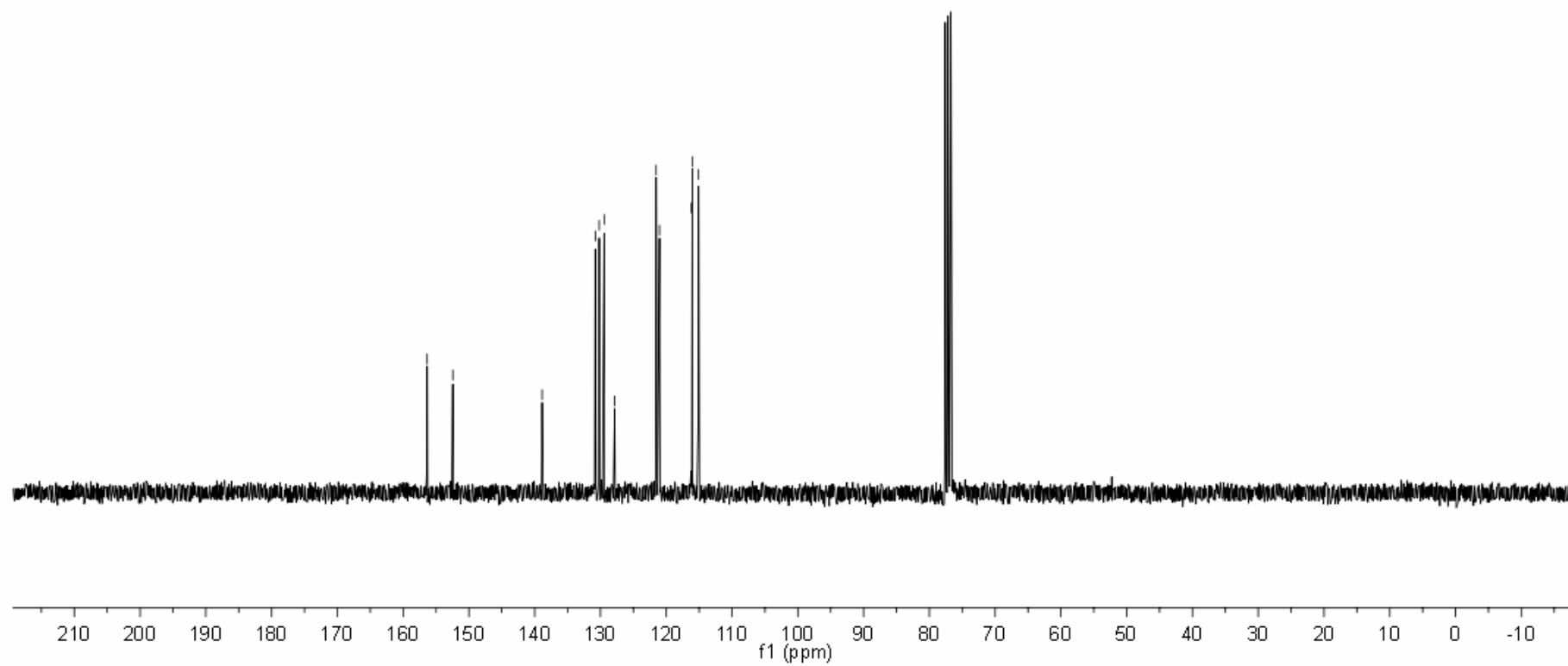
4'-Methoxybiphenyl-2-ol (17c)	S21
2'-Methoxybiphenyl-3-ol (17d)	S23
3'-Methoxybiphenyl-3-ol (17e)	S25
4'-Methoxybiphenyl-3-ol (17f)	S27
2'-Methoxybiphenyl-4-ol (17g)	S29
3'-Methoxybiphenyl-4-ol (17h)	S31
4'-Methoxybiphenyl-4-ol (17i)	S33
2,2'-Dimethoxy-1,1'-biphenyl (19a)	S35
2,3'-Dimethoxy-1,1'-biphenyl (19b)	S37
2,4'-Dimethoxy-1,1'-biphenyl (19c)	S39
3,3'-Dimethoxy-1,1'-biphenyl (19d)	S41
3,4'-Dimethoxy-1,1'-biphenyl (19e)	S43
4,4'-Dimethoxy-1,1'-biphenyl (19f)	S45
4-Bromo-2,6-dimethoxyphenol (21)	S47
5-Bromo-2-hydroxy-3-methoxybenzaldehyde (23)	S49
5-Bromo-3-methoxybenzene-1,2-diol (24)	S51
6-Bromo-4-methoxybenzo[d][1,3]dioxole (25)	S53
Aucuparin (7a)	S55
2'-Methoxyaucuparin (<i>o</i> -5)	S57
4'-Methoxyaucuparin (<i>p</i> -5)	S59
2'-Hydroxyaucuparin (<i>o</i> -3)	S61
3'-Hydroxyaucuparin (<i>m</i> -3)	S63
Garcibiphenyl C (<i>p</i> -3)	S65
Rhaphiolepsin (4)	S67
3-De-O-methylaucuparin (7b)	S69
3-(7-Methoxybenzo[d][1,3]dioxol-5-yl)phenol (6)	S71

^1H NMR (CDCl_3 , 300 MHz) of **10b**

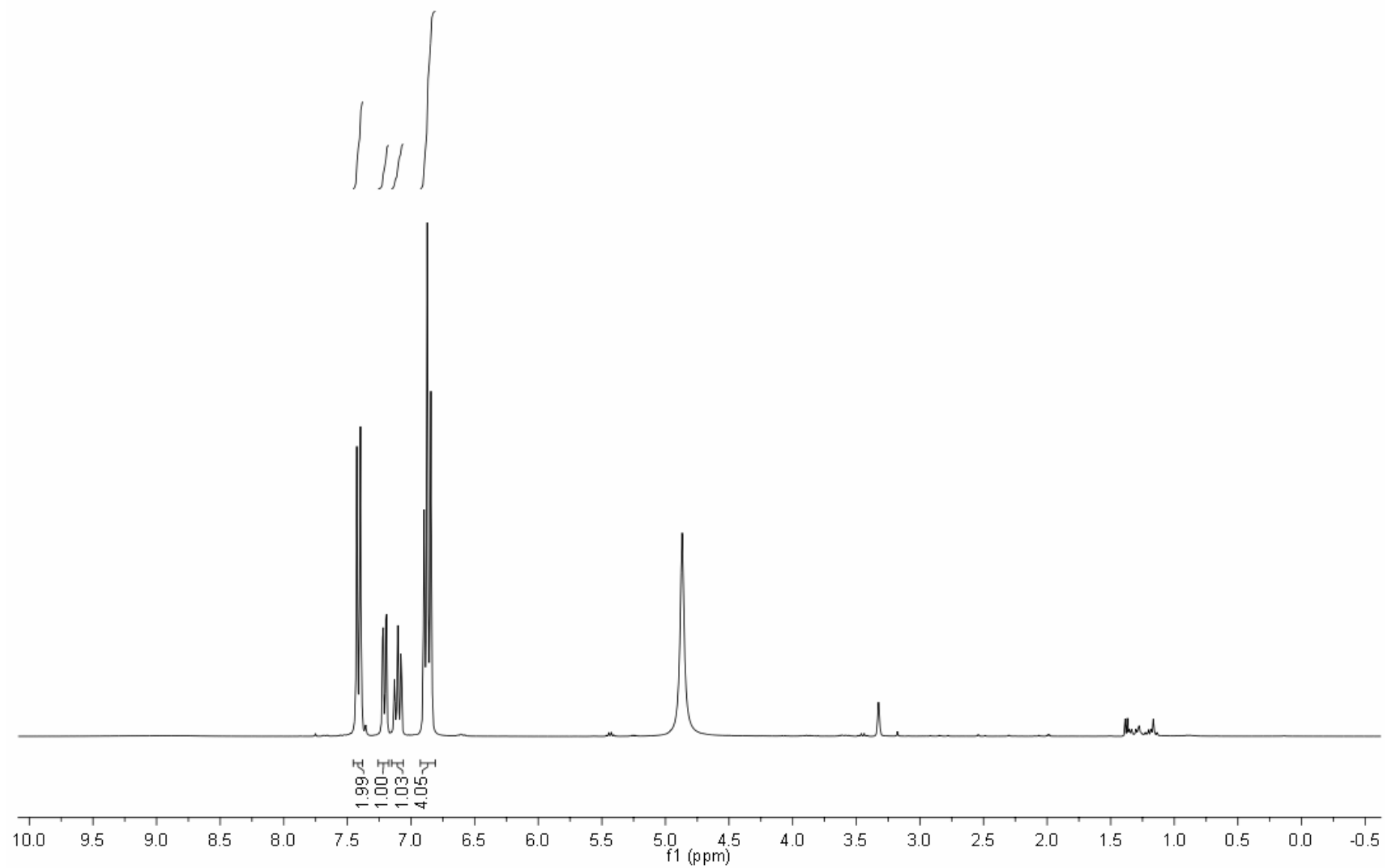


^{13}C NMR (CDCl_3 , 75 MHz) of **10b**

156.4
152.5
138.9
130.8
130.2
129.4
127.8
121.5
121.0
116.2
116.0
115.1

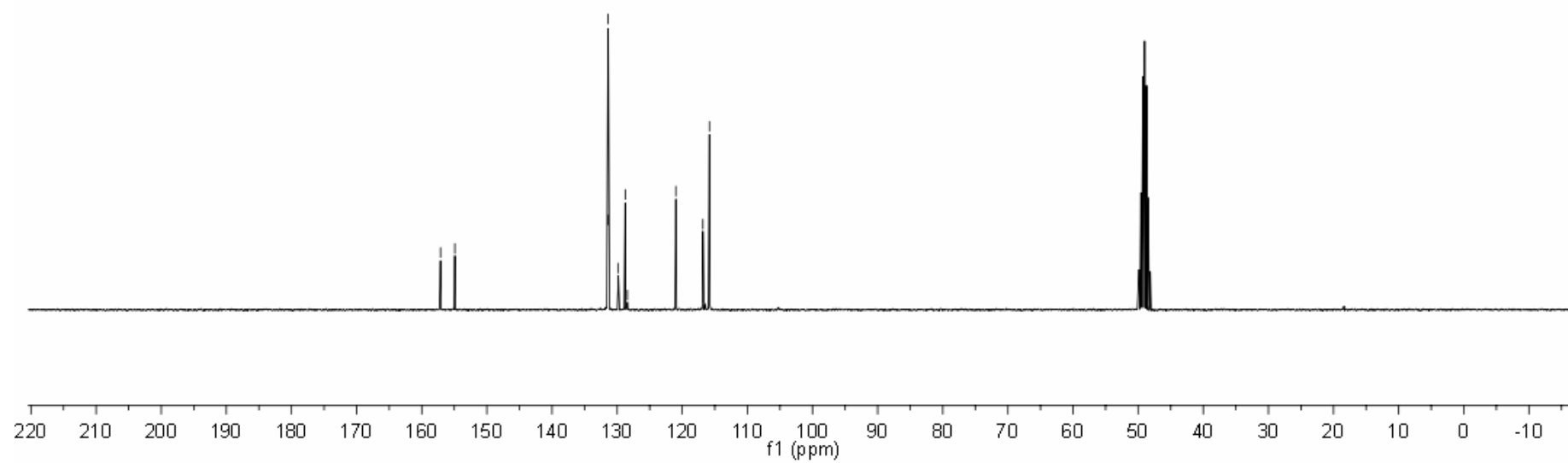


^1H NMR (methanol- d_4 , 300 MHz) of **10c**

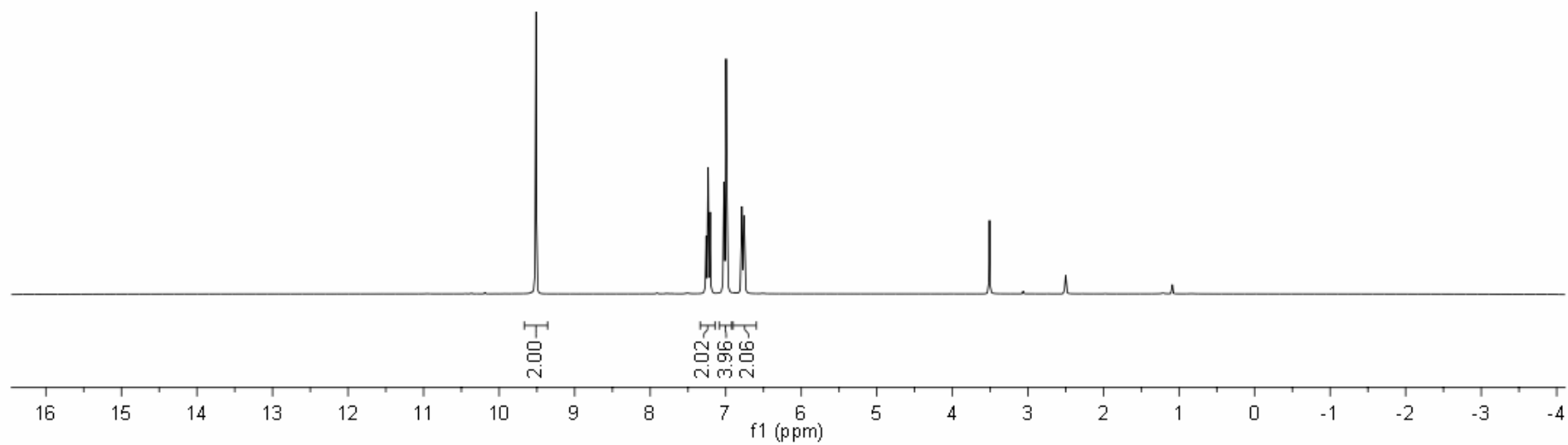
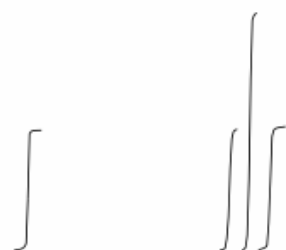


