

Supporting Information

Metal-free Chlorodeboronation of Organotrifluoroborates

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Roy and Diana Vagelos Laboratories, Department of Chemistry,

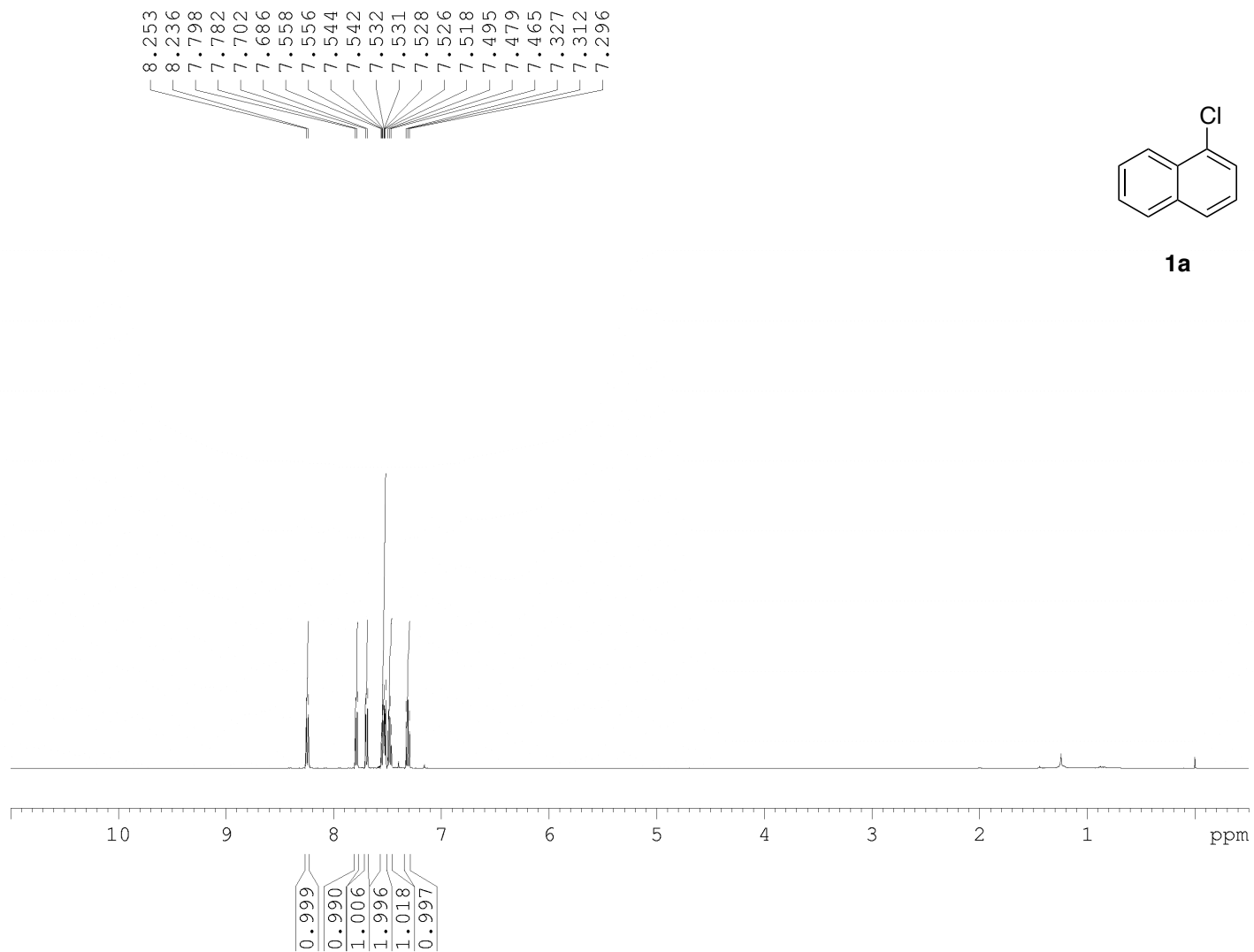
University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323

gmolandr@sas.upenn.edu

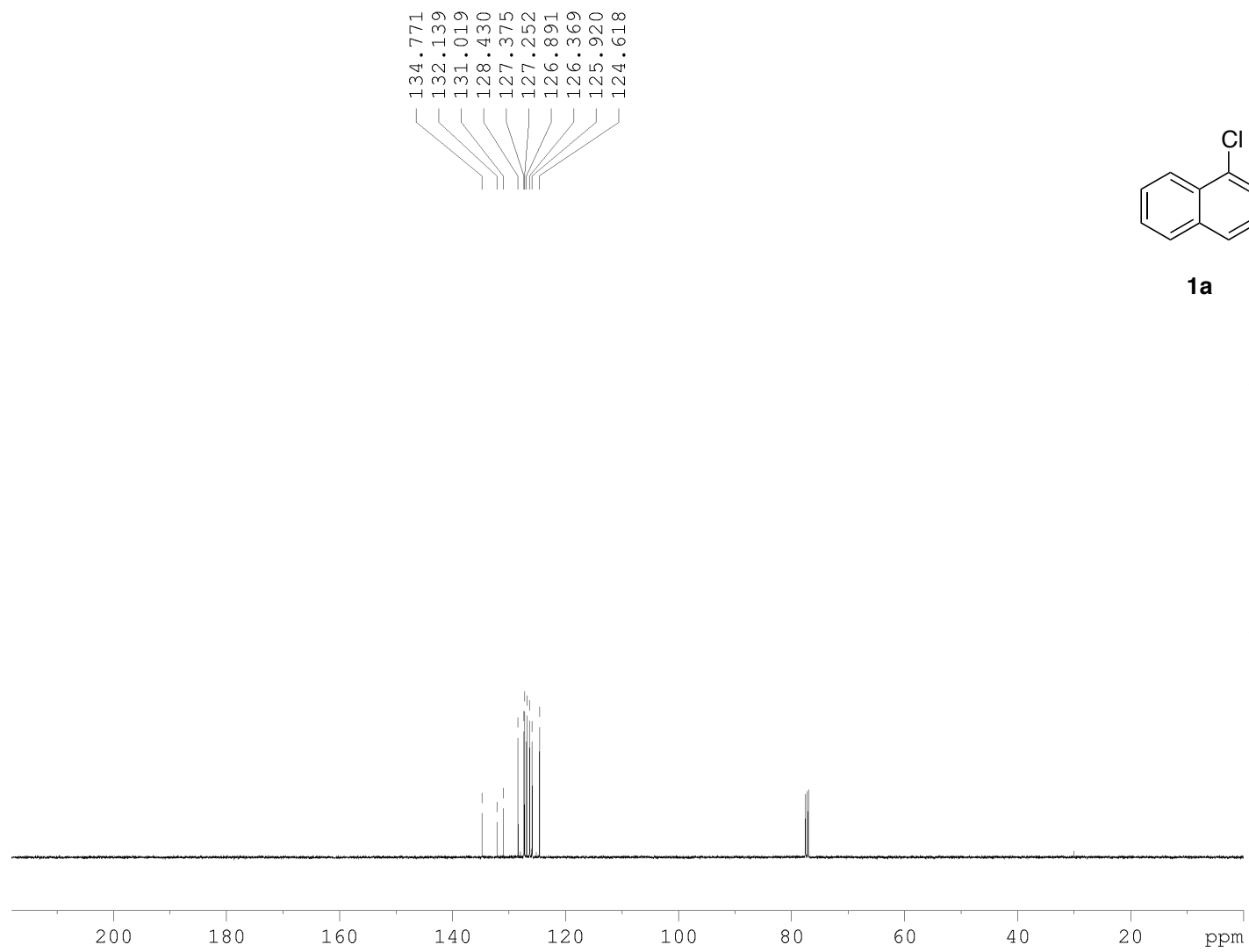
Contents:

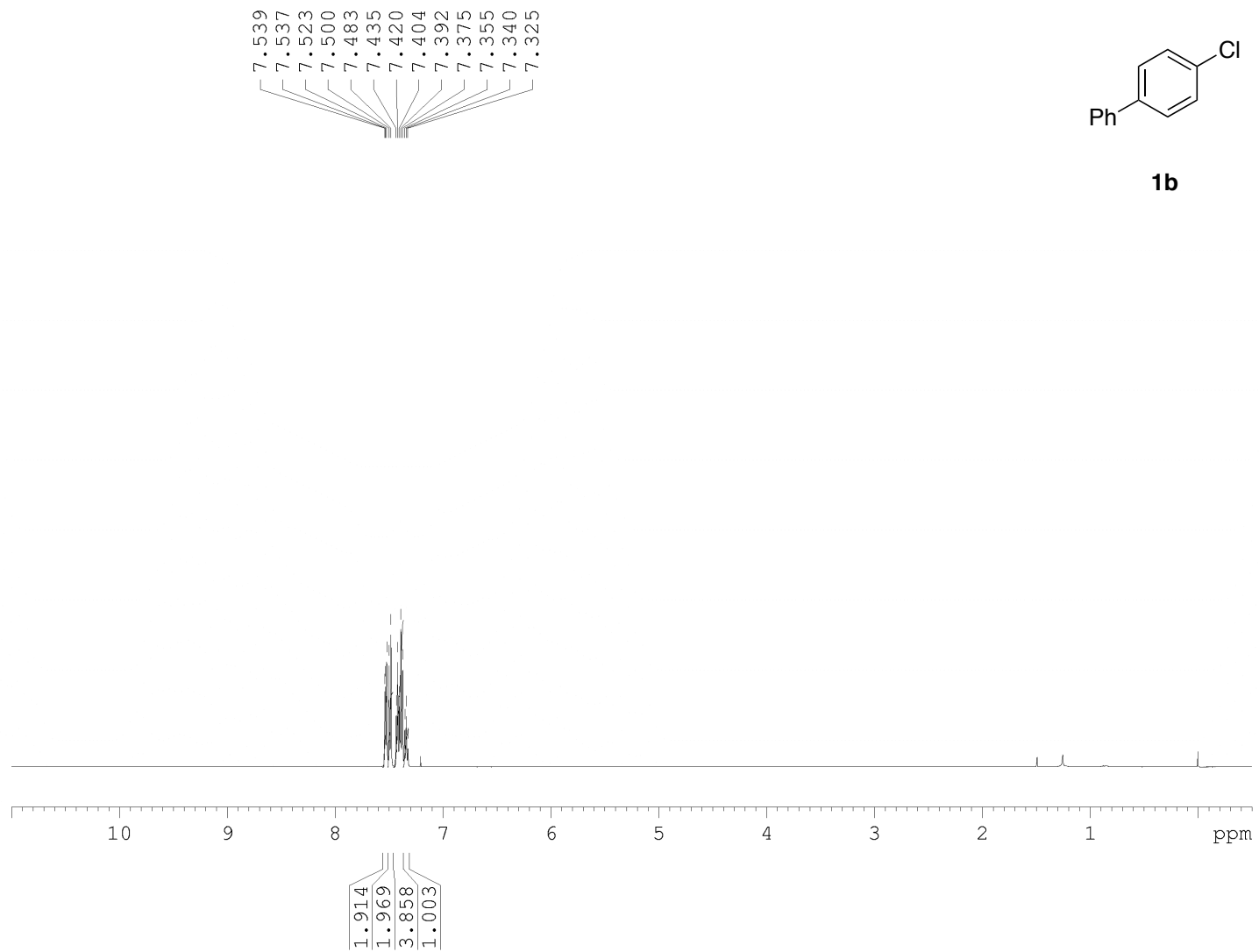
General Considerations.....	S2
NMR spectras	S2-S62

General Considerations: All of the reagents and HPLC grade acetone were used as received. Melting points (°C) are uncorrected. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. ¹⁹F NMR chemical shifts were referenced to external CFCl₃ (0.0 ppm). Compounds **4d** and **4e** were characterized by comparison of their NMR data with commercially available samples.

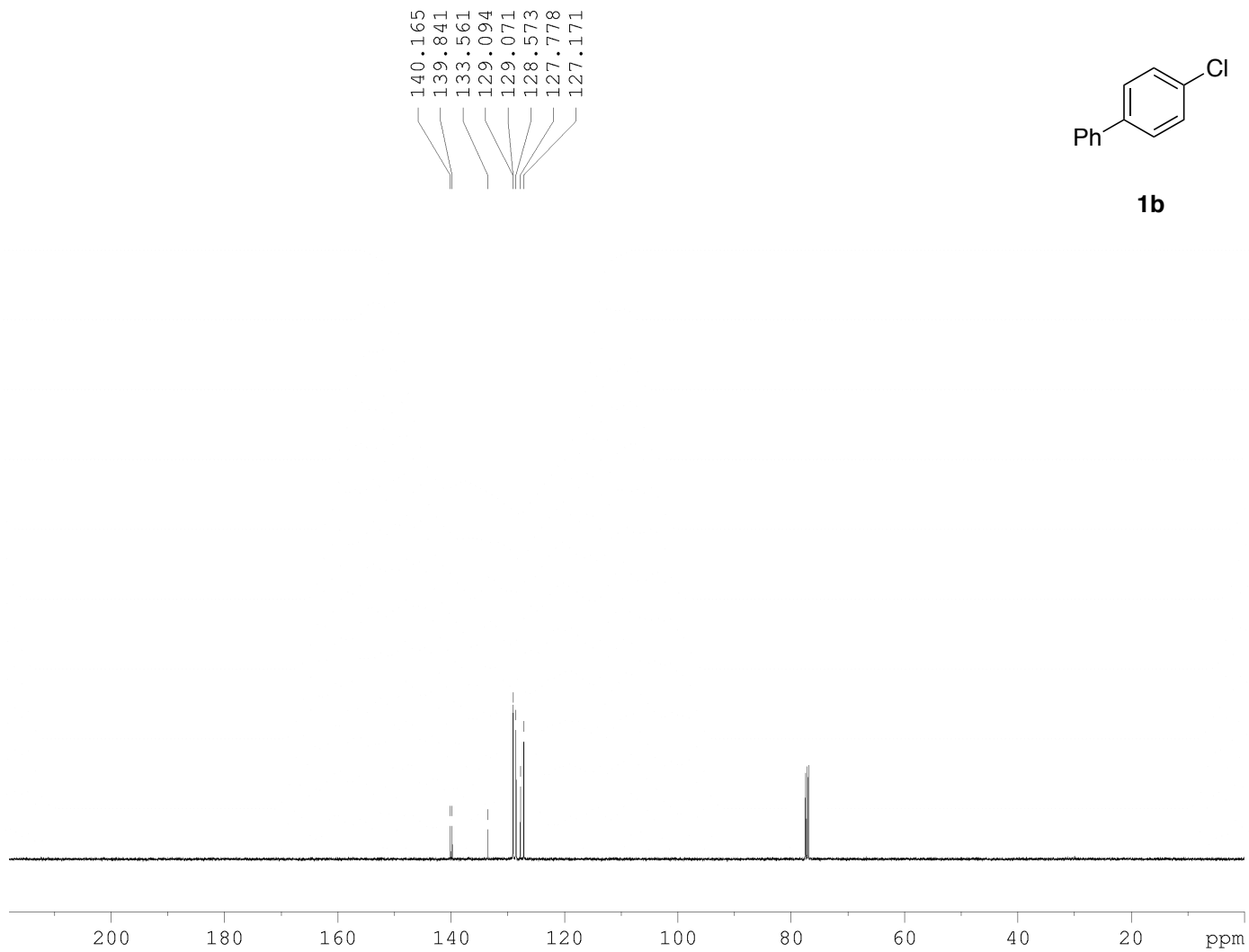


¹H NMR (500 MHz, CDCl₃) Spectrum of 1-Chloronaphthalene (1a)

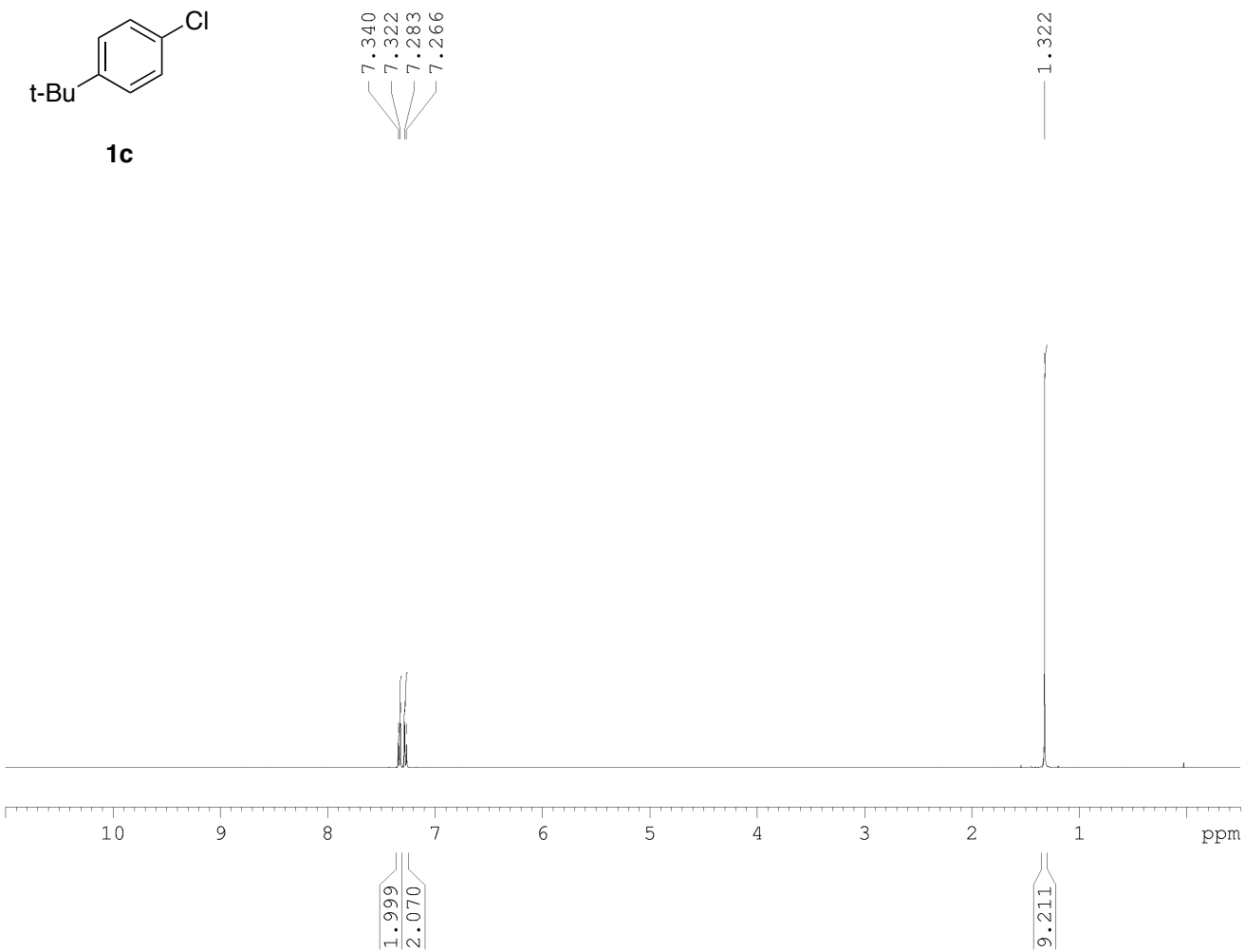




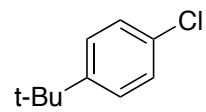
^1H NMR (500 MHz, CDCl_3) Spectrum of 4-Chlorobiphenyl (1b)



^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-Chlorobiphenyl (1b)



¹H NMR (500 MHz, CDCl₃) Spectrum of 1-*tert*-butyl-4-chlorobenzene (**1c**)



1c

149.747

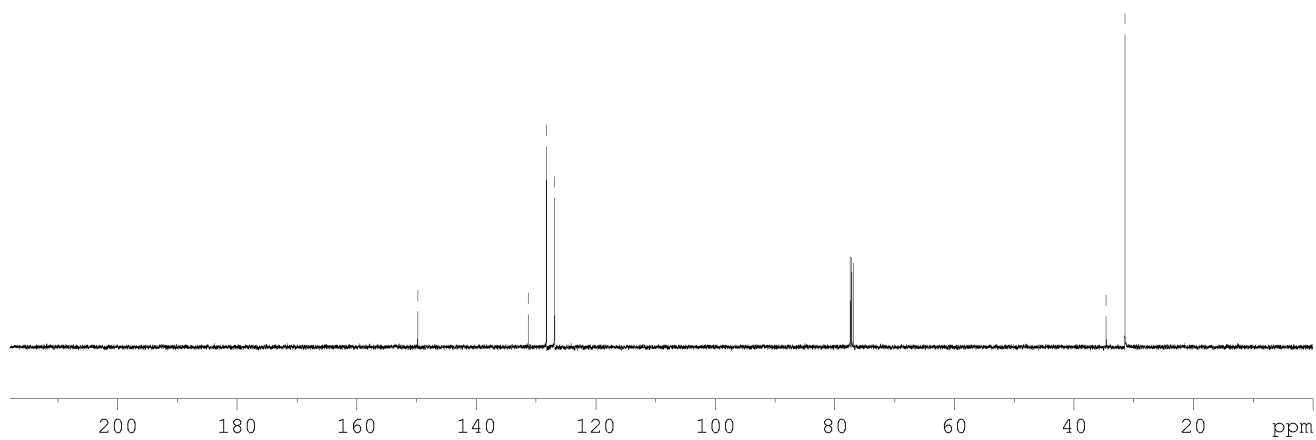
131.283

128.231

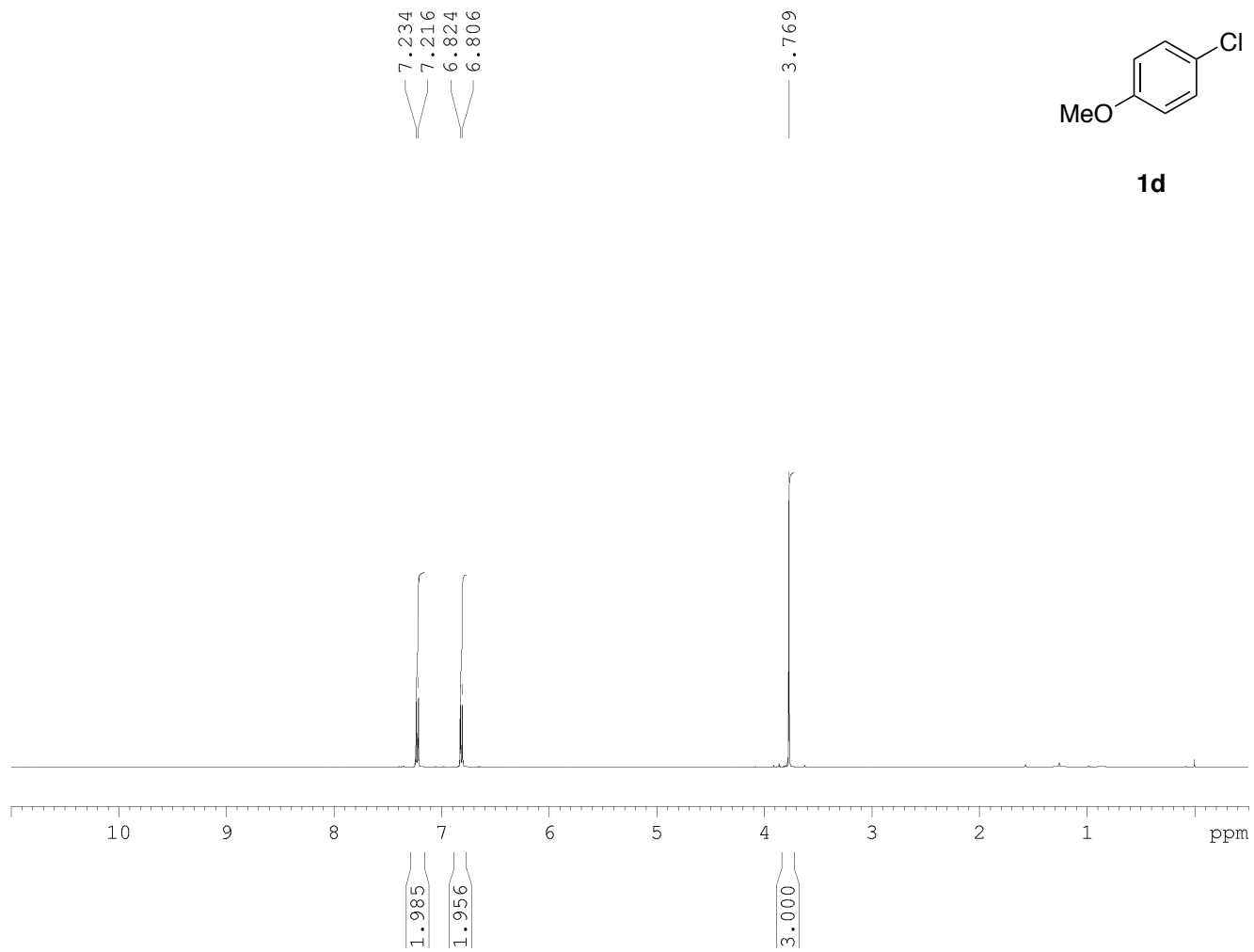
126.922

34.624

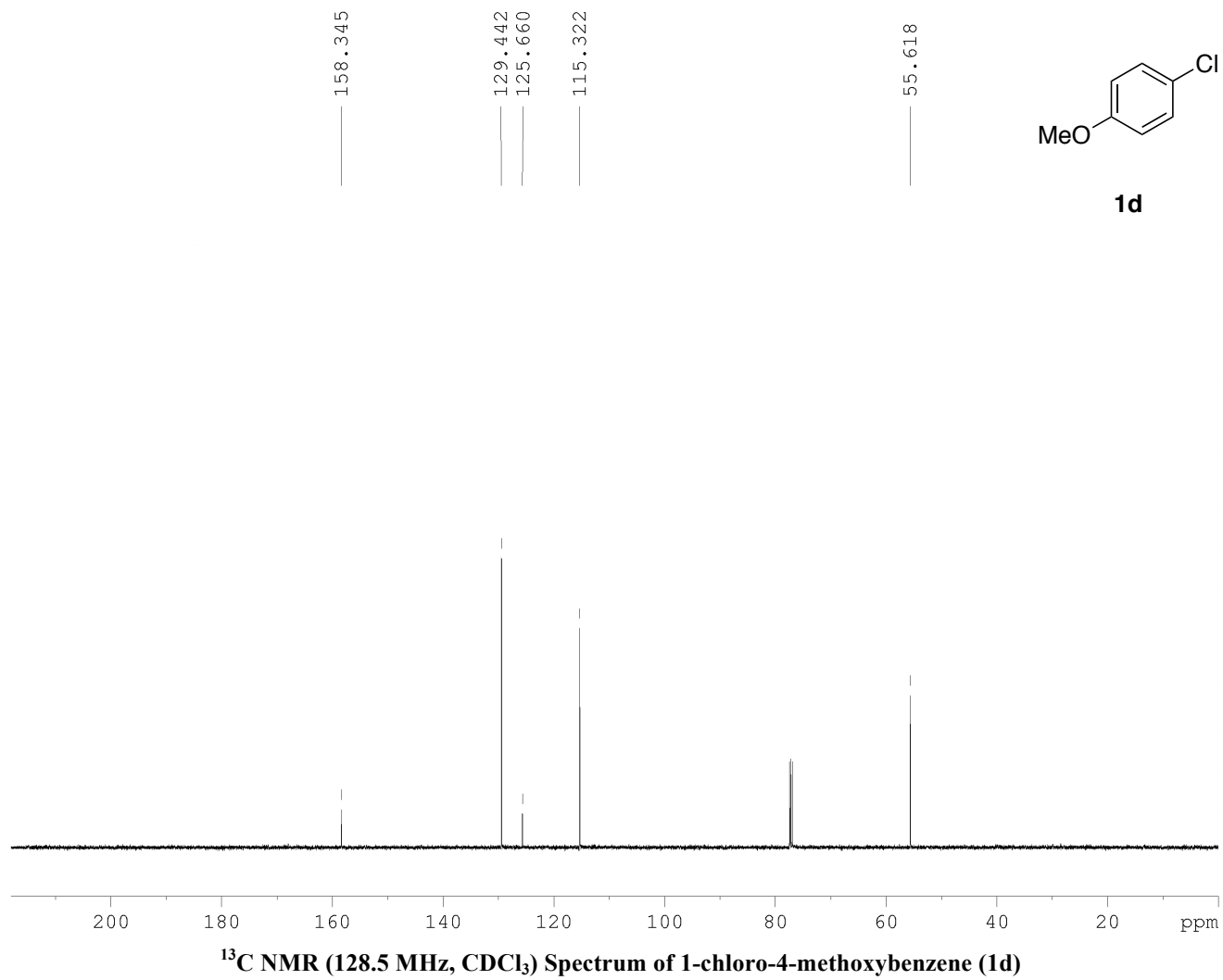
31.438

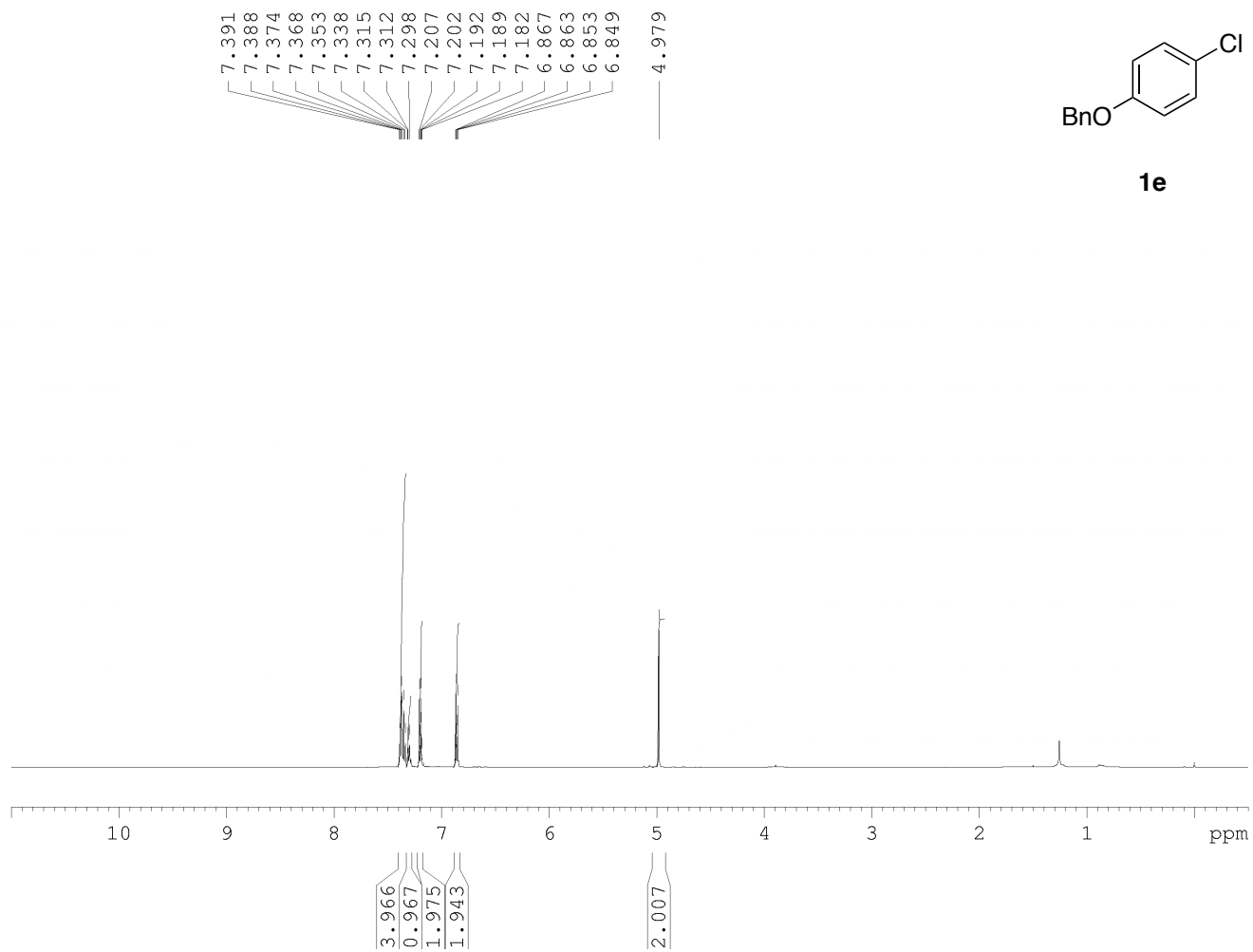


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1-*tert*-butyl-4-chlorobenzene (1c)

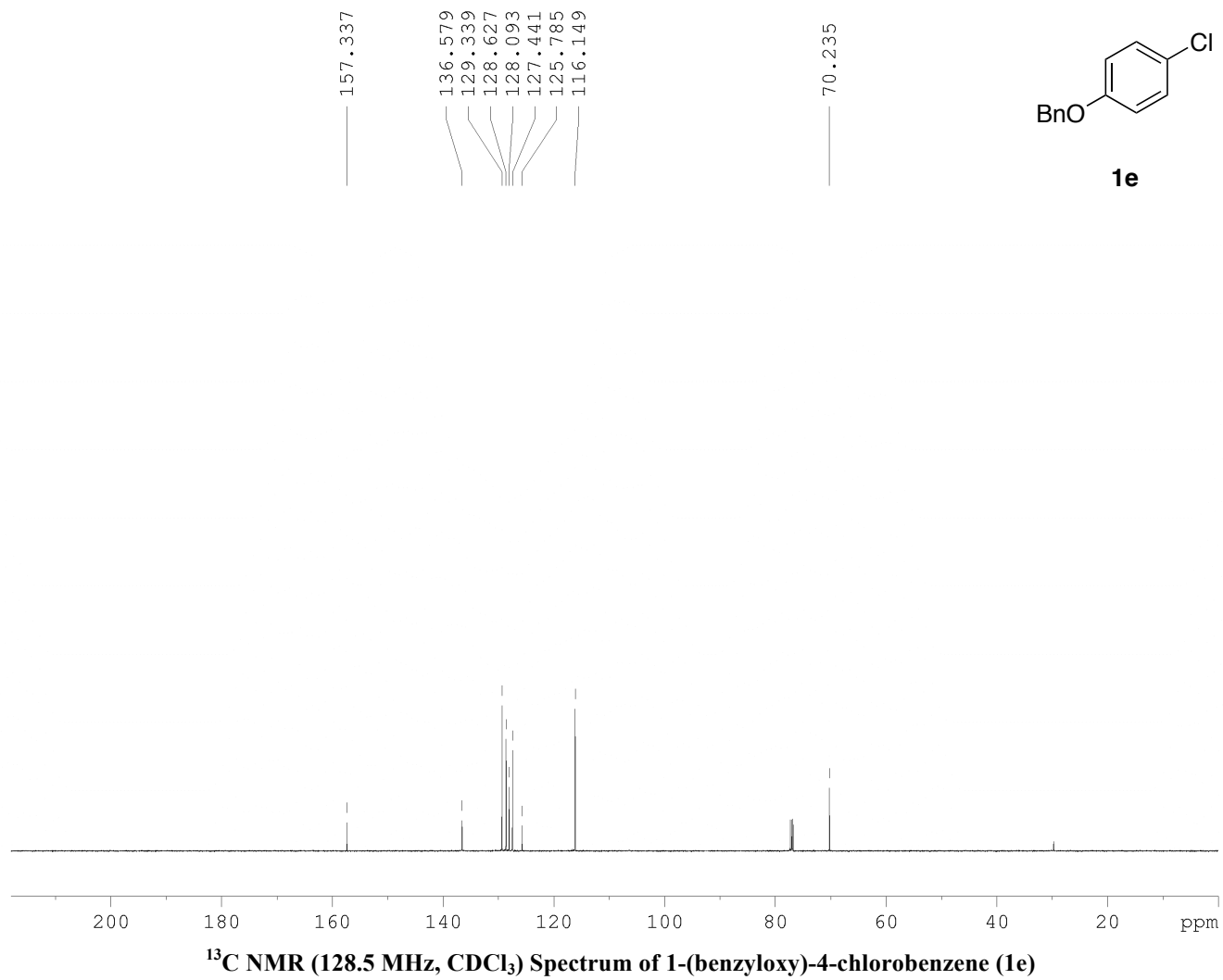


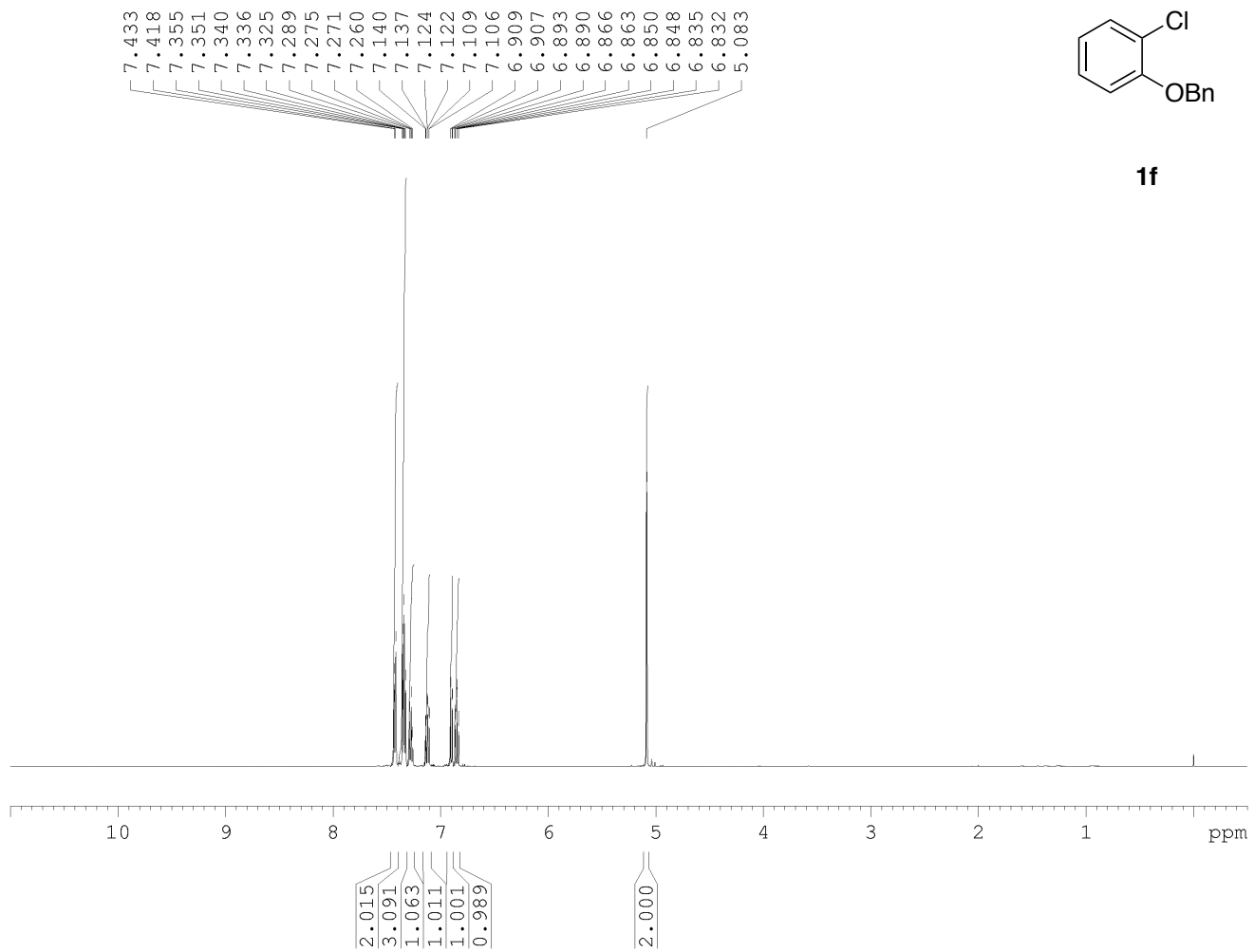
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-chloro-4-methoxybenzene (1d)



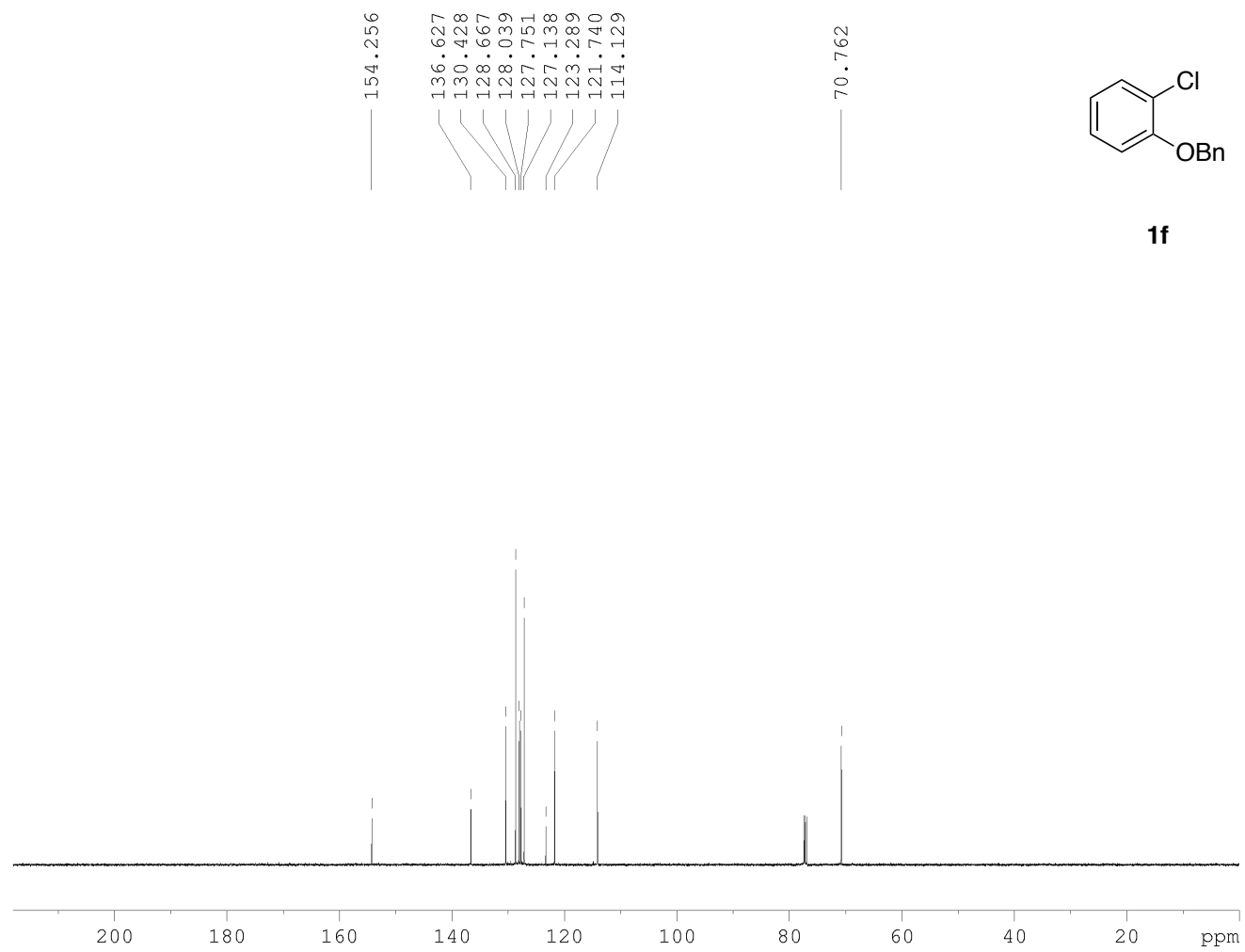


¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(benzyloxy)-4-chlorobenzene (1e)

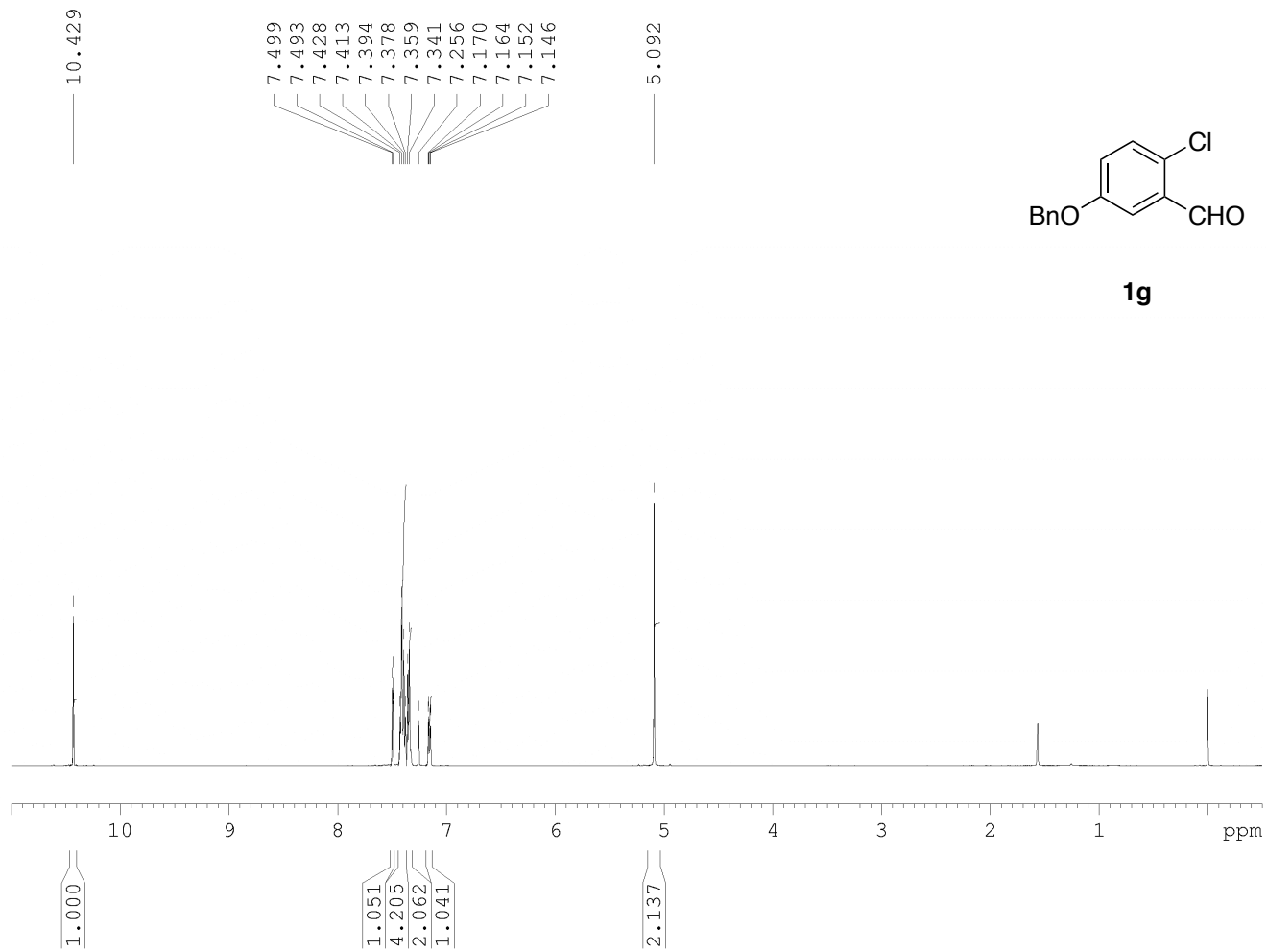




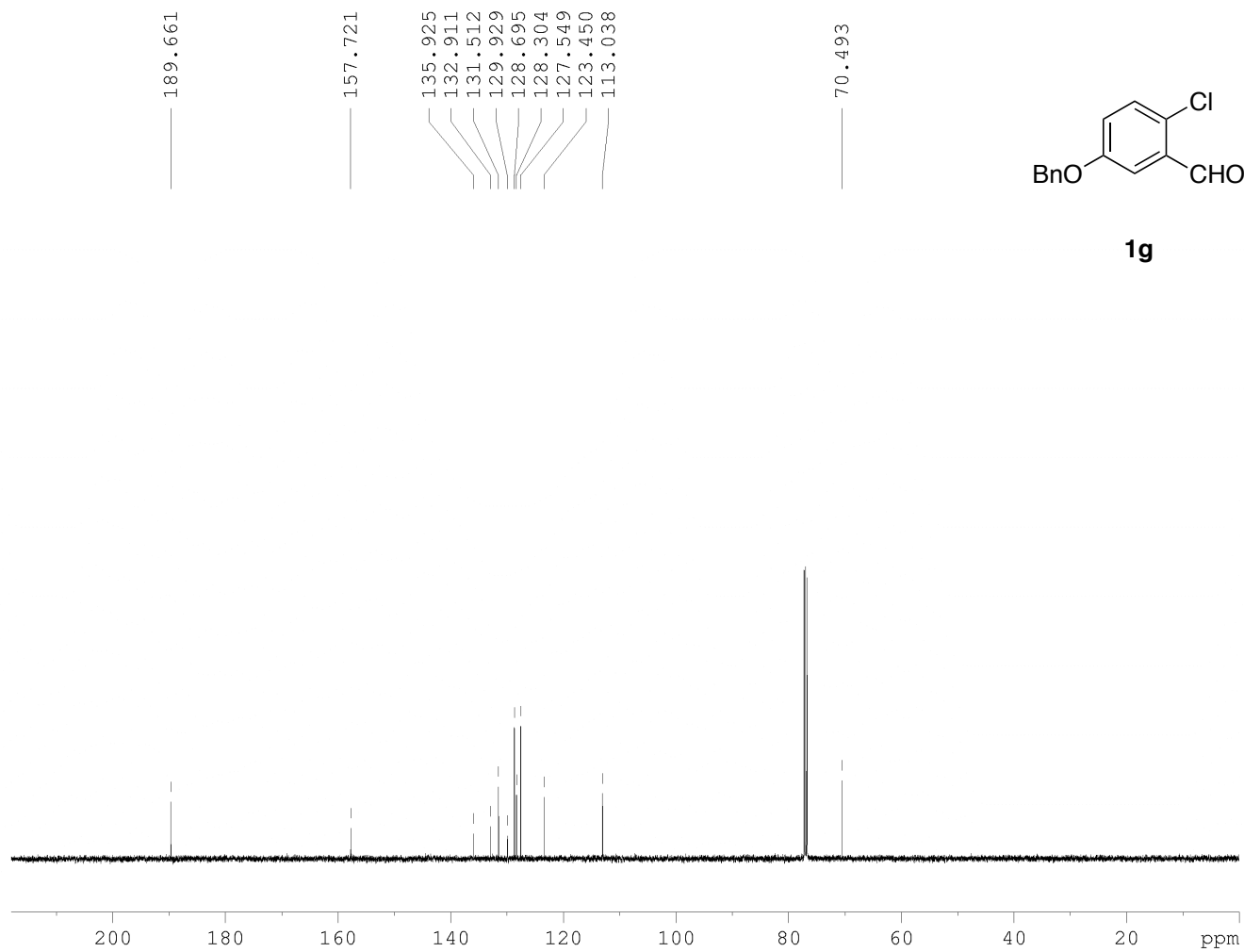
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(benzyloxy)-2-chlorobenzene (1f)