^{13}C NMR (methanol- d_4 , 75 MHz) of **10c**

157.1
154.9
131.4
131.4
129.8
128.8
128.4
121.0
116.8
115.8

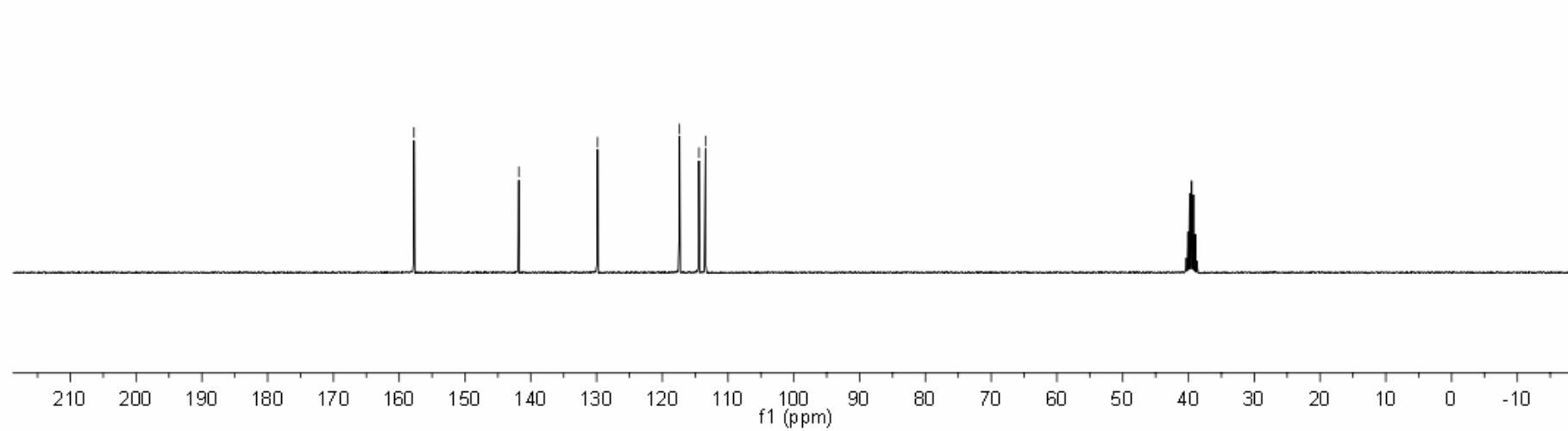


^1H NMR ($\text{DMSO}-d_6$, 300 MHz) of **10d**

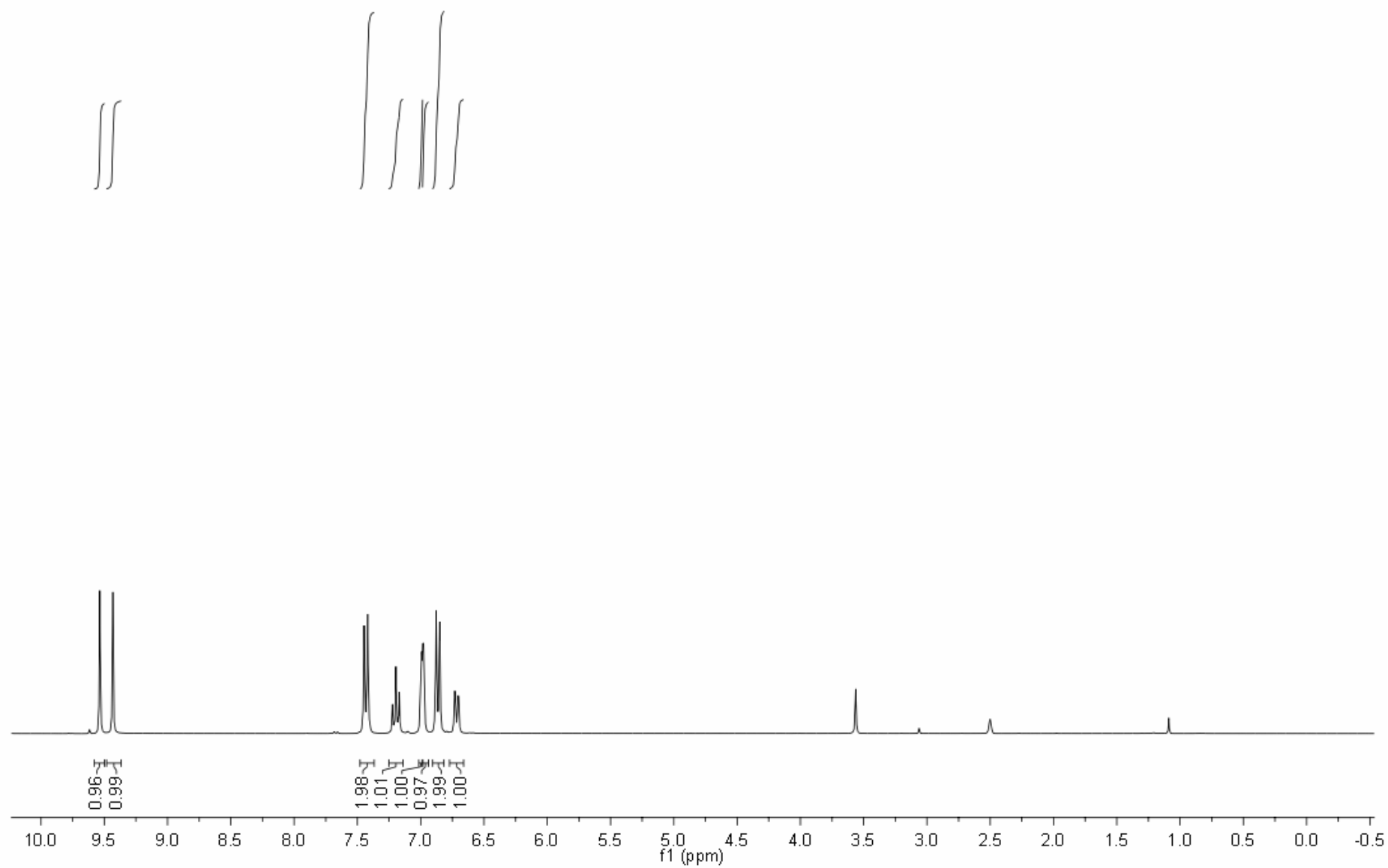


^{13}C NMR (DMSO- d_6 , 75 MHz) of **10d**

—157.7
—141.8
—129.8
✓117.4
✓114.4
✓113.4

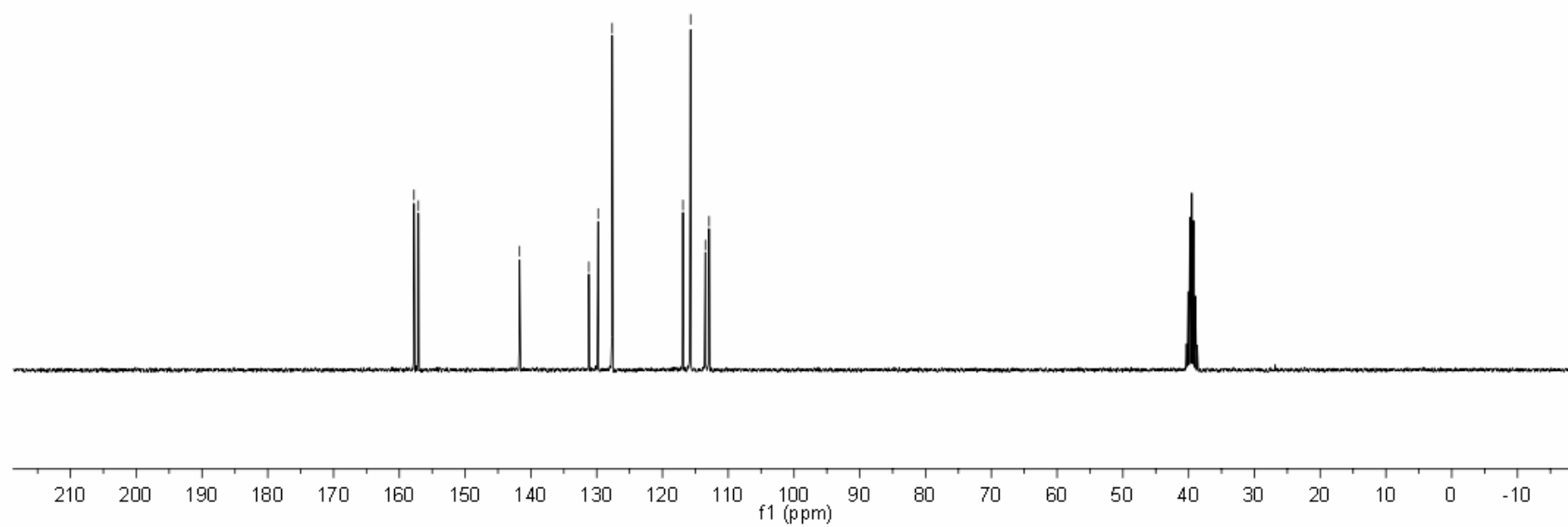


^1H NMR (DMSO- d_6 , 300 MHz) of **10e**

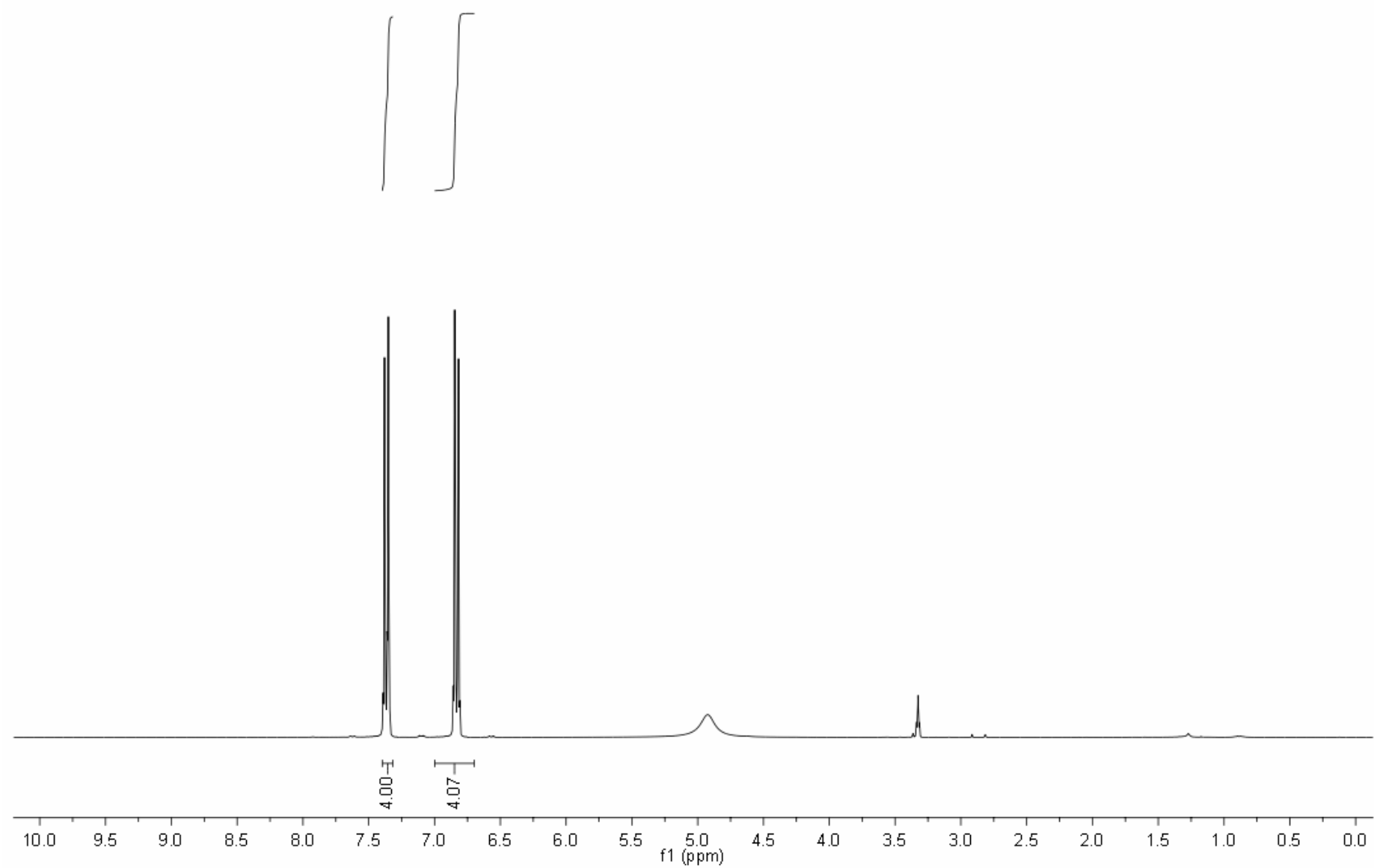


^{13}C NMR (DMSO- d_6 , 75 MHz) of **10e**

157.8
157.1
141.7
131.2
129.8
127.7
116.9
115.7
113.5
112.9

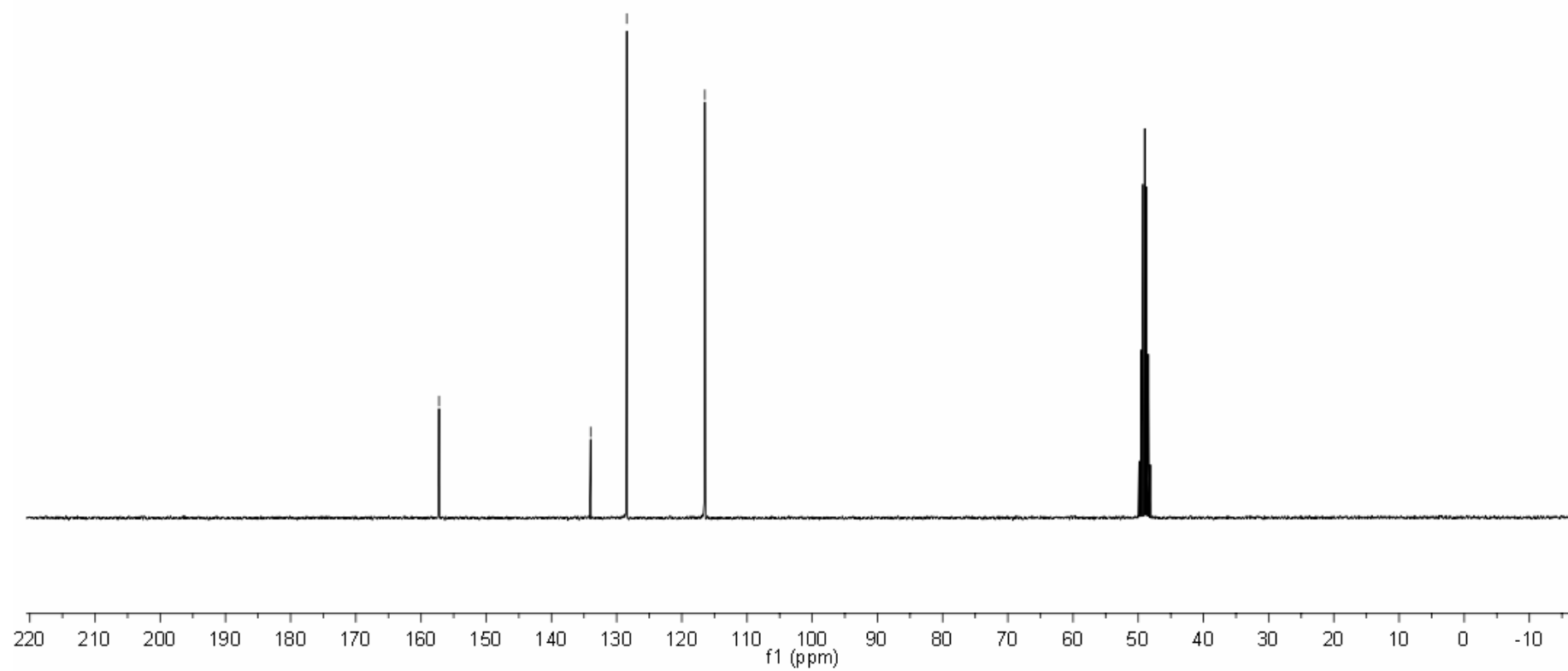


^1H NMR (methanol- d_4 , 300 MHz) of **10f**

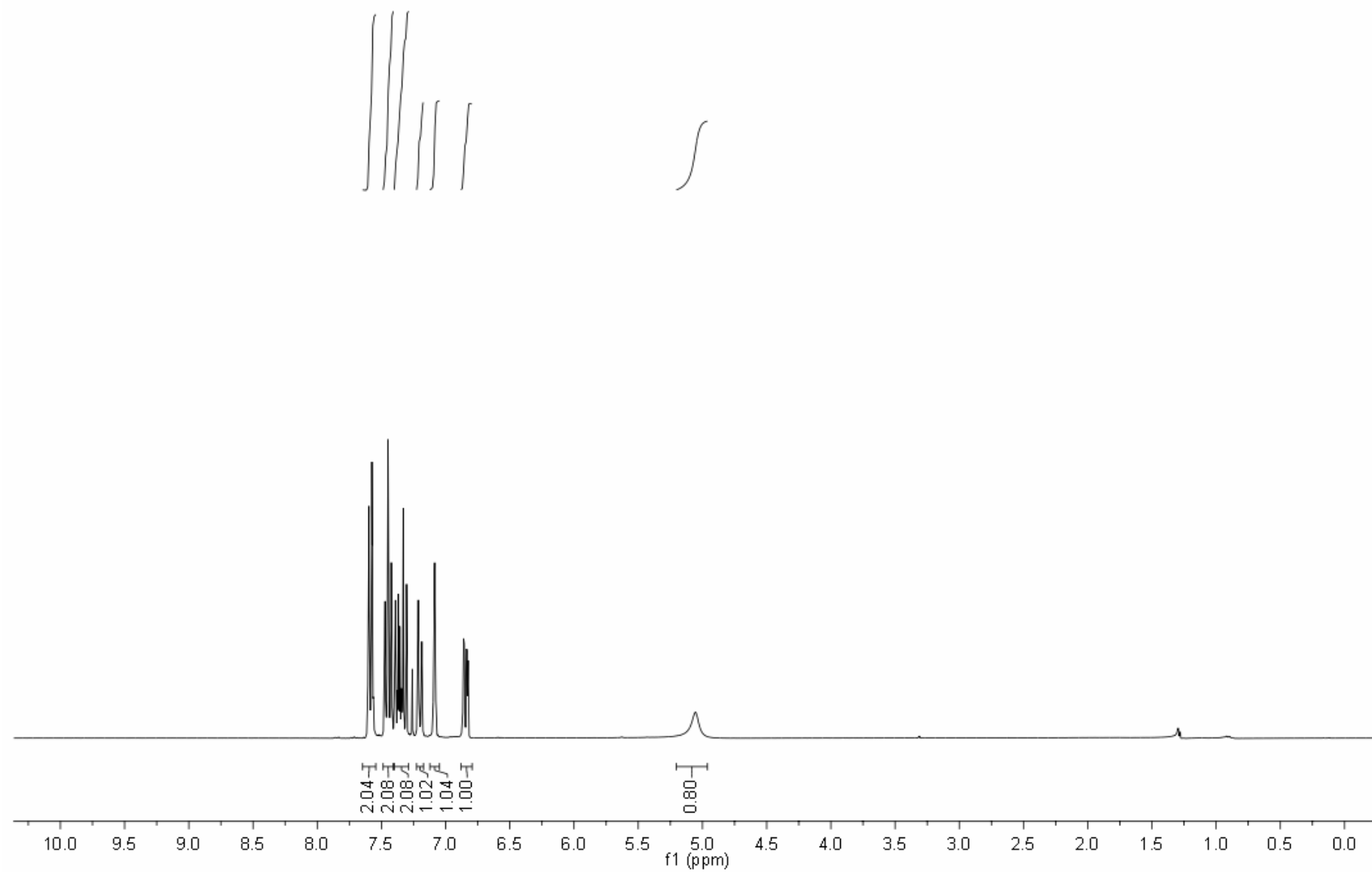


^{13}C NMR (methanol- d_4 , 75 MHz) of **10f**

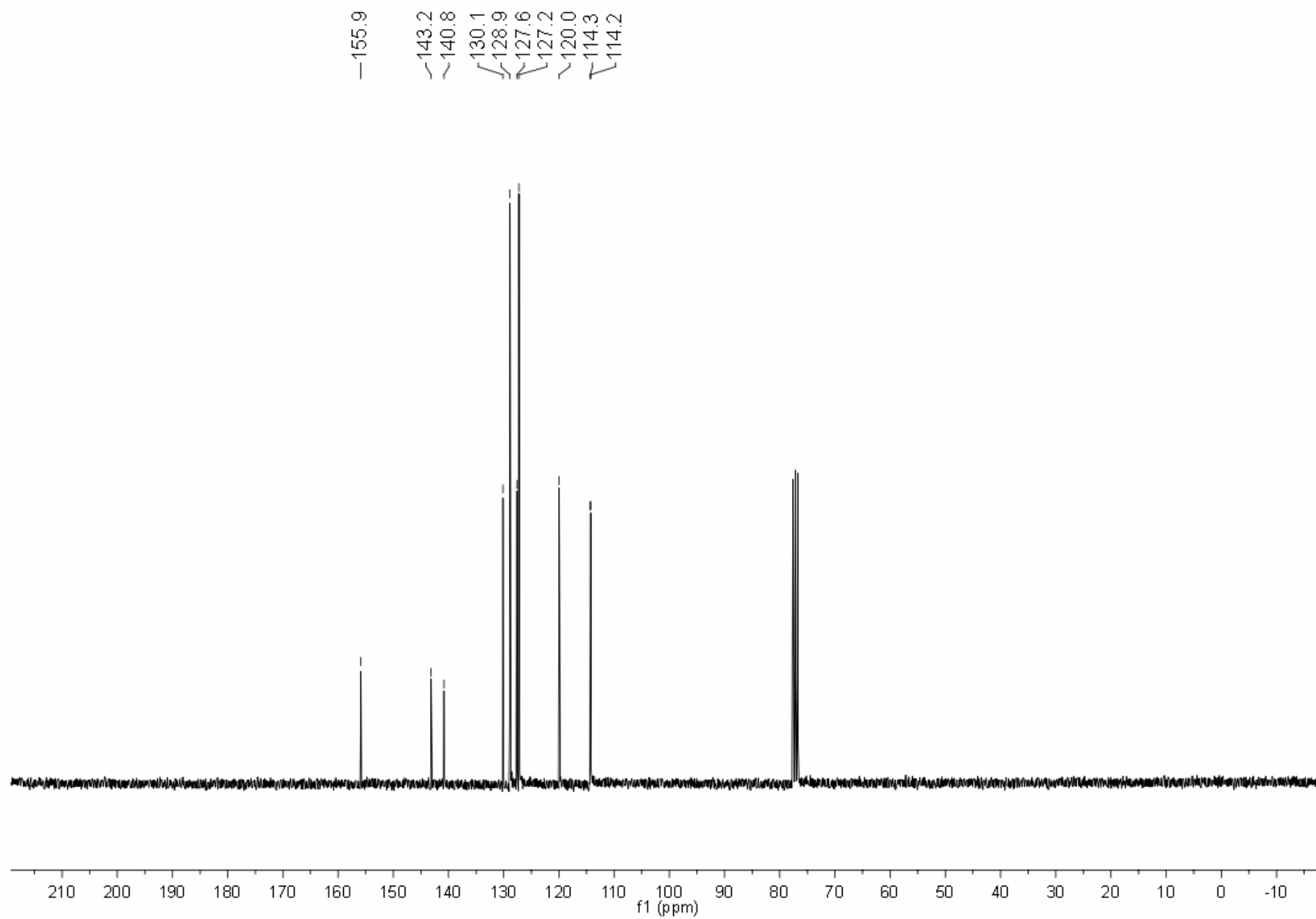
—157.2
—134.0
—128.4
—116.5



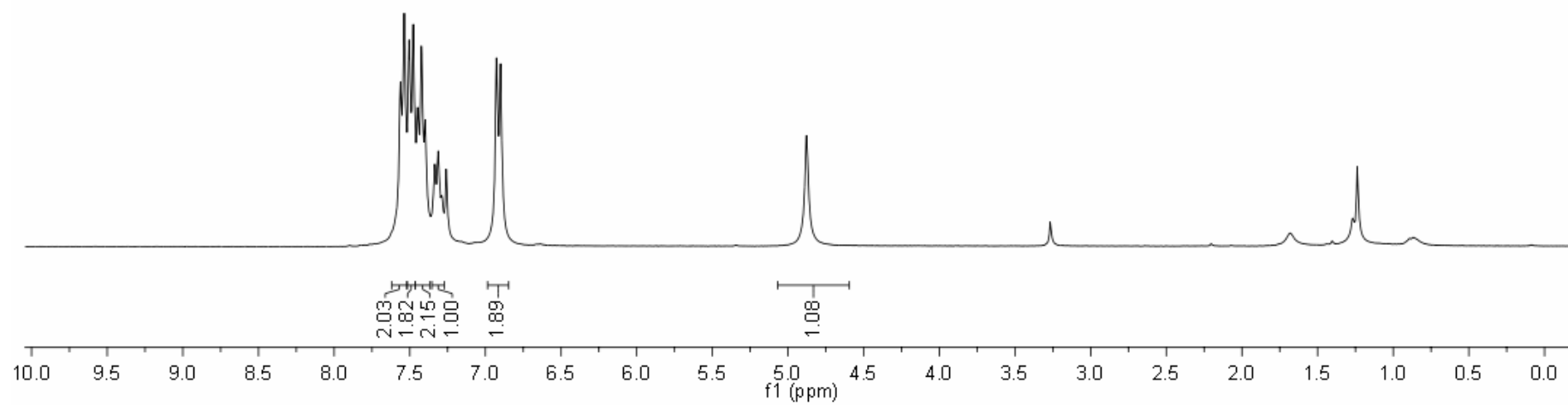
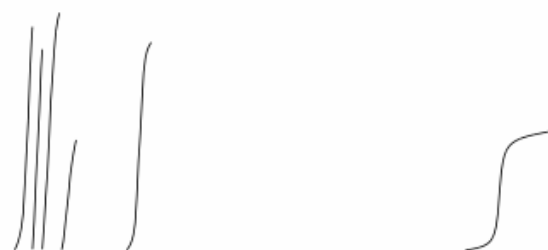
^1H NMR (CDCl_3 , 300 MHz) of *m*-12



^{13}C NMR (CDCl_3 , 75 MHz) of *m*-12

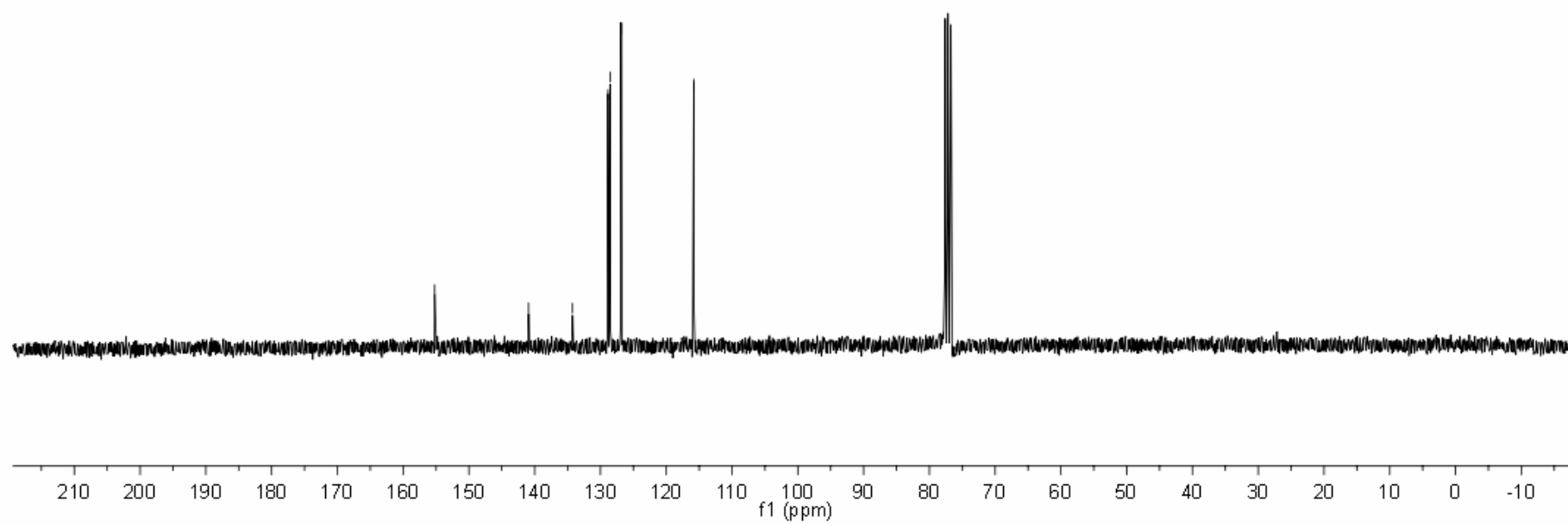


^1H NMR (CDCl_3 , 300 MHz) of *p*-12

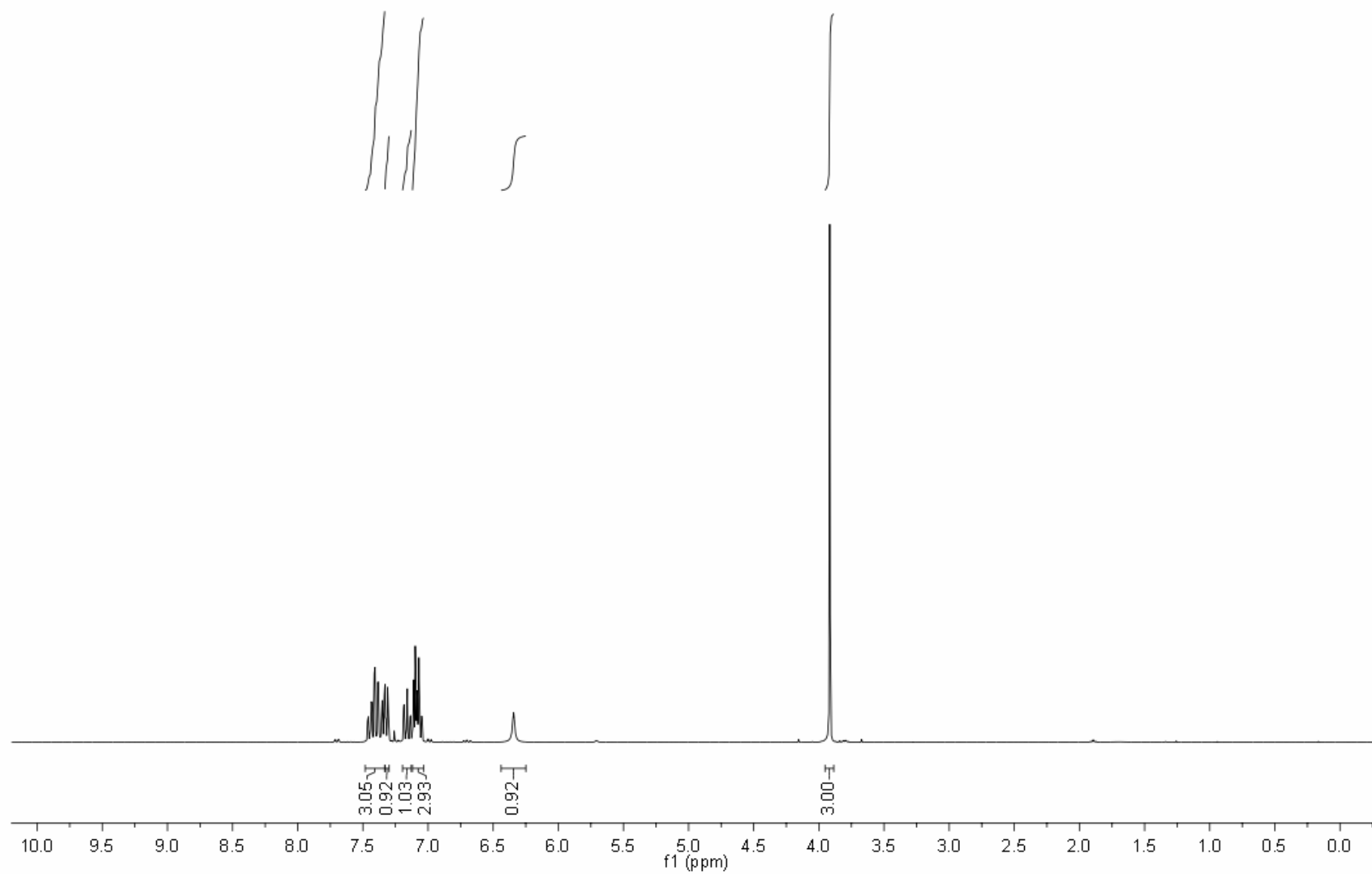


^{13}C NMR (CDCl_3 , 75 MHz) of *p*-12

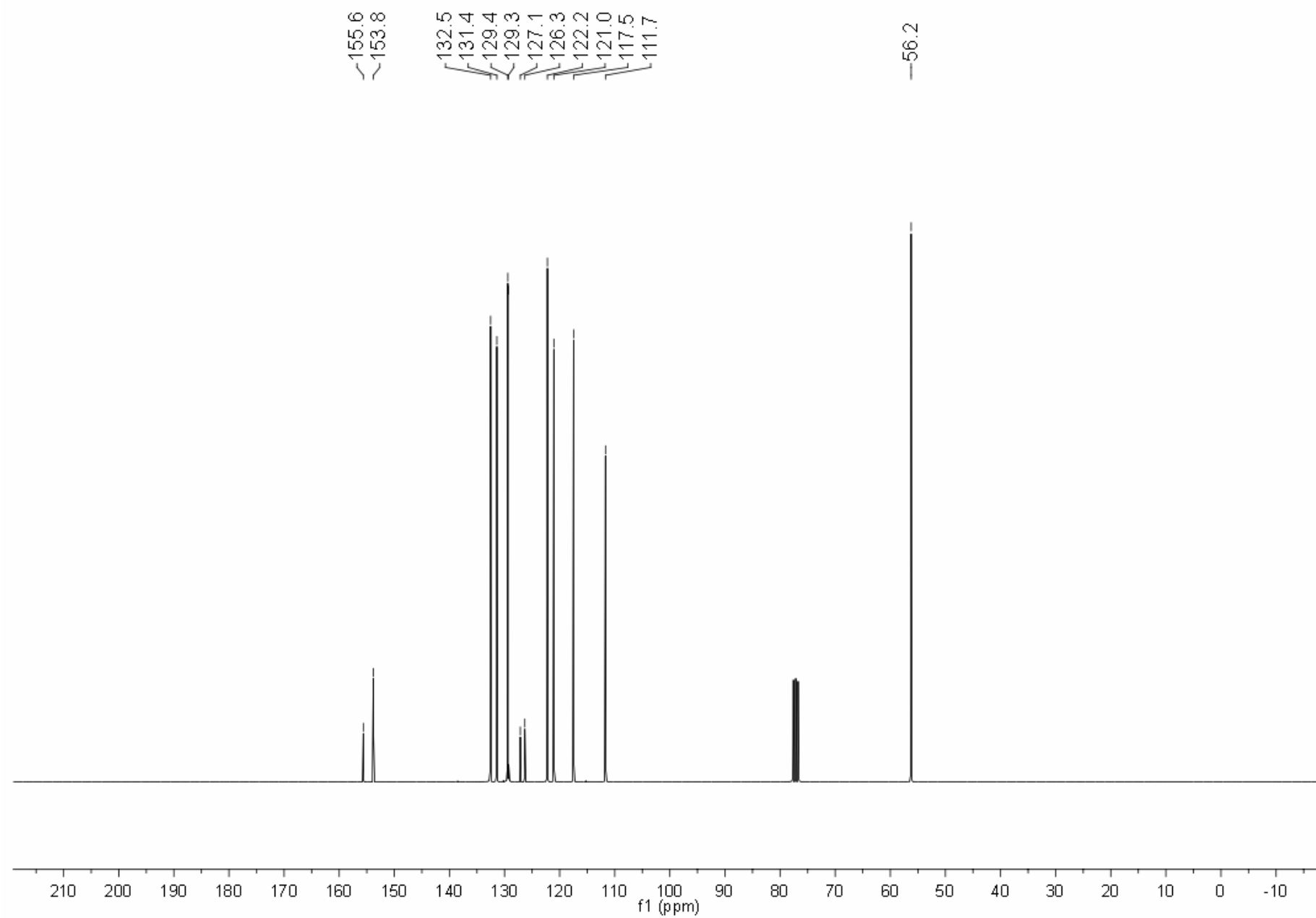
—155.2
~140.9
/134.3
/128.9
/128.5
~126.9
—115.8



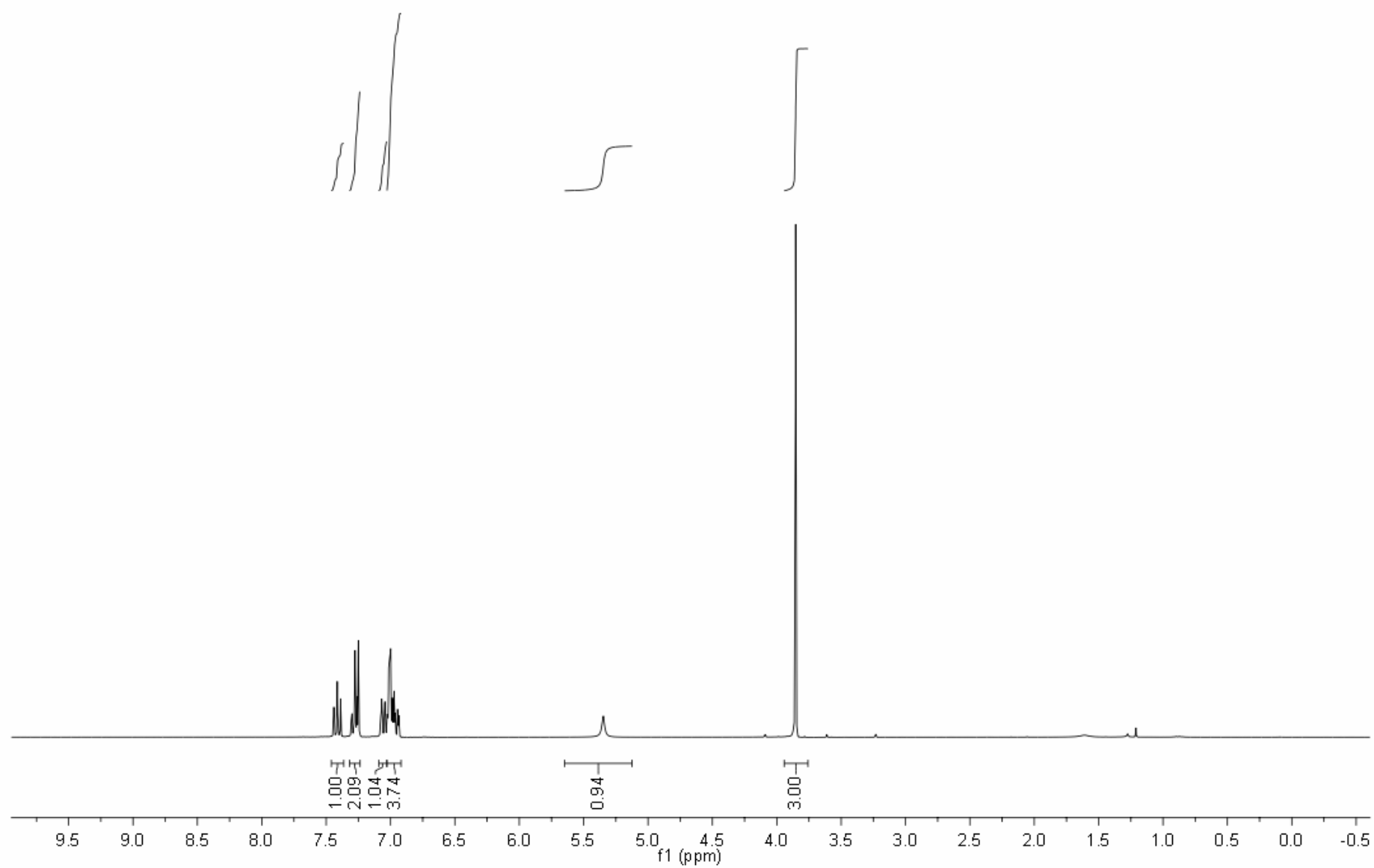
^1H NMR (CDCl_3 , 300 MHz) of **17a**



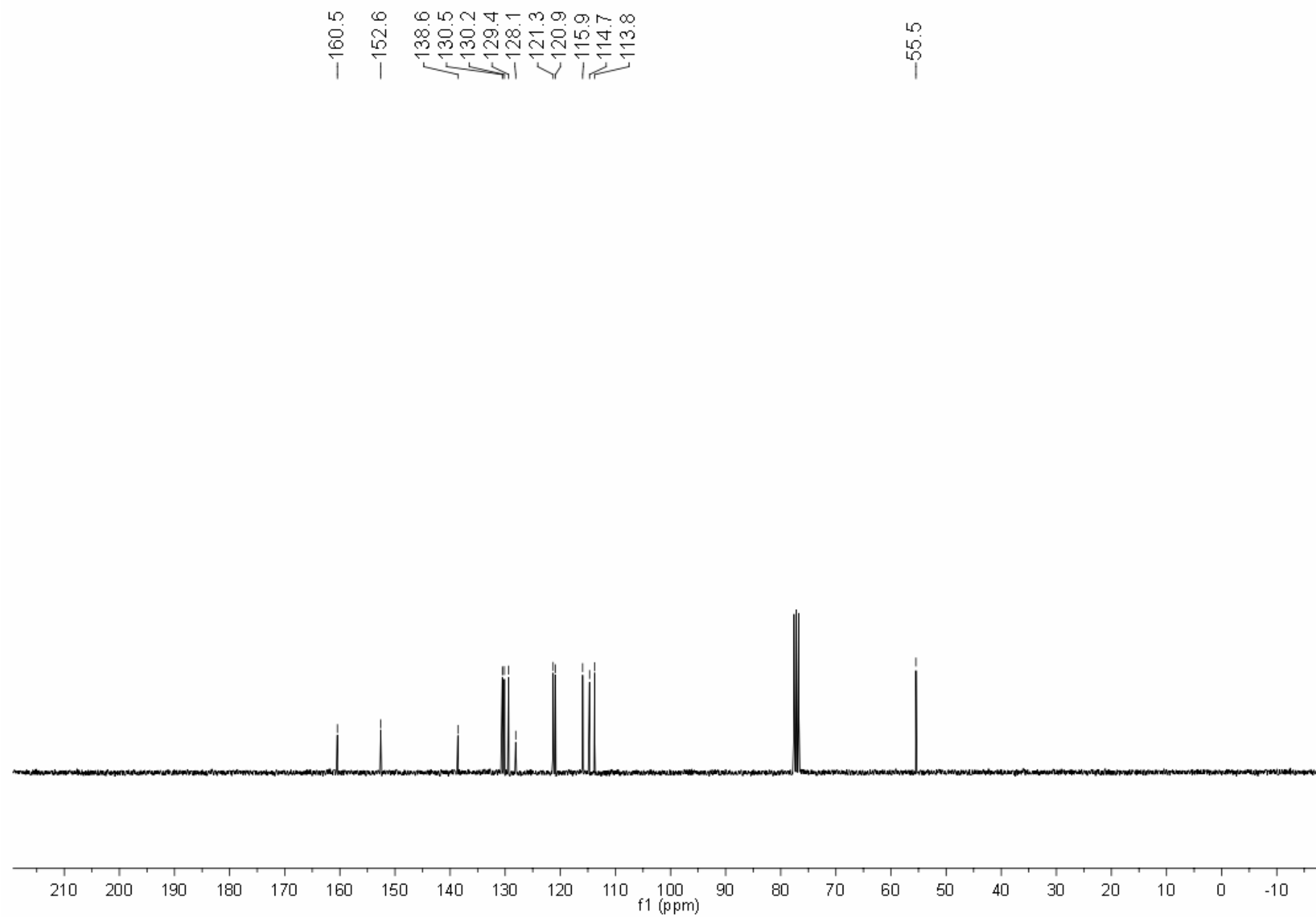
^{13}C NMR (CDCl_3 , 75 MHz) of **17a**



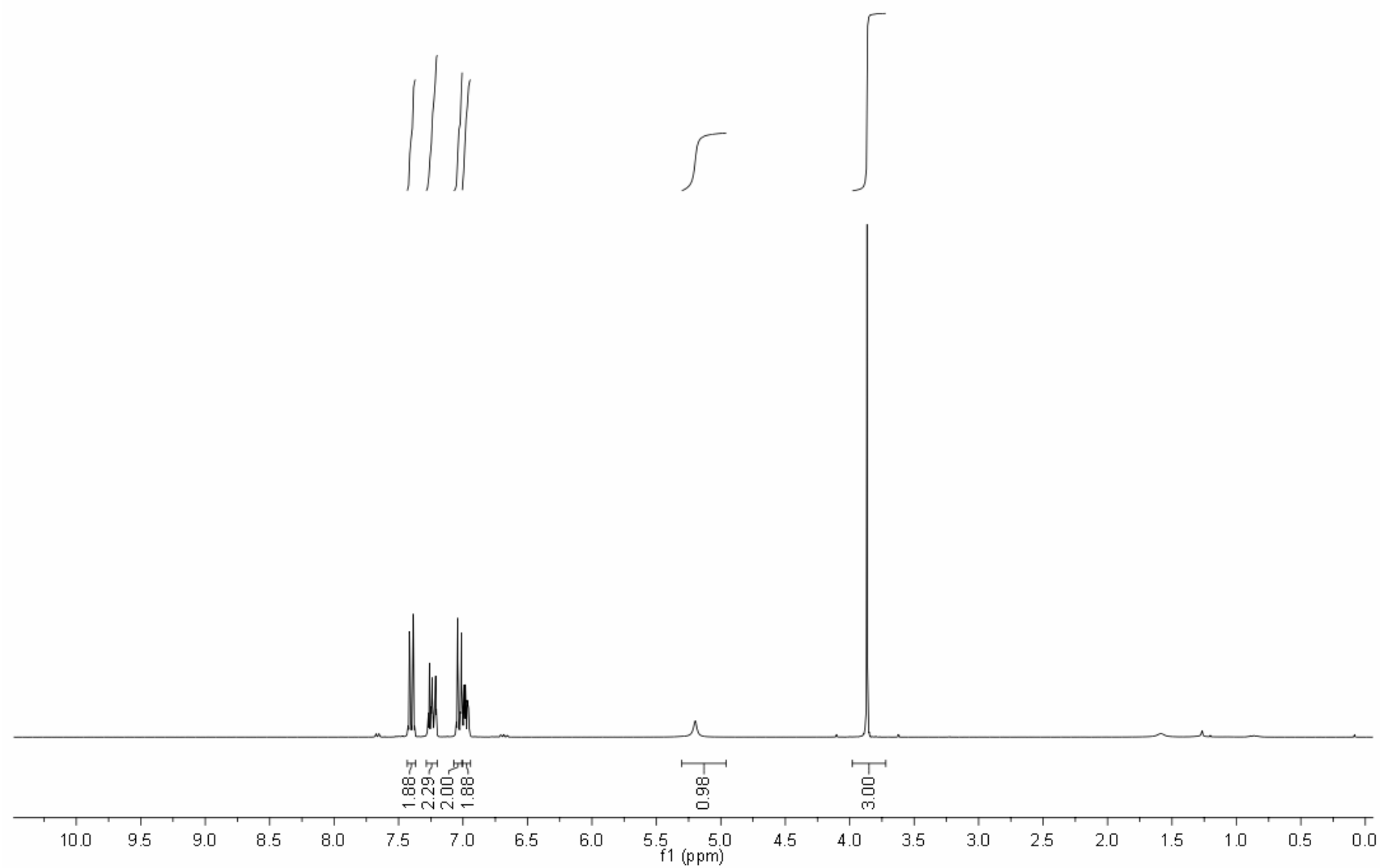
^1H NMR (CDCl_3 , 300 MHz) of **17b**



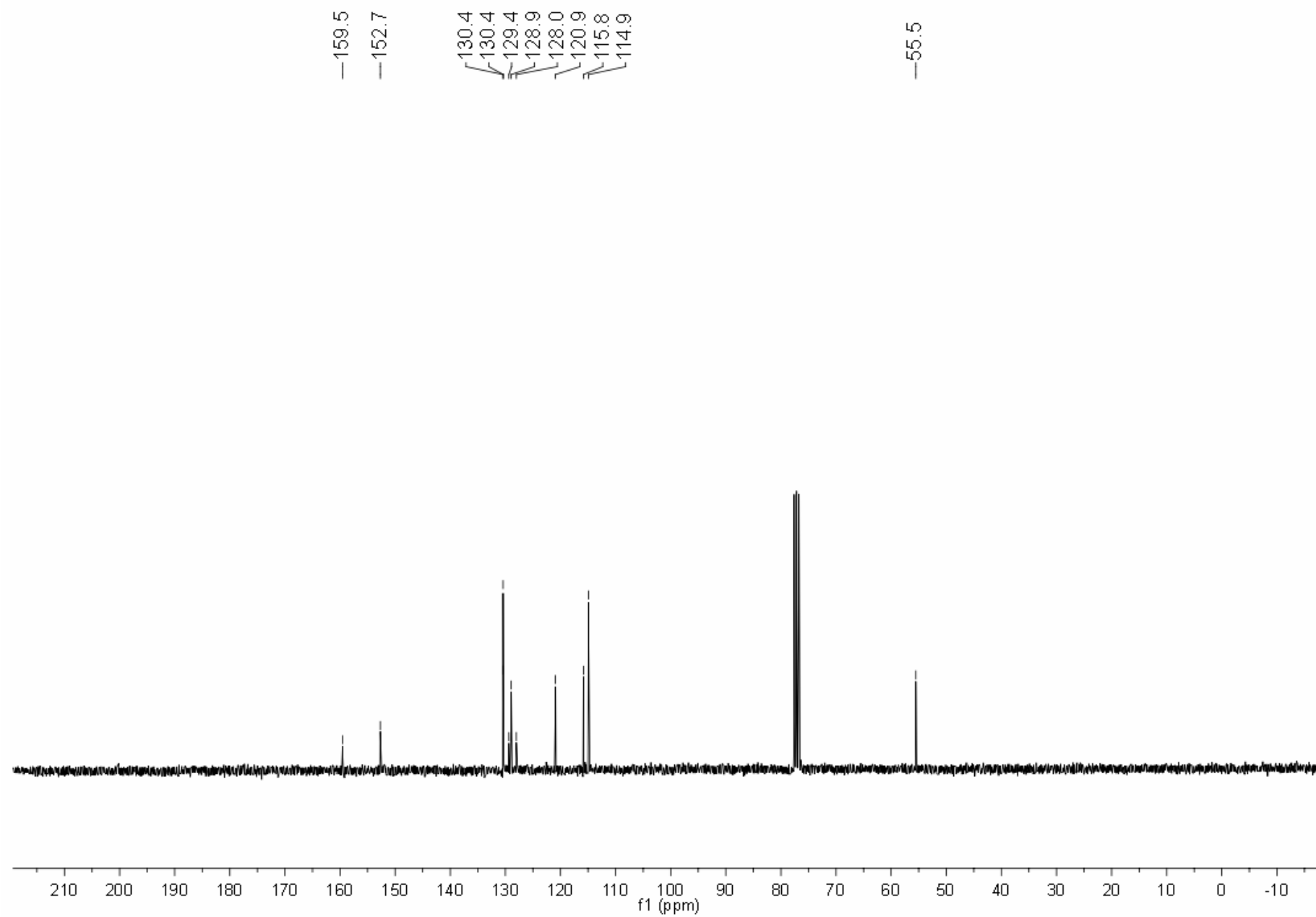
^{13}C NMR (CDCl_3 , 75 MHz) of **17b**



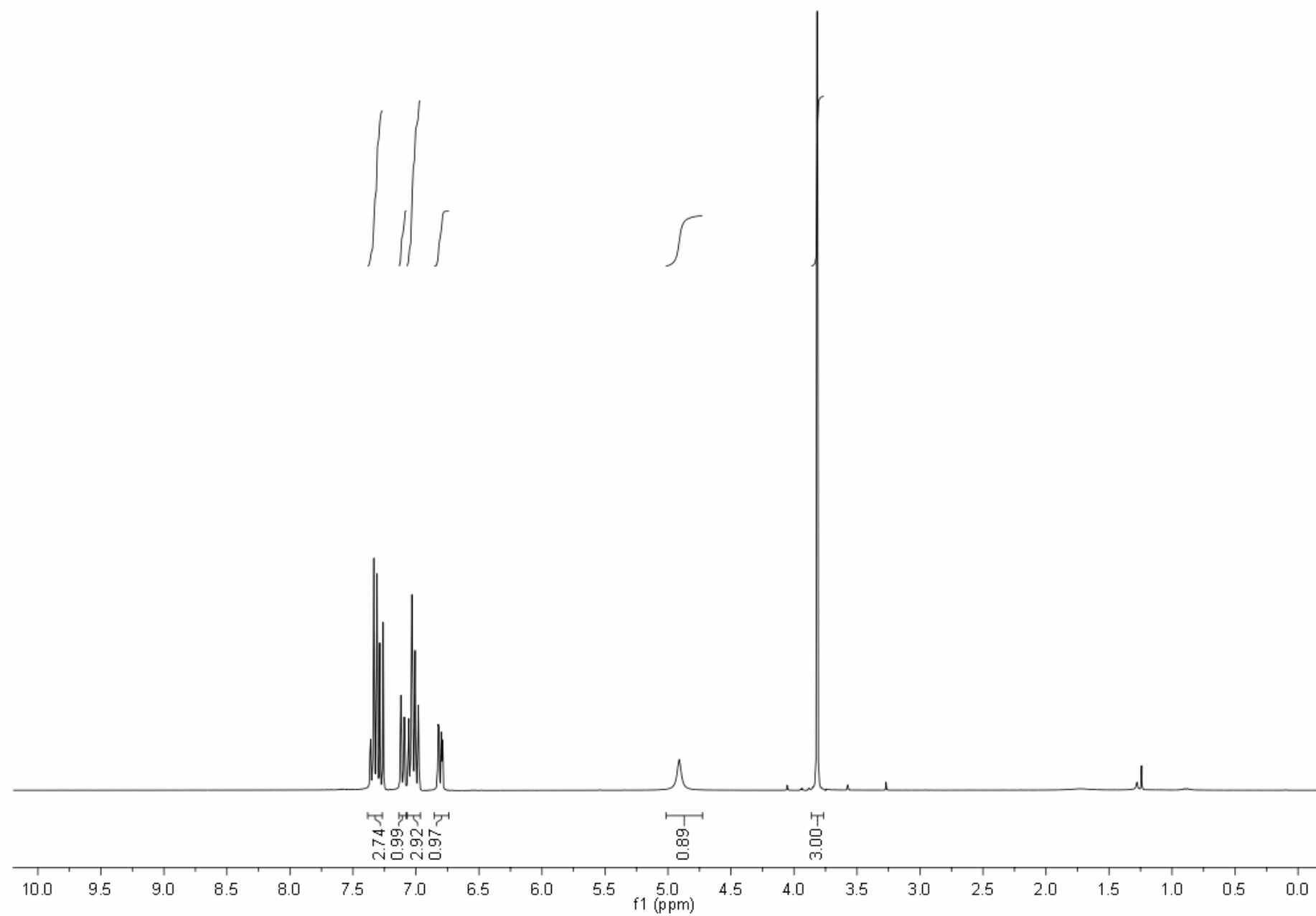
^1H NMR (CDCl_3 , 300 MHz) of **17c**



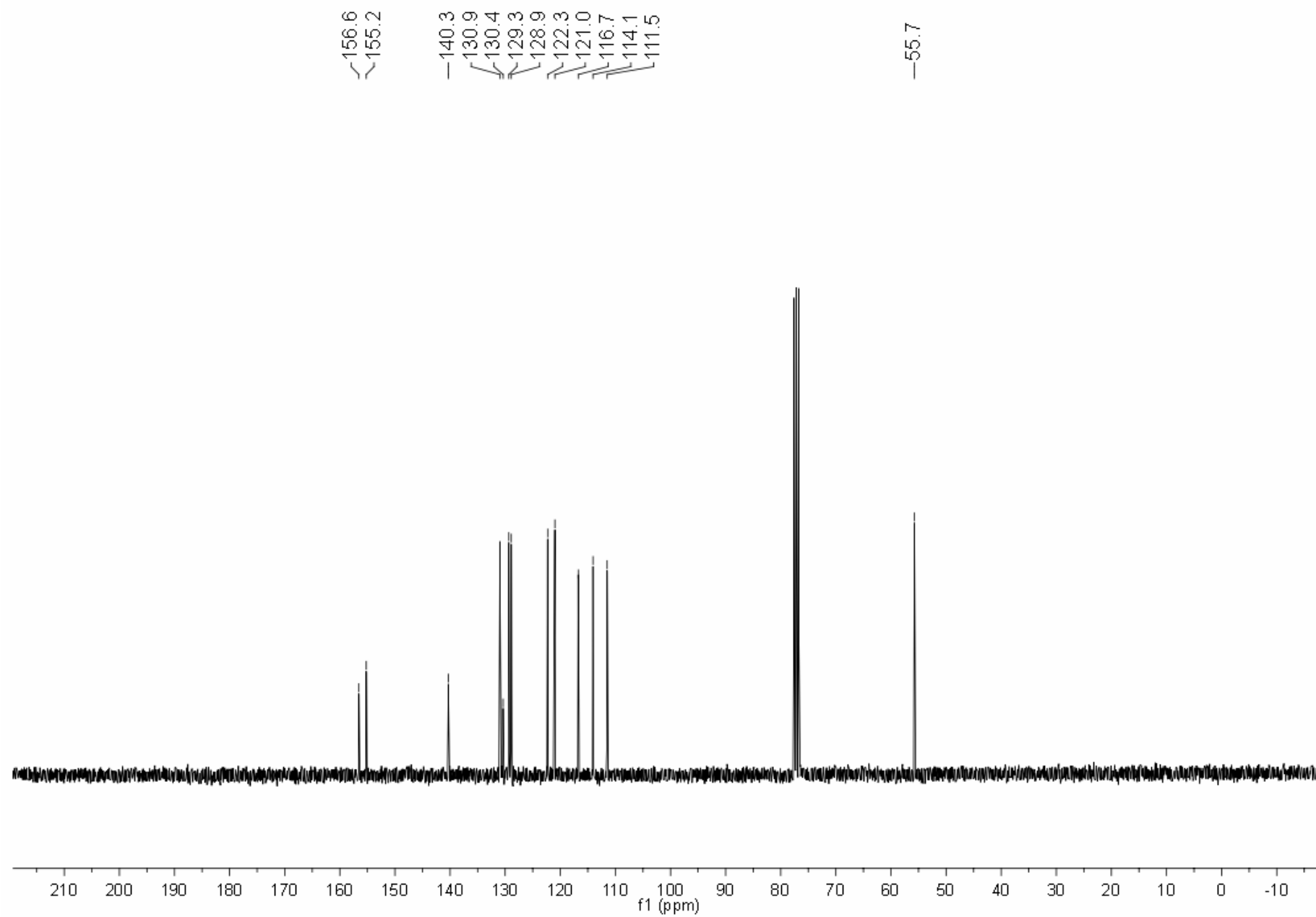
^{13}C NMR (CDCl_3 , 75 MHz) of **17c**



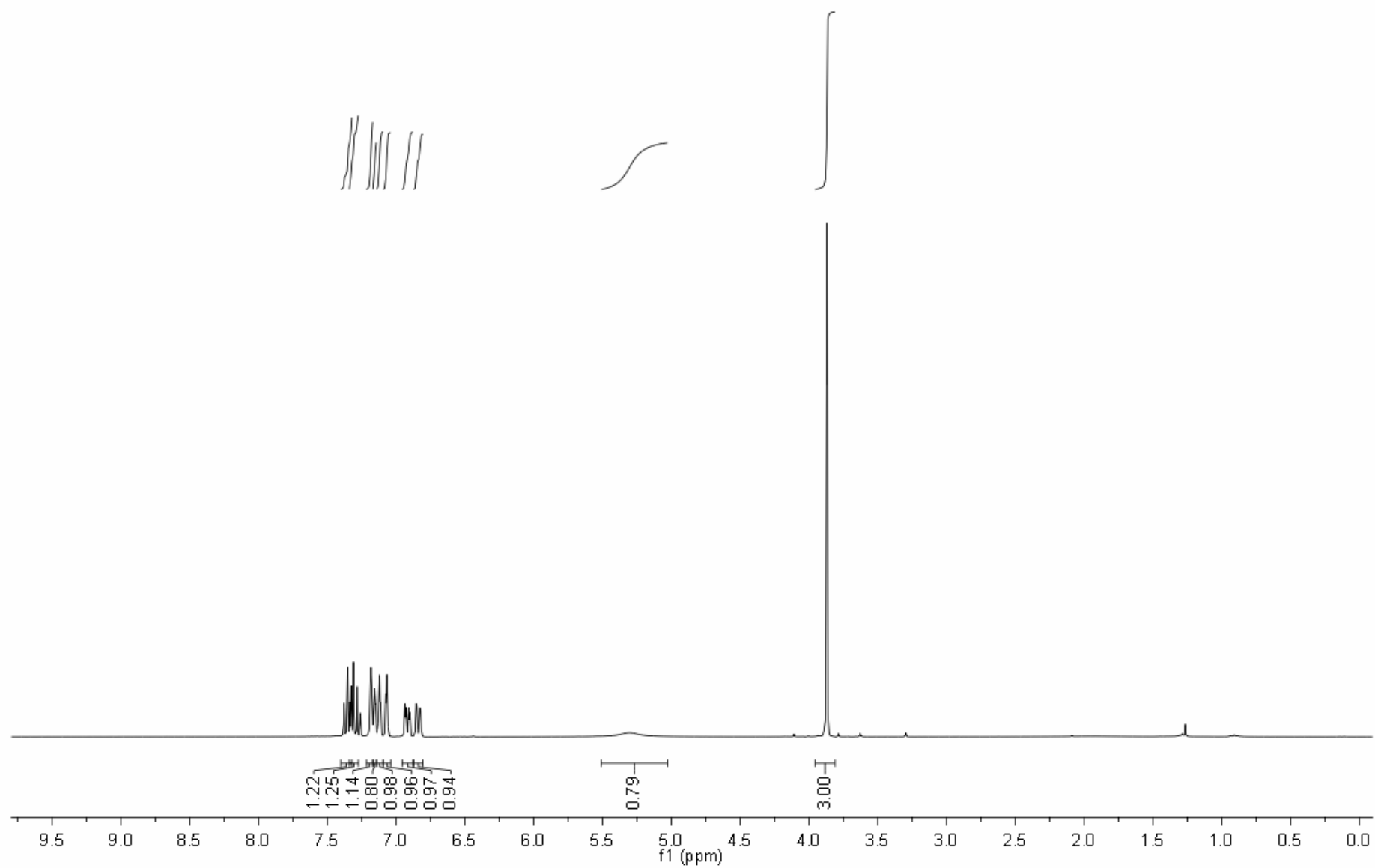
^1H NMR (CDCl_3 , 300 MHz) of **17d**



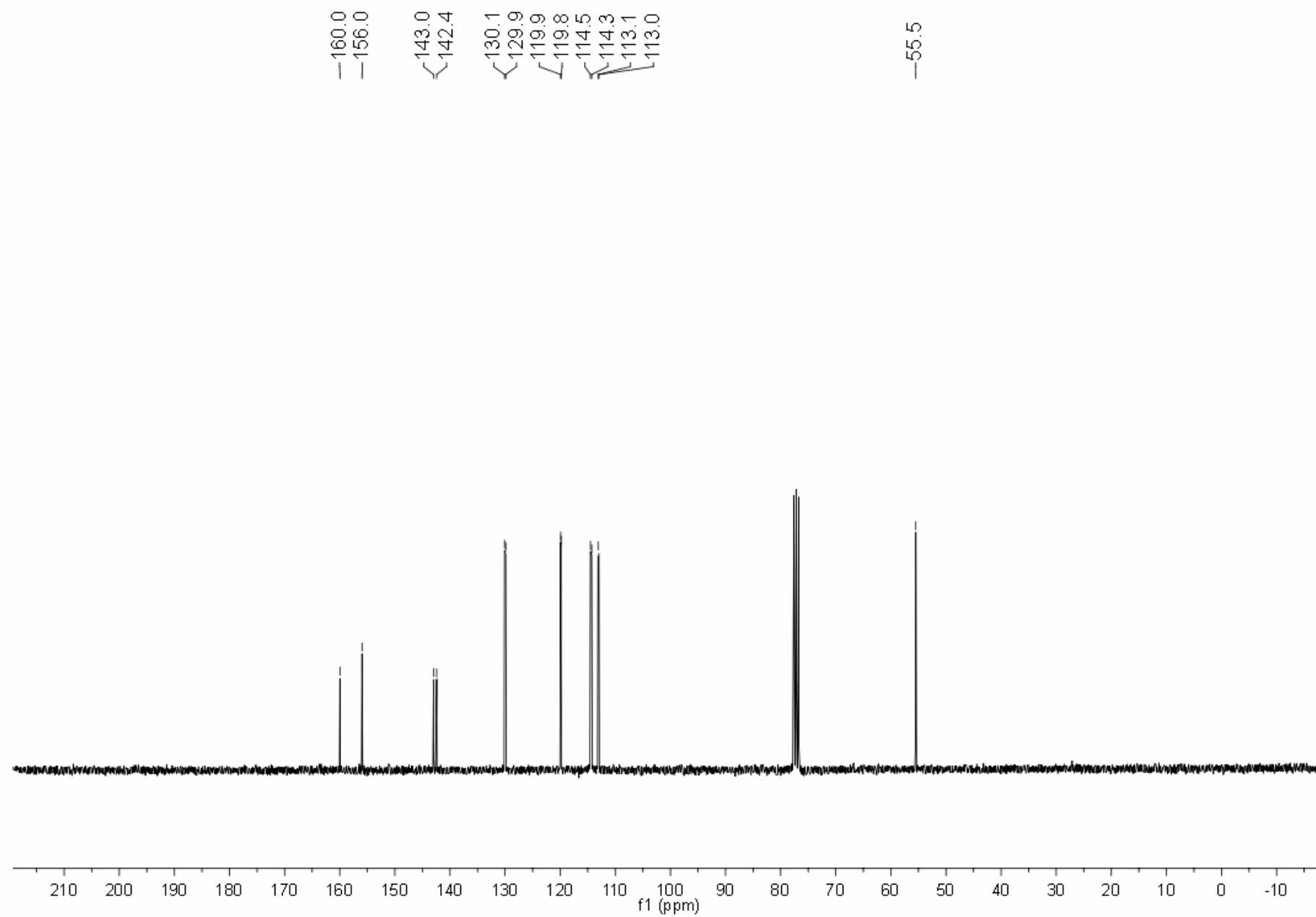
^{13}C NMR (CDCl_3 , 75 MHz) of **17d**



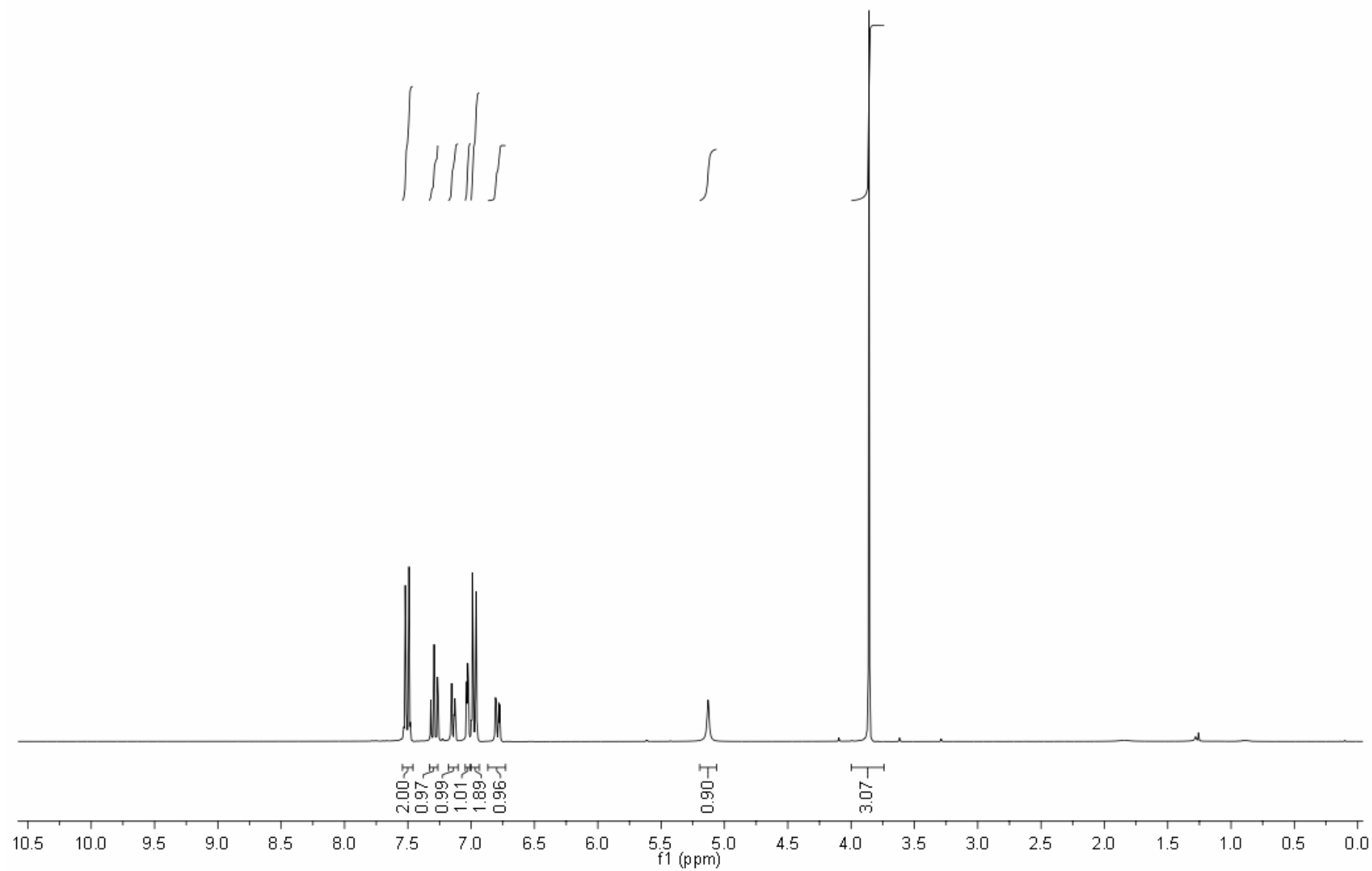
^1H NMR (CDCl_3 , 300 MHz) of **17e**