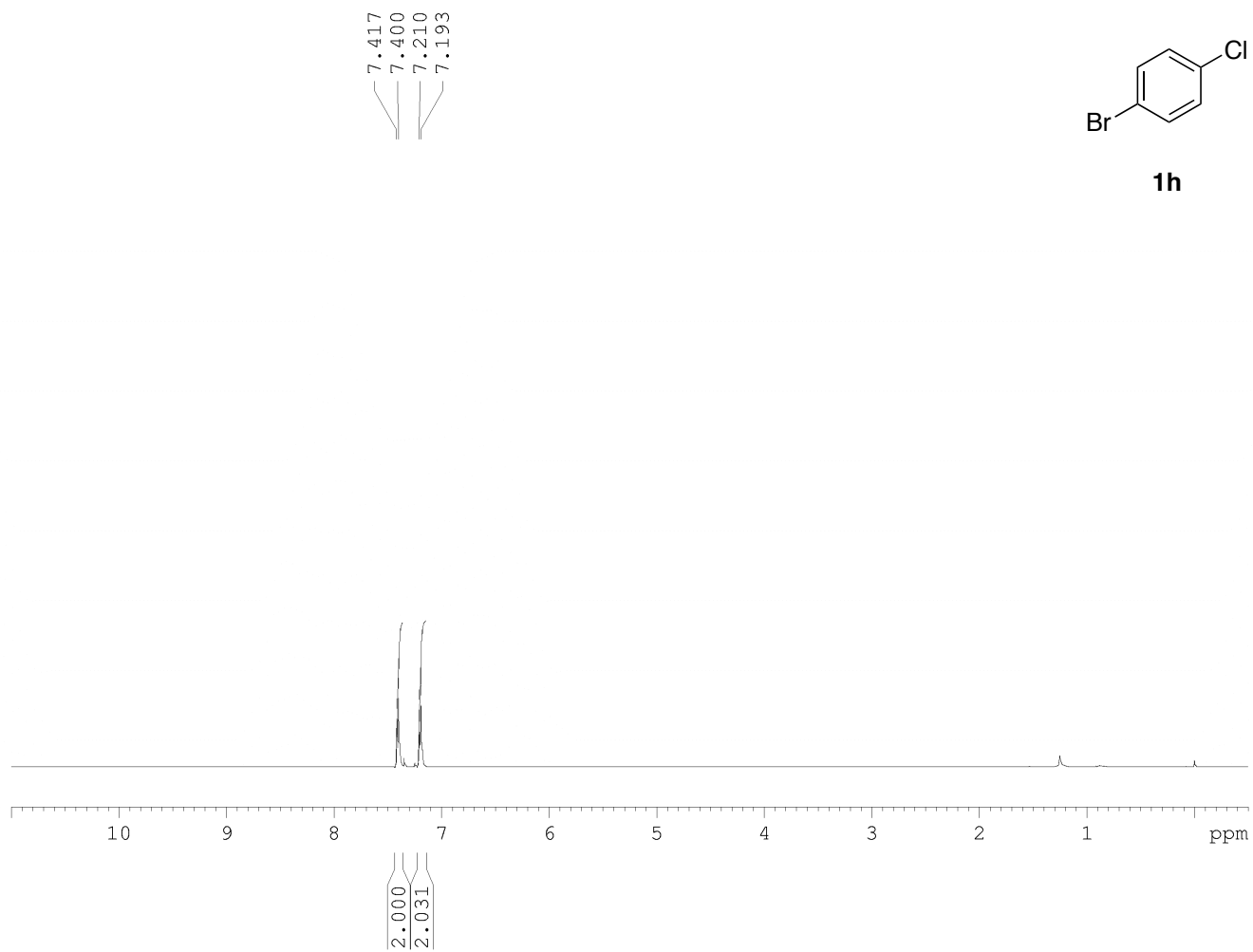
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1-(benzyloxy)-2-chlorobenzene (1f)



¹H NMR (500 MHz, CDCl₃) Spectrum of 5-(benzyloxy)-2-chlorobenzaldehyde (1g)

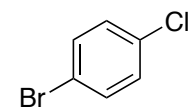


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 5-(benzyloxy)-2-chlorobenzaldehyde (1g)

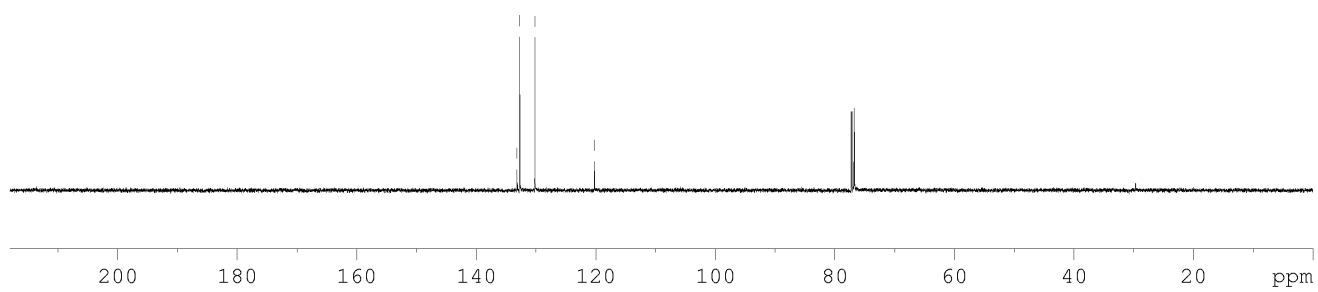


^1H NMR (500 MHz, CDCl_3) Spectrum of 1-bromo-4-chlorobenzene (1h)

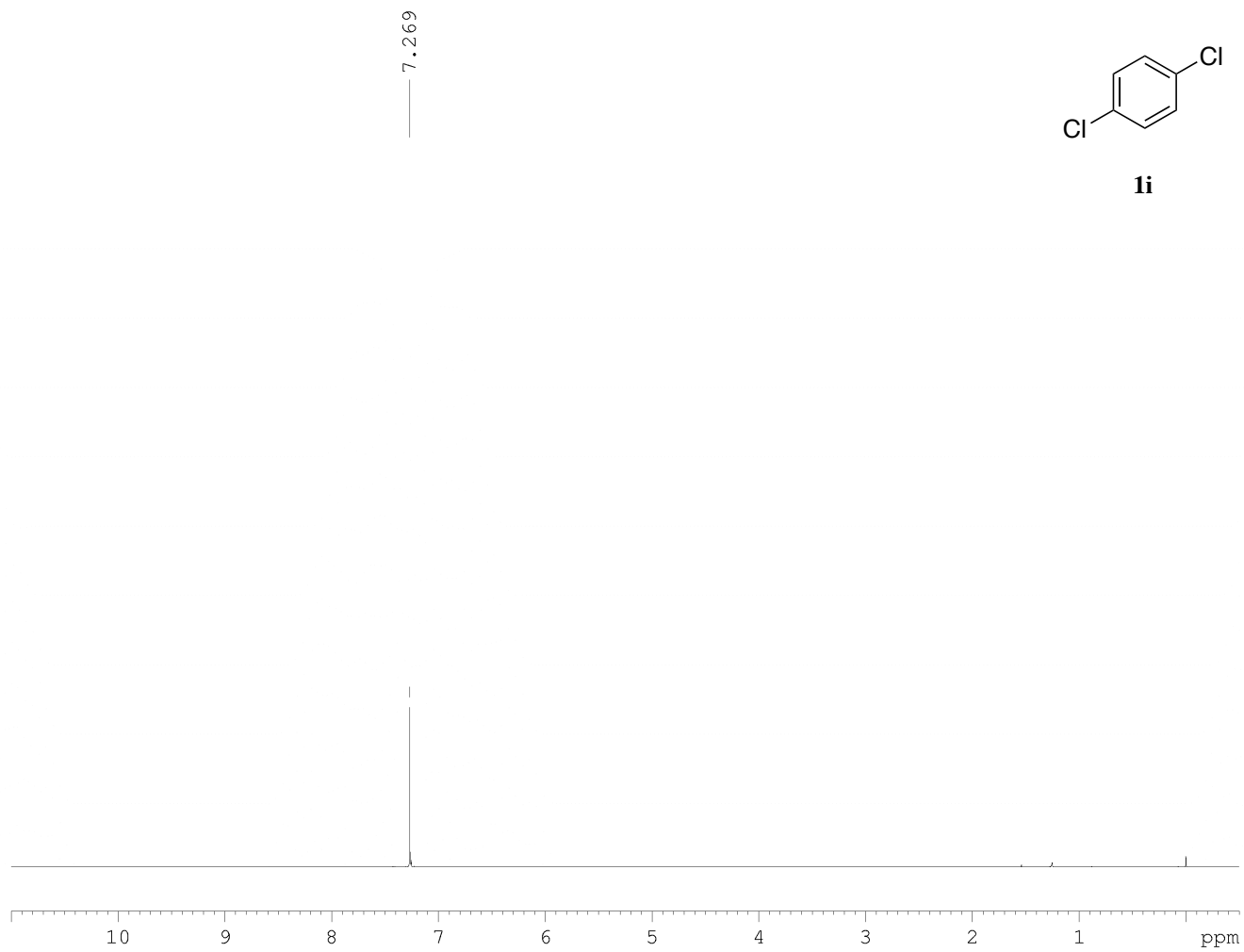
133.189
132.744
130.173
120.246



1h

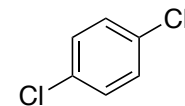


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1-bromo-4-chlorobenzene (1h)

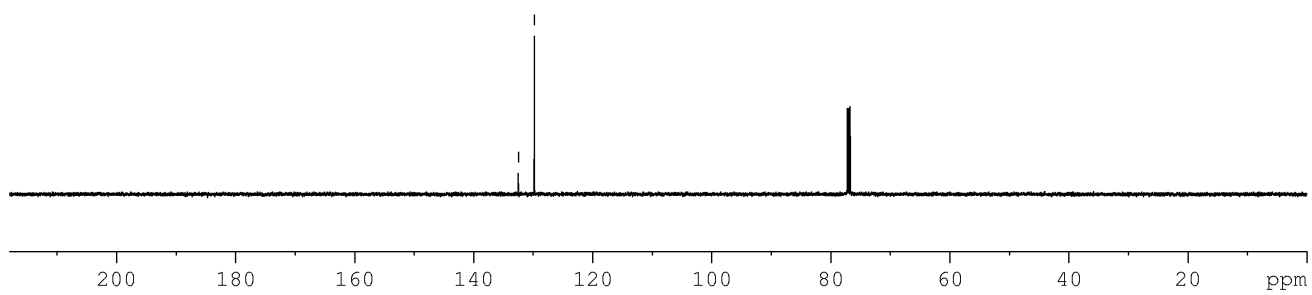


^1H NMR (500 MHz, CDCl_3) Spectrum of 1,4-dichlorobenzene (**1i**)

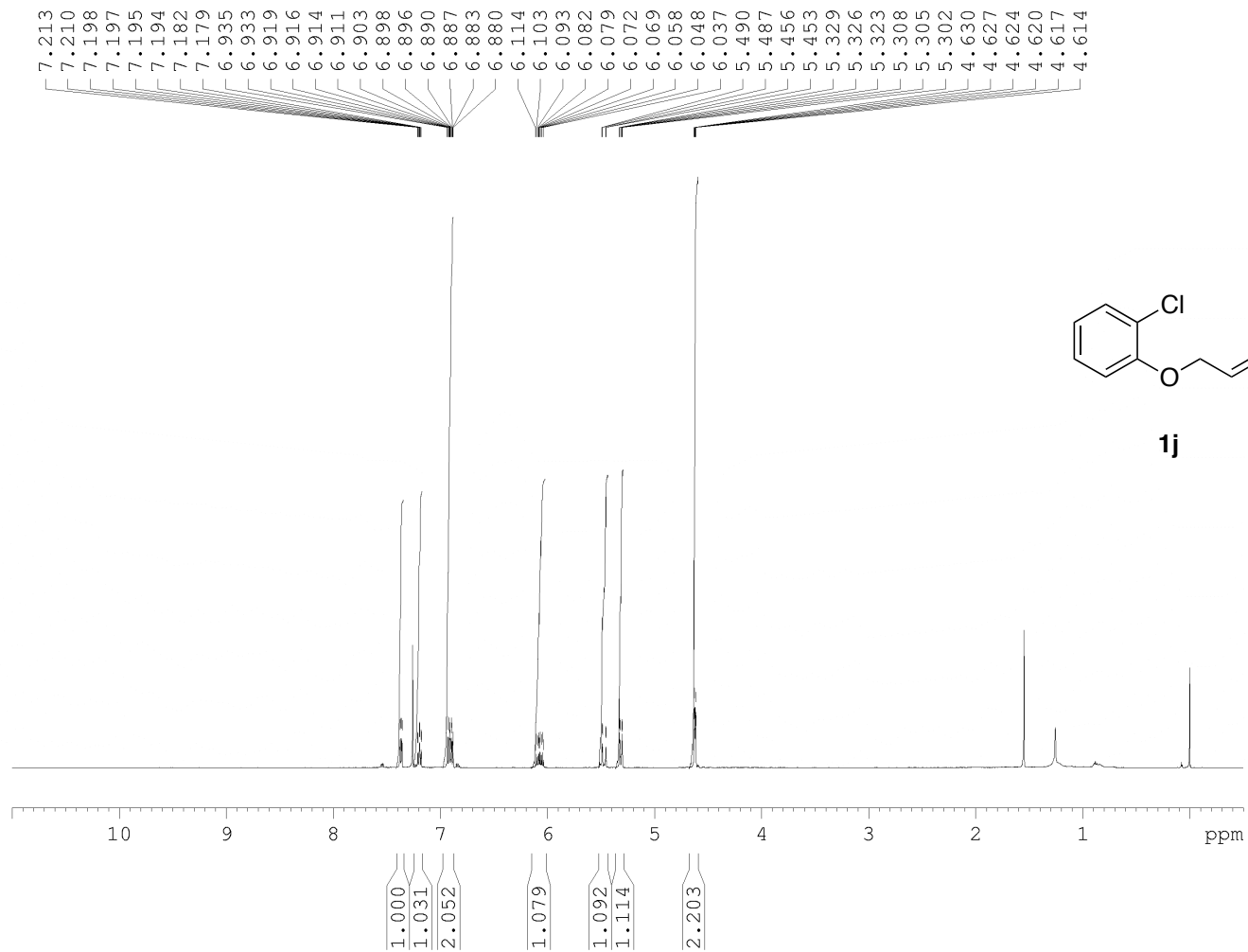
132.496
129.802



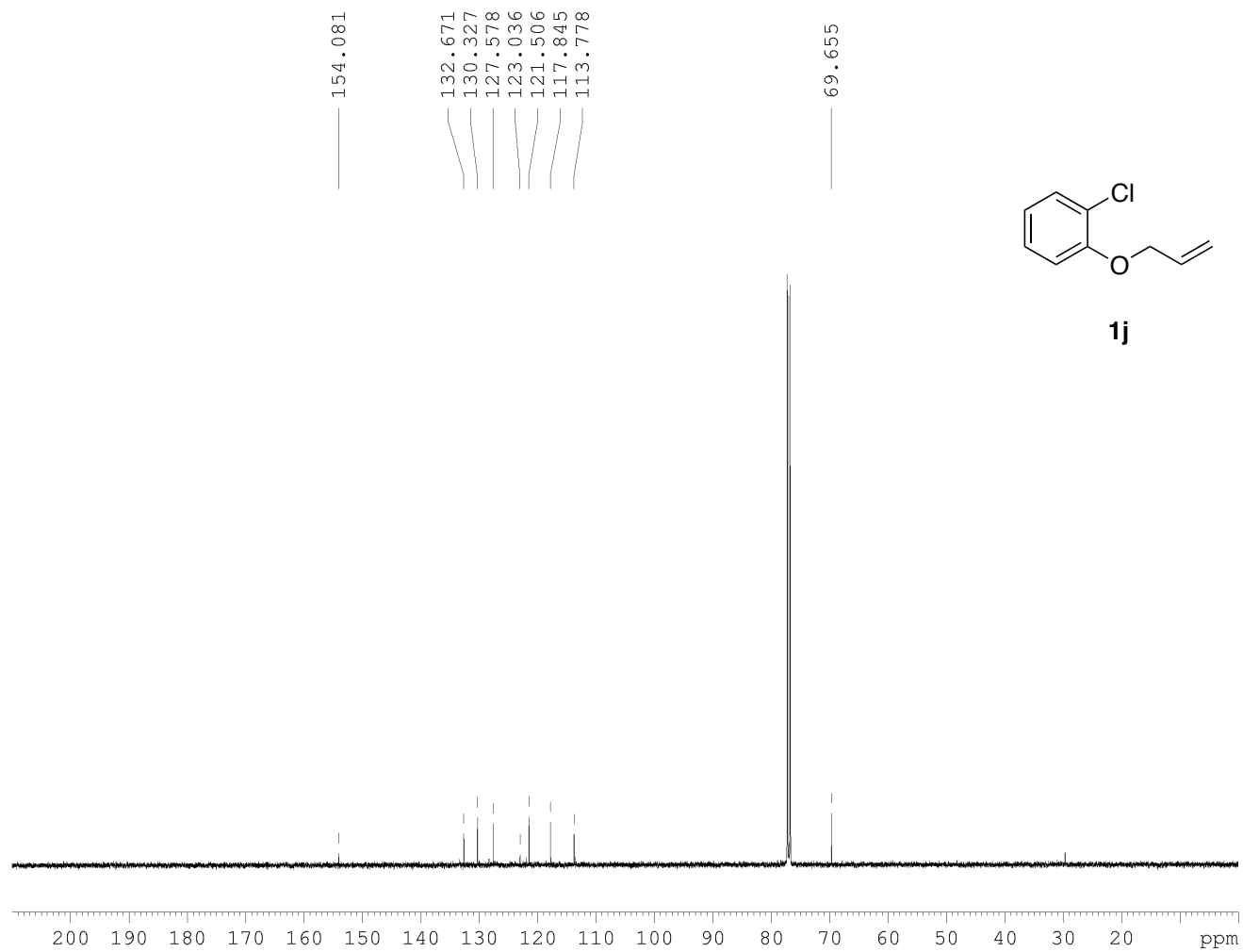
1i



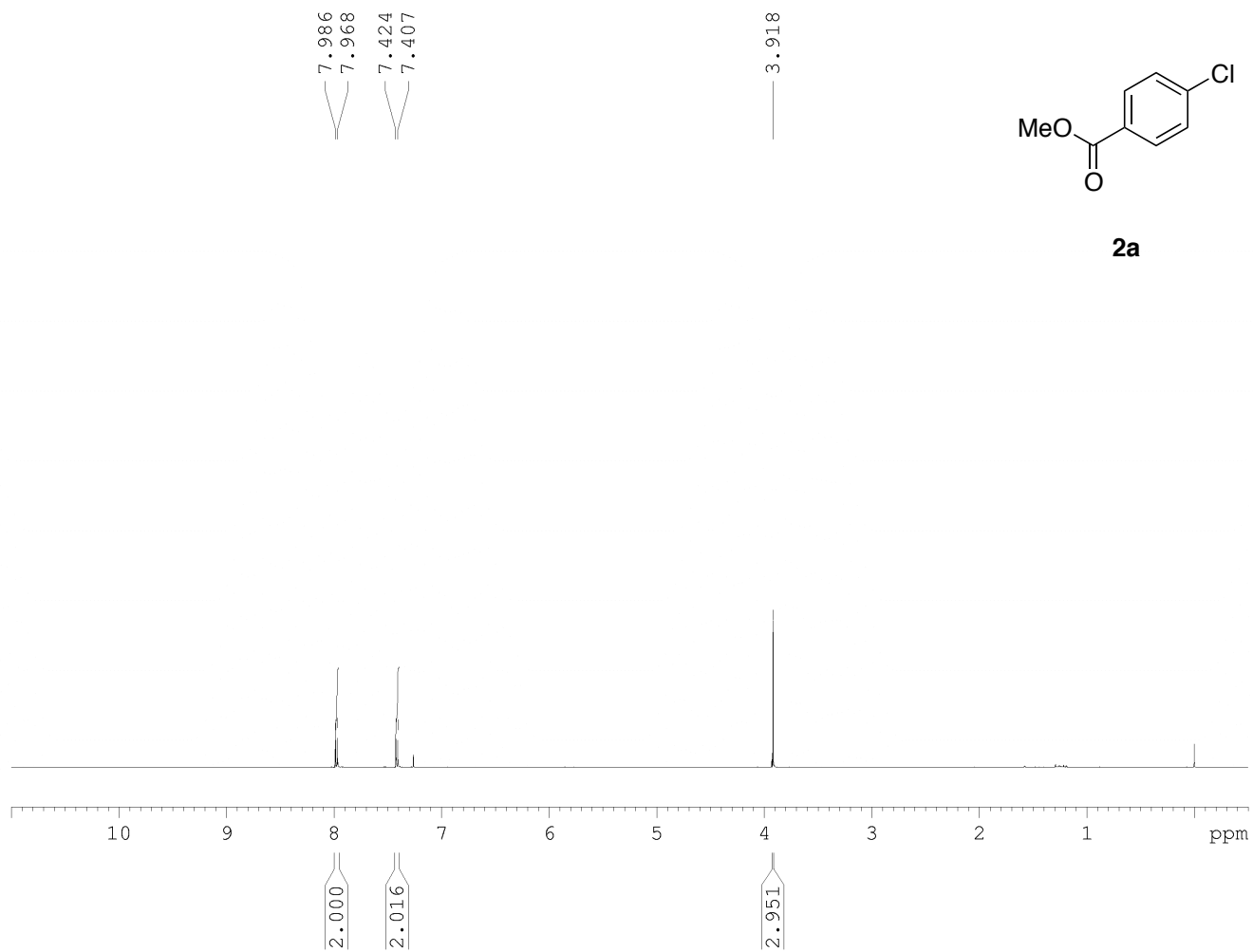
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1,4-dichlorobenzene (1i)