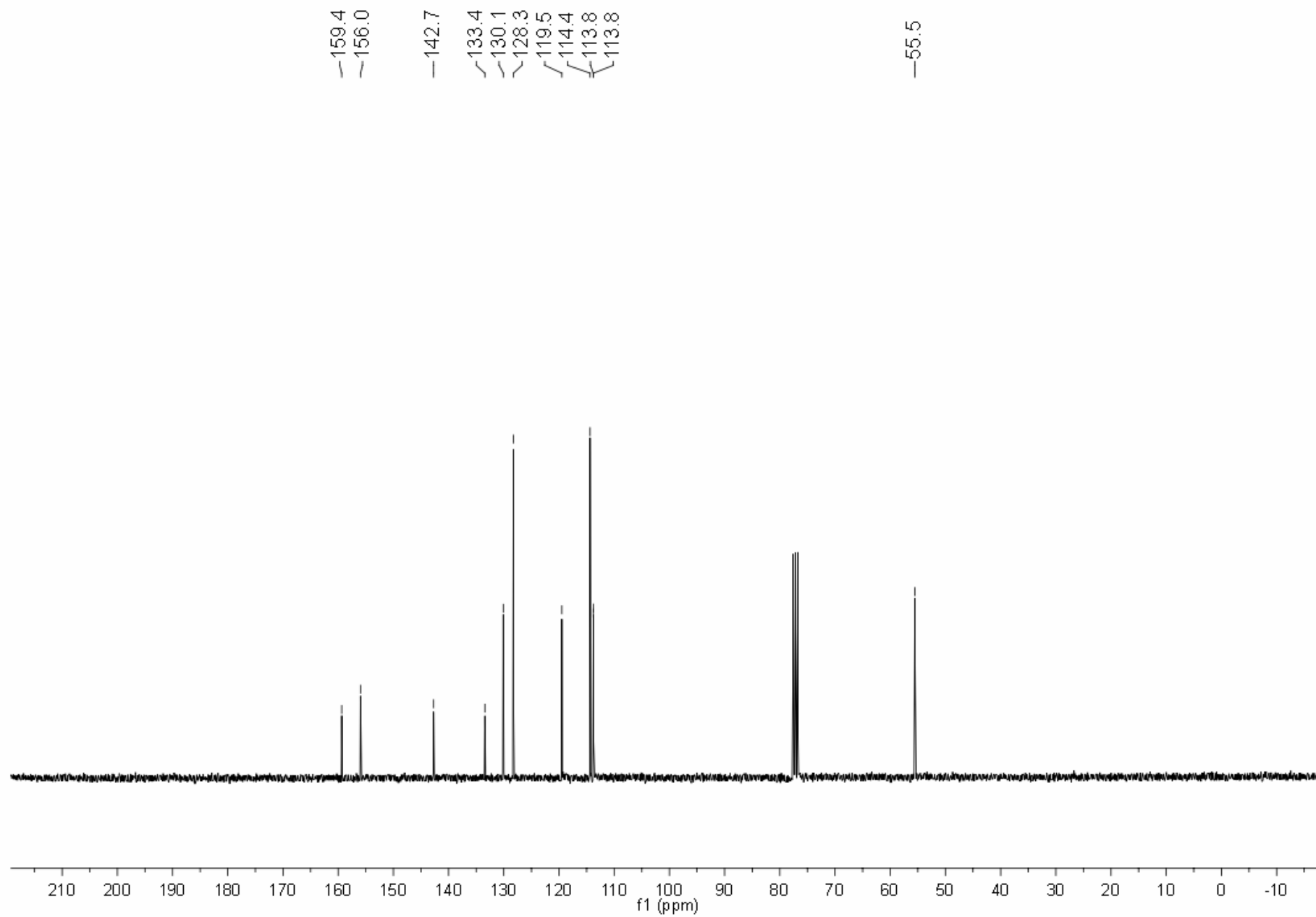
^{13}C NMR (CDCl_3 , 75 MHz) of **17e**



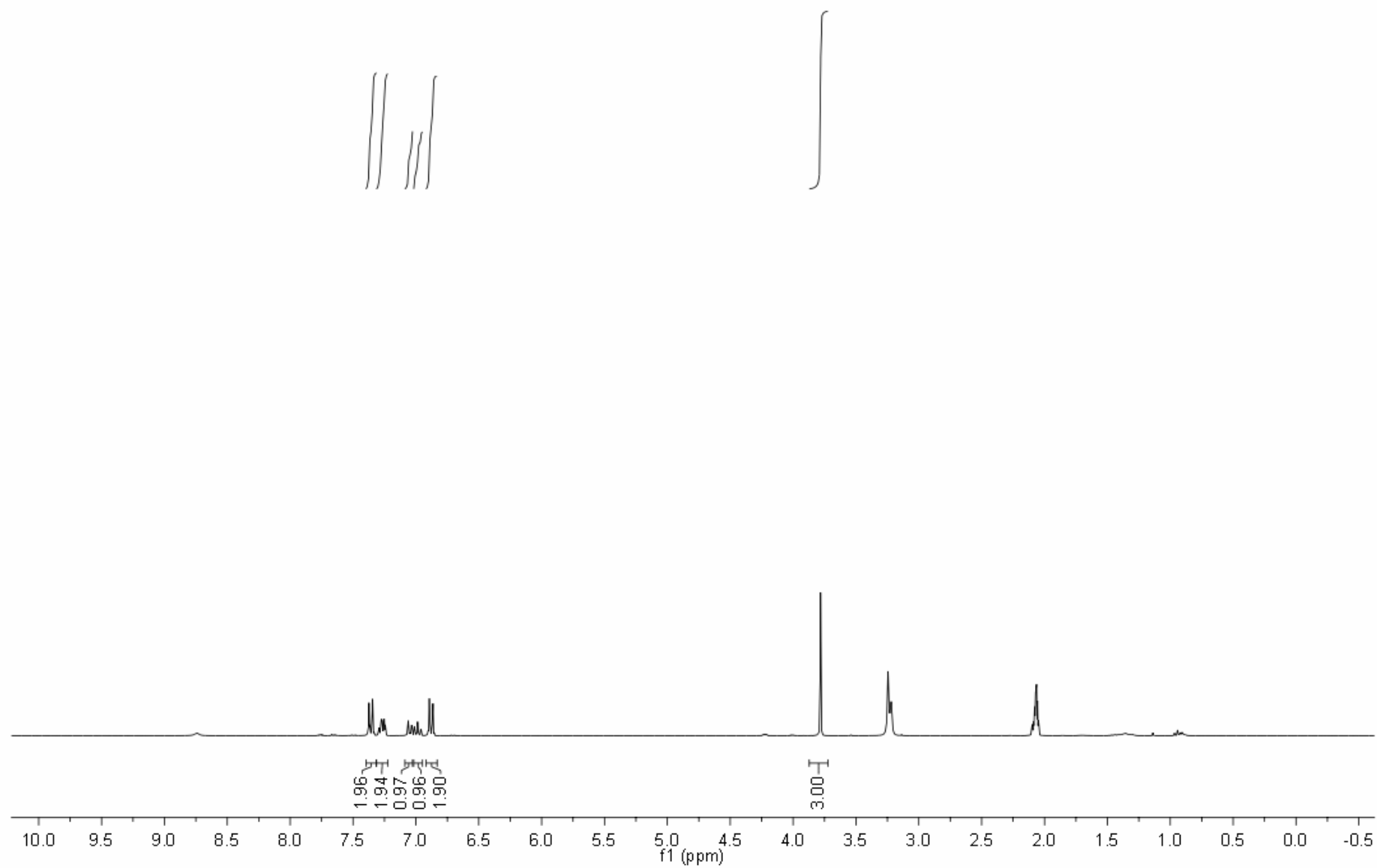
^1H NMR (CDCl_3 , 300 MHz) of **17f**



^{13}C NMR (CDCl_3 , 75 MHz) of **17f**



^1H NMR (acetone- d_6 , 300 MHz) of **17g**

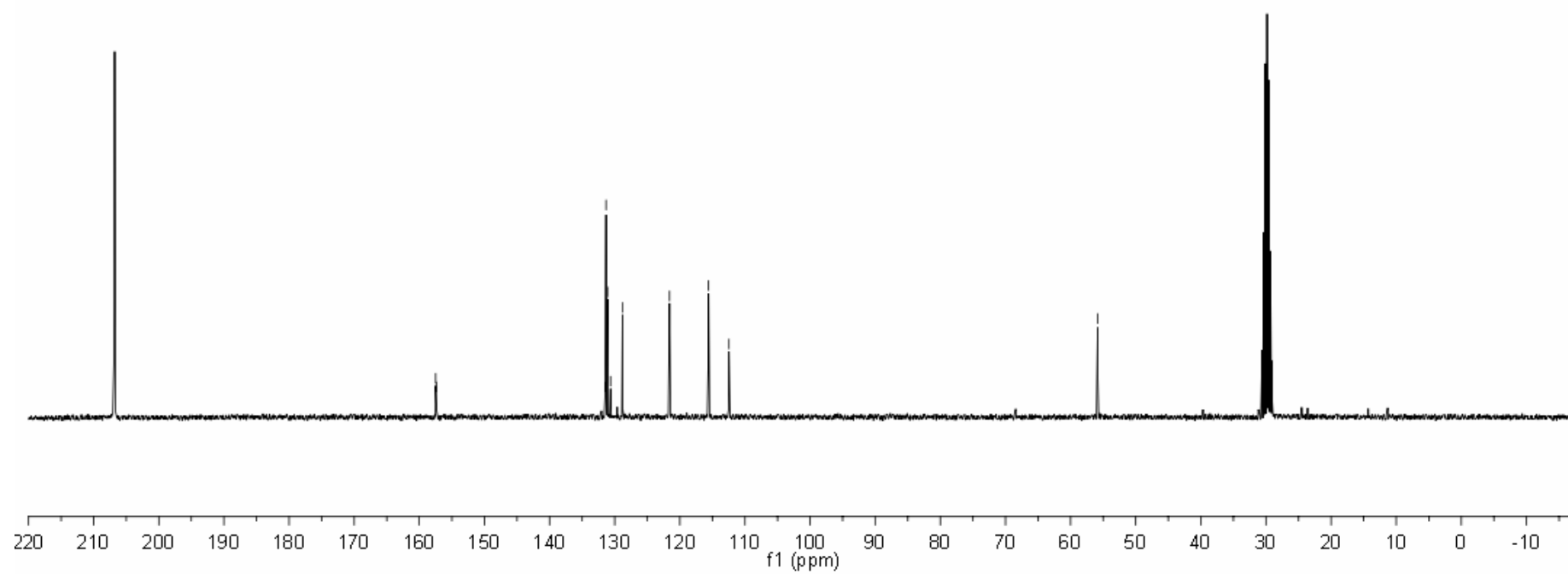


^{13}C NMR (acetone- d_6 , 75 MHz) of **17g**

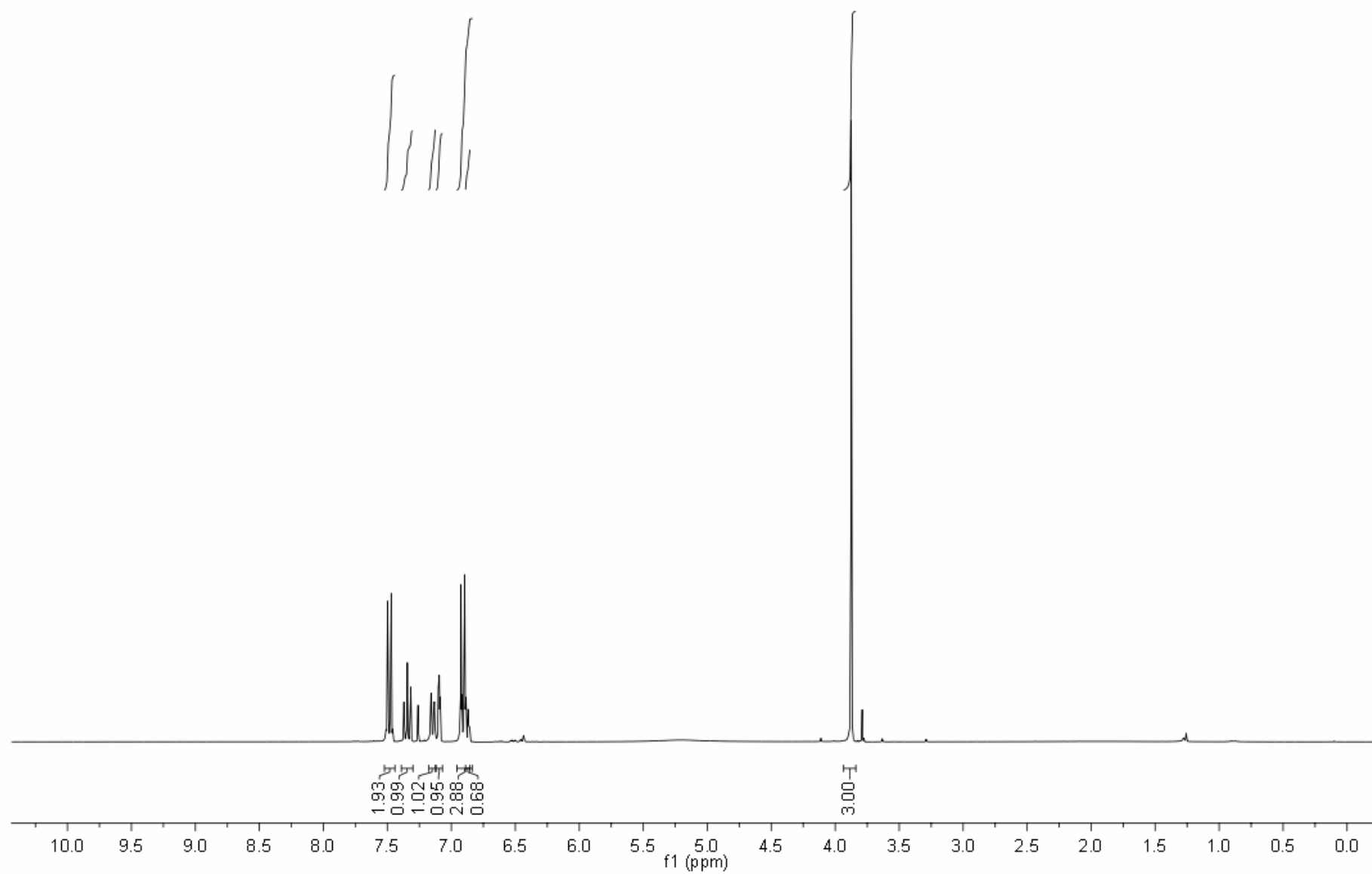
157.5
157.4

131.5
131.3
131.1
130.6
128.8
121.6
115.6
112.5

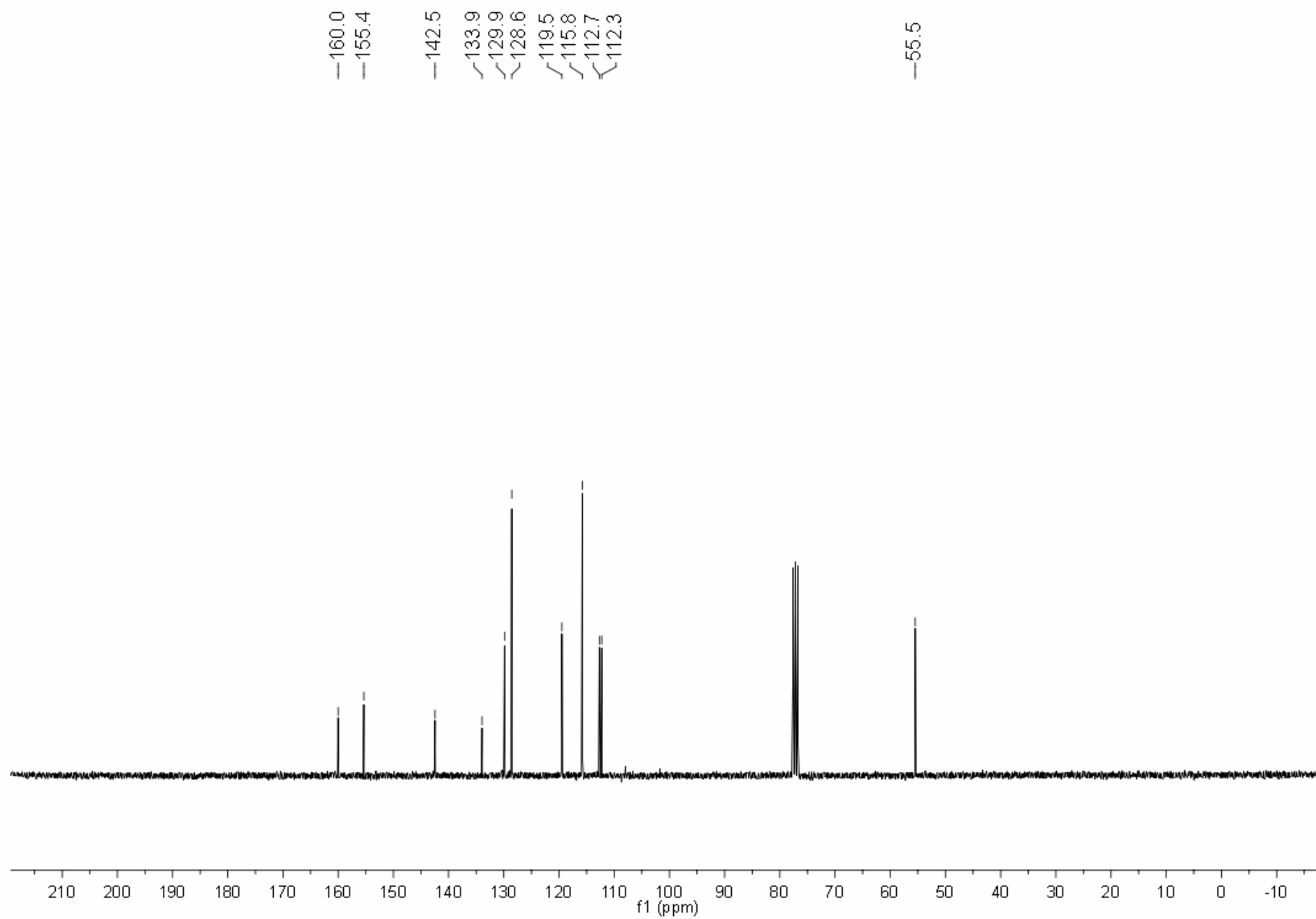
55.8



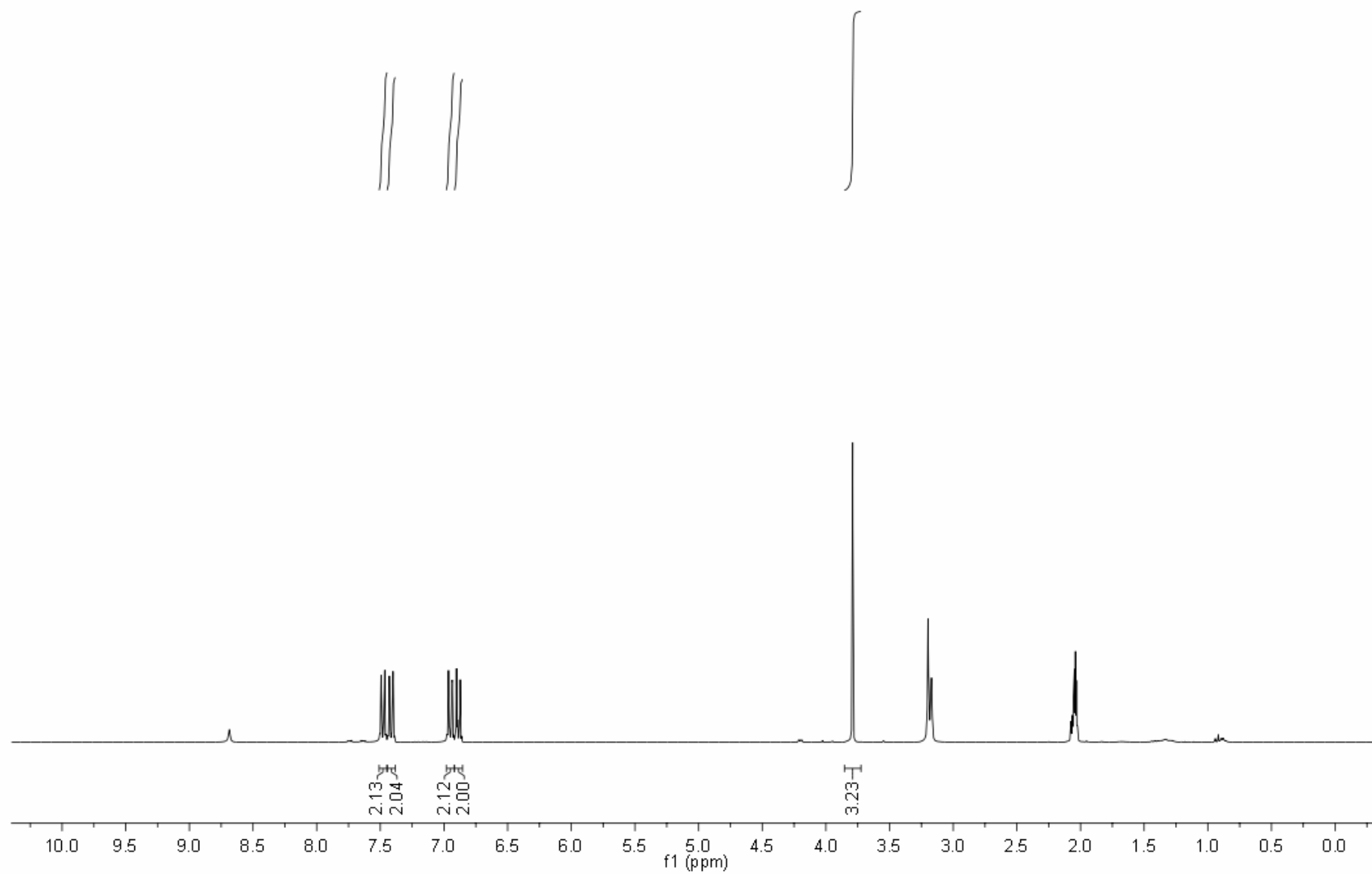
^1H NMR (CDCl_3 , 300 MHz) of **17h**



^{13}C NMR (CDCl_3 , 75 MHz) of **17h**



^1H NMR (acetone- d_6 , 300 MHz) of **17i**



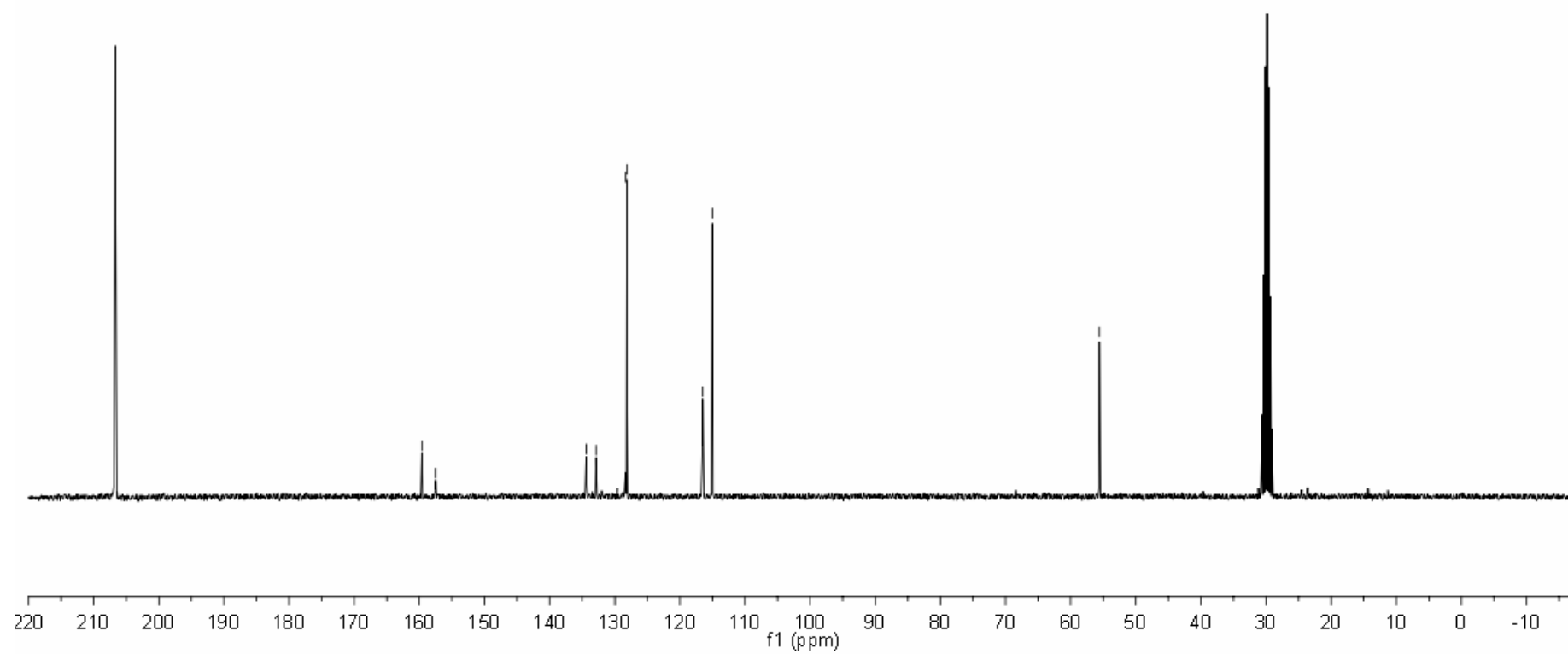
^{13}C NMR (acetone- d_6 , 75 MHz) of **17i**