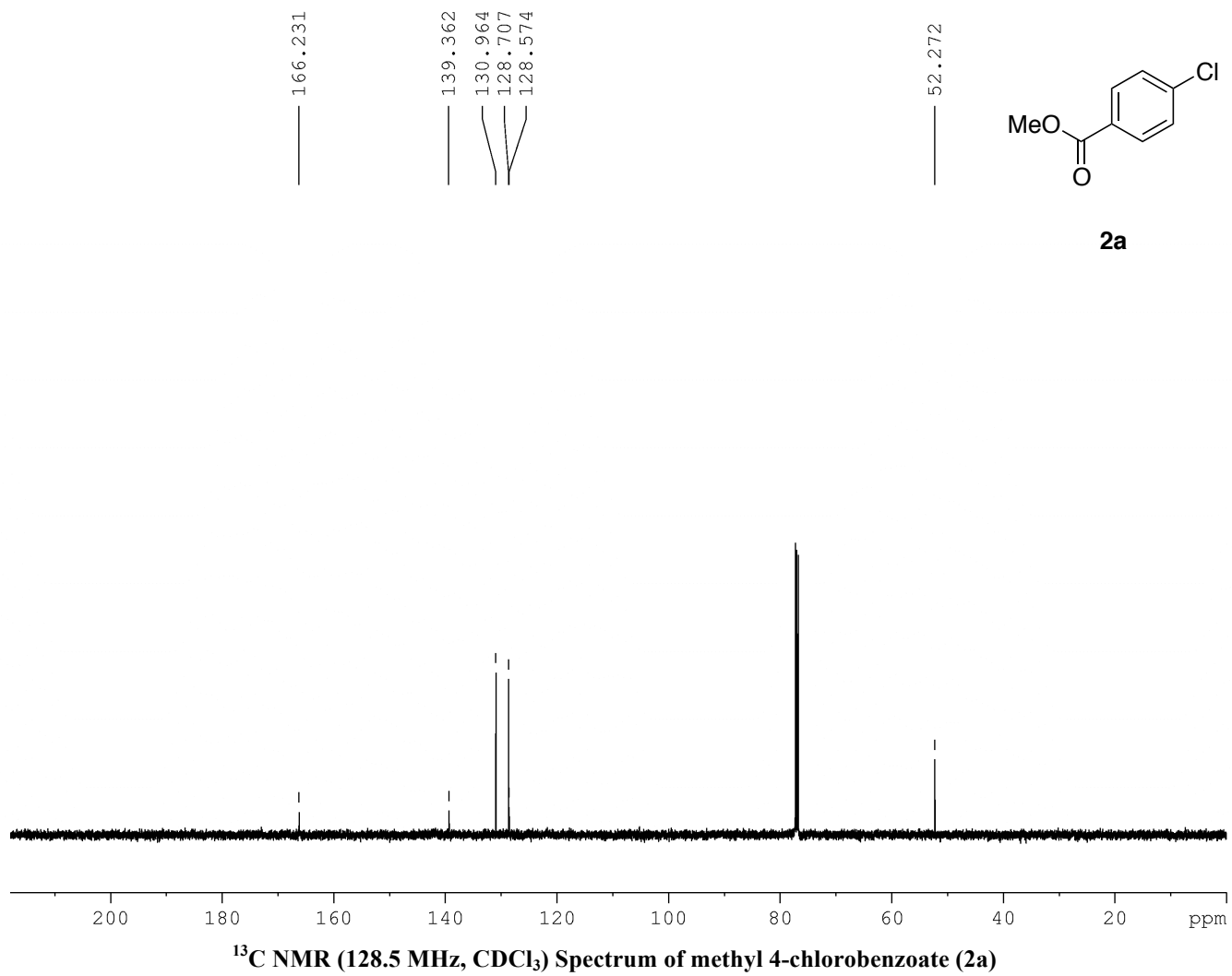
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(allyloxy)-2-chlorobenzene (1j)

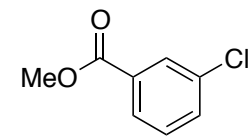
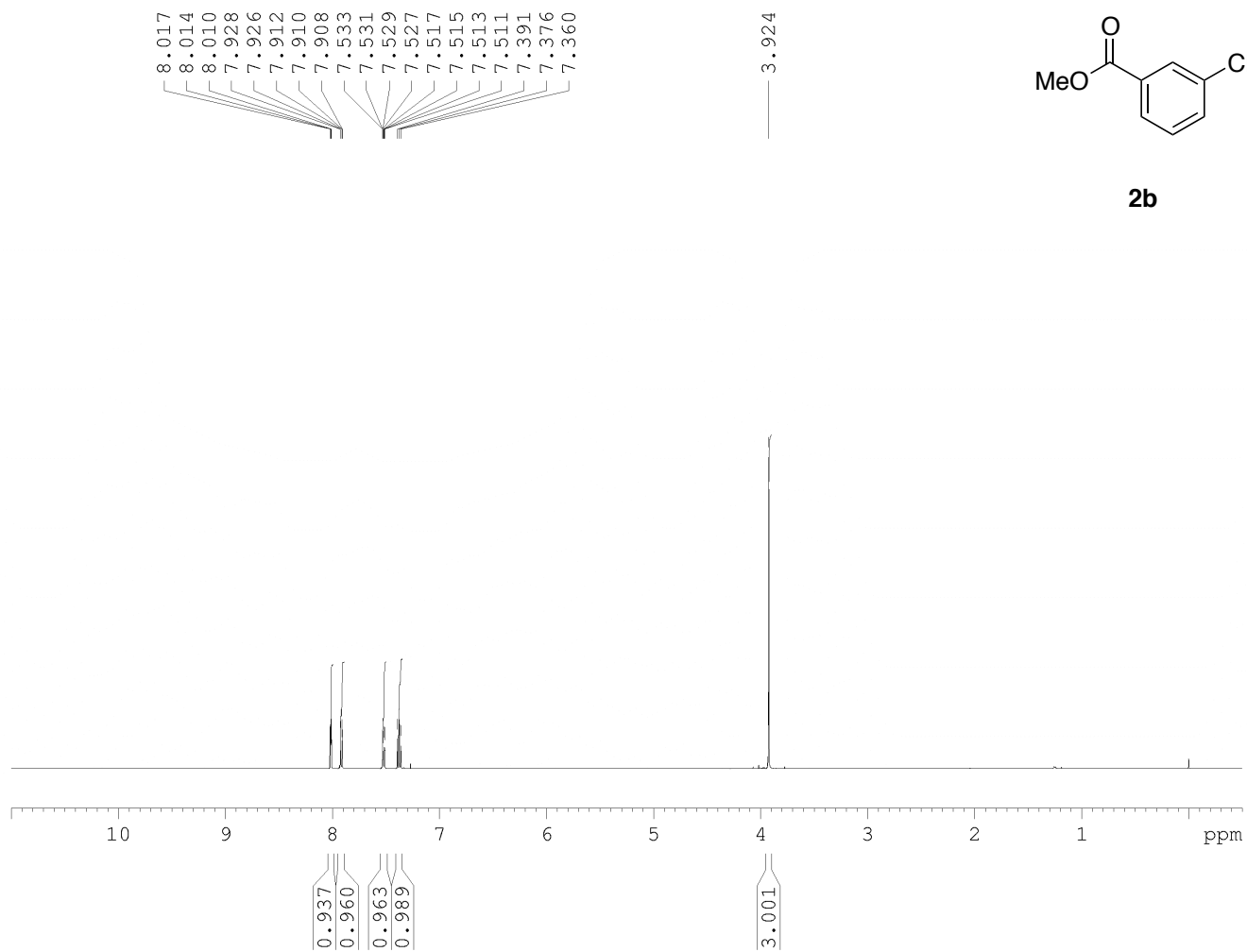


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-(allyloxy)-2-chlorobenzene (1j)



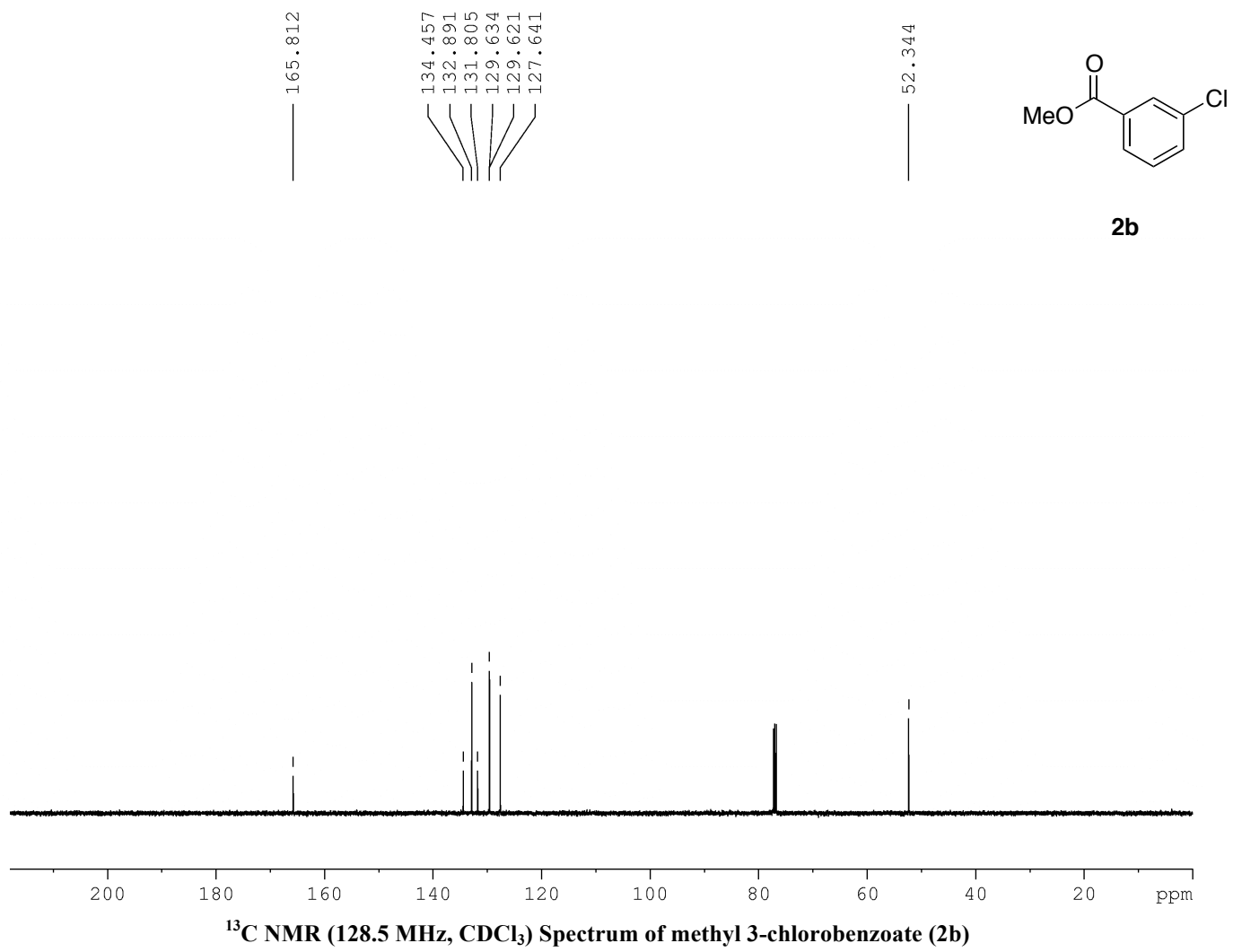
¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 4-chlorobenzoate (2a)

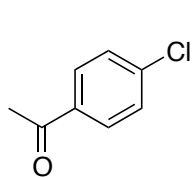




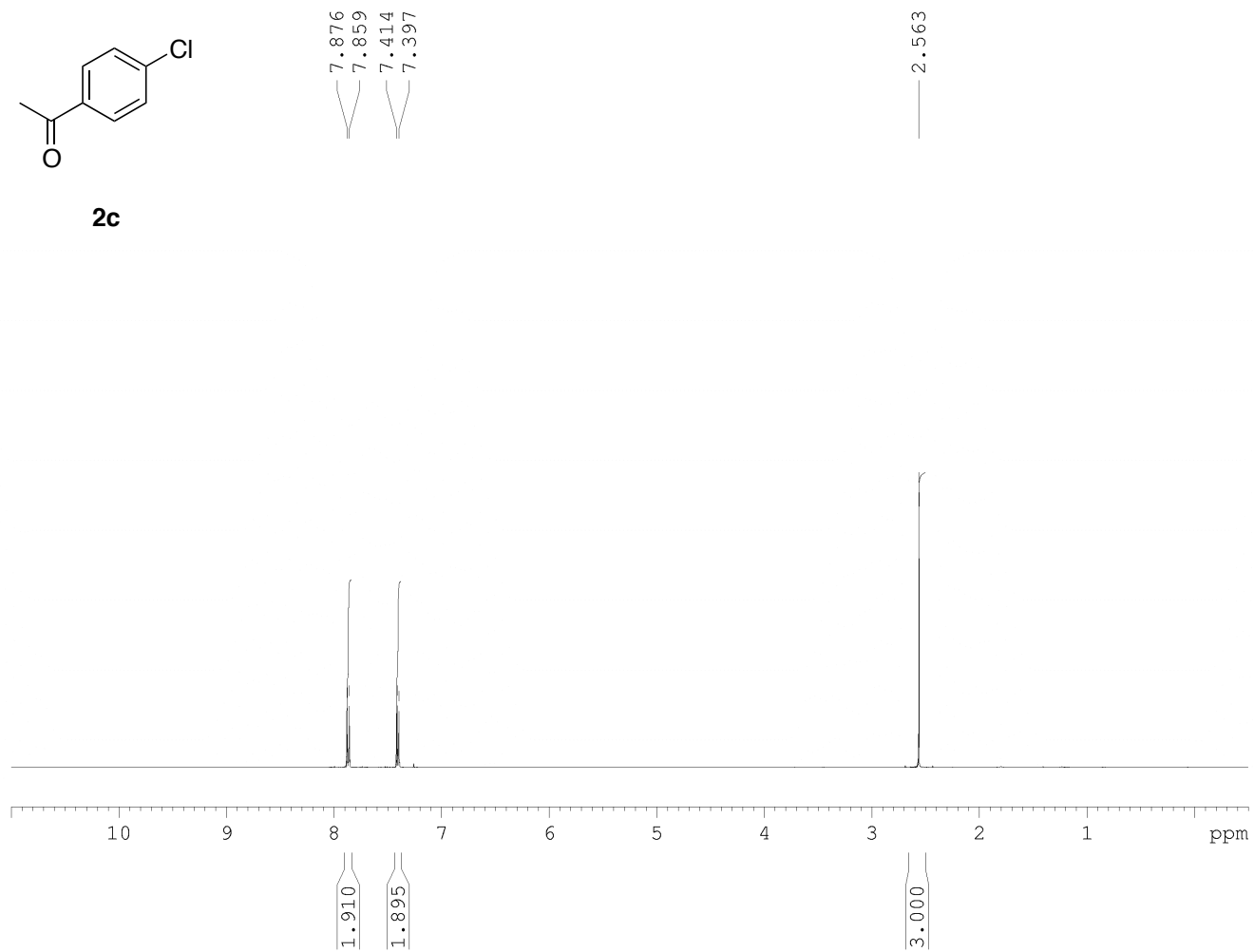
2b

^1H NMR (500 MHz, CDCl_3) Spectrum of methyl 3-chlorobenzoate (2b)

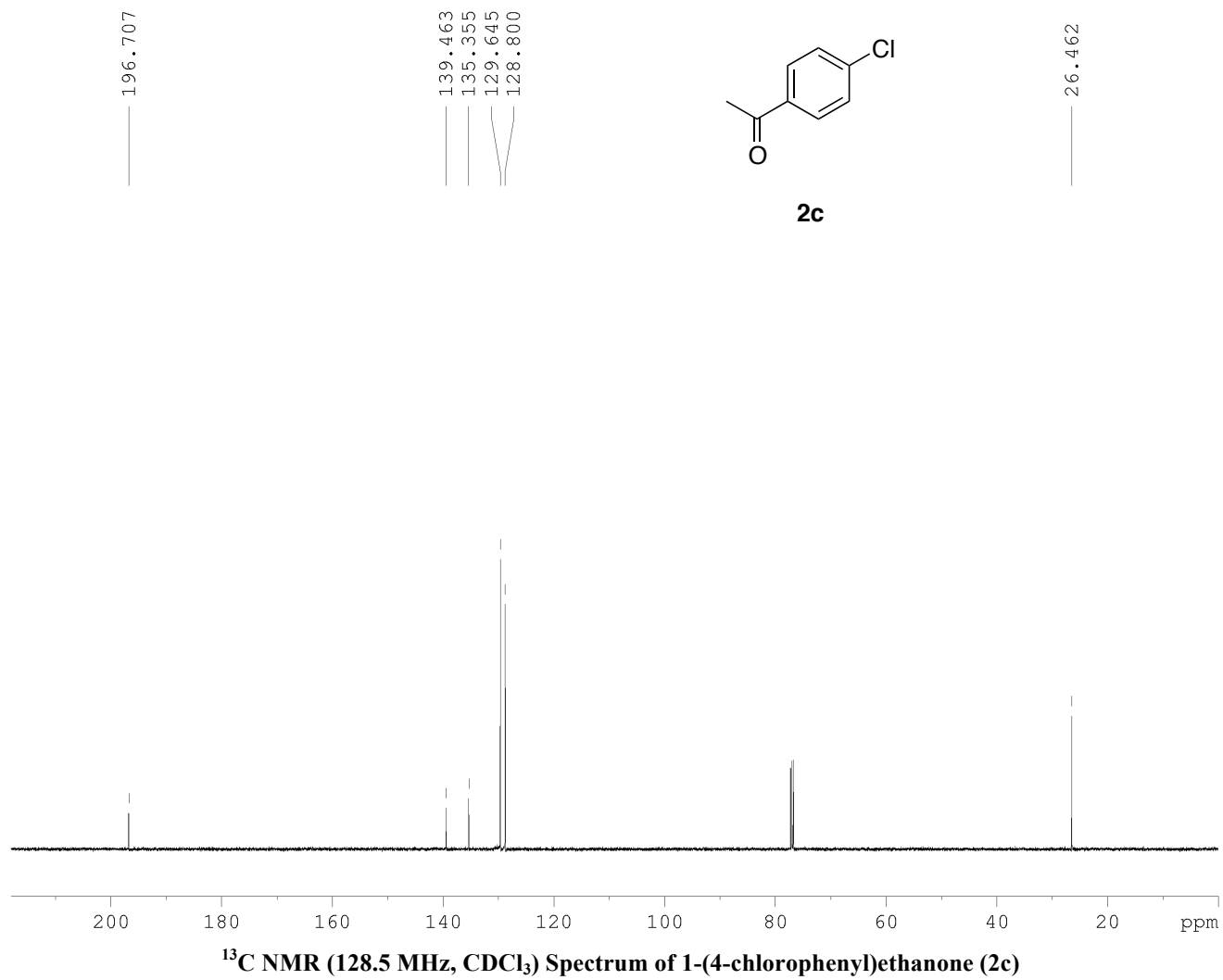


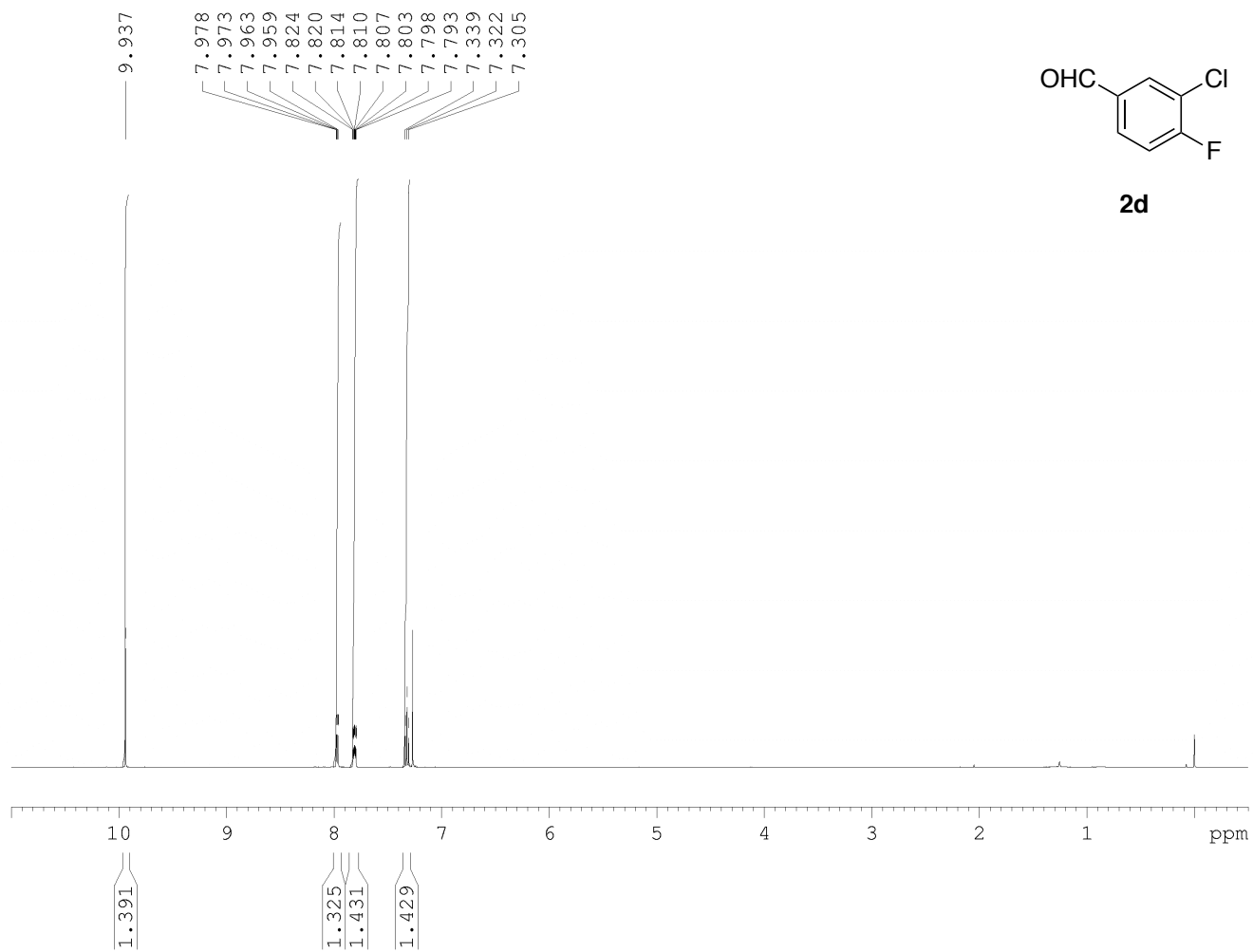


2c

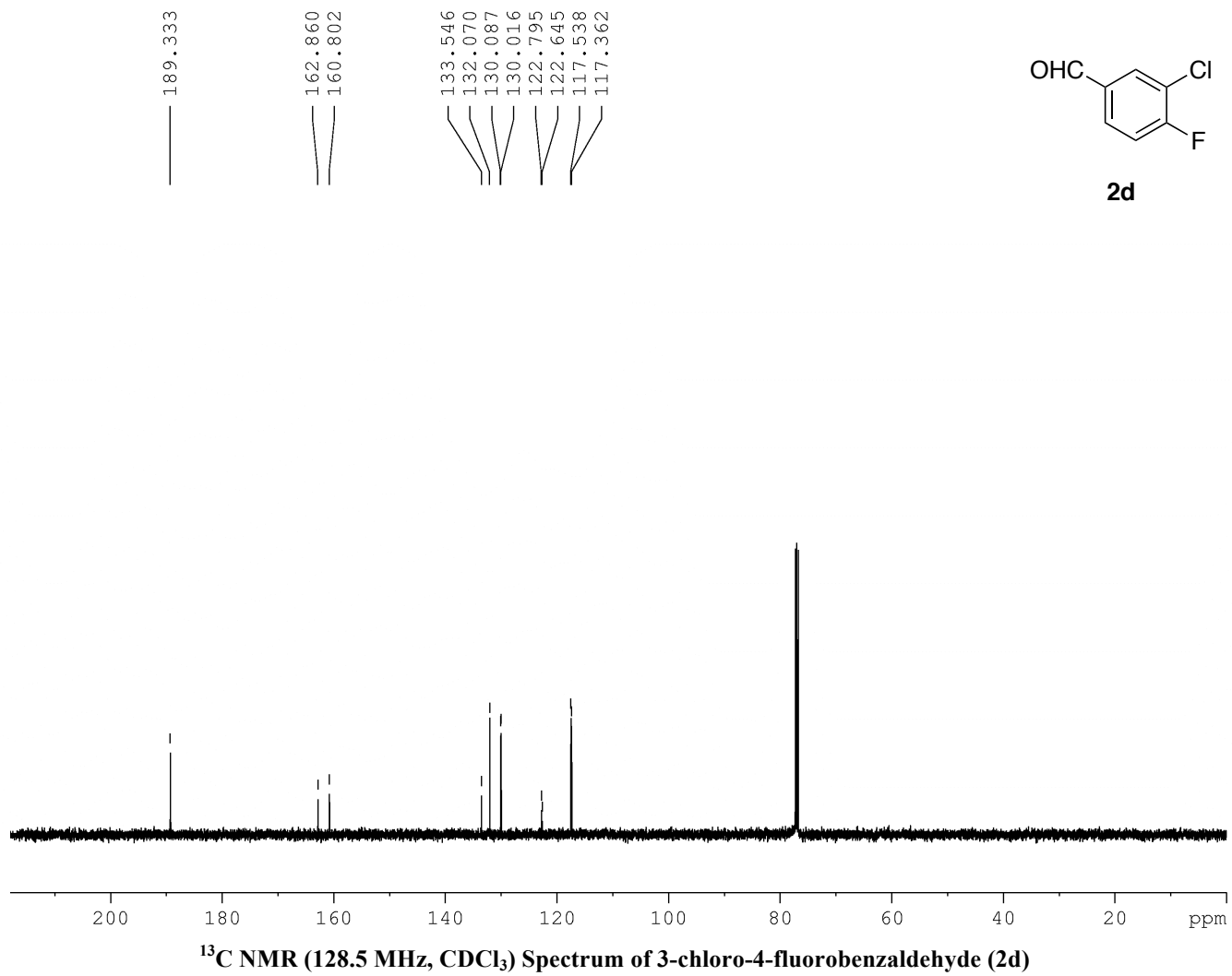


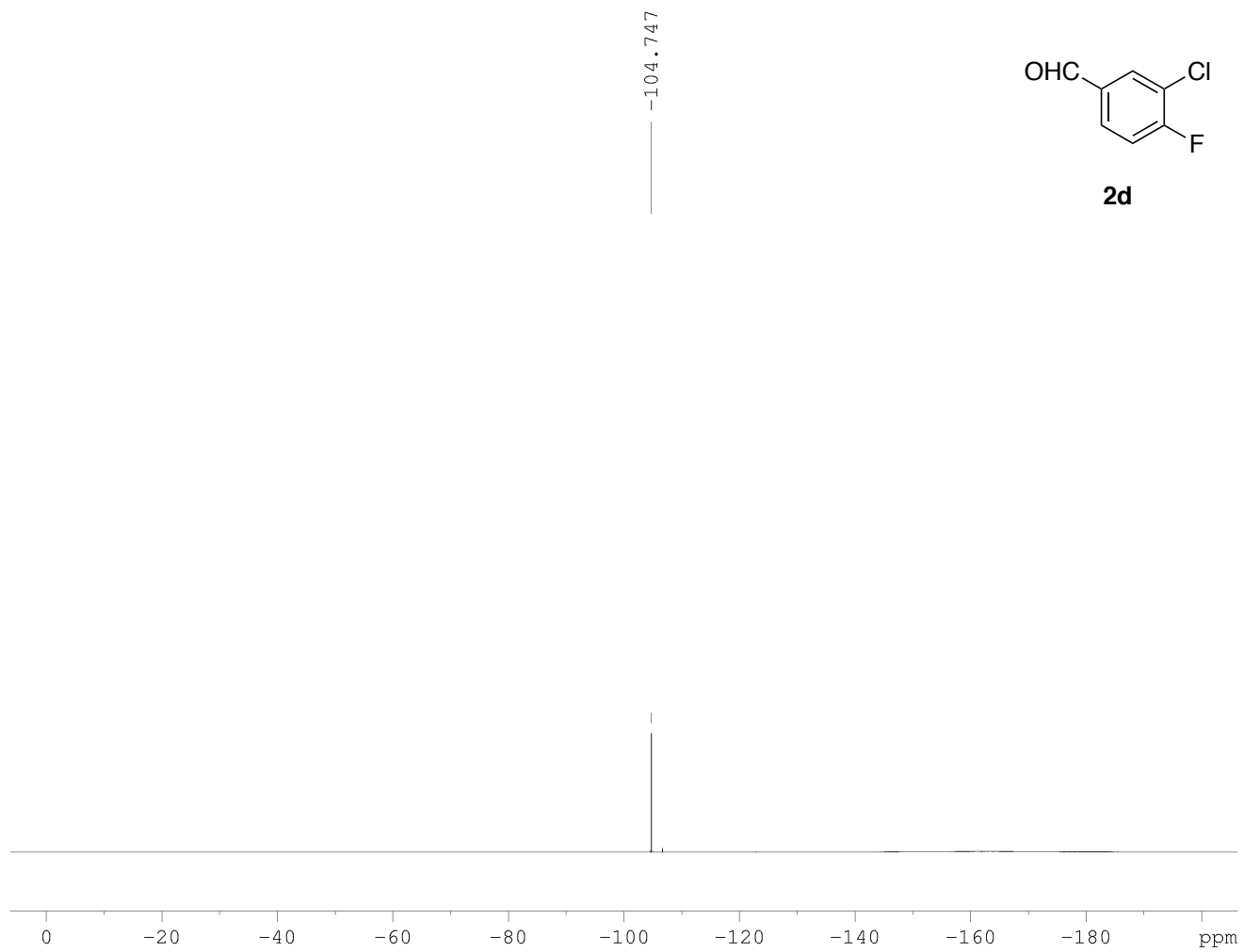
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(4-chlorophenyl)ethanone (2c)



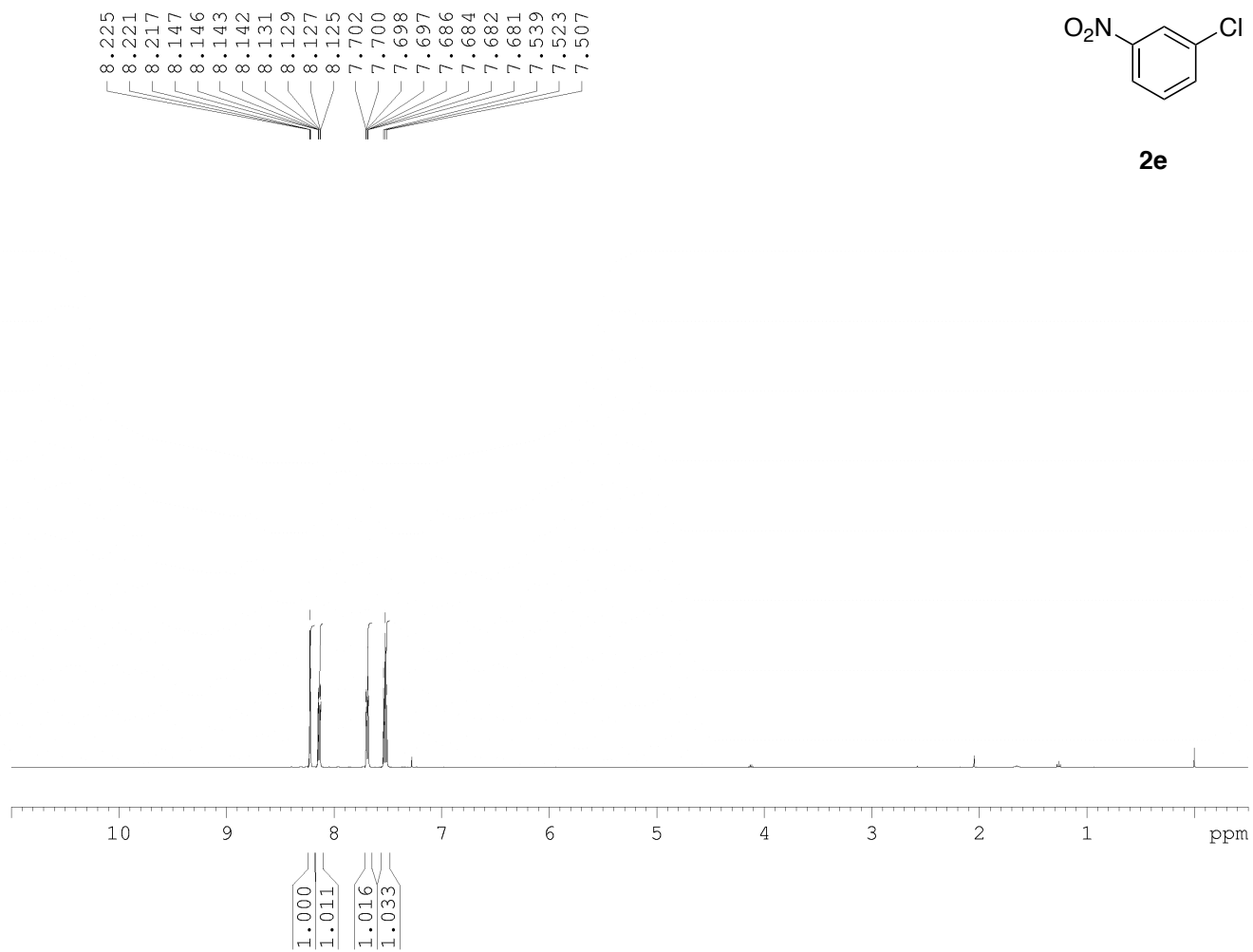


¹H NMR (500 MHz, CDCl₃) Spectrum of 3-chloro-4-fluorobenzaldehyde (2d)

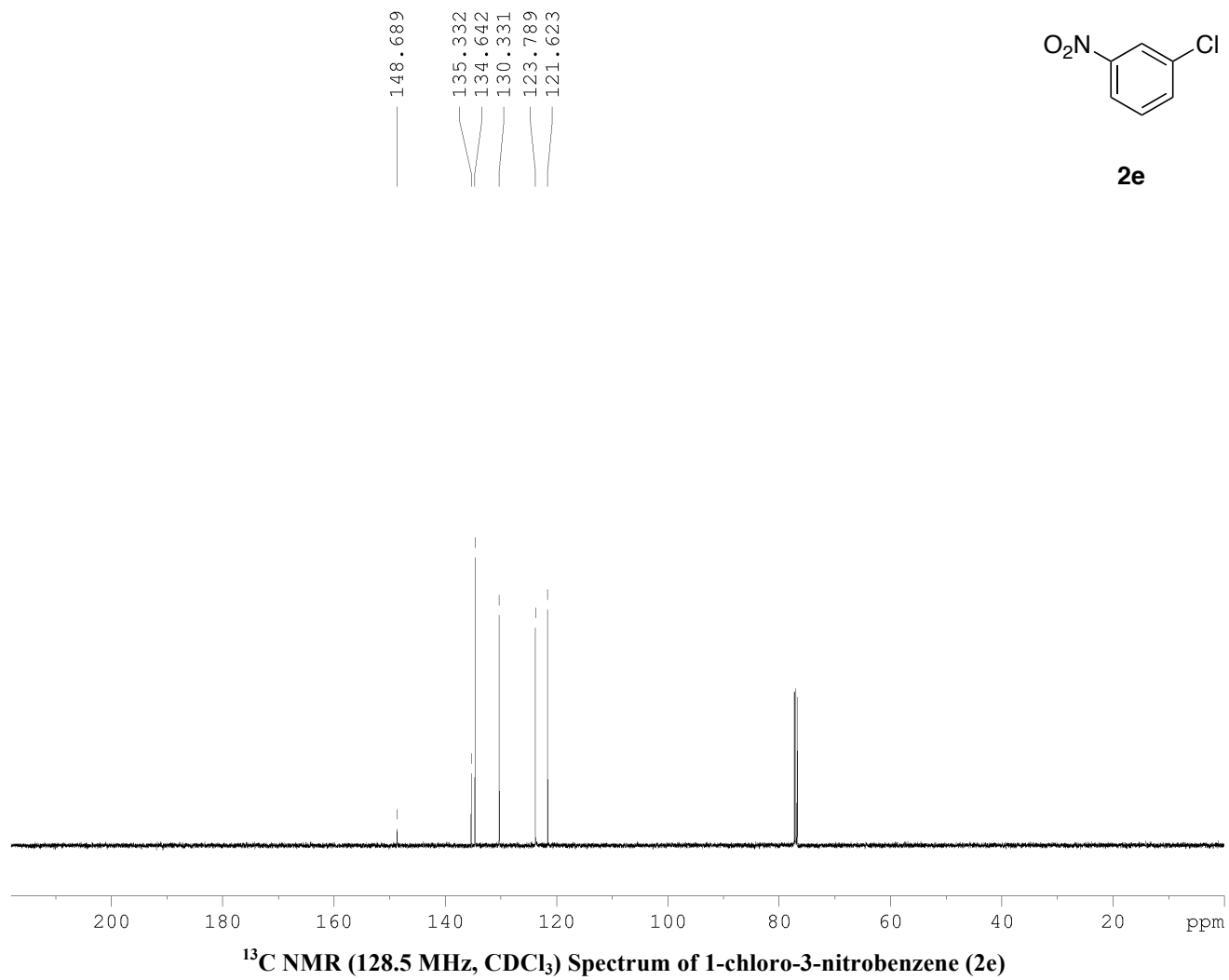


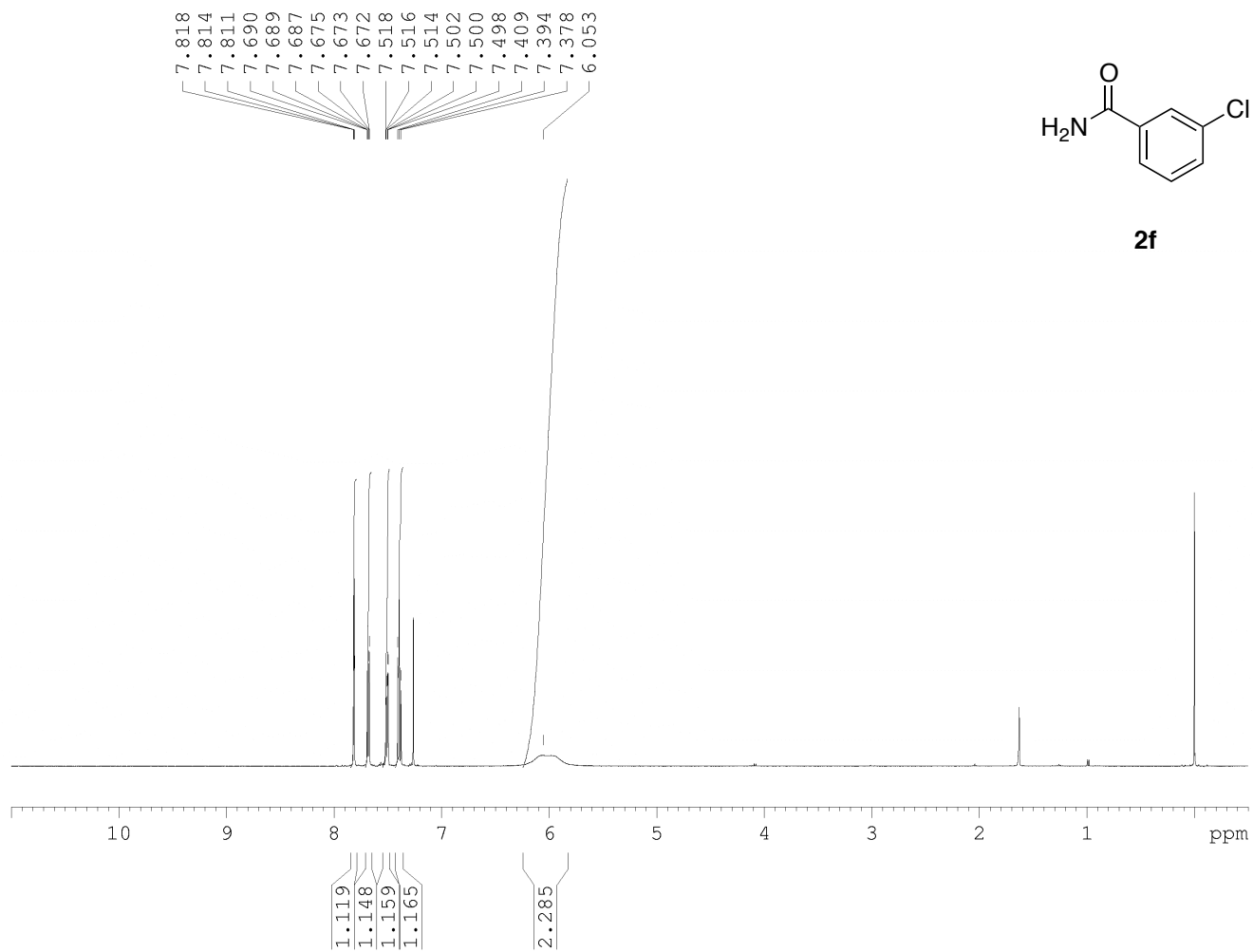


^{19}F NMR (470.8 MHz, CDCl_3) Spectrum of 3-chloro-4-fluorobenzaldehyde (2d)

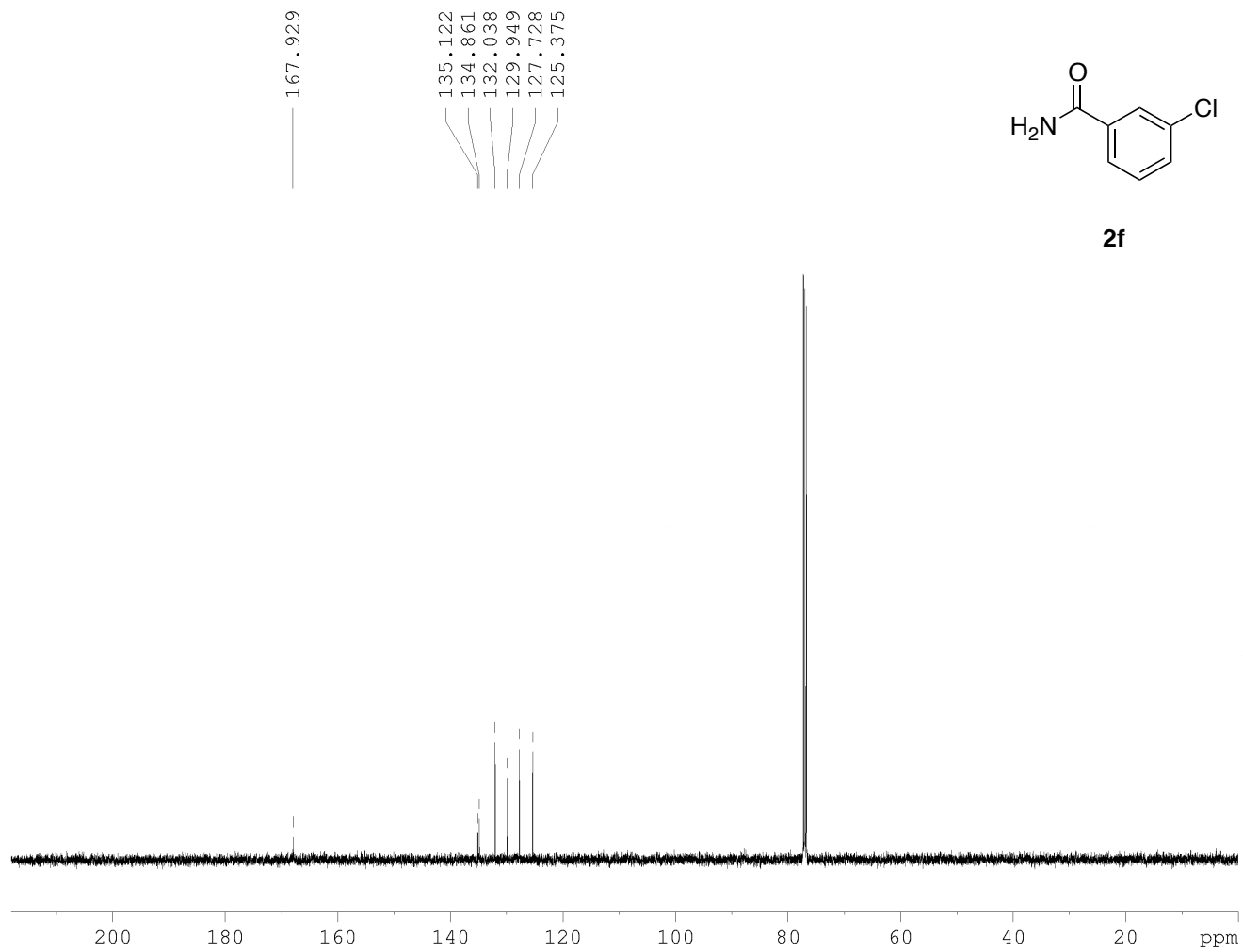


¹H NMR (500 MHz, CDCl₃) Spectrum of 1-chloro-3-nitrobenzene (2e)

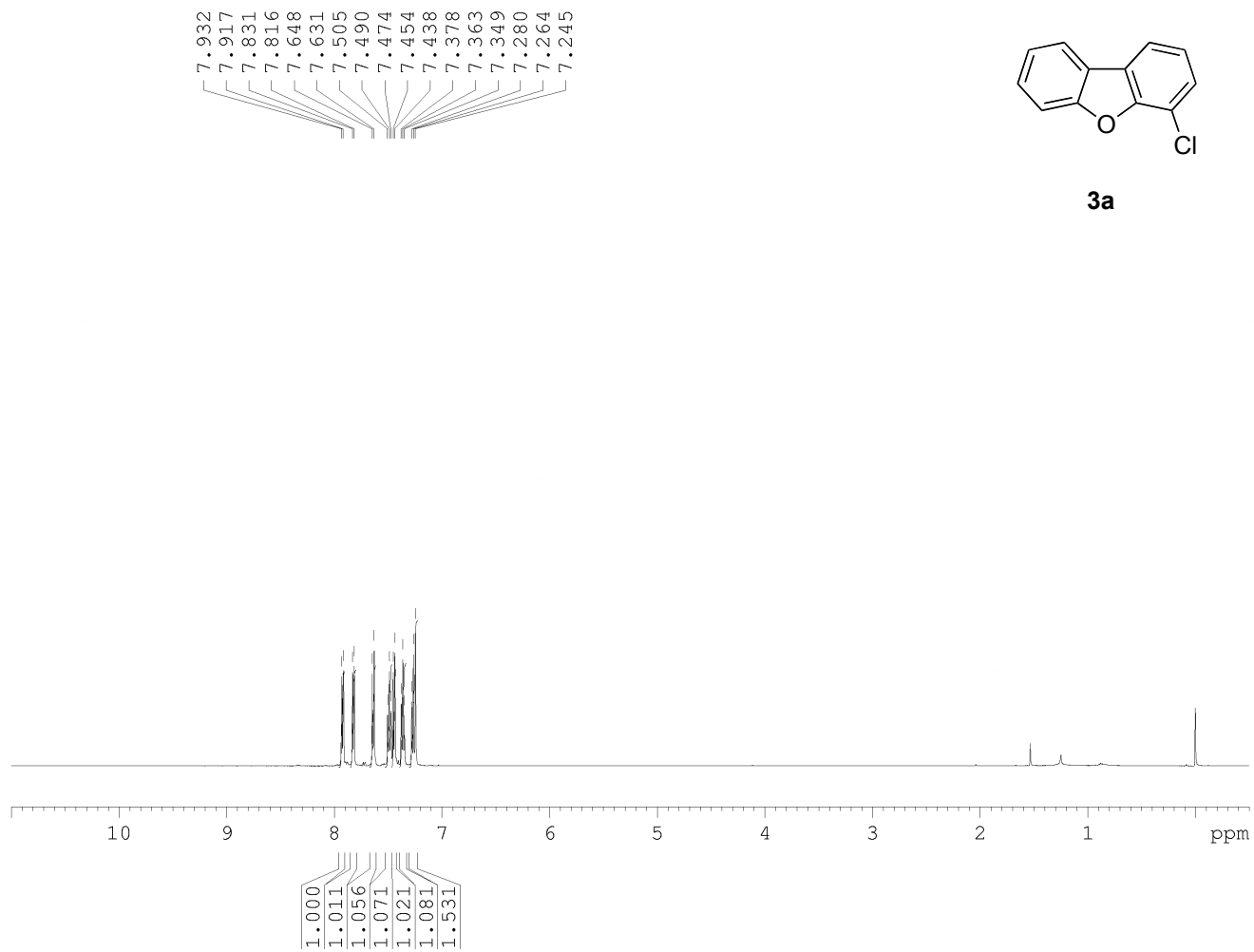




¹H NMR (500 MHz, CDCl₃) Spectrum of 3-chlorobenzamide (2f)

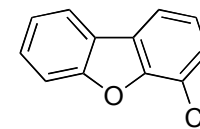


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 3-chlorobenzamide (2f)

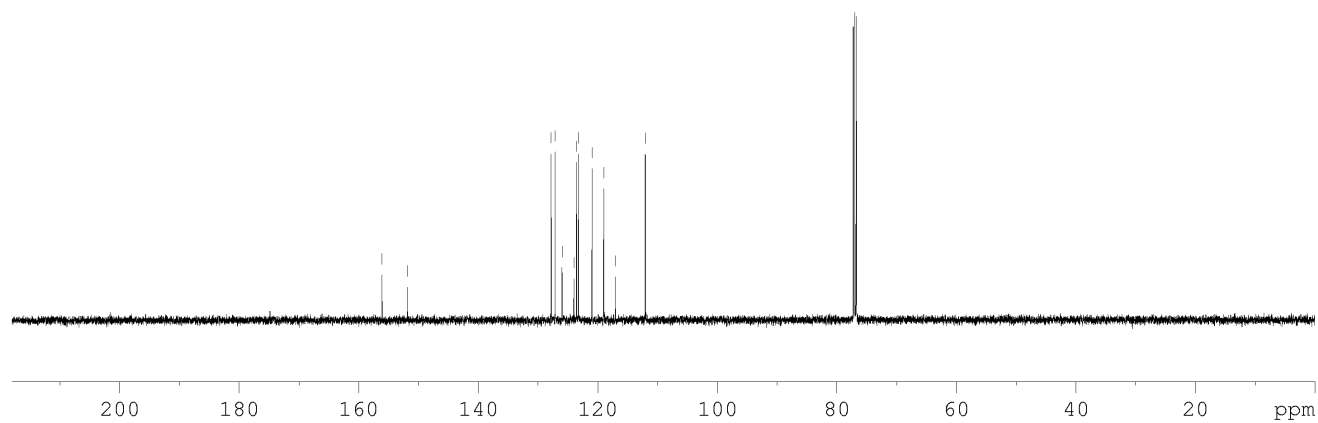


¹H NMR (500 MHz, CDCl₃) Spectrum of 4-chlorodibenzo[*b,d*]furan (3a)