159.6
157.5

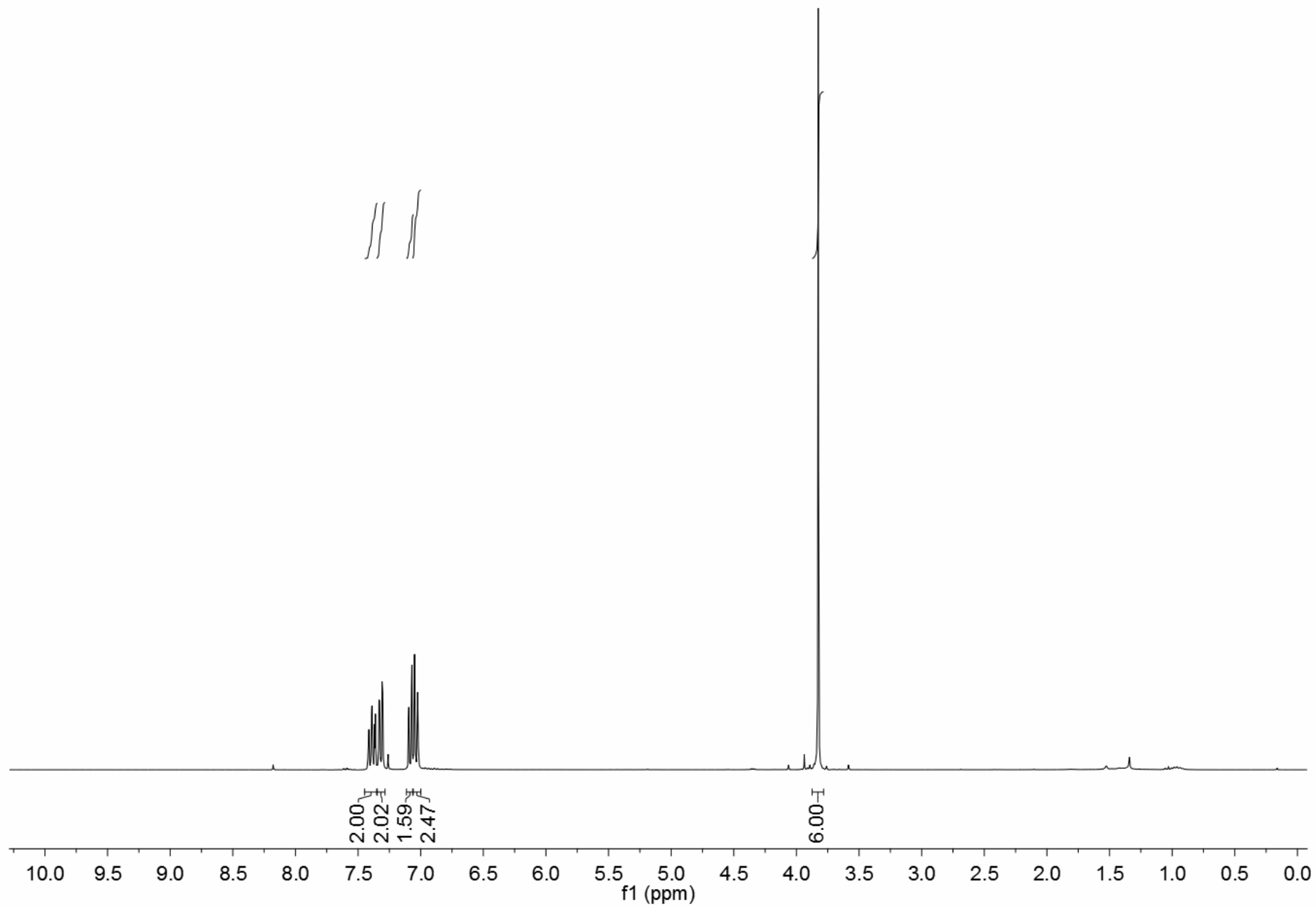
134.4
132.9
128.3
128.1

116.5
115.0

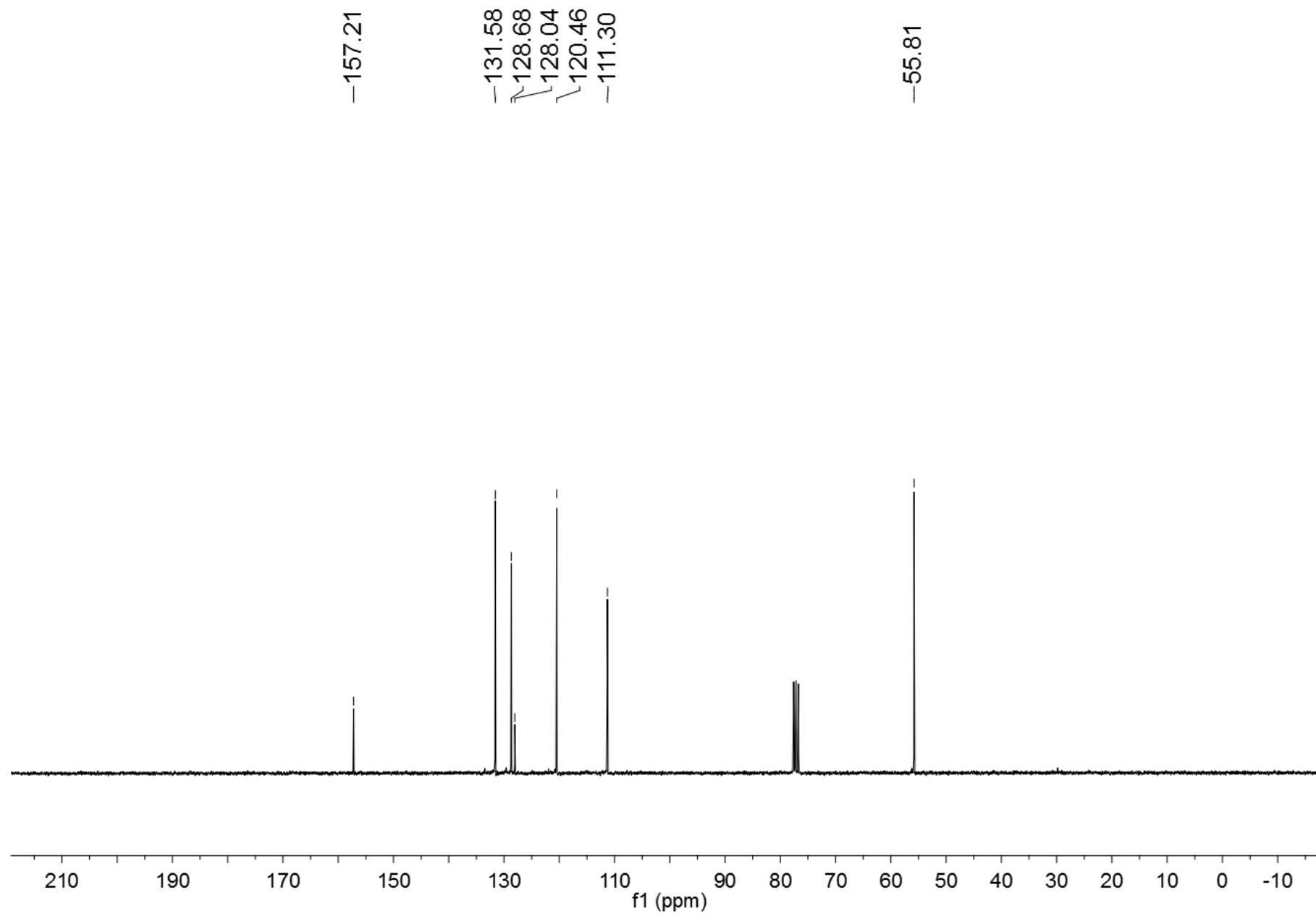
55.6



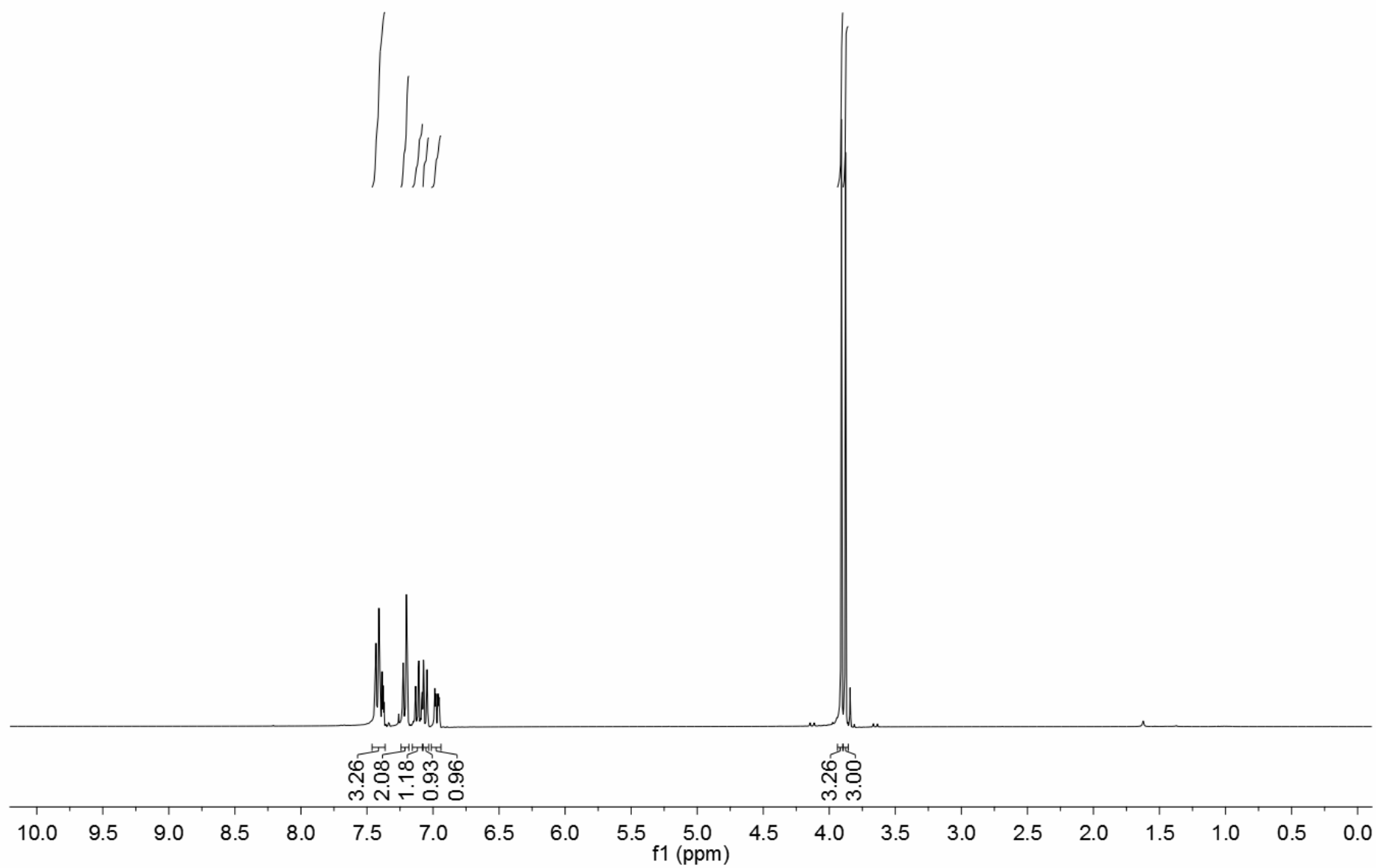
^1H NMR (CDCl_3 , 300 MHz) of **19a**



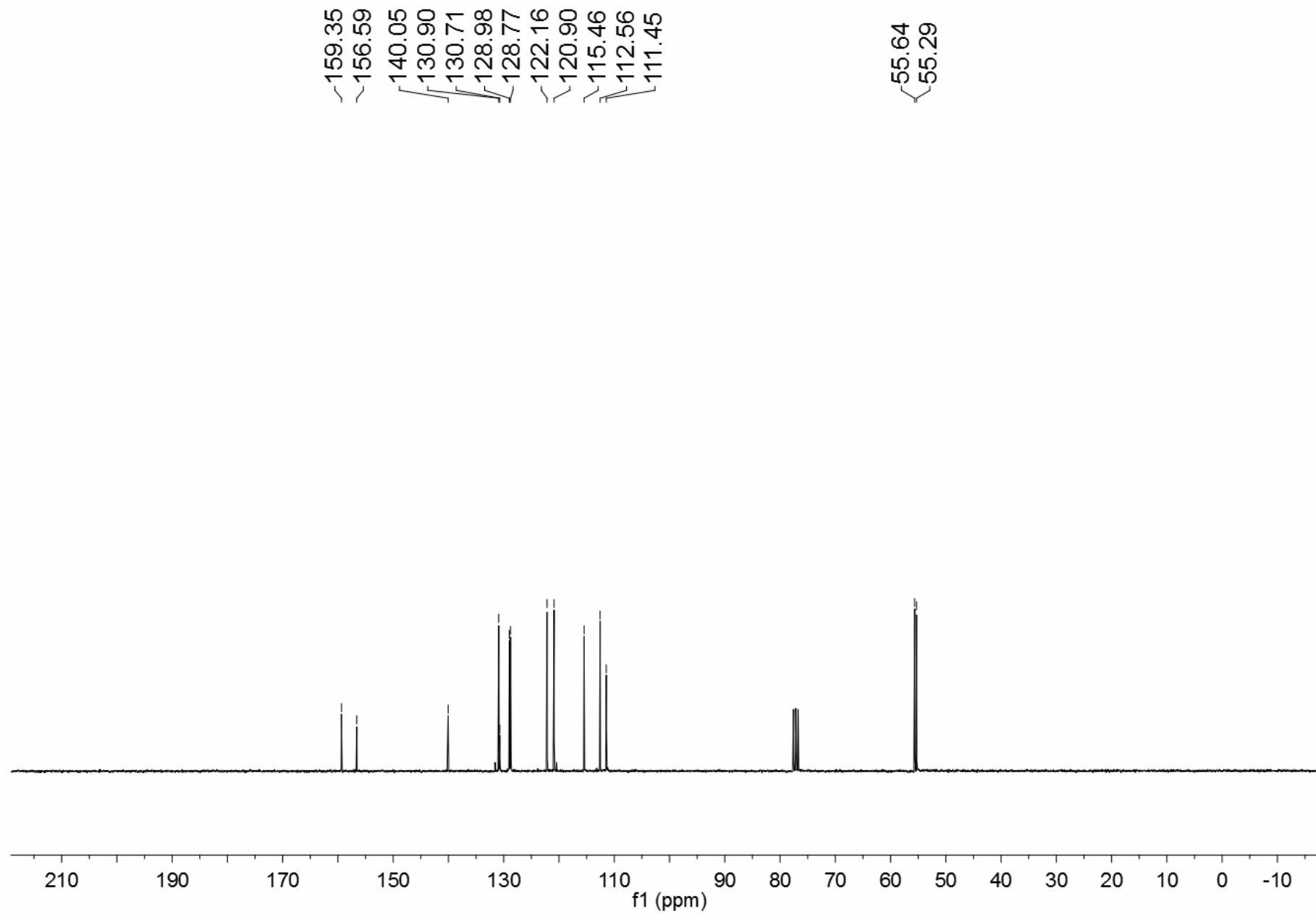
^{13}C NMR (CDCl_3 , 75 MHz) of **19a**



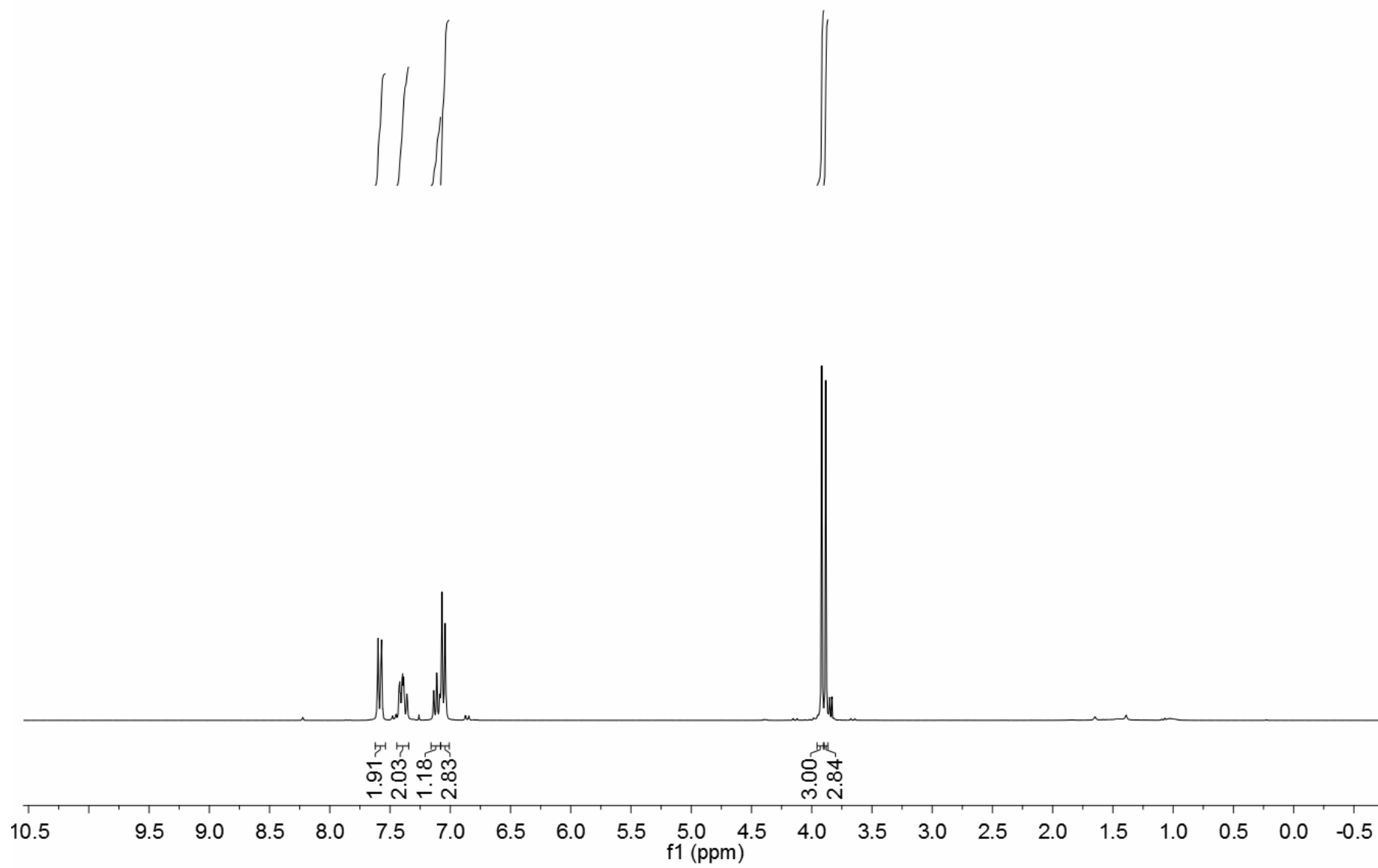
^1H NMR (CDCl_3 , 300 MHz) of **19b**



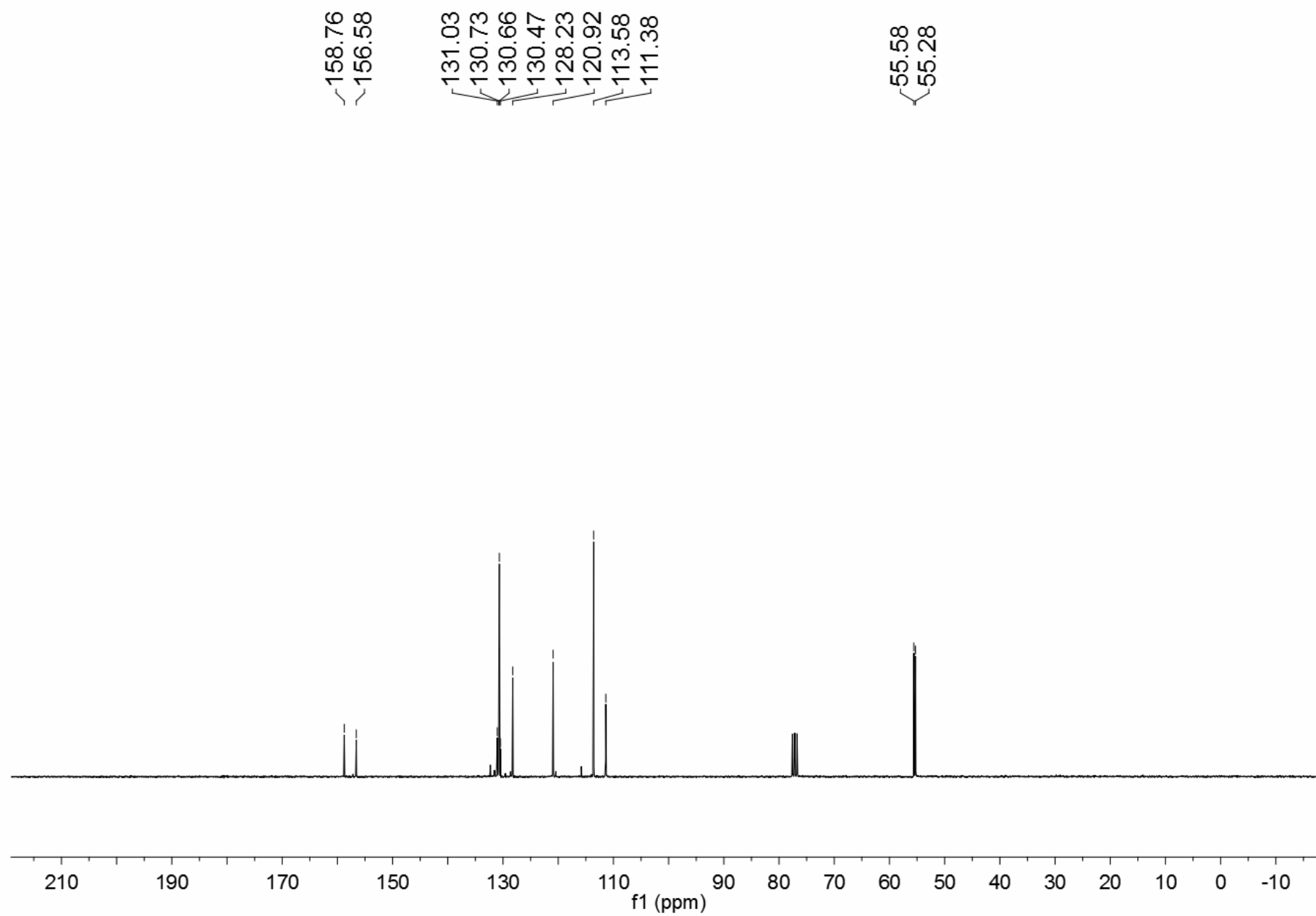
^{13}C NMR (CDCl_3 , 75 MHz) of **19b**



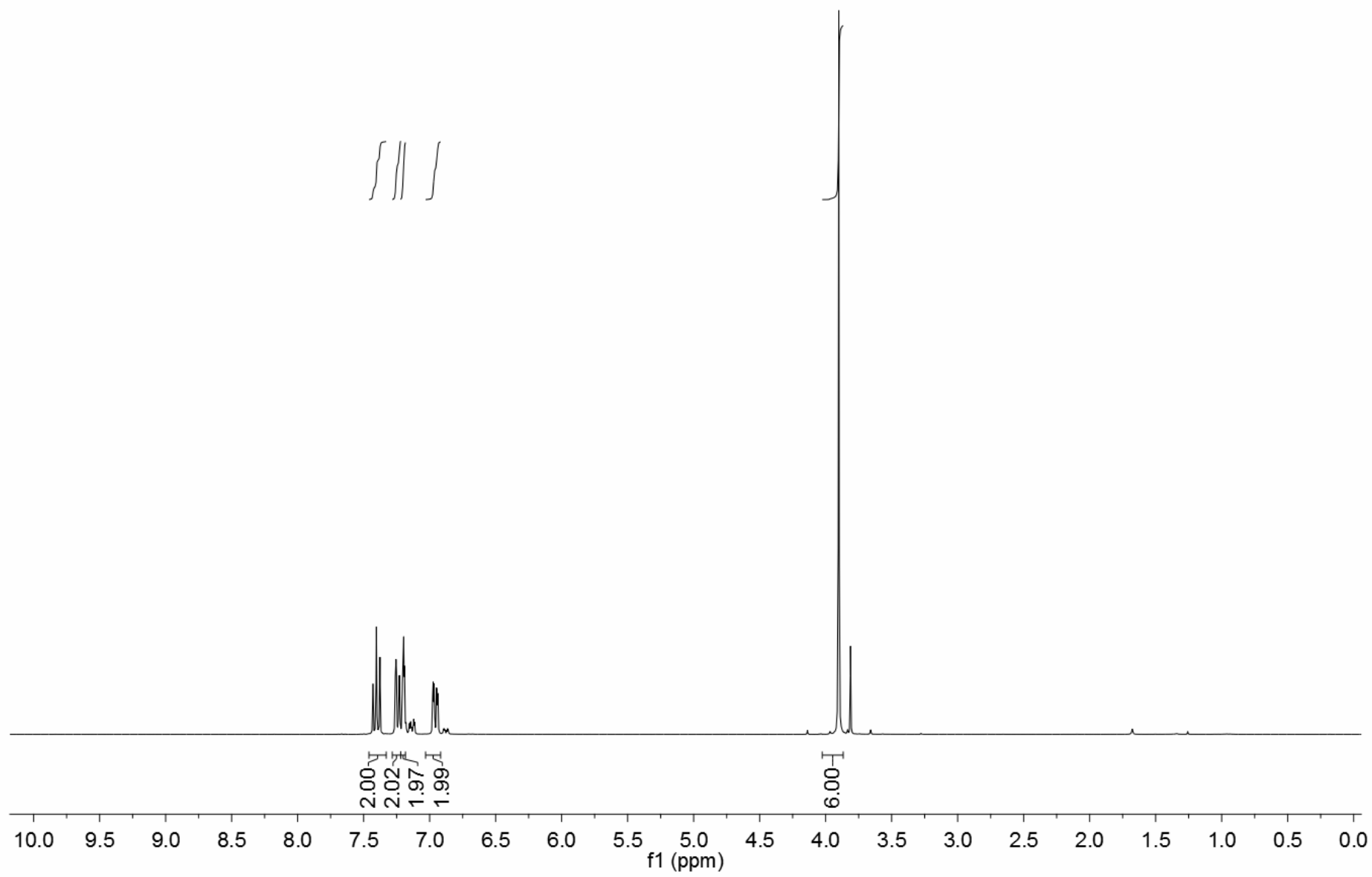
^1H NMR (CDCl_3 , 300 MHz) of **19c**



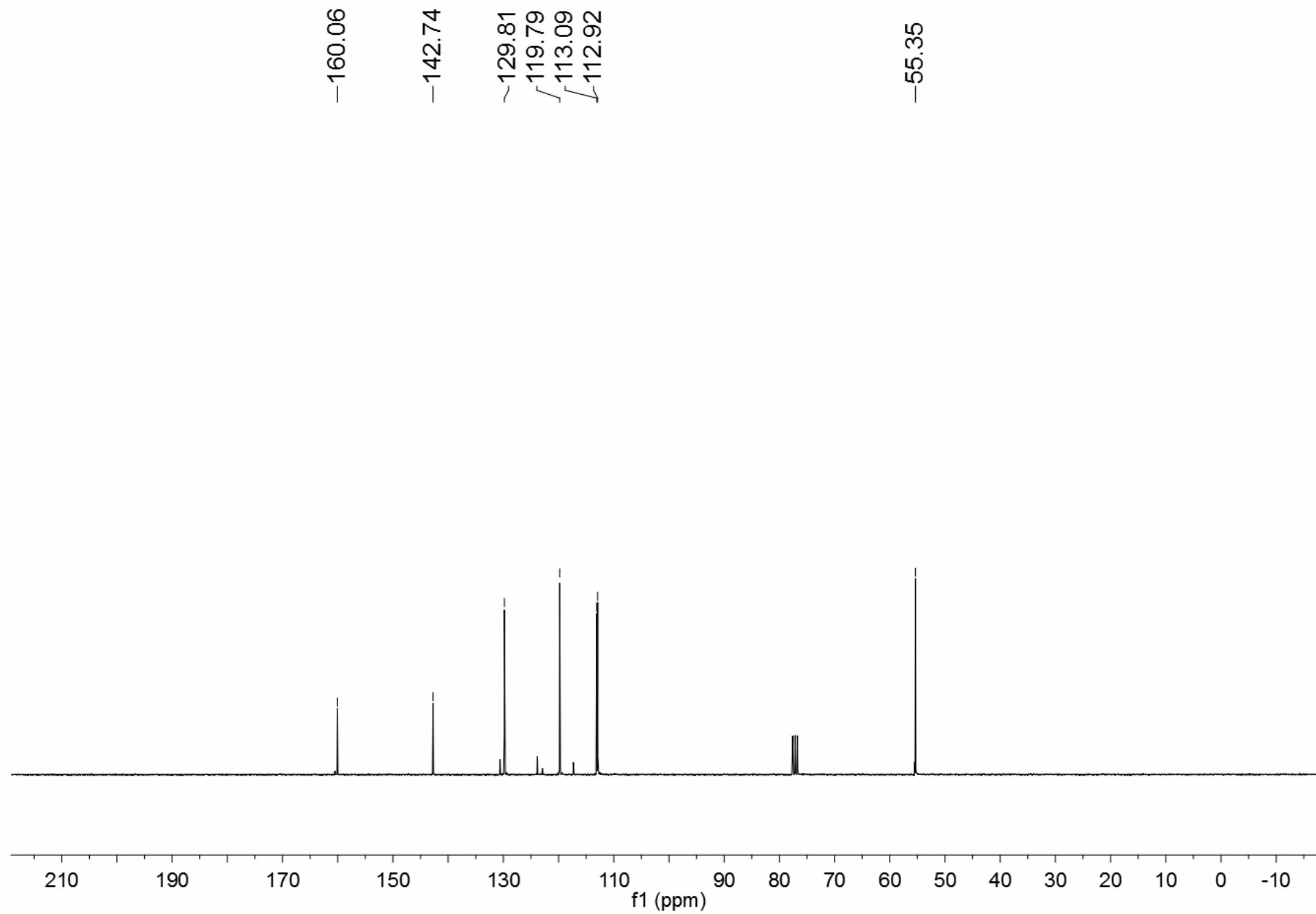
^{13}C NMR (CDCl_3 , 75 MHz) of **19c**



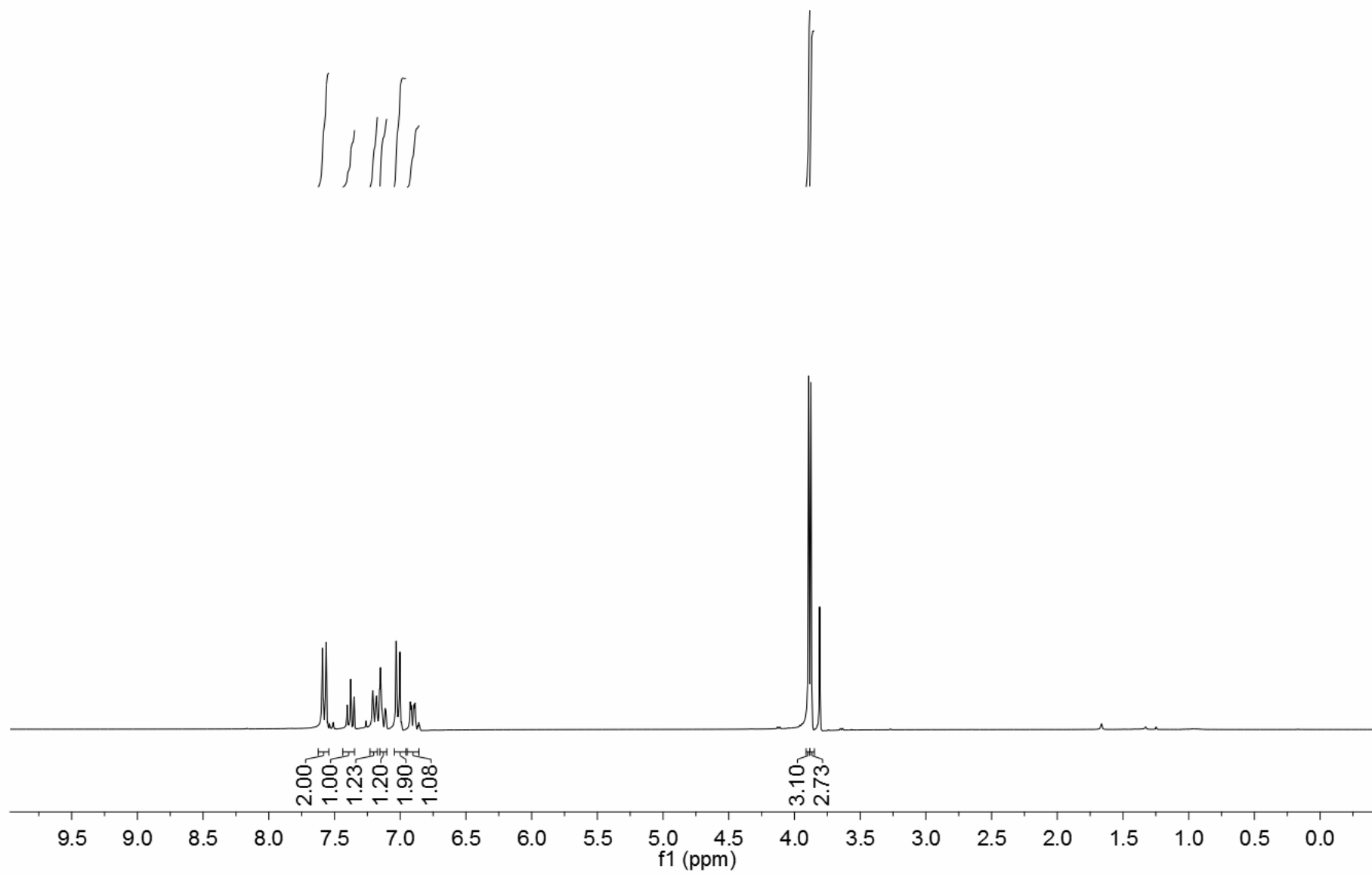