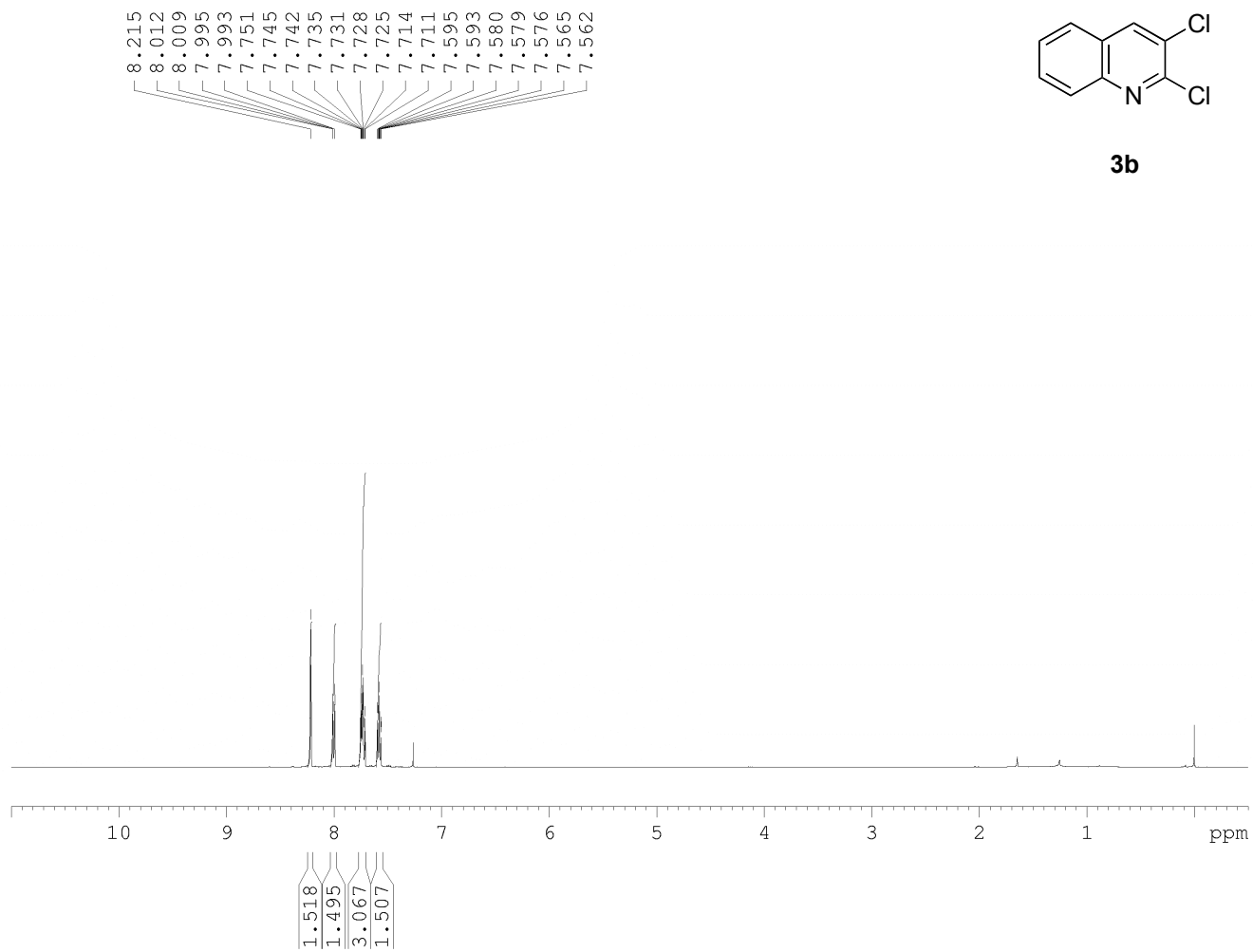
156.133
151.888
127.821
127.136
125.966
124.002
123.556
123.245
120.971
119.003
117.101
112.057



3a

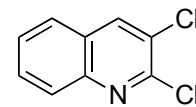


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 4-chlorodibenzo[*b,d*]furan (3a)

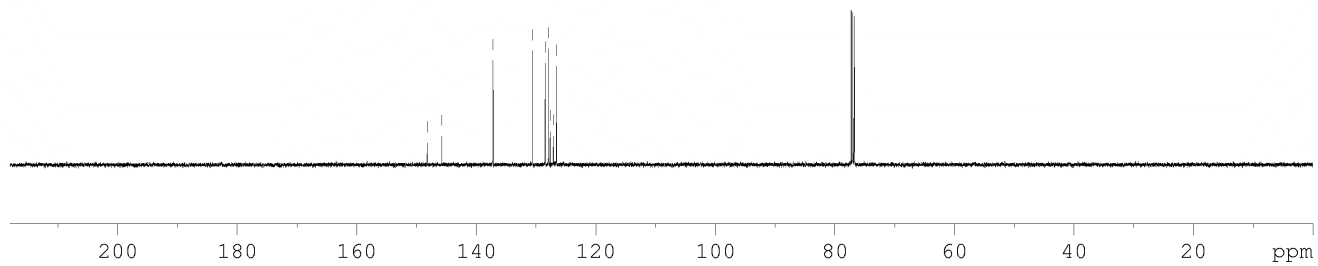


¹H NMR (500 MHz, CDCl₃) Spectrum of 2,3-dichloroquinoline (3b)

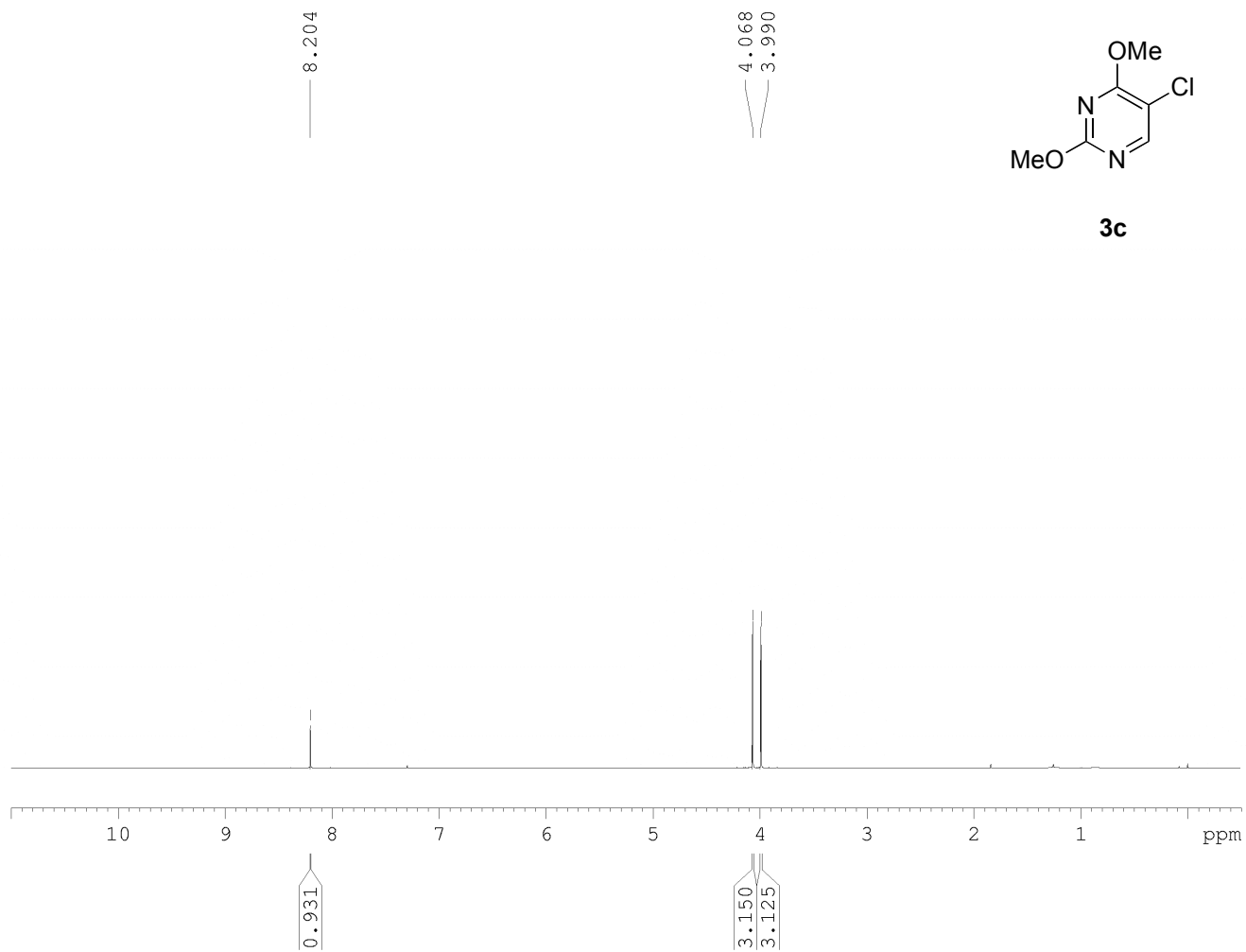
148.199
145.781
137.185
130.602
128.466
127.881
127.633
127.094
126.612

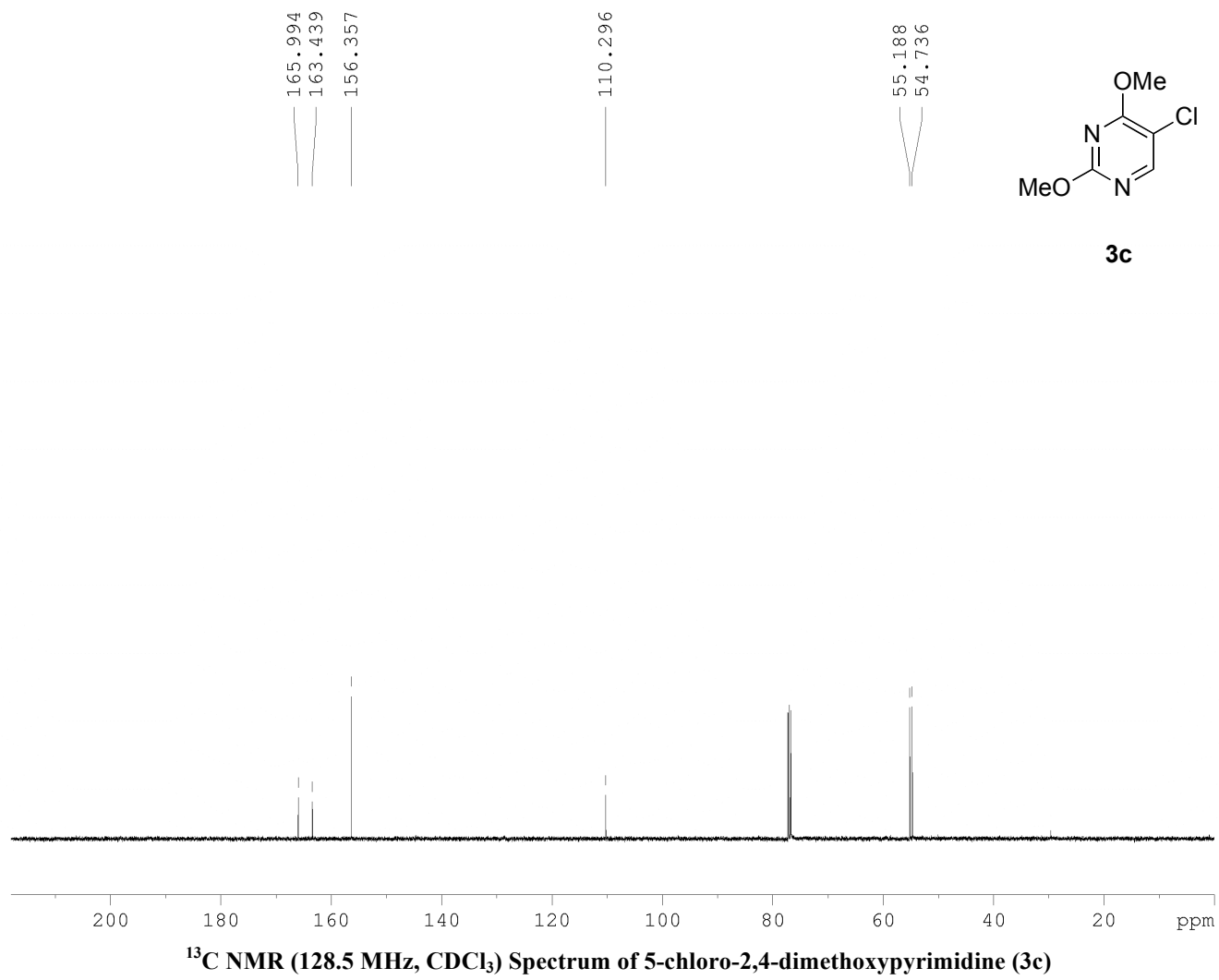


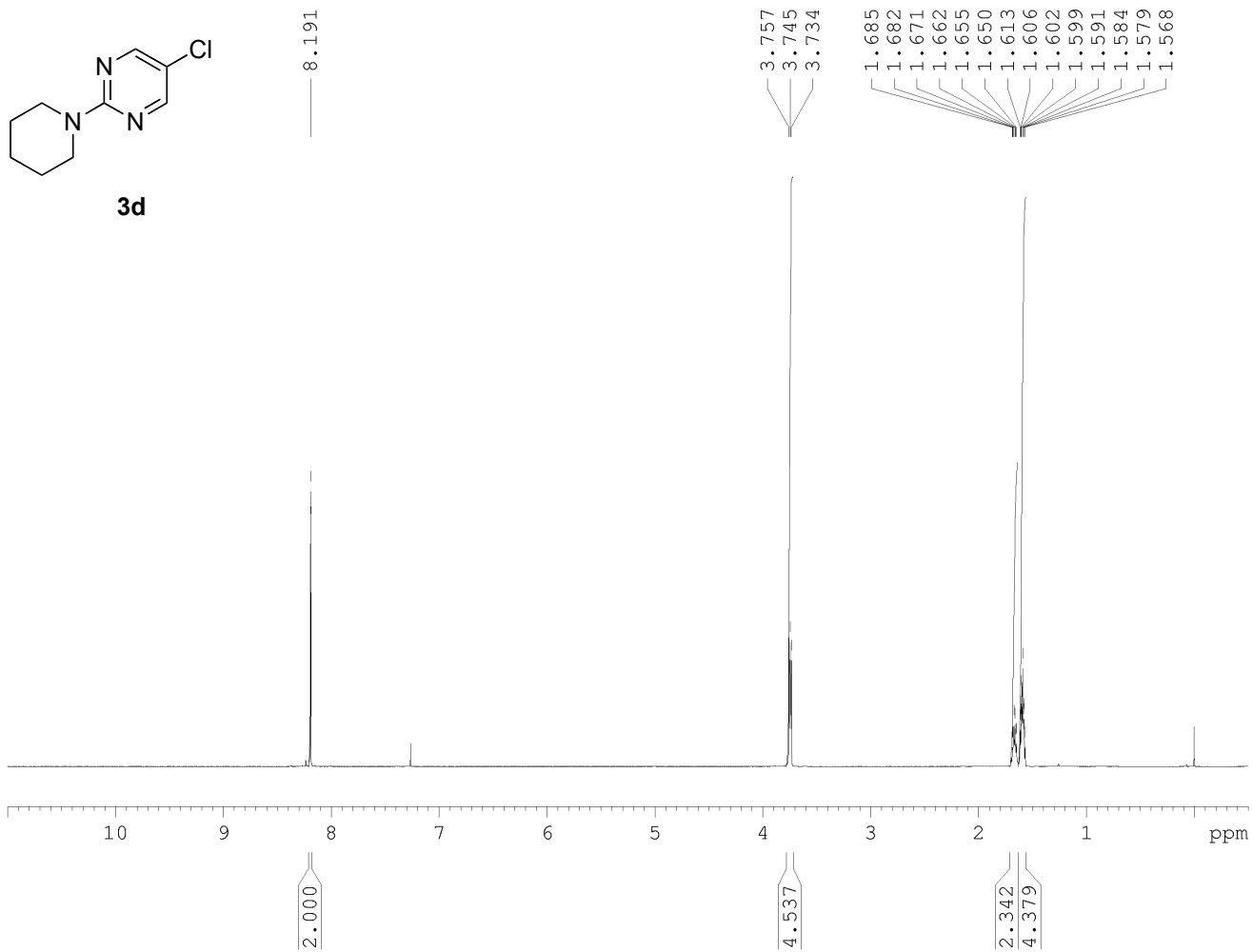
3b

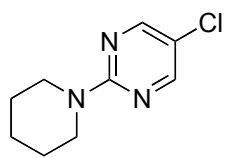


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 2,3-dichloroquinoline (3b)









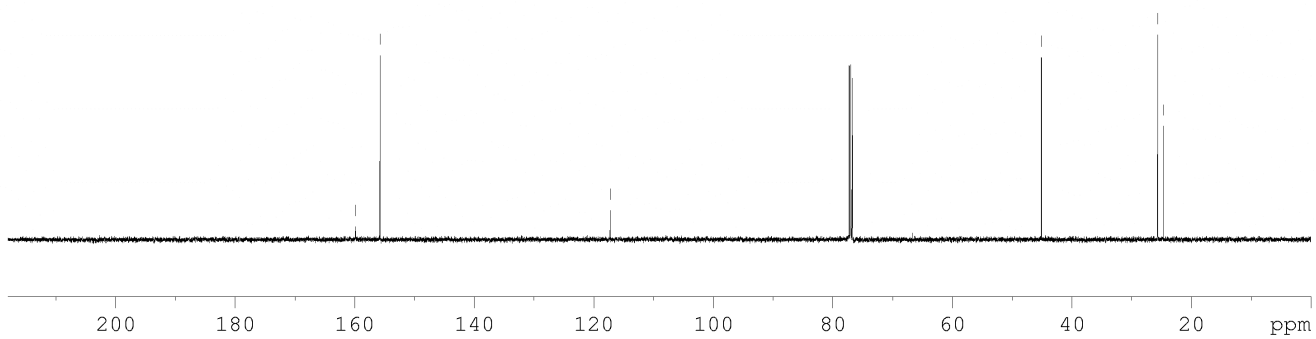
3d

159.892
155.758

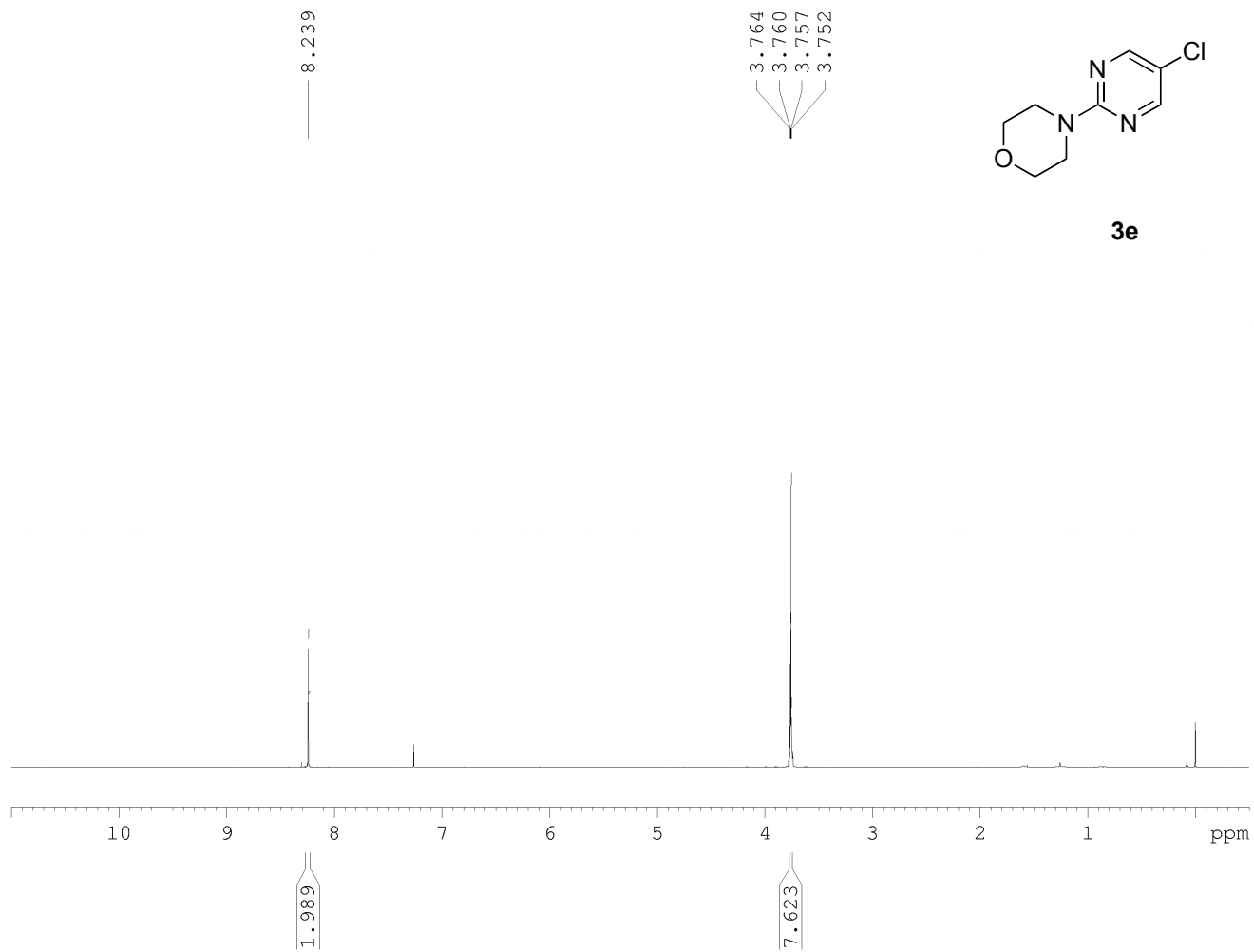
117.254

45.090

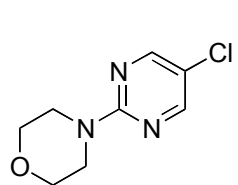
25.629
24.713



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 5-chloro-2-(piperidin-1-yl)pyrimidine (3d)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(5-chloropyrimidin-2-yl)morpholine (3e)