^1H NMR (CDCl_3 , 300 MHz) of **19d**



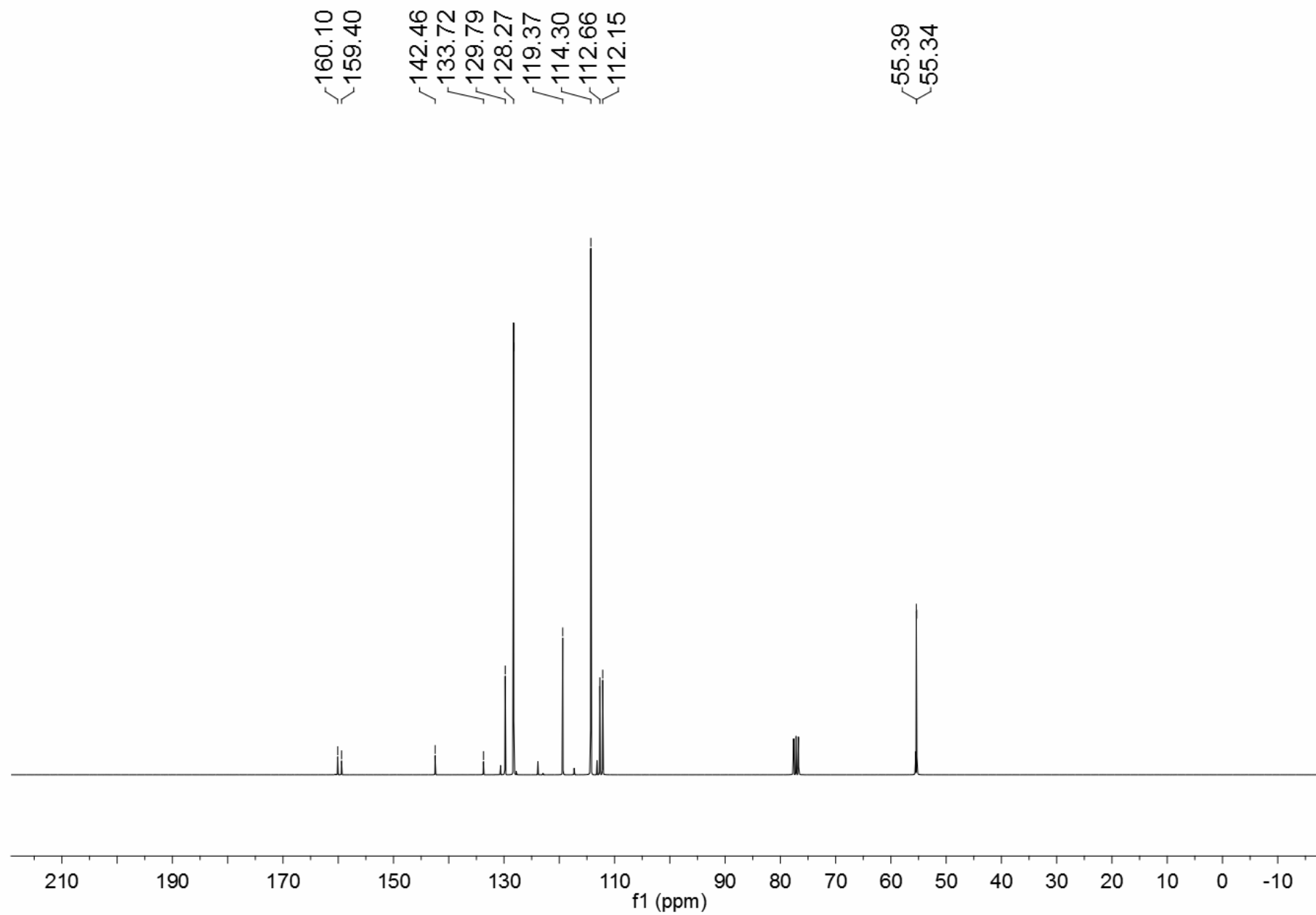
^{13}C NMR (CDCl_3 , 75 MHz) of **19d**



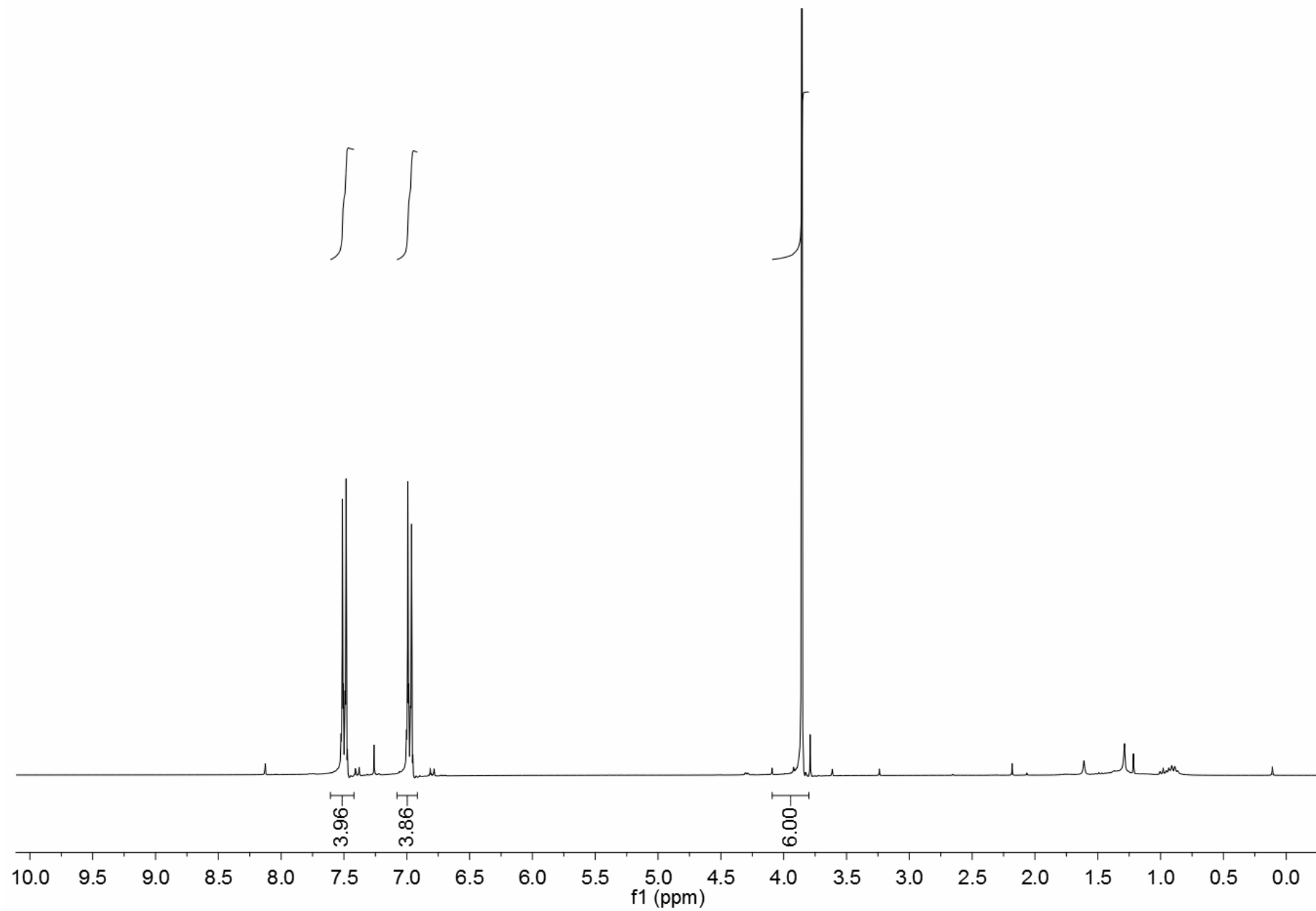
^1H NMR (CDCl_3 , 300 MHz) of **19e**



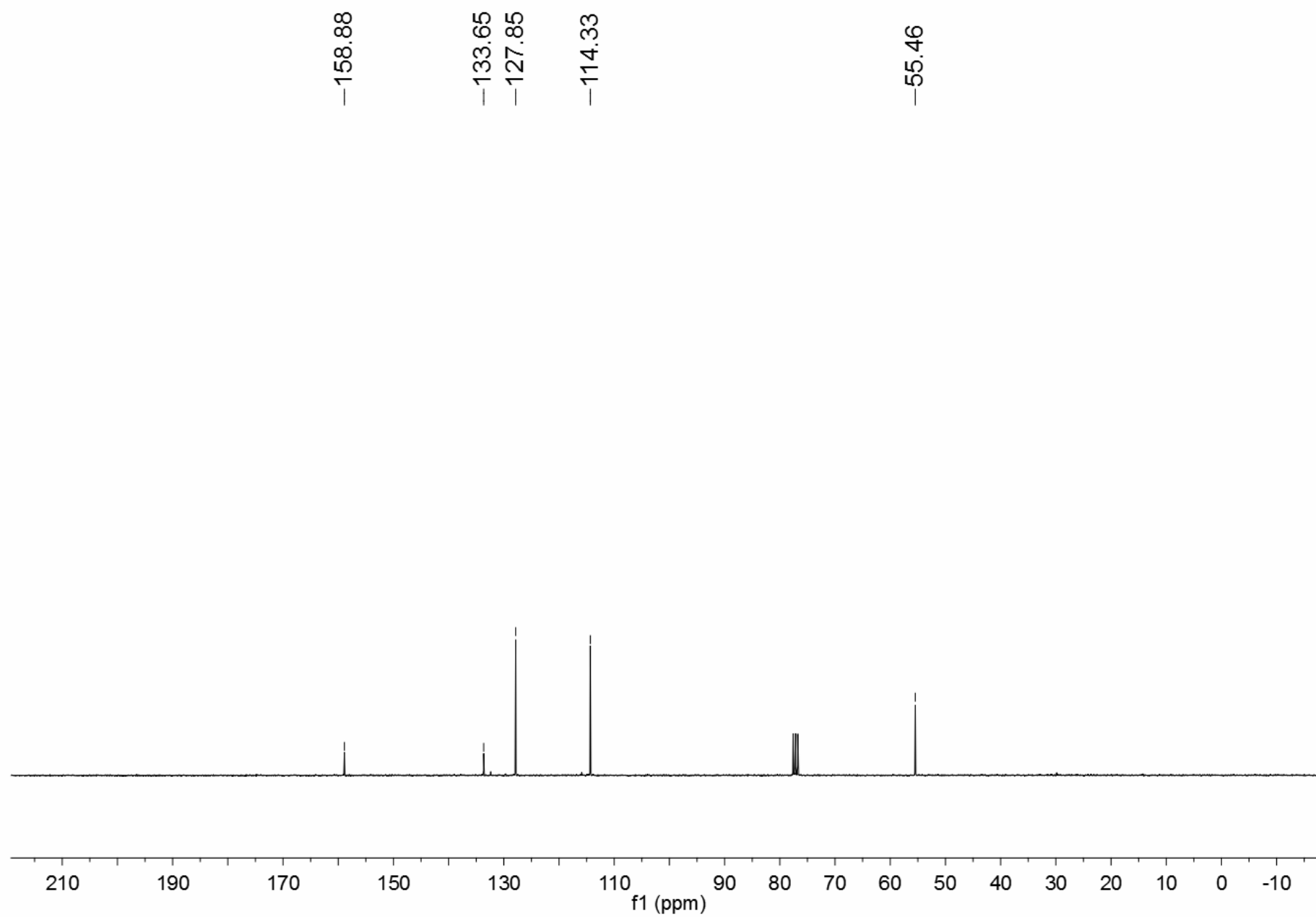
^{13}C NMR (CDCl_3 , 75 MHz) of **19e**



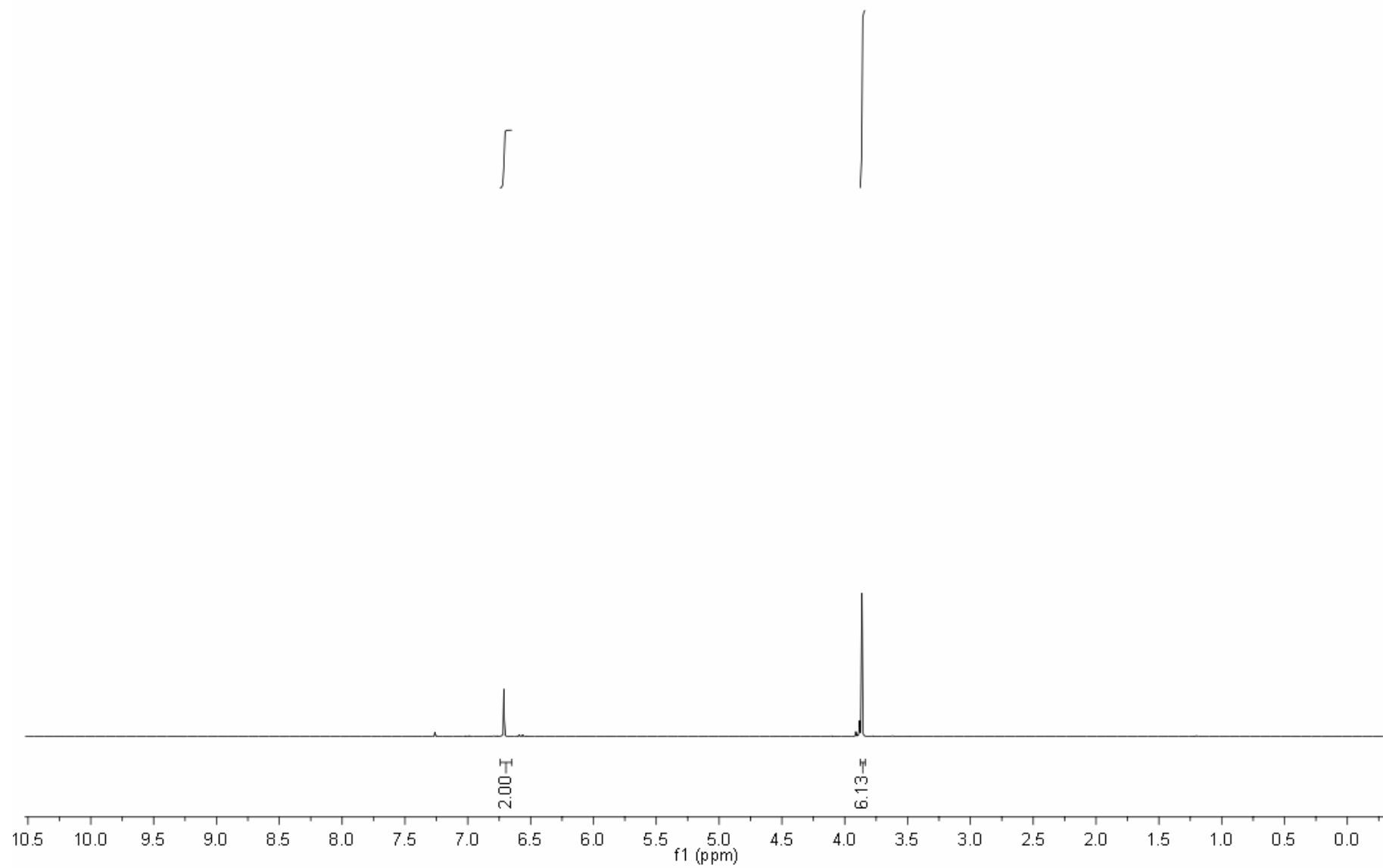
^1H NMR (CDCl_3 , 300 MHz) of **19f**



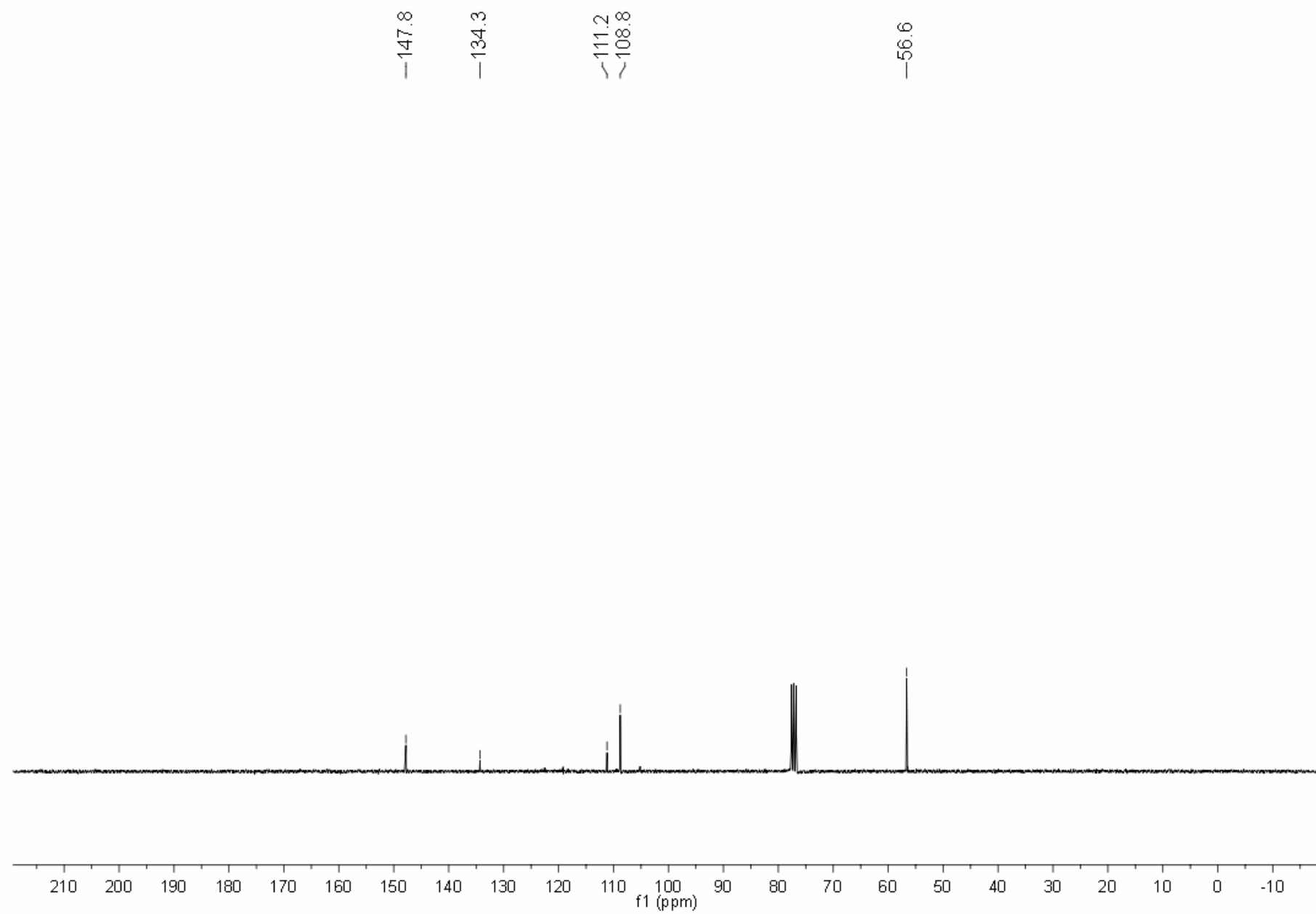
^{13}C NMR (CDCl_3 , 75 MHz) of **19f**



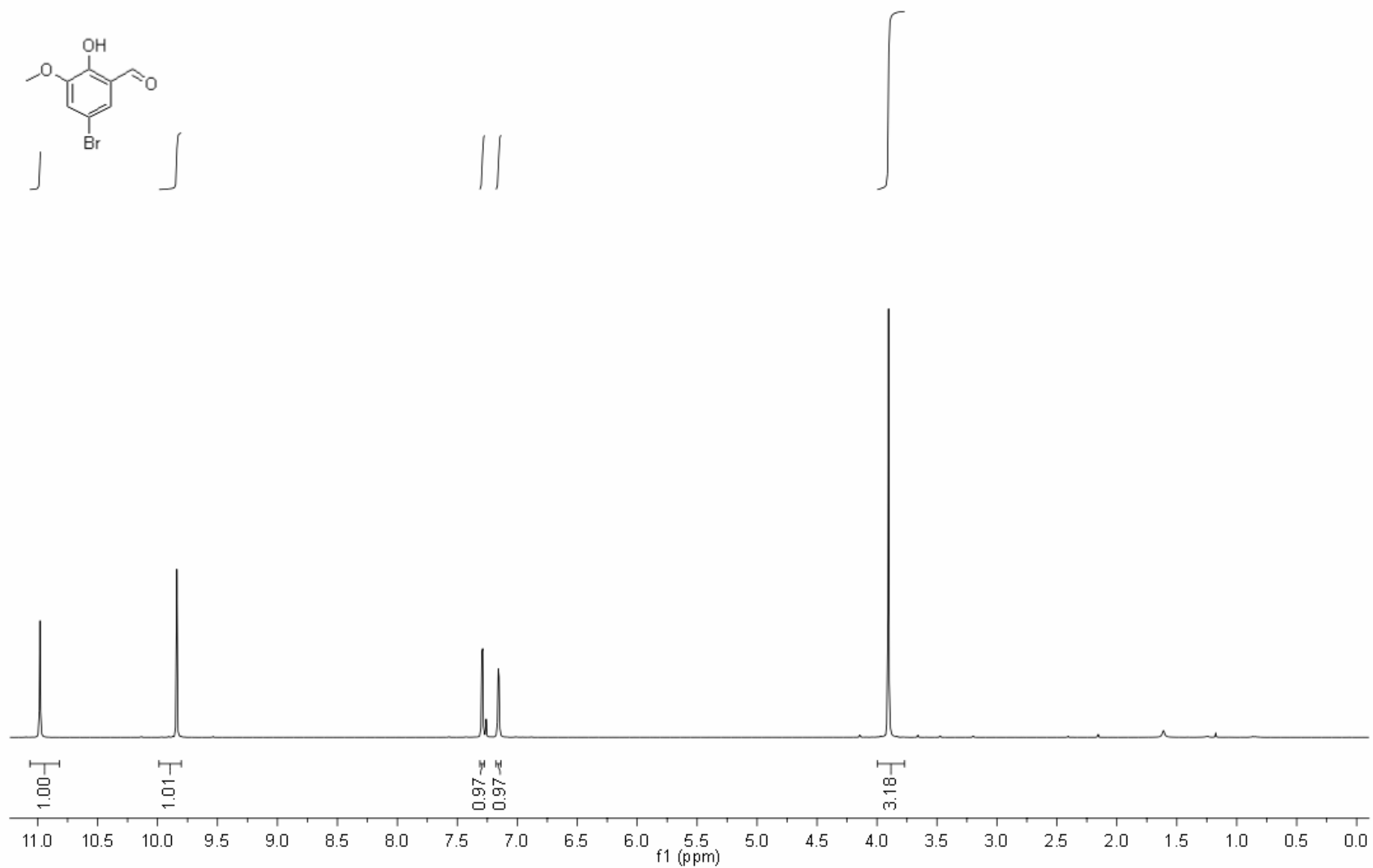
^1H NMR (CDCl_3 , 300 MHz) of **21**



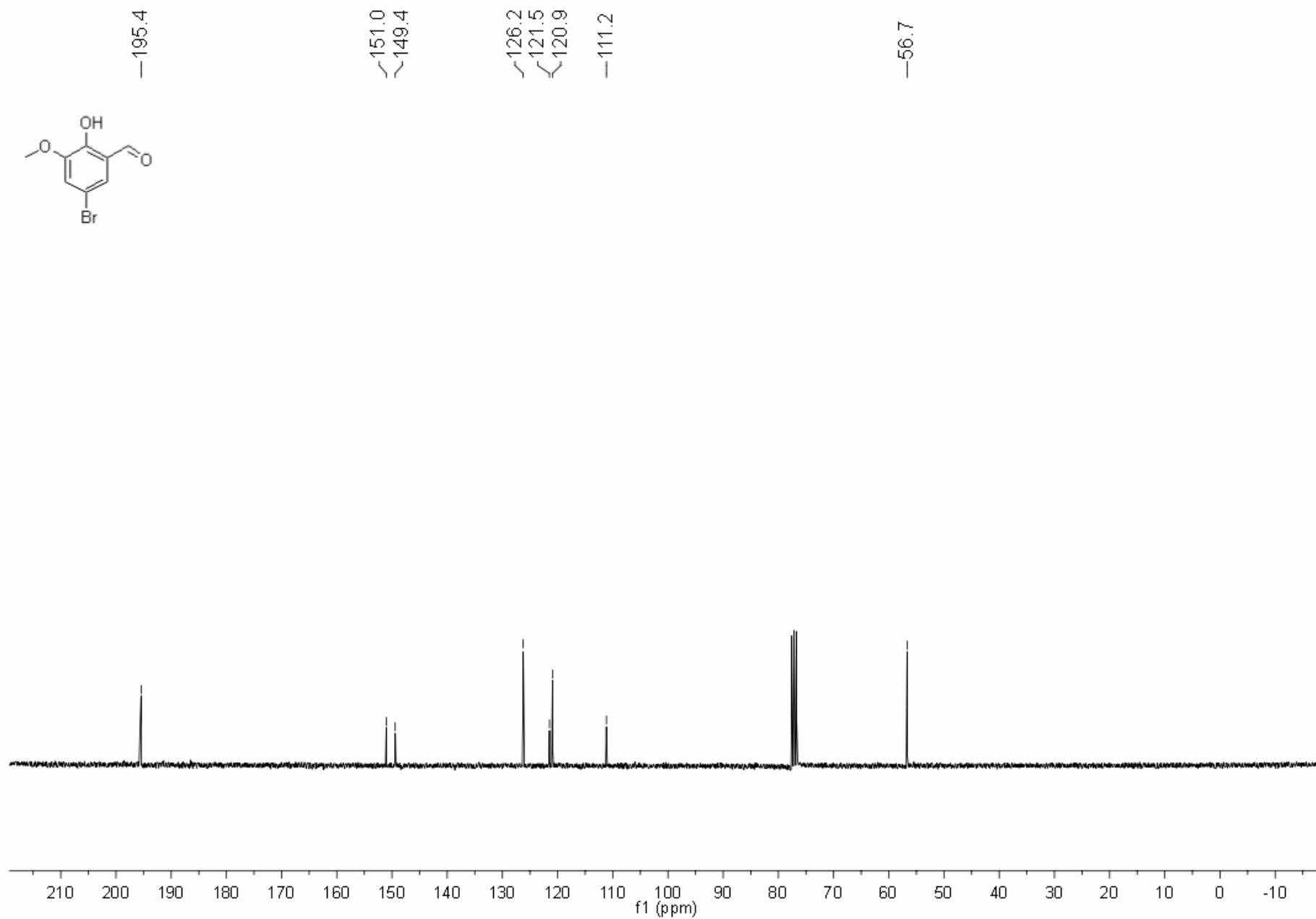
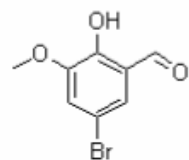
^{13}C NMR (CDCl_3 , 75 MHz) of **21**