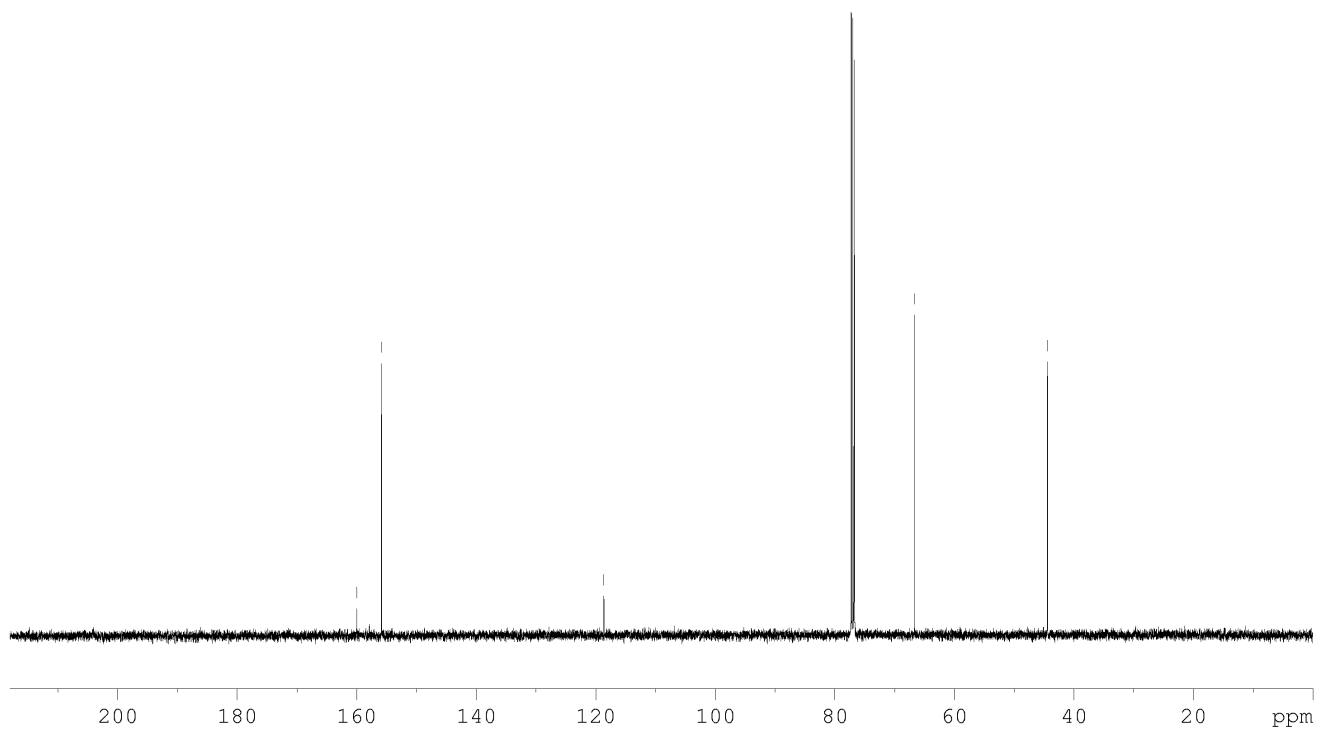
3e

159.967
155.867

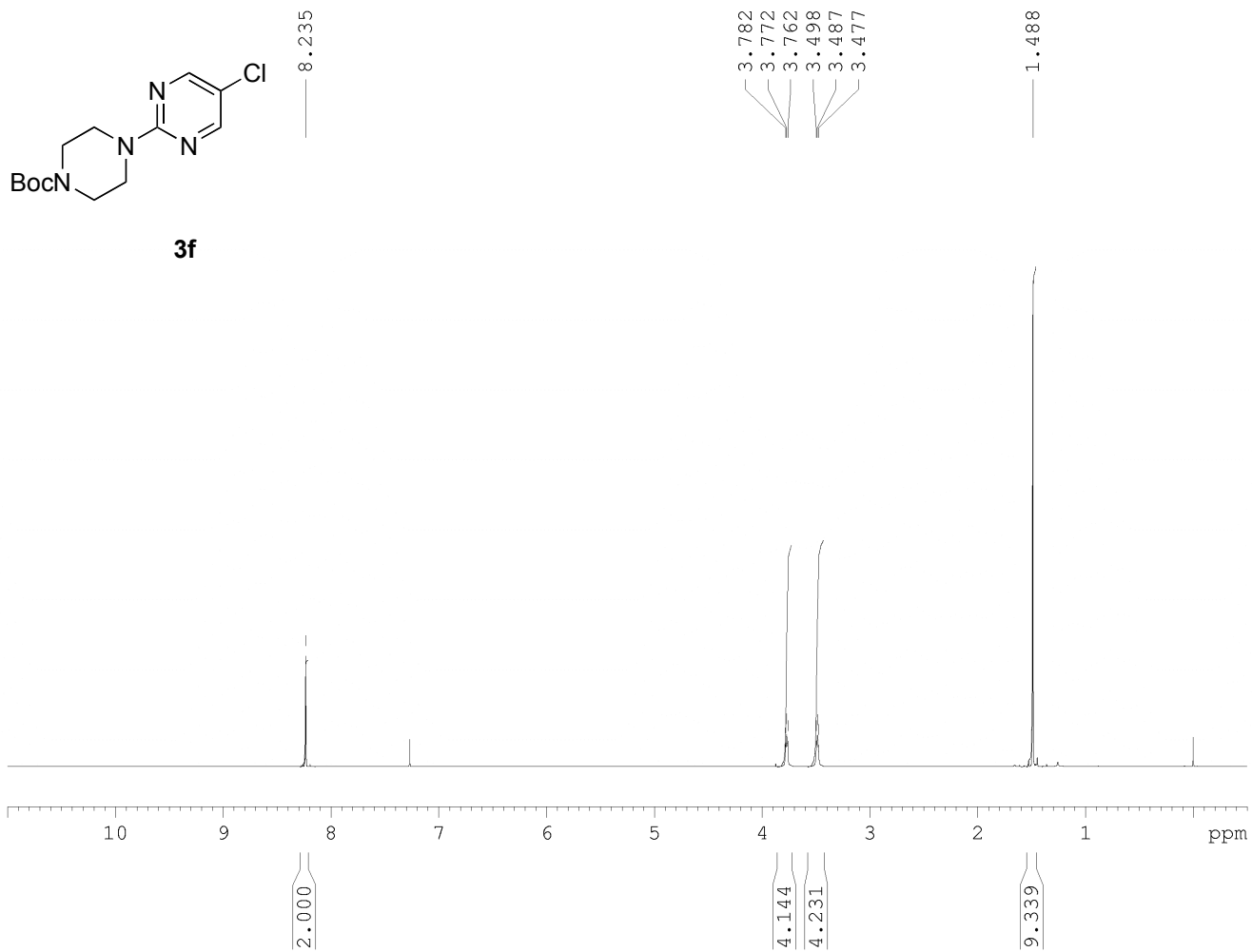
118.652

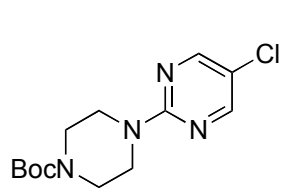
66.689

44.442



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 4-(5-chloropyrimidin-2-yl)morpholine (3e)





3f

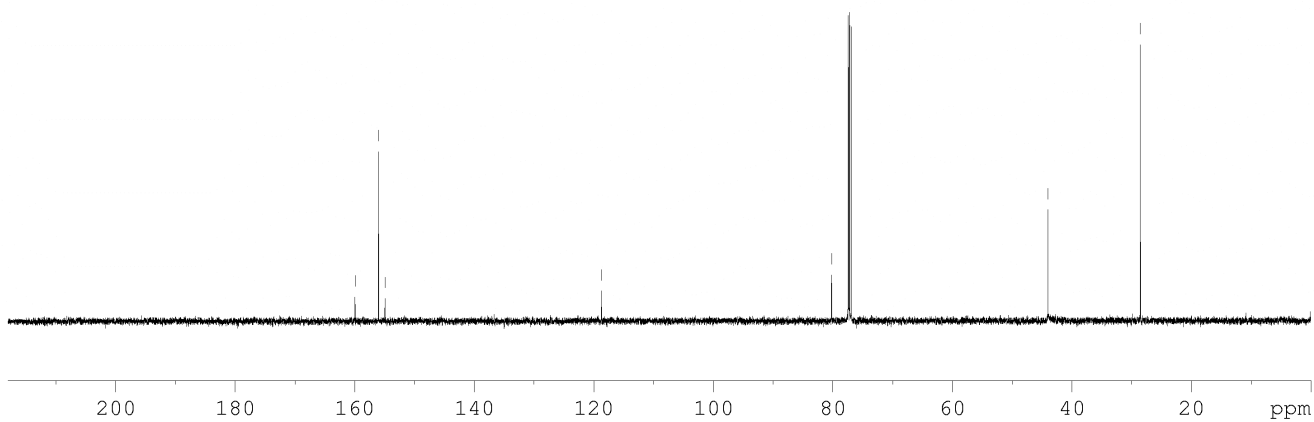
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154.930

118.684

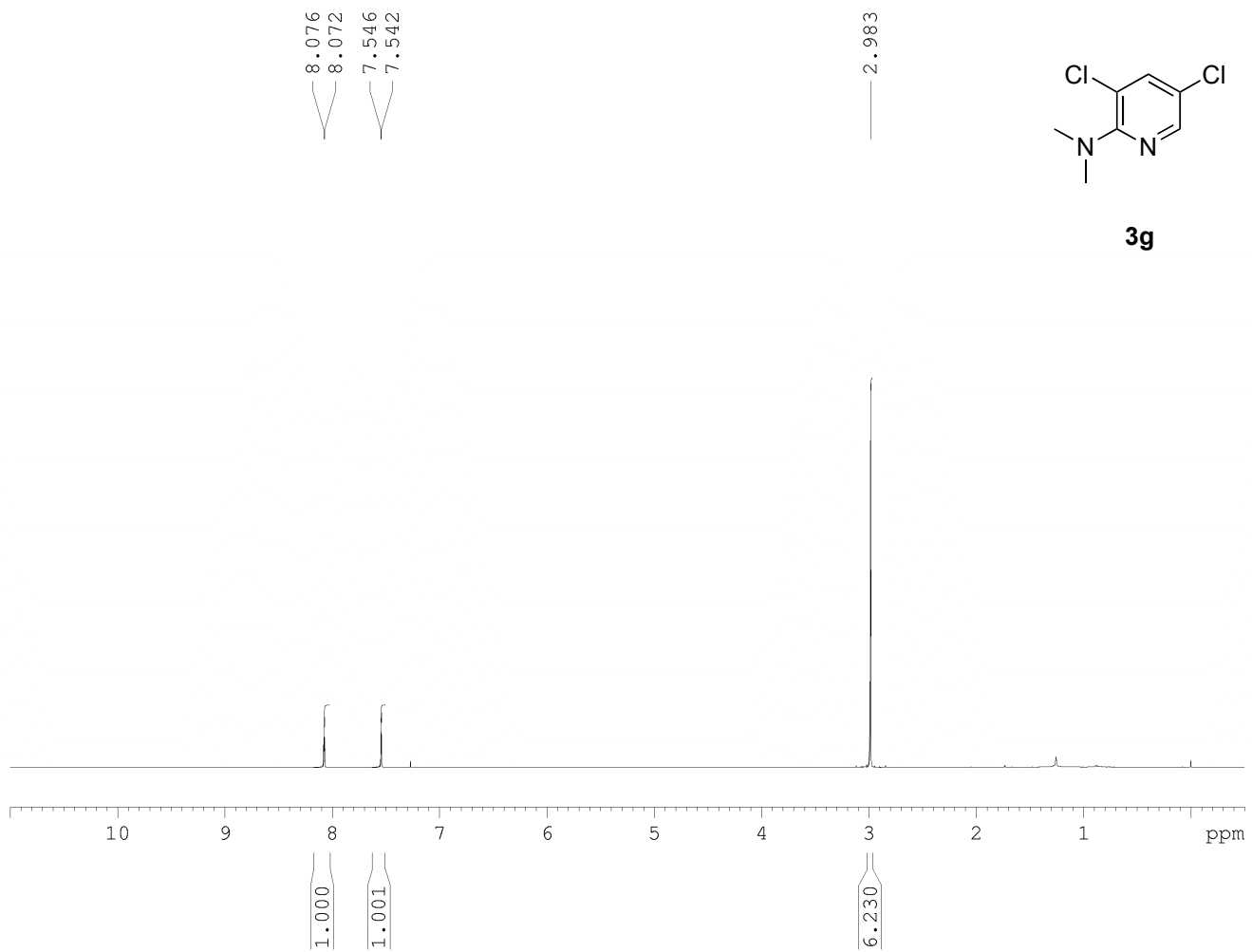
80.206

43.991

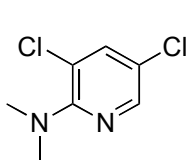
28.567



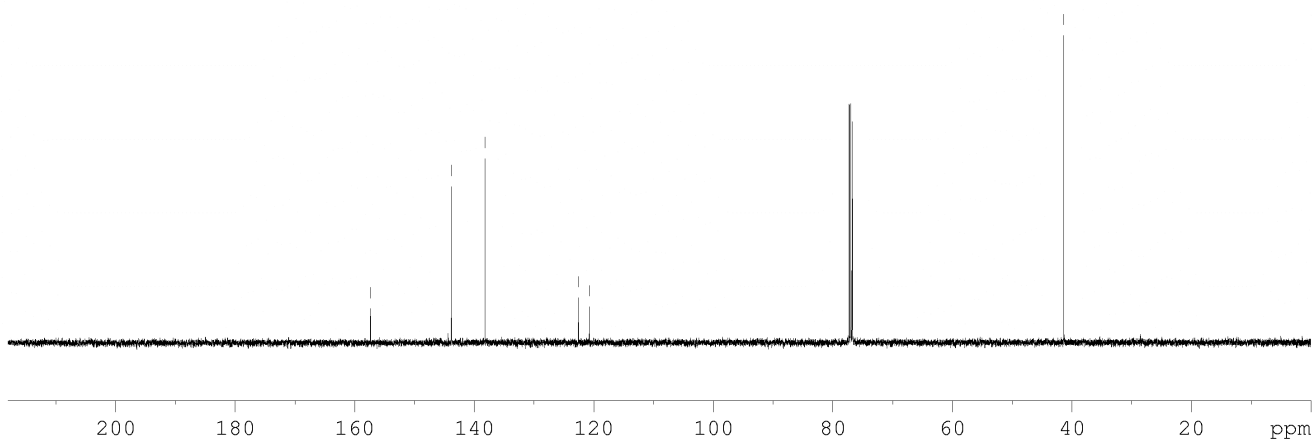
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of *tert*-butyl 4-(5-chloropyrimidin-2-yl)piperazine-1-carboxylate (**3f**)



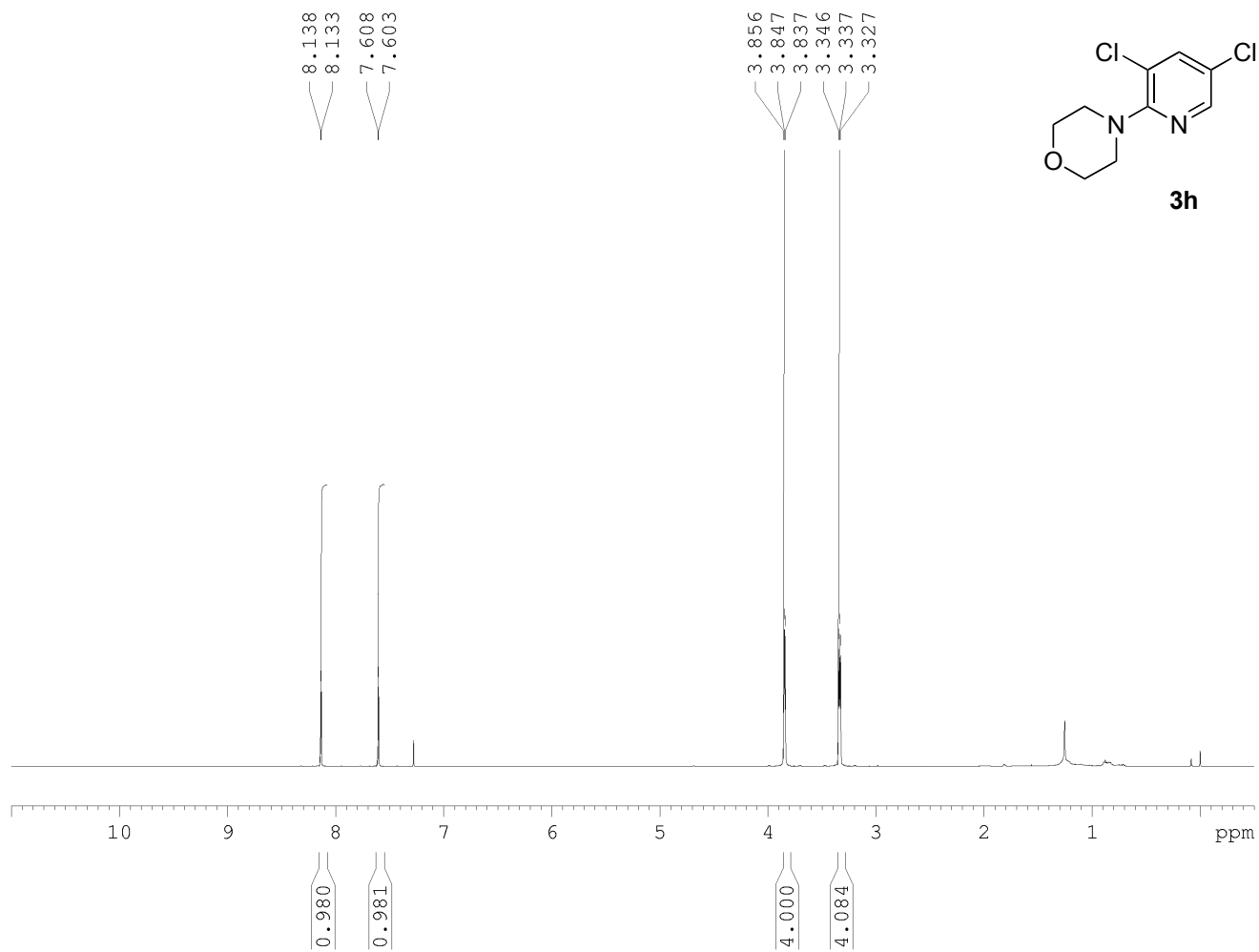
¹H NMR (500 MHz, CDCl₃) Spectrum of 3,5-dichloro-*N,N*-dimethylpyridin-2-amine (3g)



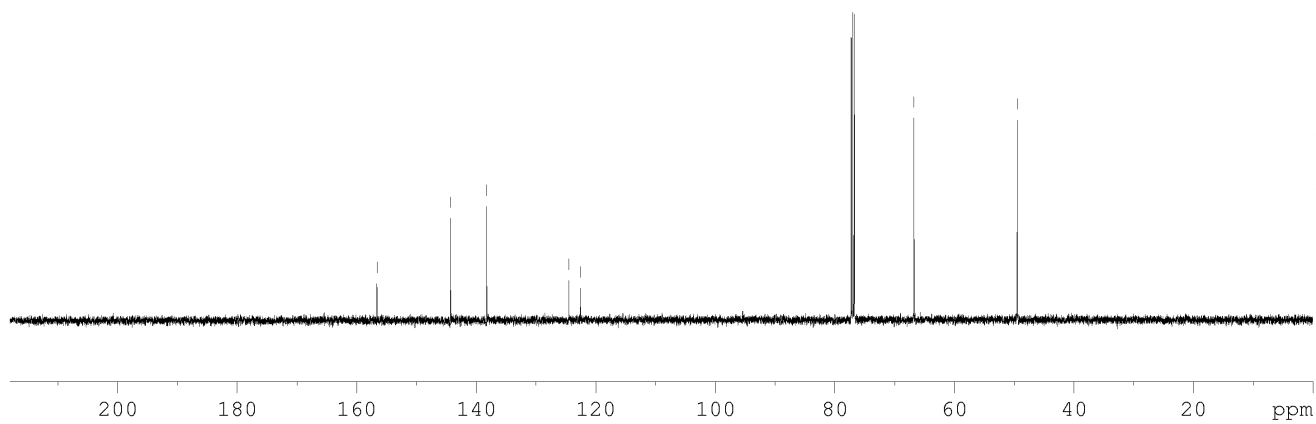
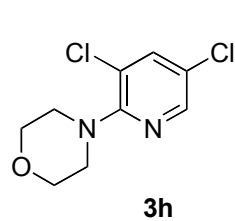
3g



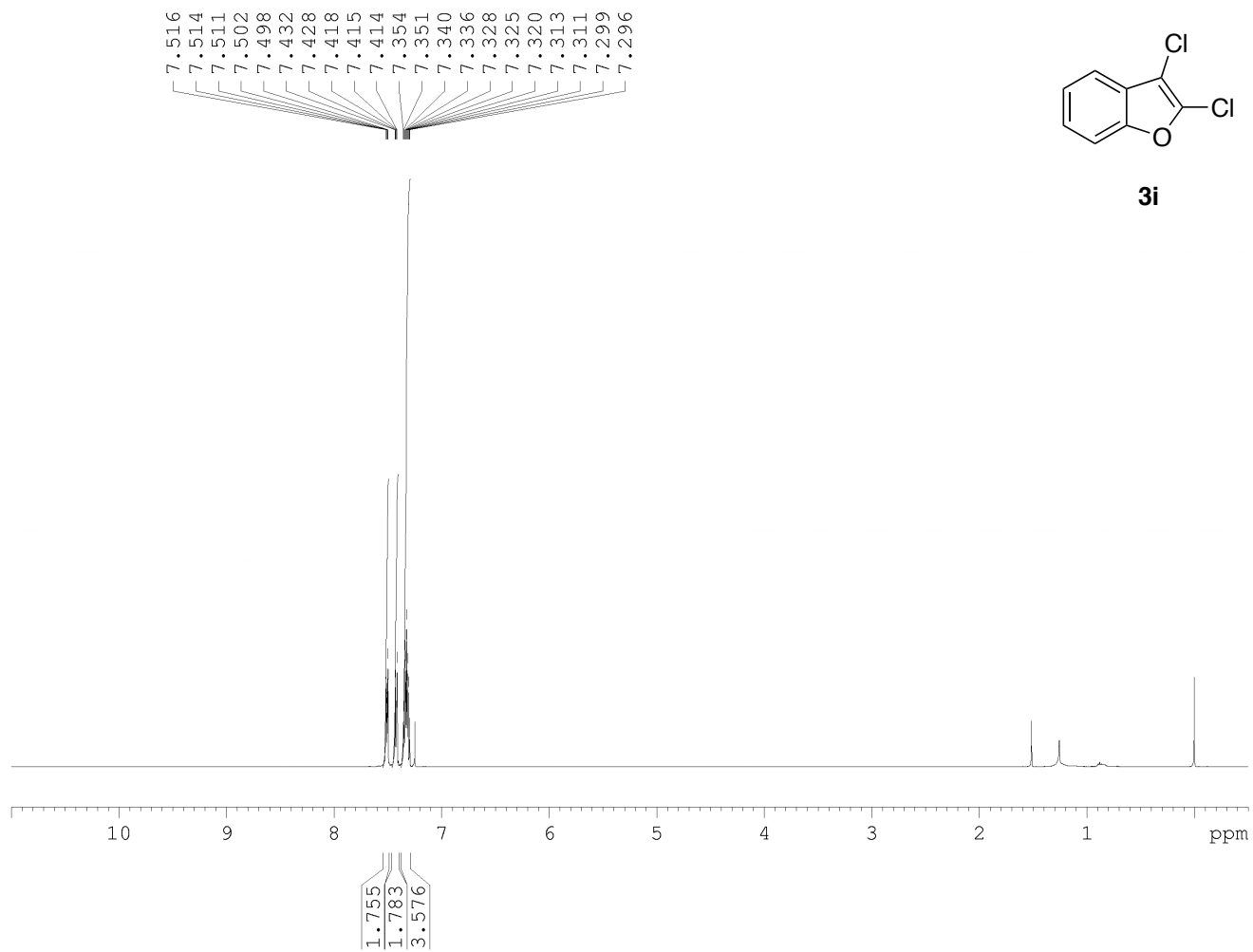
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 3,5-dichloro-*N,N*-dimethylpyridin-2-amine (3g)

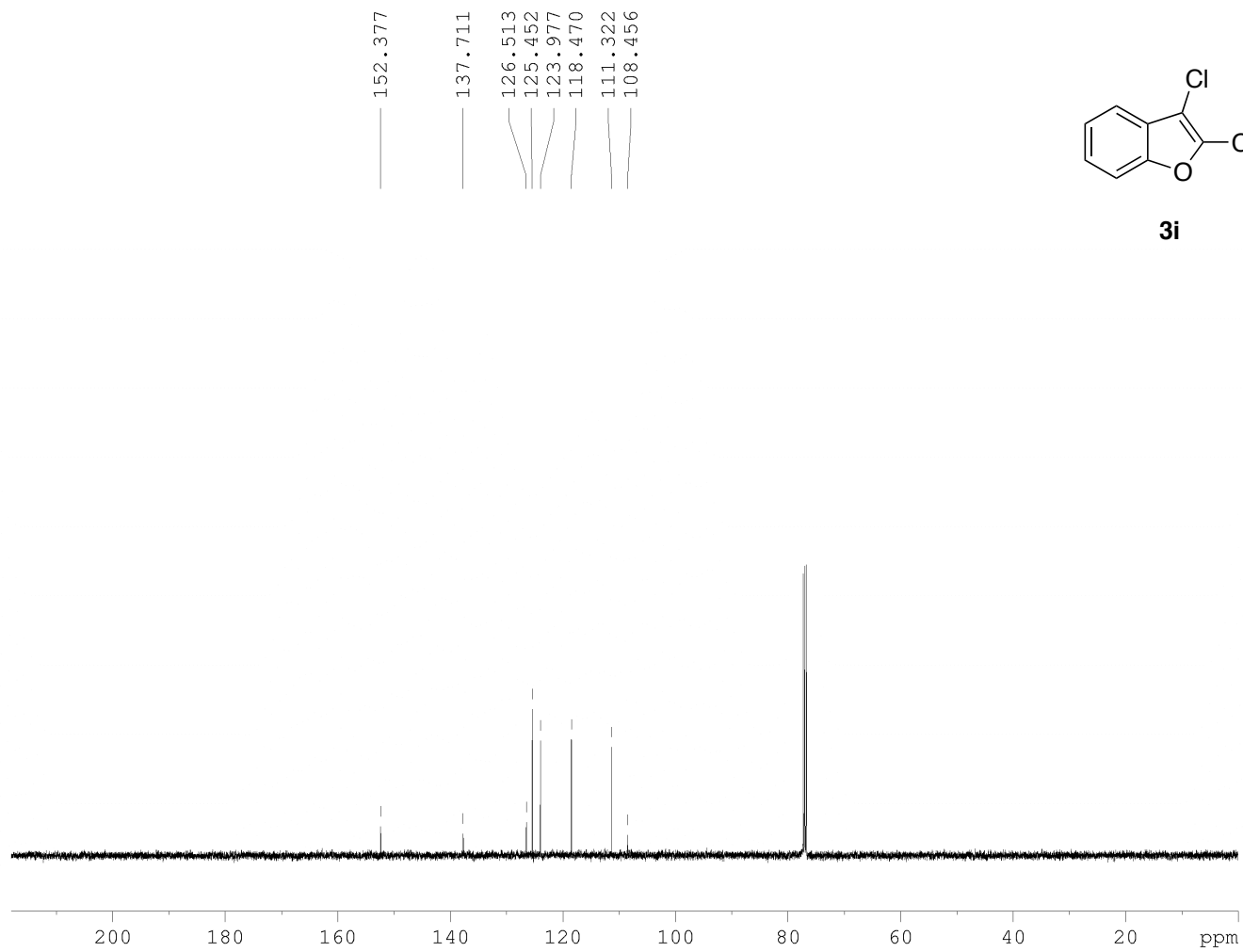


¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(3,5-dichloropyridin-2-yl)morpholine (3h)



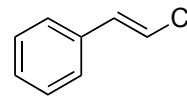
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 4-(3,5-dichloropyridin-2-yl)morpholine (3h)