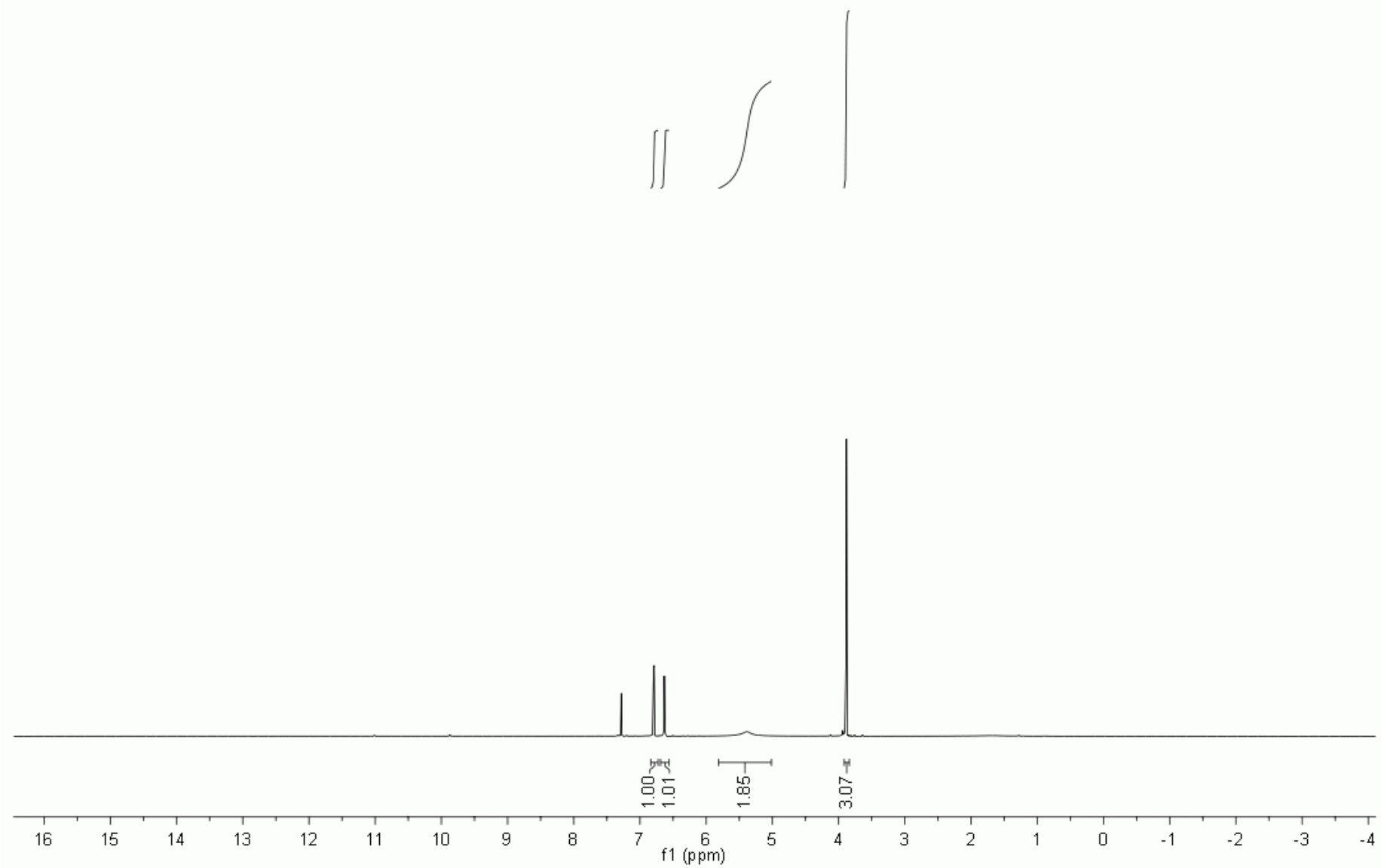
^1H NMR (CDCl_3 , 300 MHz) of **23**



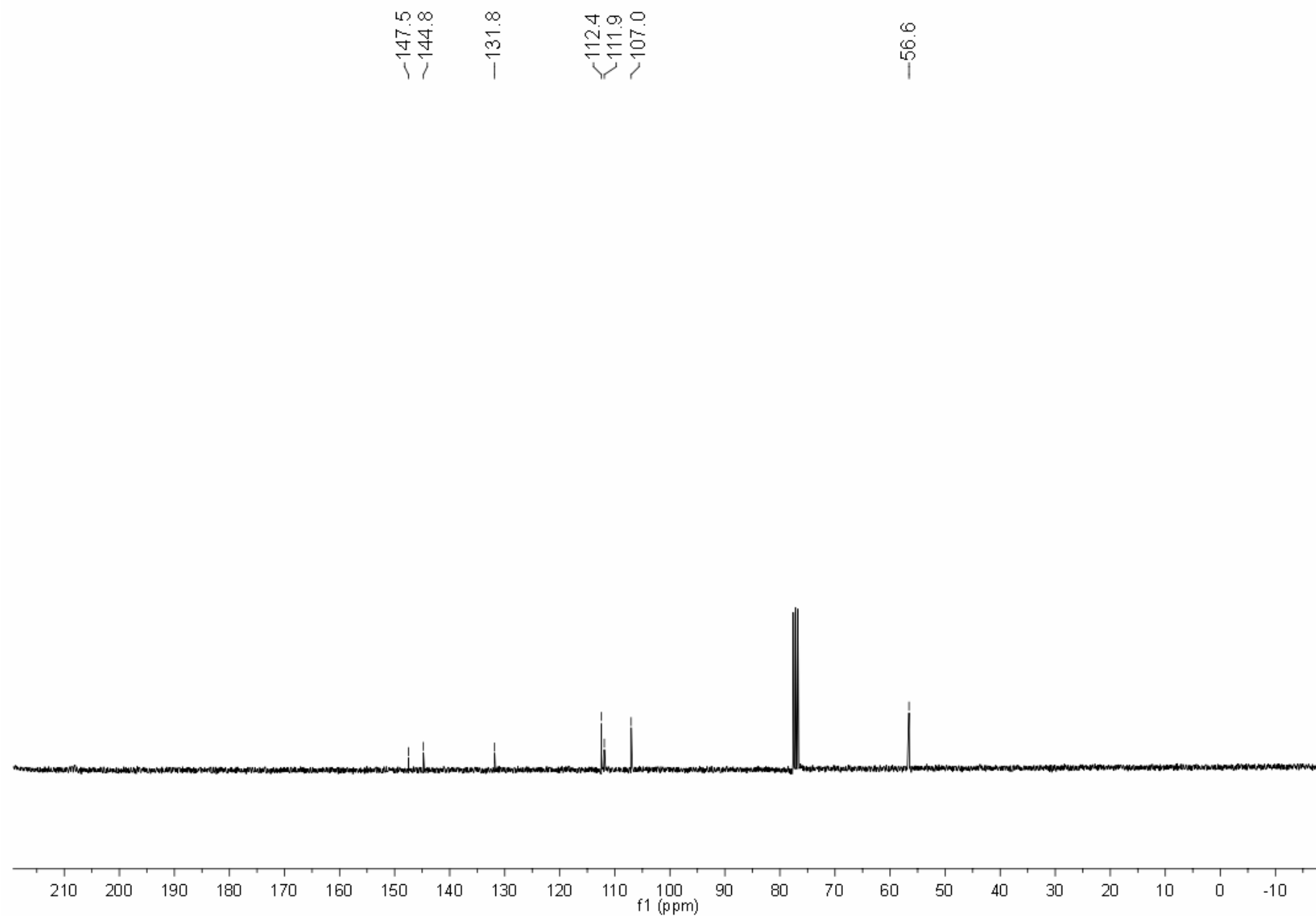
^{13}C NMR (CDCl_3 , 75 MHz) of **23**



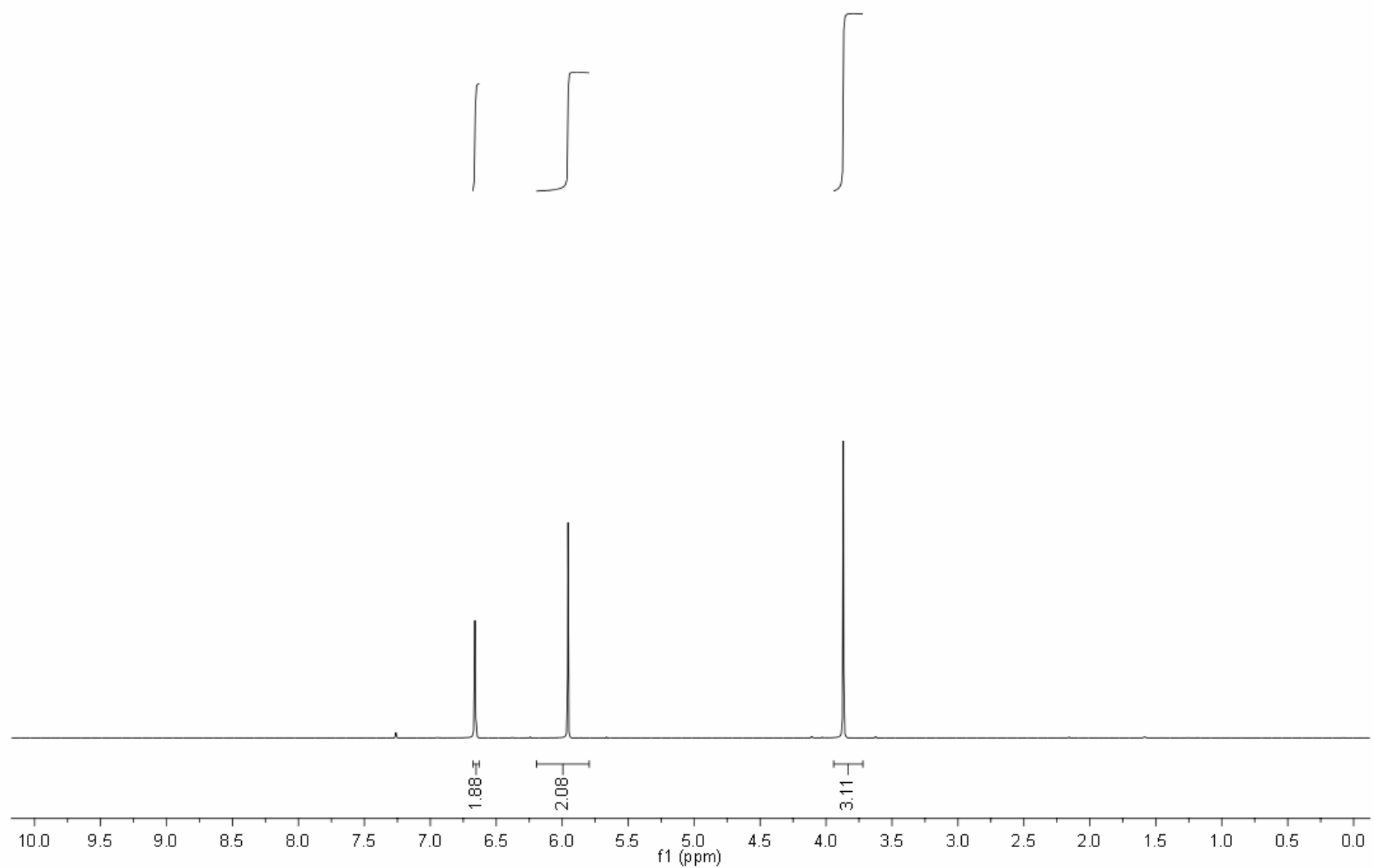
^1H NMR (CDCl_3 , 300 MHz) of **24**



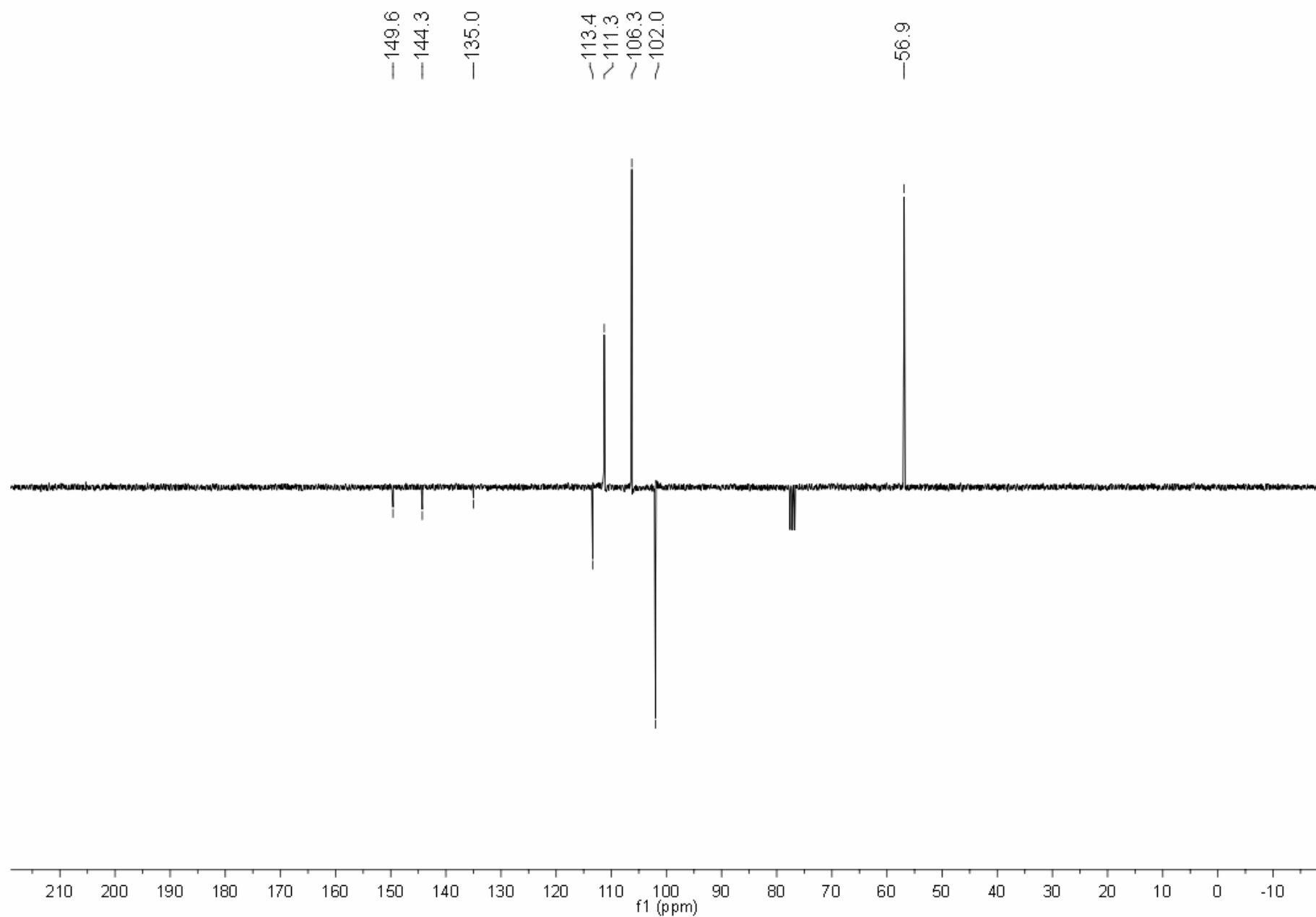
^{13}C NMR (CDCl_3 , 75 MHz) of **24**



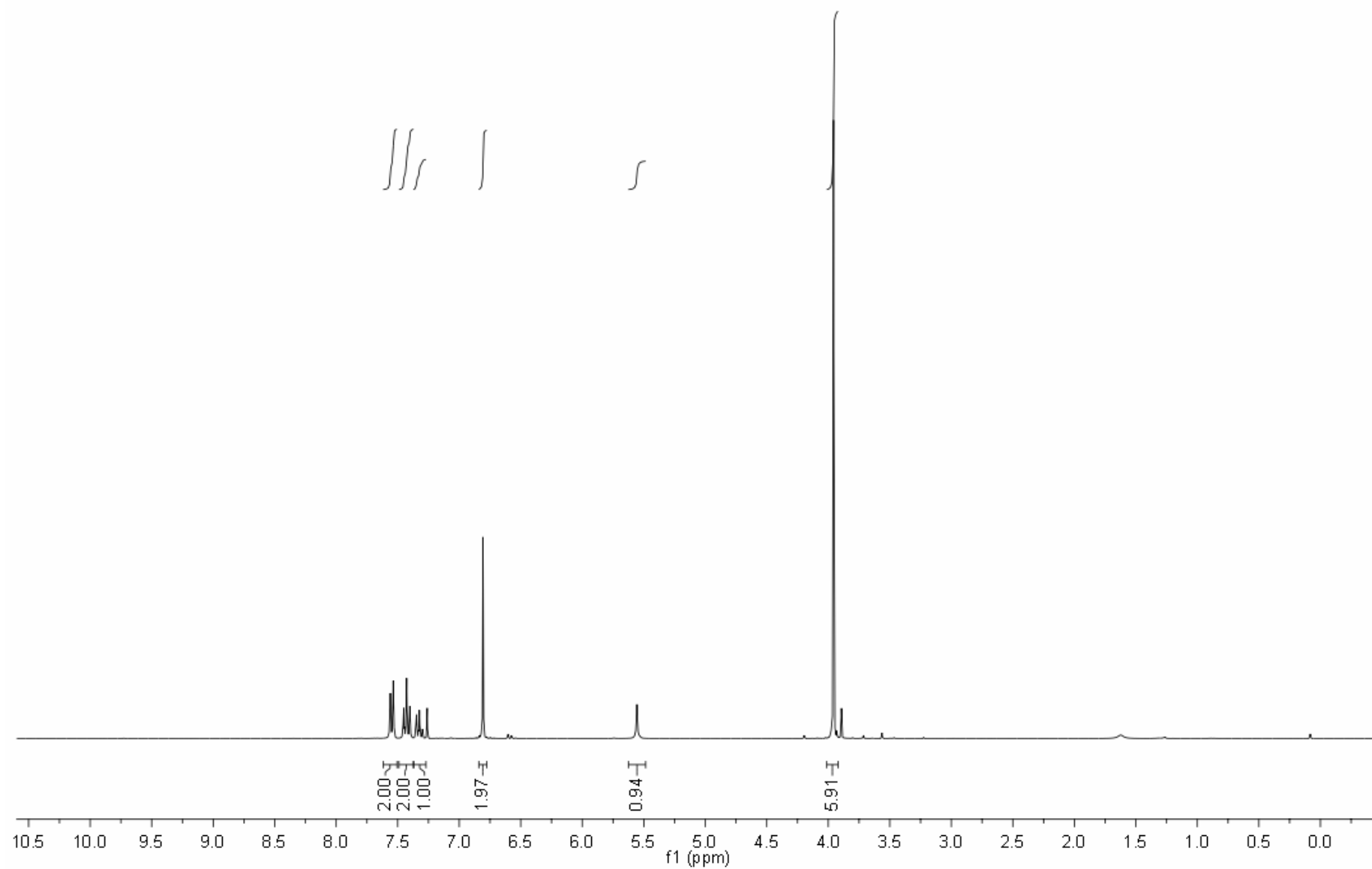
^1H NMR (CDCl_3 , 300 MHz) of 25



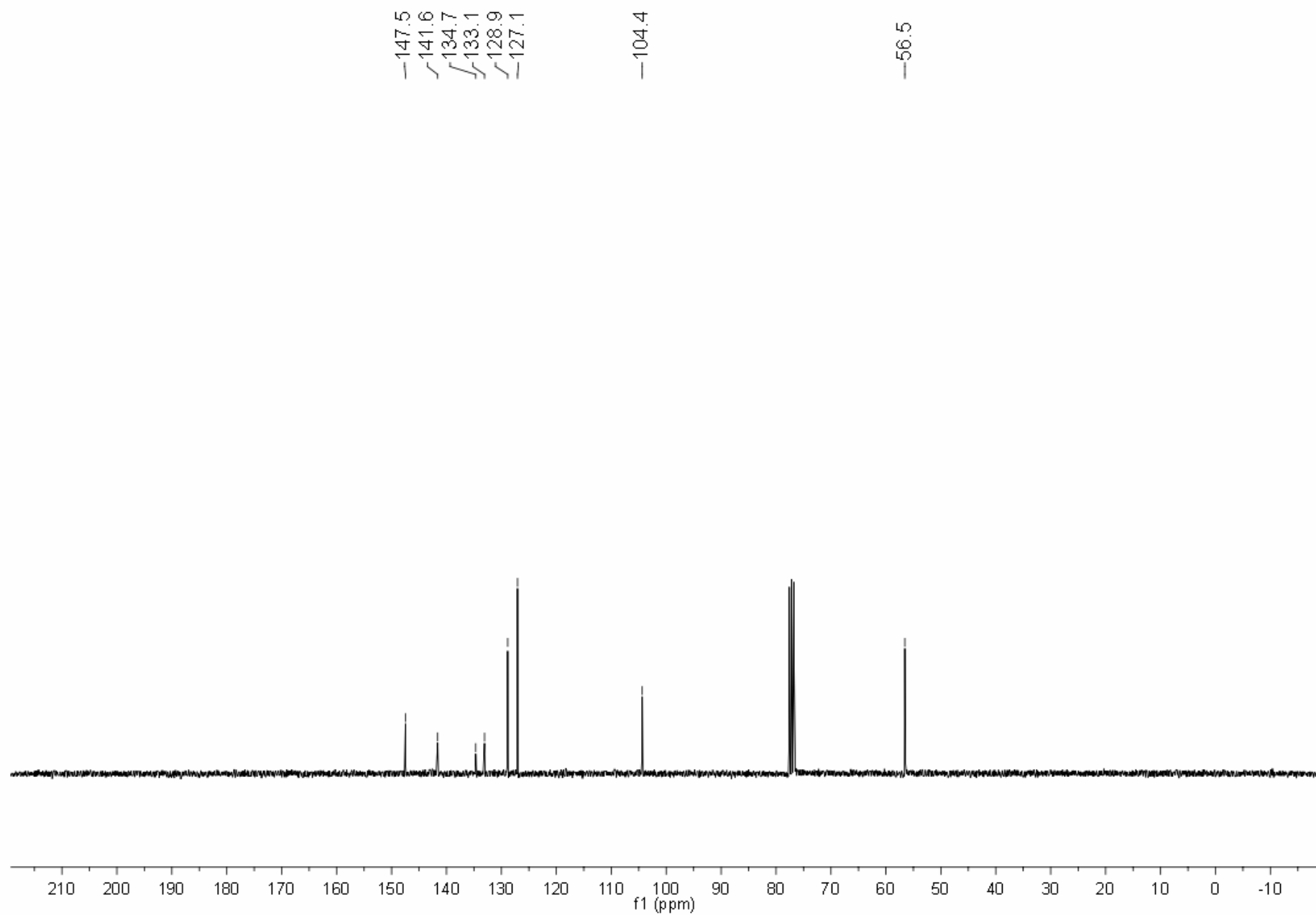
^{13}C NMR-APT (CDCl_3 , 75 MHz) of **25**



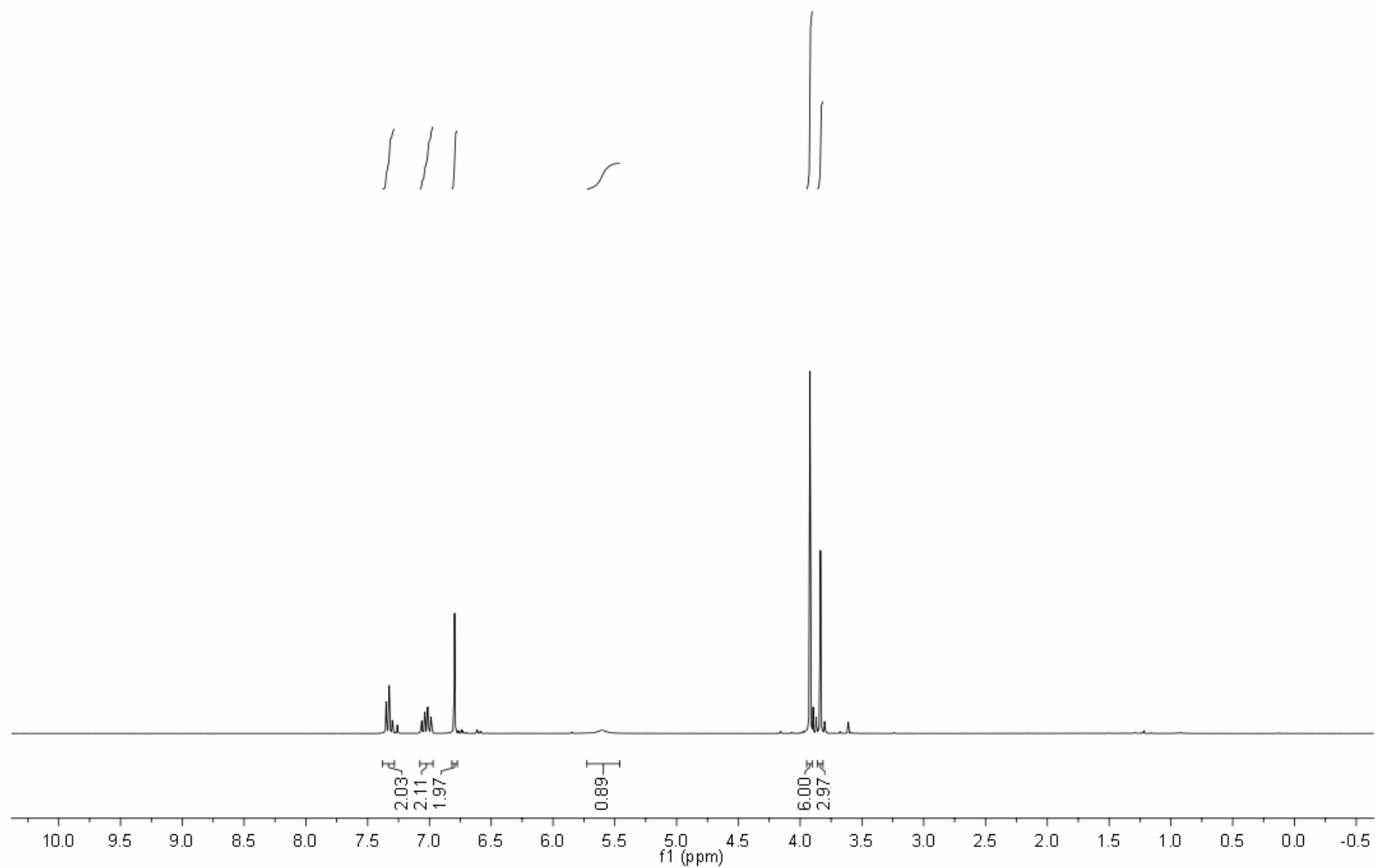
^1H NMR (CDCl_3 , 300 MHz) of aucuparin (**7a**)



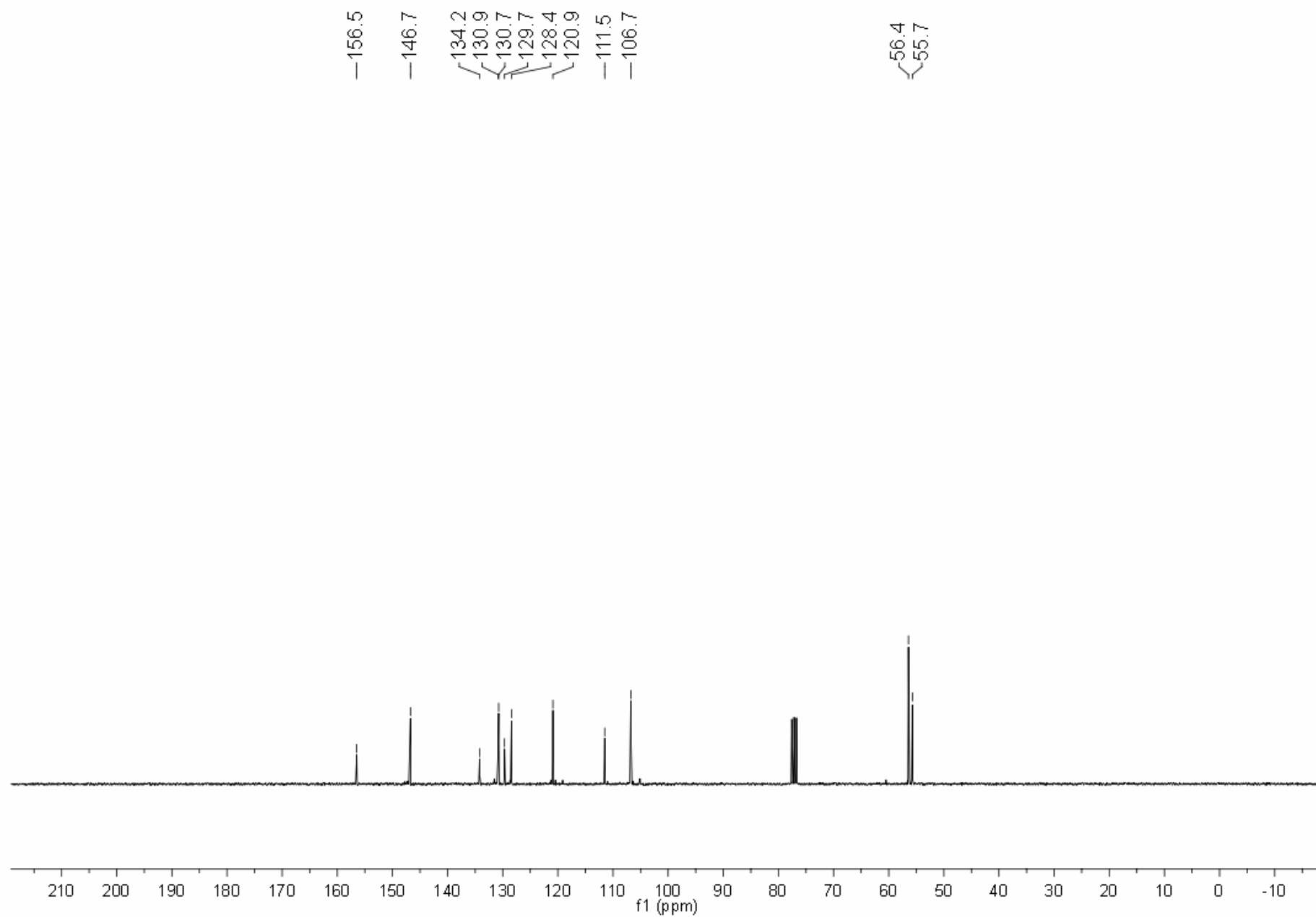
^{13}C NMR (CDCl_3 , 75 MHz) of aucuparin (**7a**)



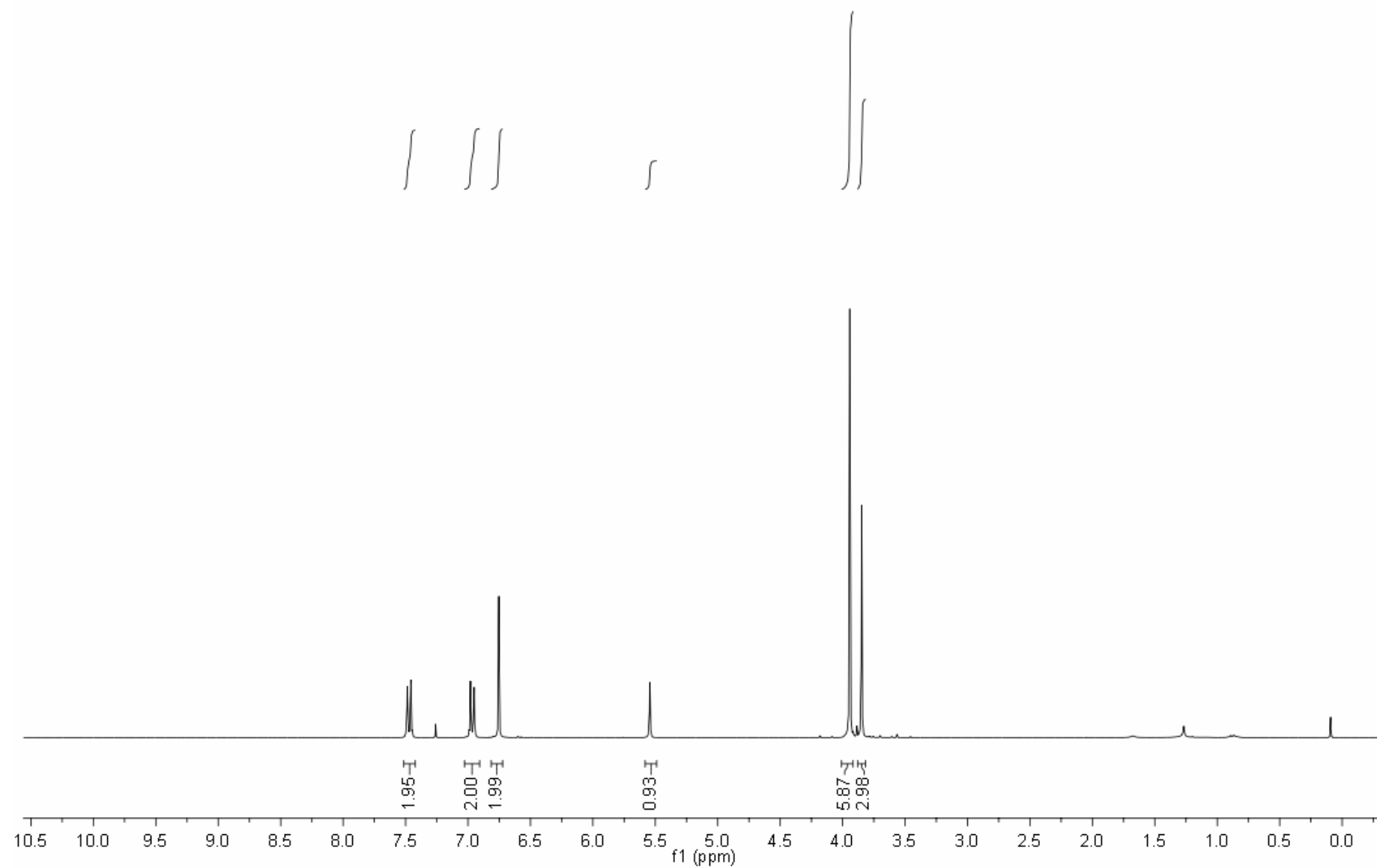
^1H NMR (CDCl_3 , 300 MHz) of 2'-methoxyaucuparin (o-5)



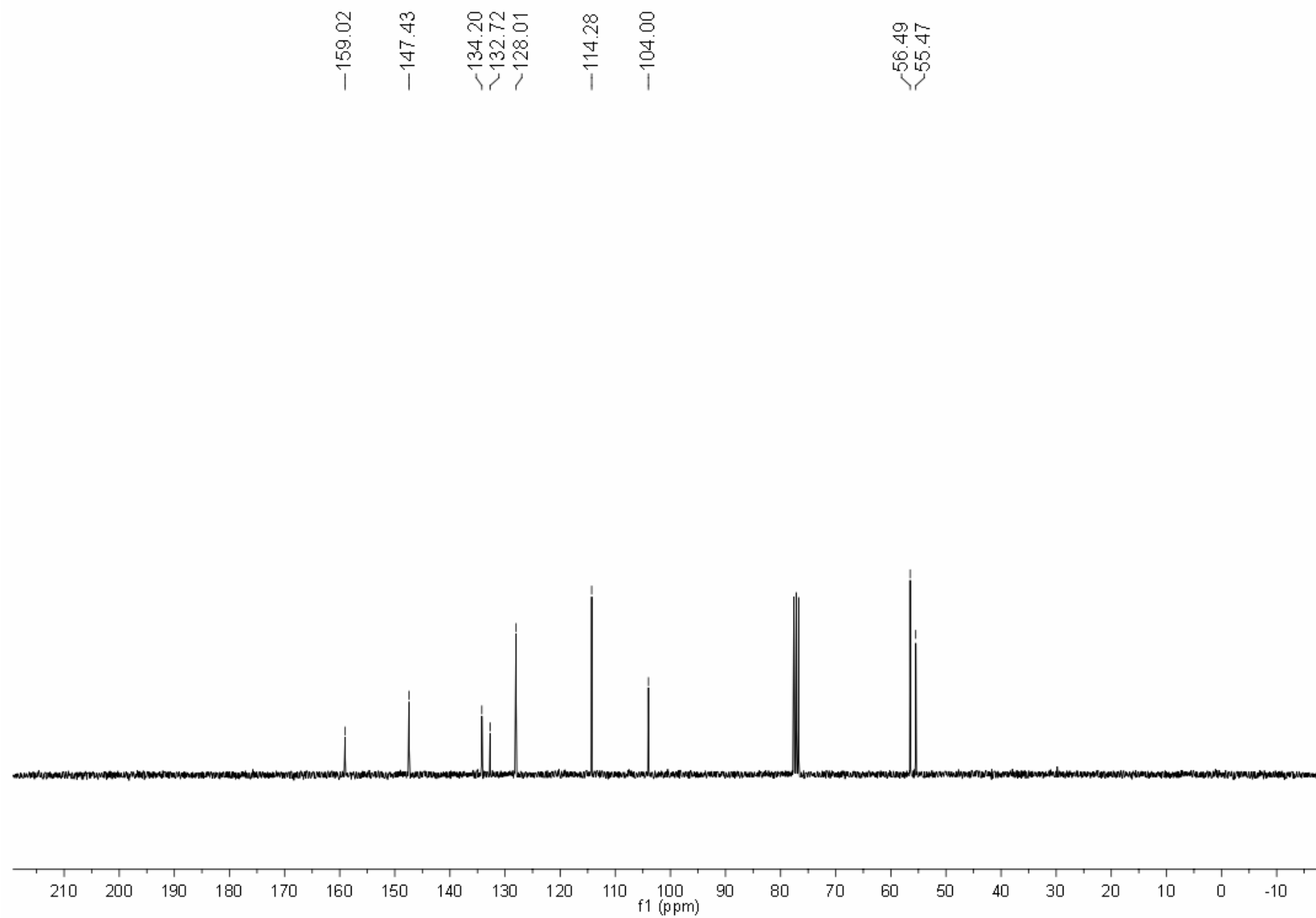
^{13}C NMR (CDCl_3 , 75 MHz) of 2'-methoxyaucuparin (*o*-5)



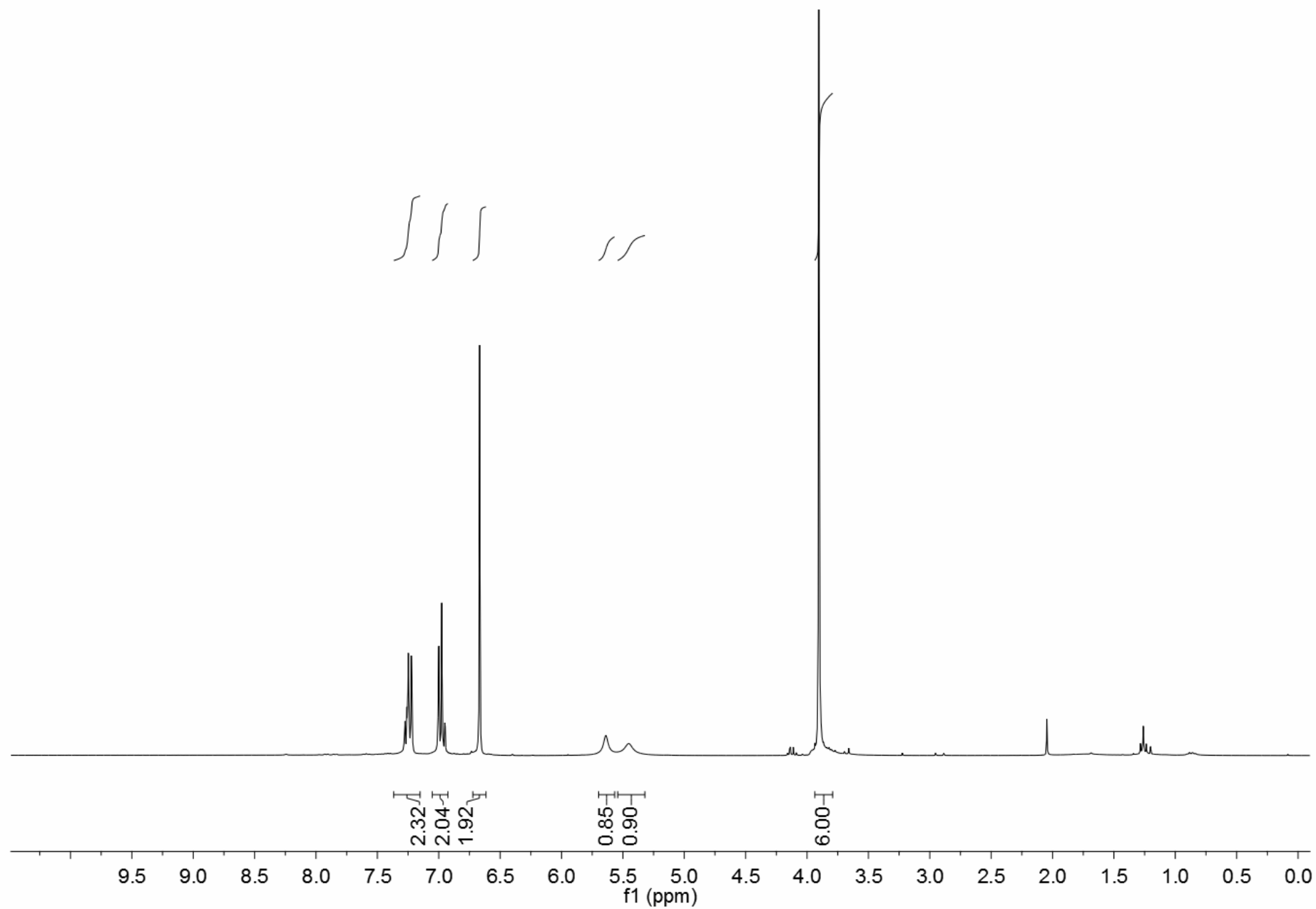
^1H NMR (CDCl_3 , 300 MHz) of 4'-methoxyaucuparin (*p*-5)



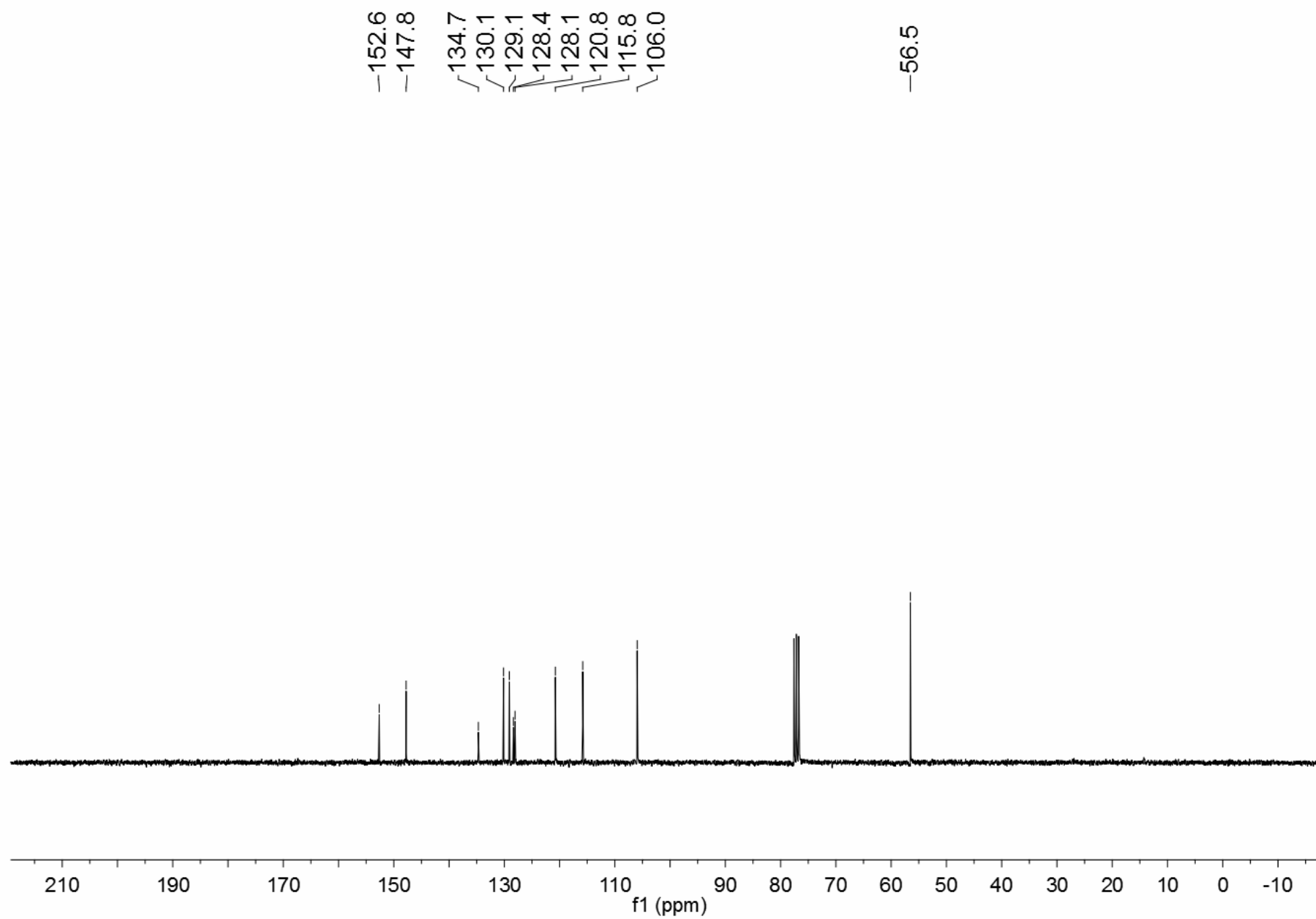
^{13}C NMR (CDCl_3 , 75 MHz) of 4'-methoxyaucuparin (*p*-5)



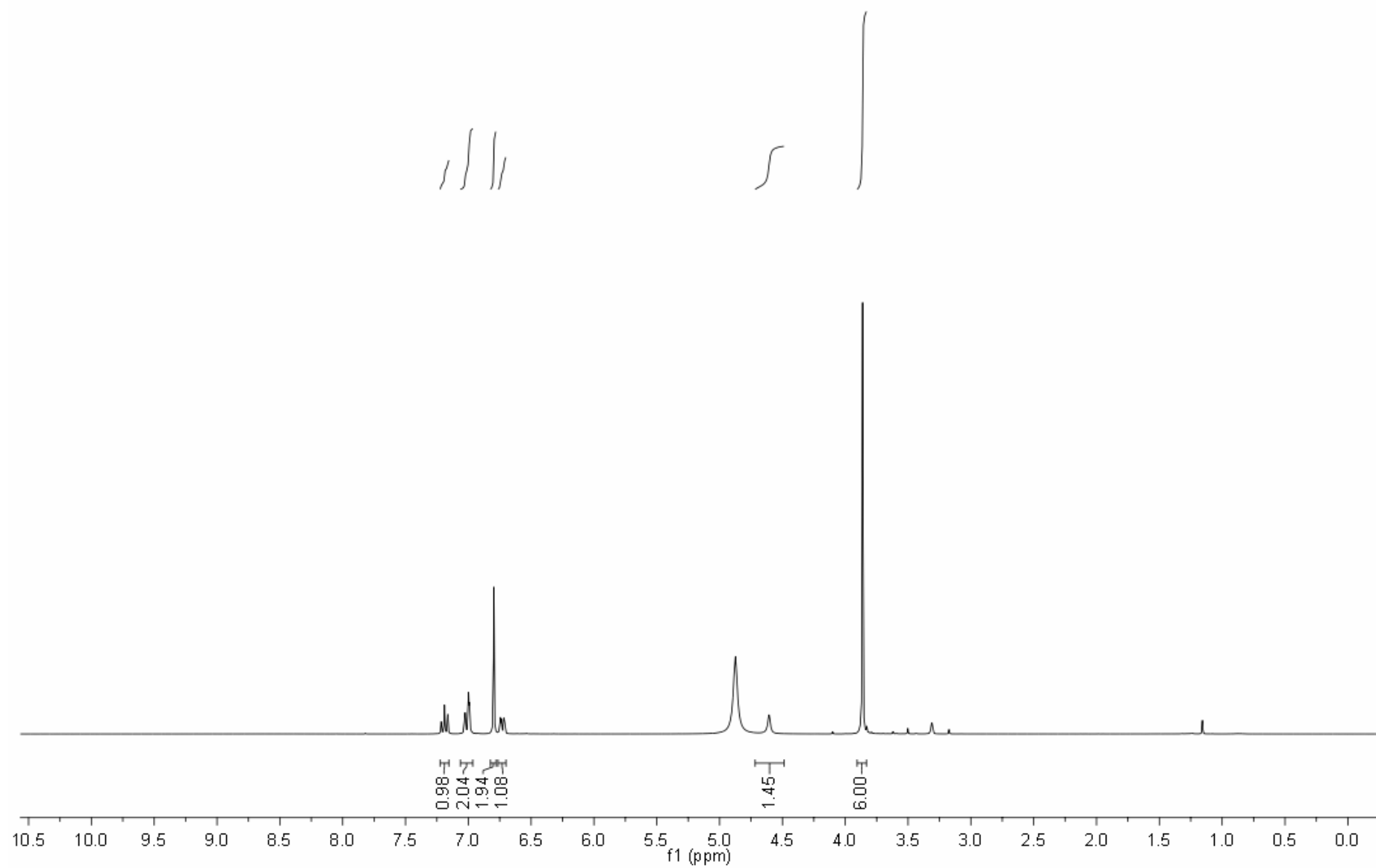
^1H NMR (CDCl_3 , 300 MHz) of 2'-hydroxyaucuparin (*o*-3)



^{13}C NMR (CDCl_3 , 75 MHz) of 2'-hydroxyaucuparin (*o*-3)



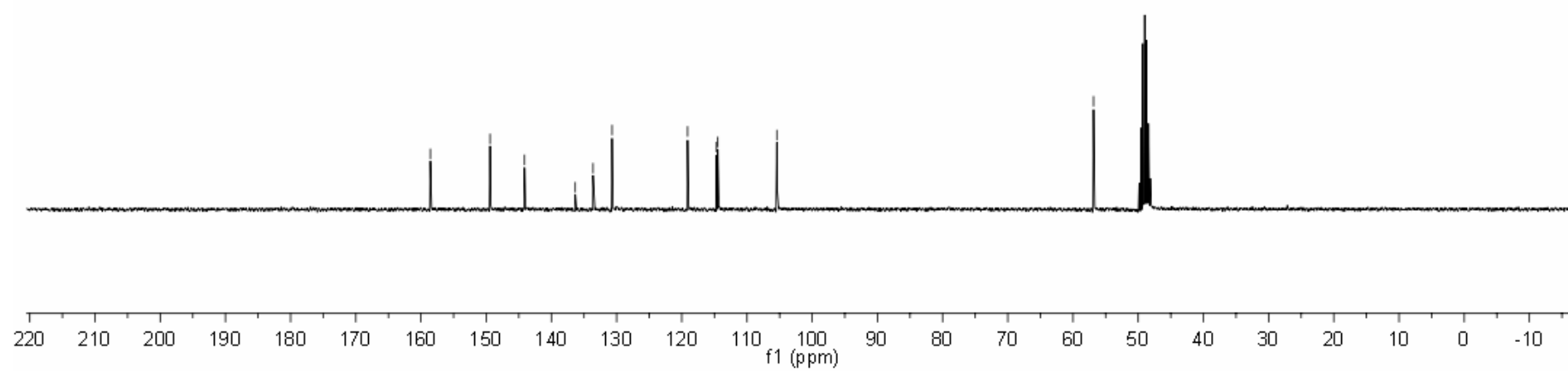
^1H NMR (methanol- d_4 , 300 MHz) of 3'-hydroxyaucuparin (*m*-**3**)



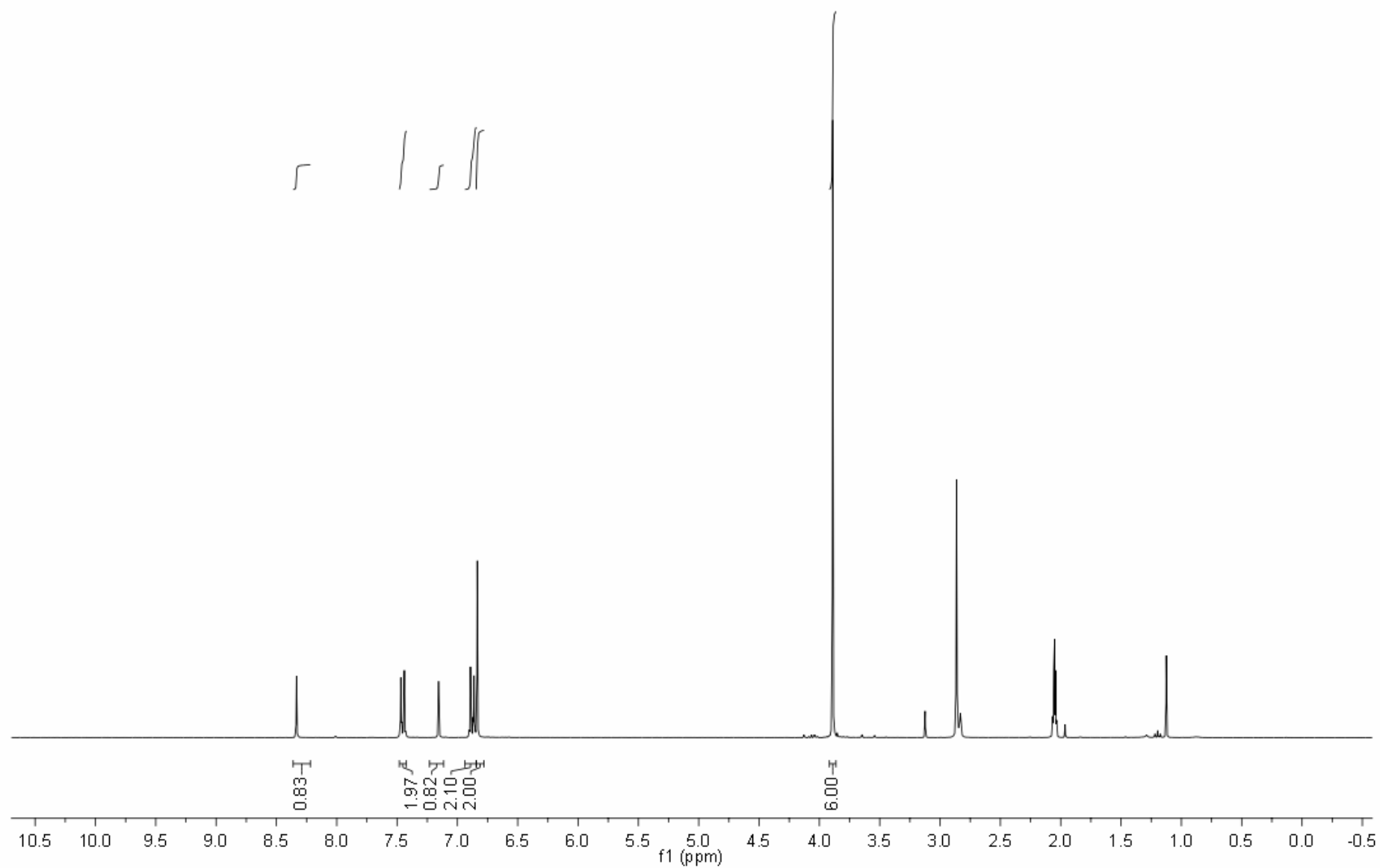
^{13}C NMR (methanol- d_4 , 75 MHz) of 3'-hydroxyaucuparin (*m*-3)

—158.6
~149.4
—144.1
/136.3
/133.6
~130.7
/119.1
/114.7
/114.5
—105.4

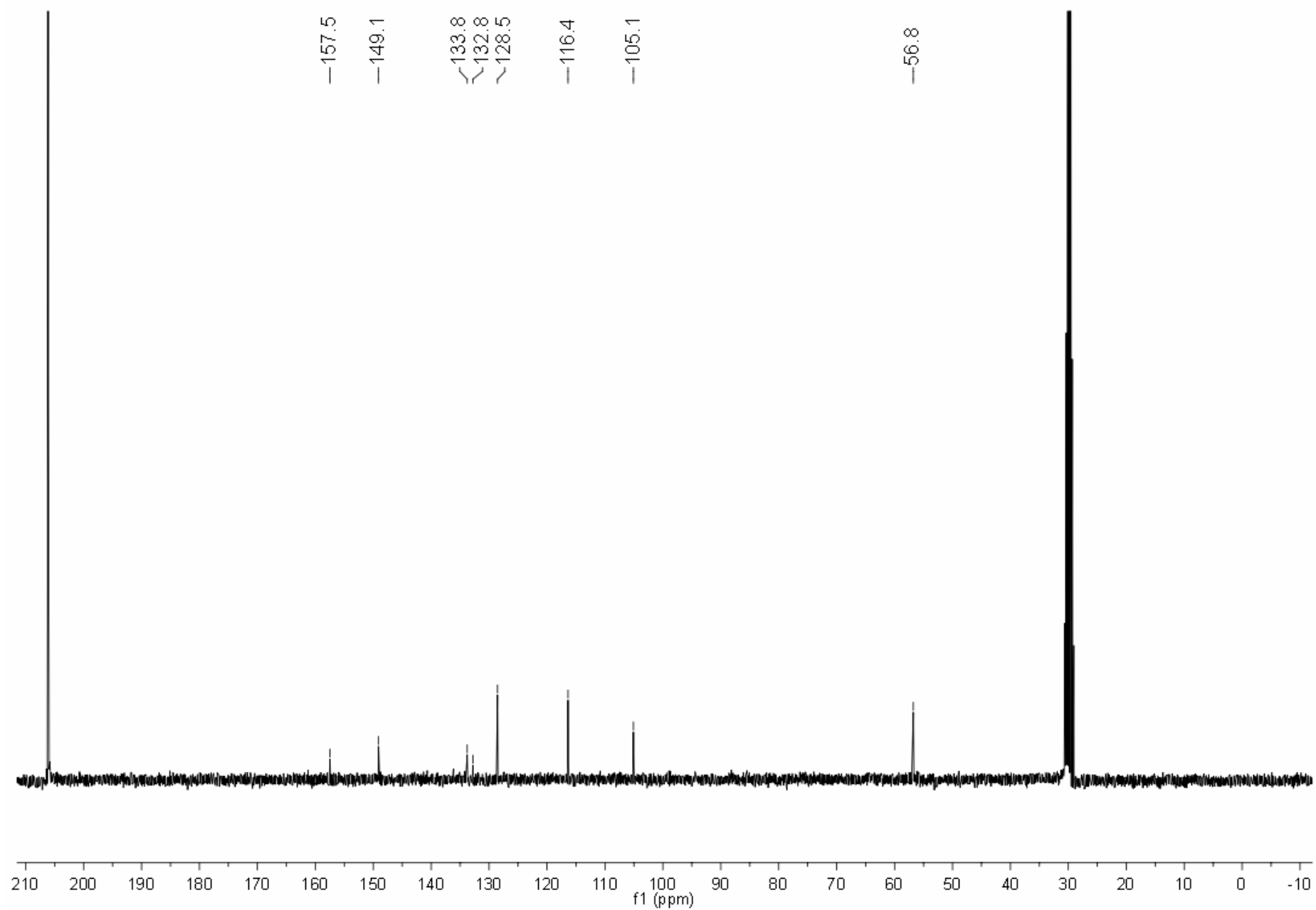
—56.9



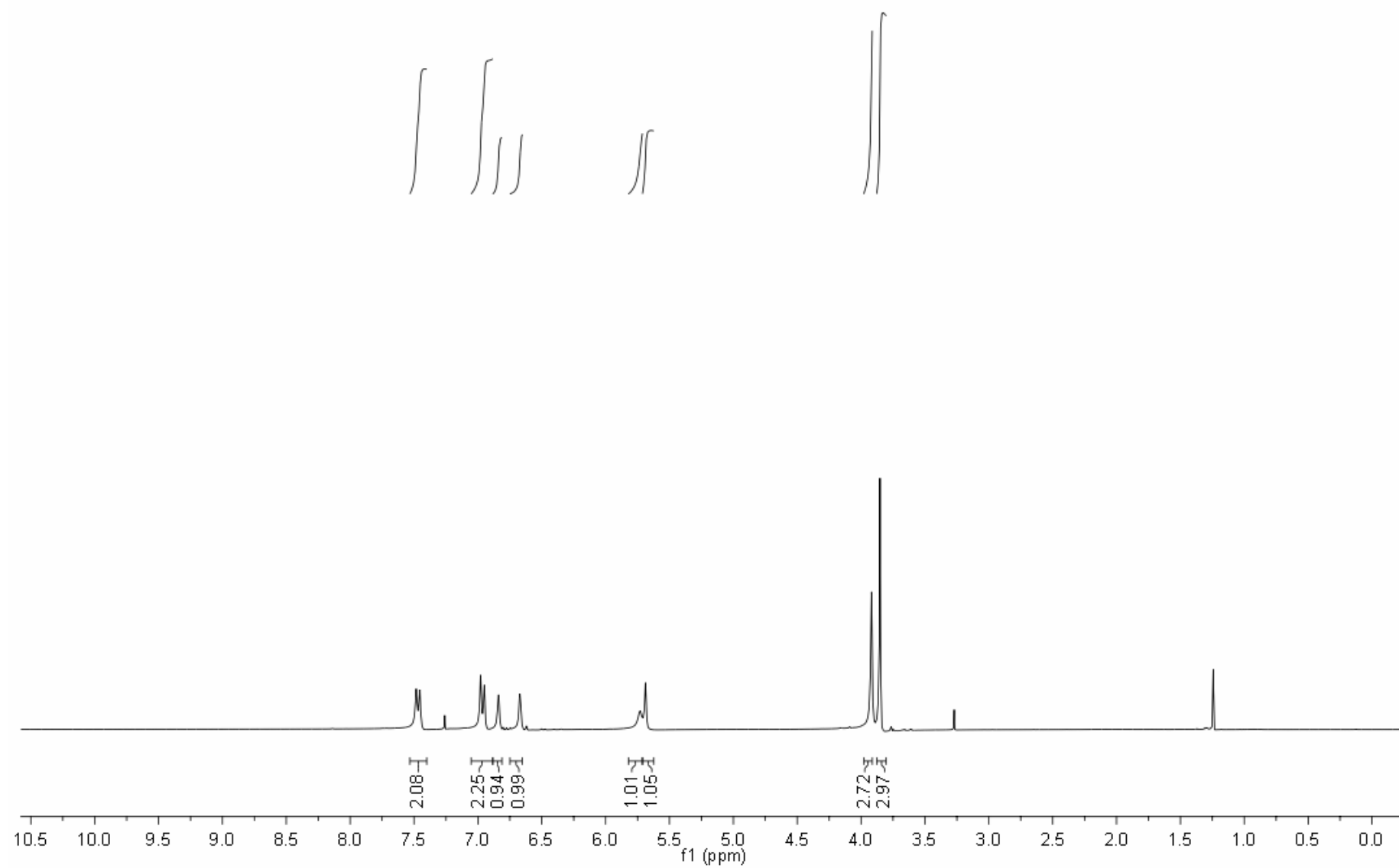
^1H NMR (acetone- d_6 , 300 MHz) of garcibiphenyl (*p*-3)



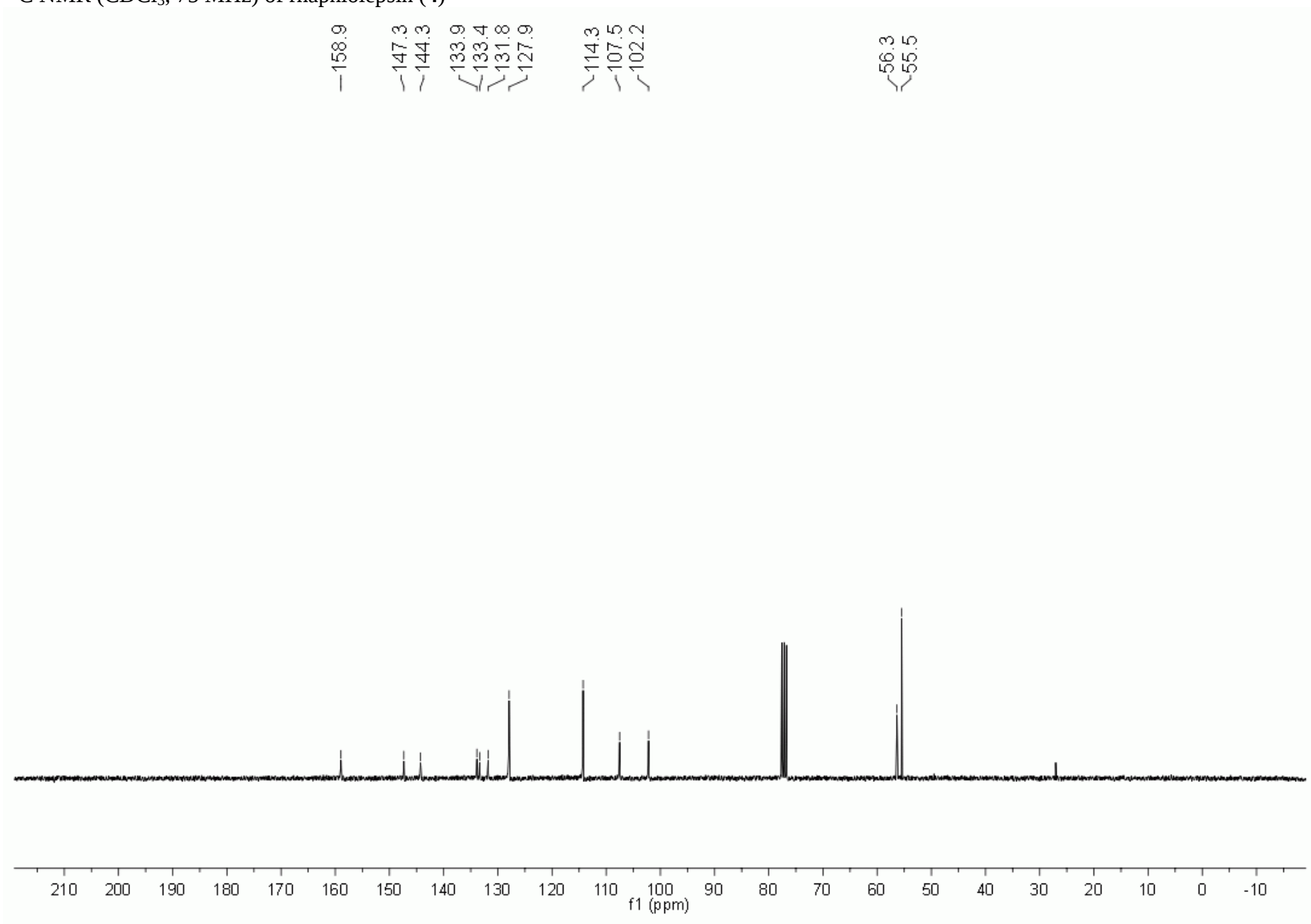
^{13}C NMR (acetone- d_6 , 75 MHz) of garcibiphenyl (*p*-3)



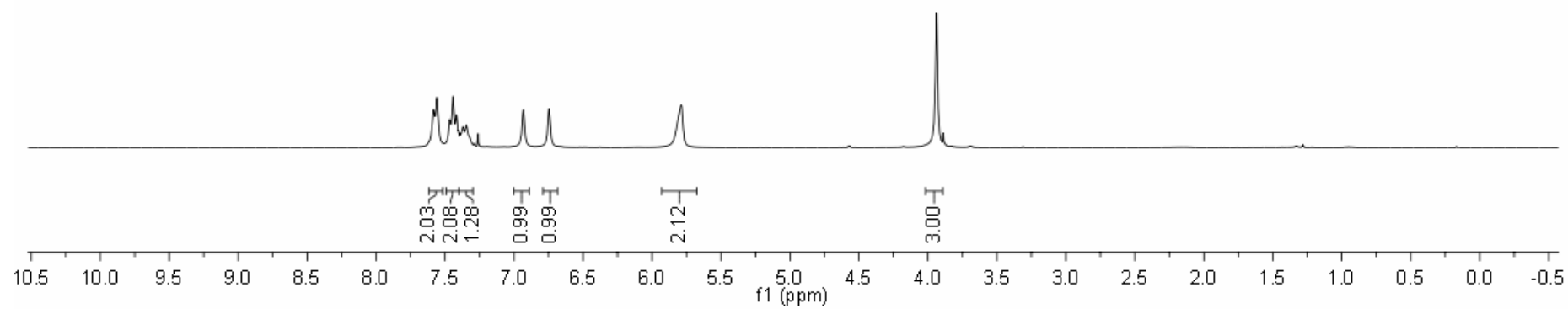
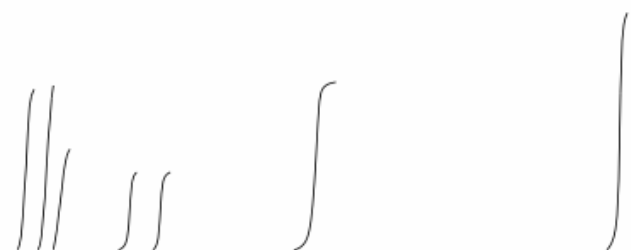
^1H NMR (CDCl_3 , 300 MHz) of raphiolepsin (**4**)



^{13}C NMR (CDCl_3 , 75 MHz) of raphiolepsin (**4**)



^1H NMR (CDCl_3 , 300 MHz) of 3-de-*O*-methylaucuparin (**7b**)

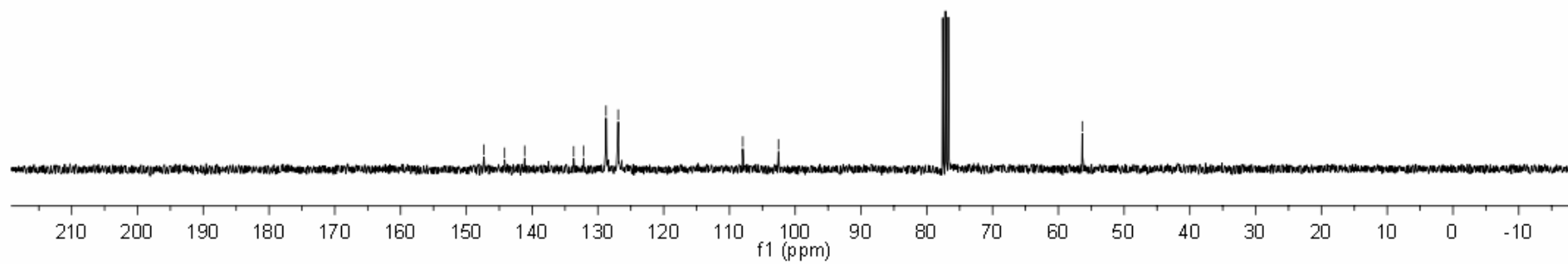


^{13}C NMR (CDCl_3 , 75 MHz) of 3-de-*O*-methylaucuparin (**7b**)

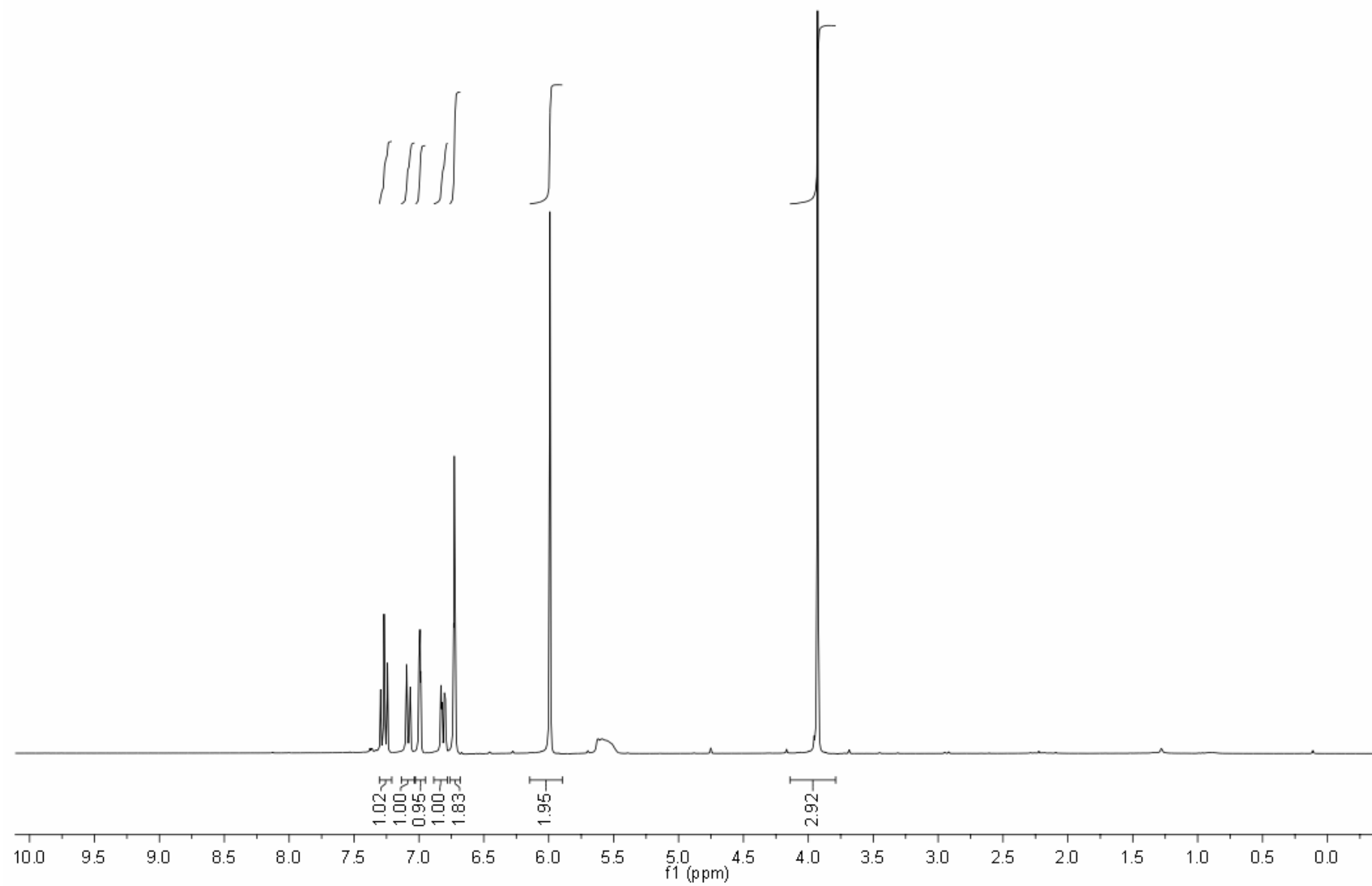
147.3
144.2
141.1
133.7
132.2
128.8
126.9

108.0
102.6

56.4



^1H NMR (CDCl_3 , 300 MHz) of **6**



^{13}C NMR-APT (CDCl_3 , 75 MHz) of **6**