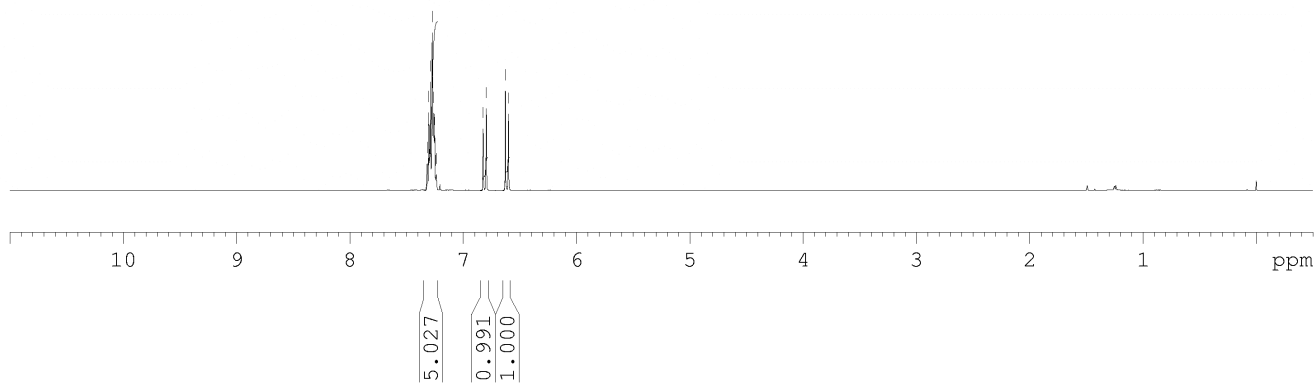


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 2,3-dichlorobenzofuran (3i)

7.319
7.304
7.290
7.274
7.269
7.260
7.253
7.247
7.239
6.824
6.797
6.628
6.601

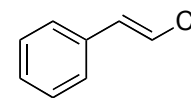


4a

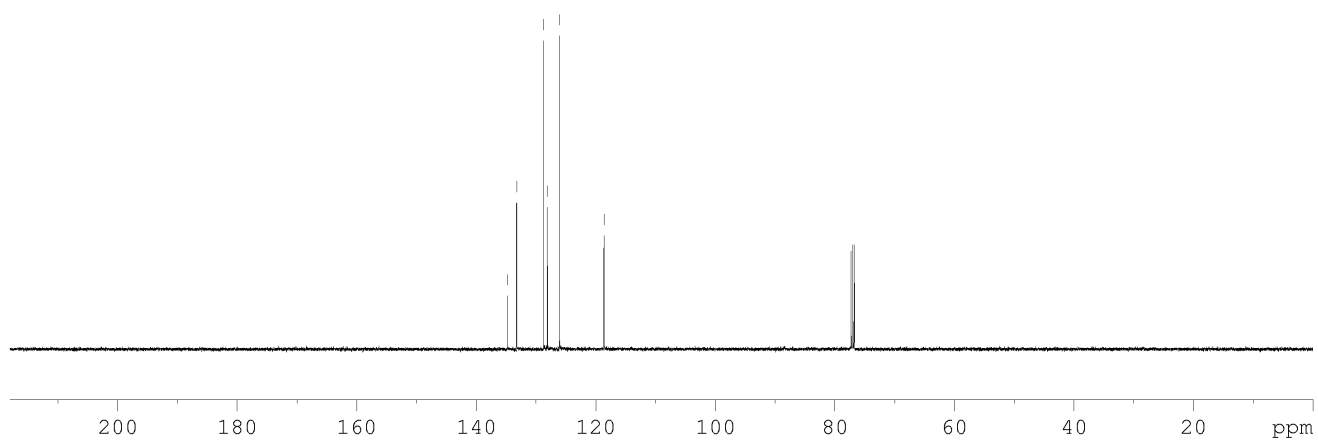


¹H NMR (500 MHz, CDCl₃) Spectrum of (*E*)-(2-chlorovinyl)benzene (4a)

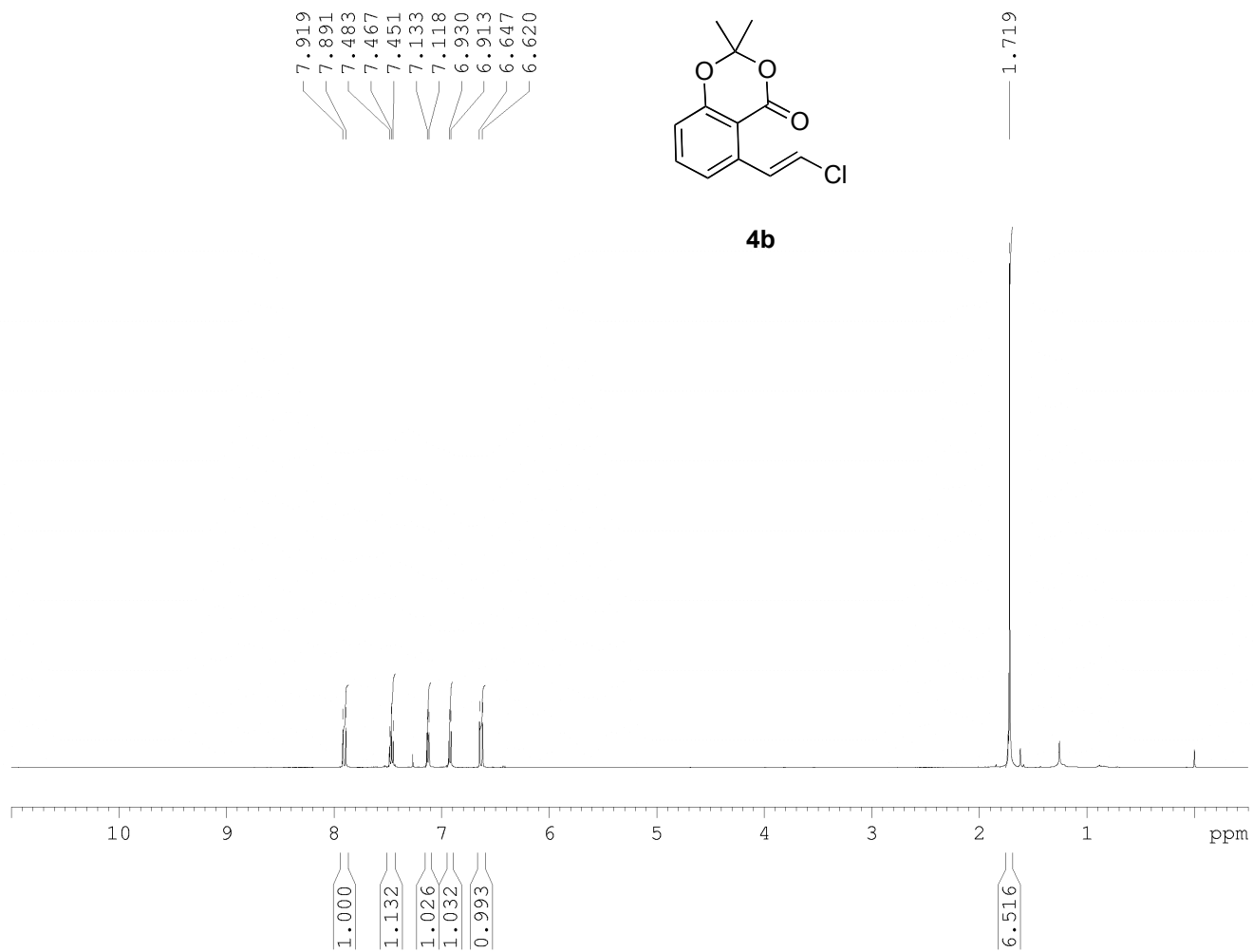
134.814
133.232
128.742
128.109
126.072
118.645



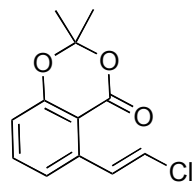
4a



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of (*E*)-(2-chlorovinyl)benzene (4a)



¹H NMR (500 MHz, CDCl₃) Spectrum of (E)-5-(2-chlorovinyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (4b)



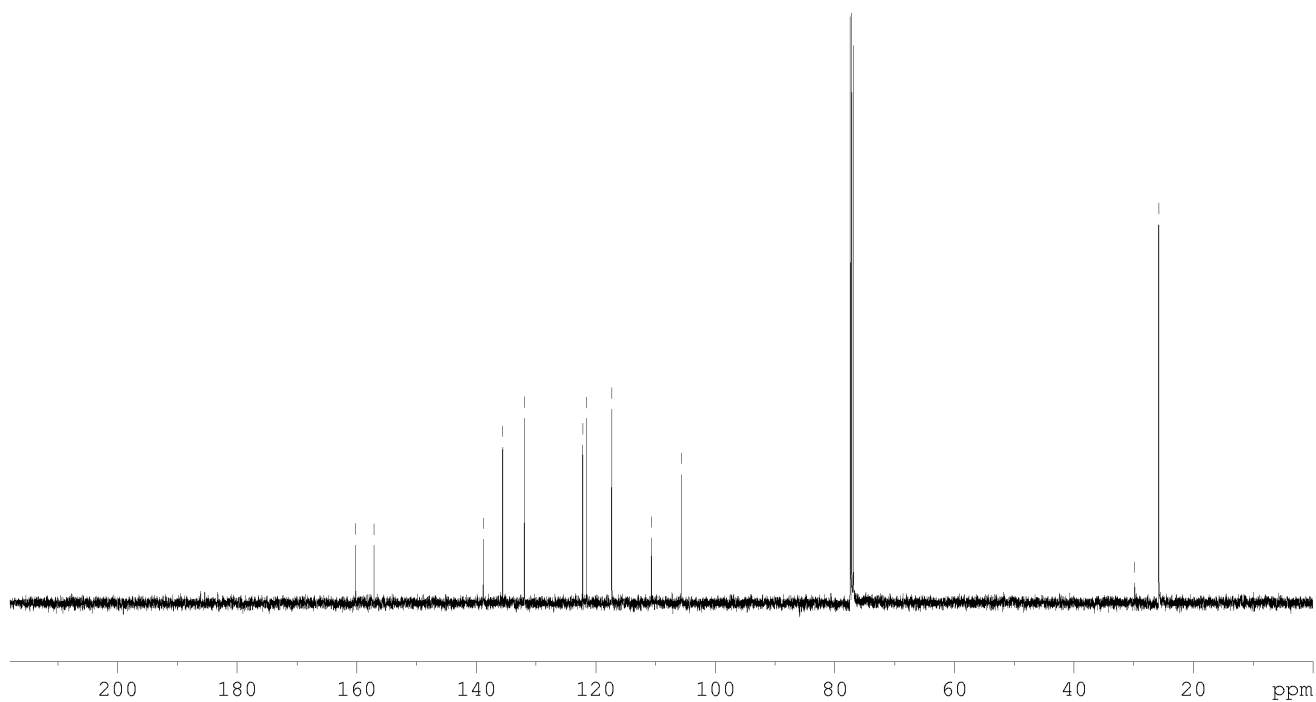
4b

160.215
157.113

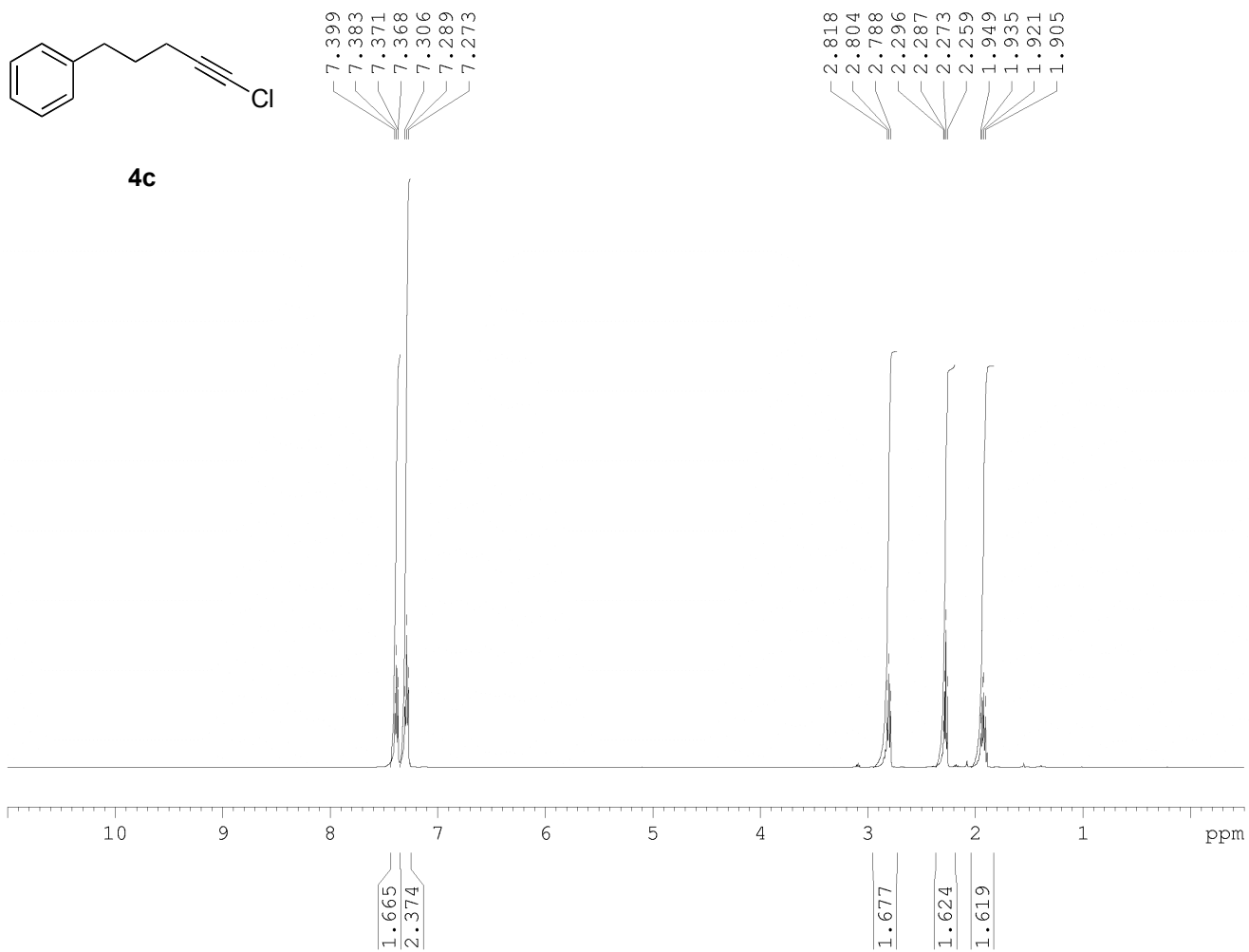
138.806
135.605
131.925

122.179
121.566
117.316
110.694
105.672

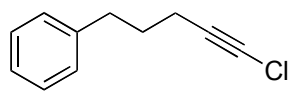
29.846
25.782



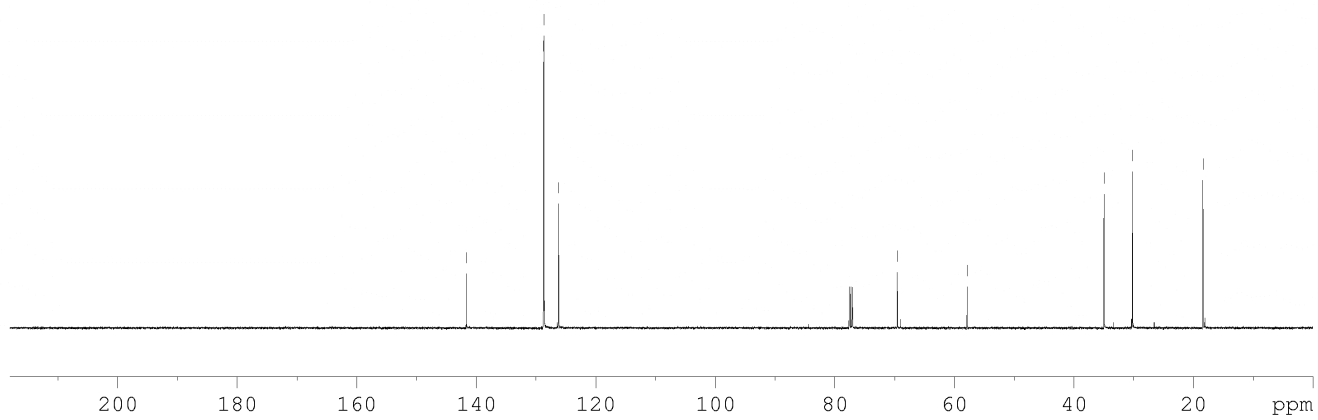
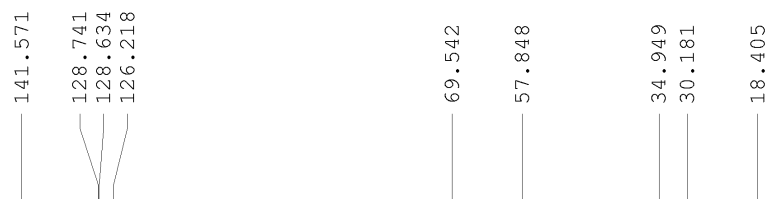
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of (*E*)-5-(2-chlorovinyl)-2,2-dimethyl-4H-benzo[d][1,3]dioxin-4-one (**4b**)

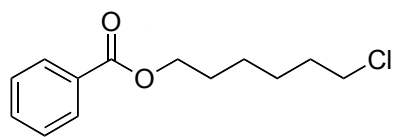


¹H NMR (500 MHz, CDCl₃) Spectrum of (5-chloropent-4-yn-1-yl)benzene (4c)

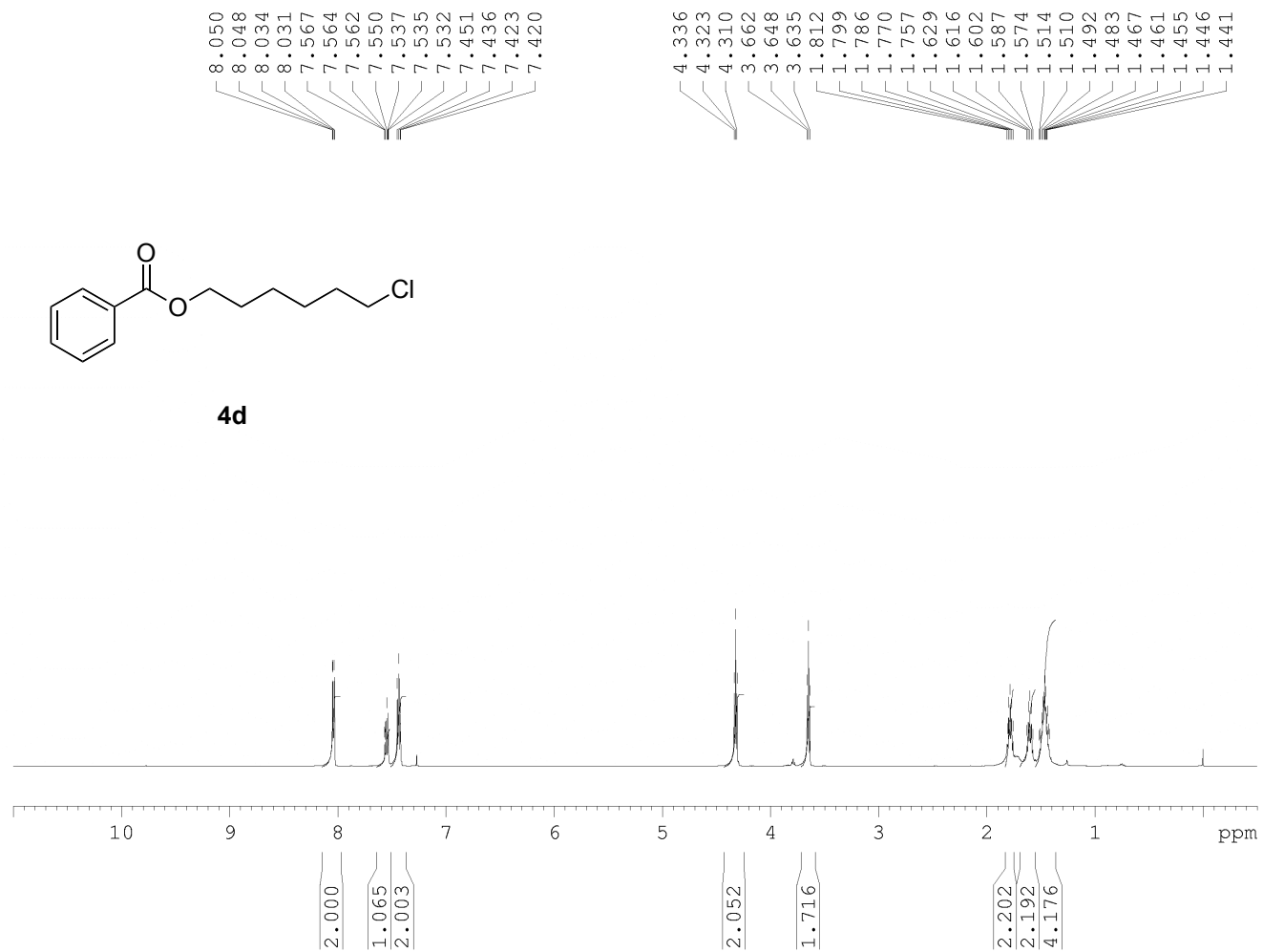


4c

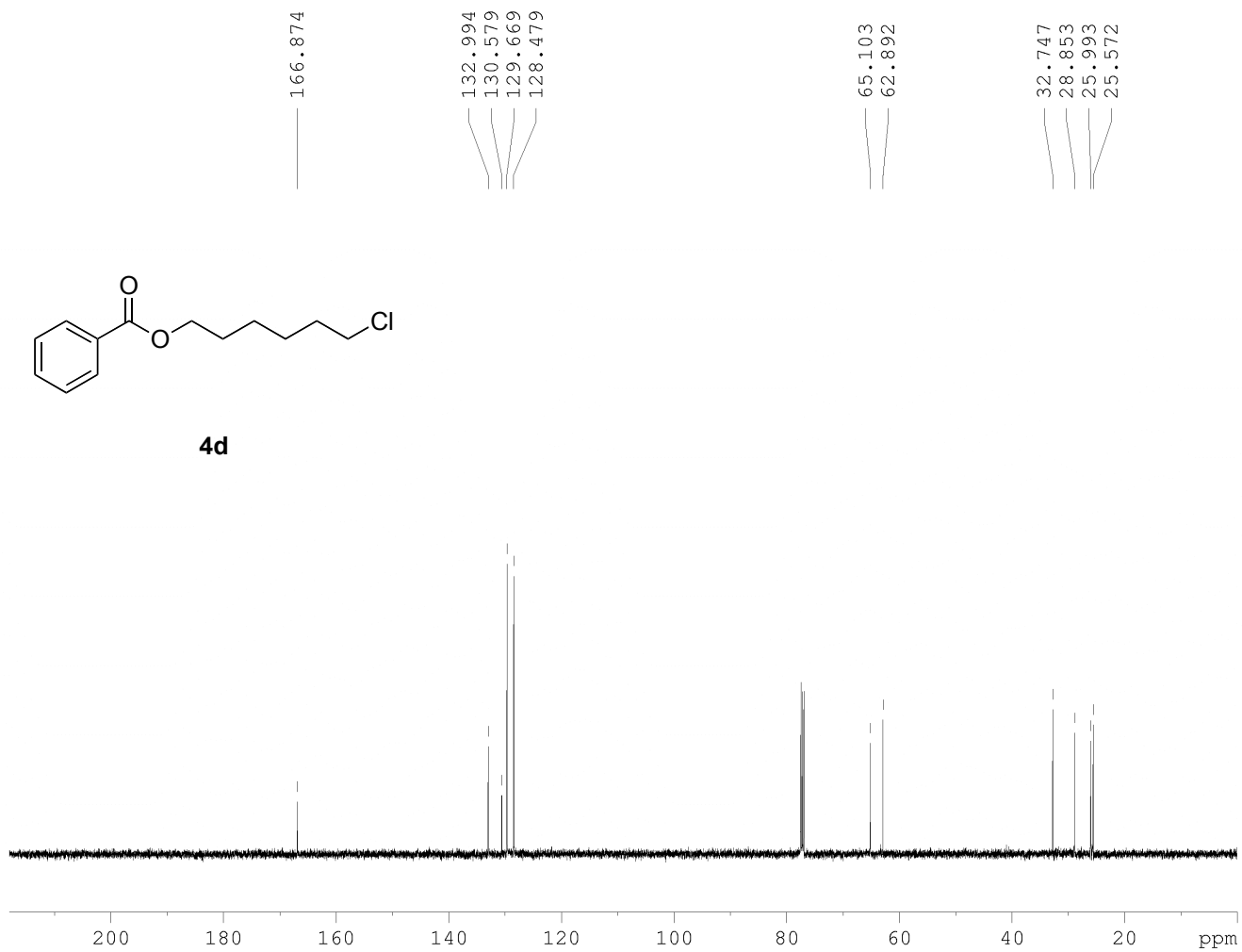




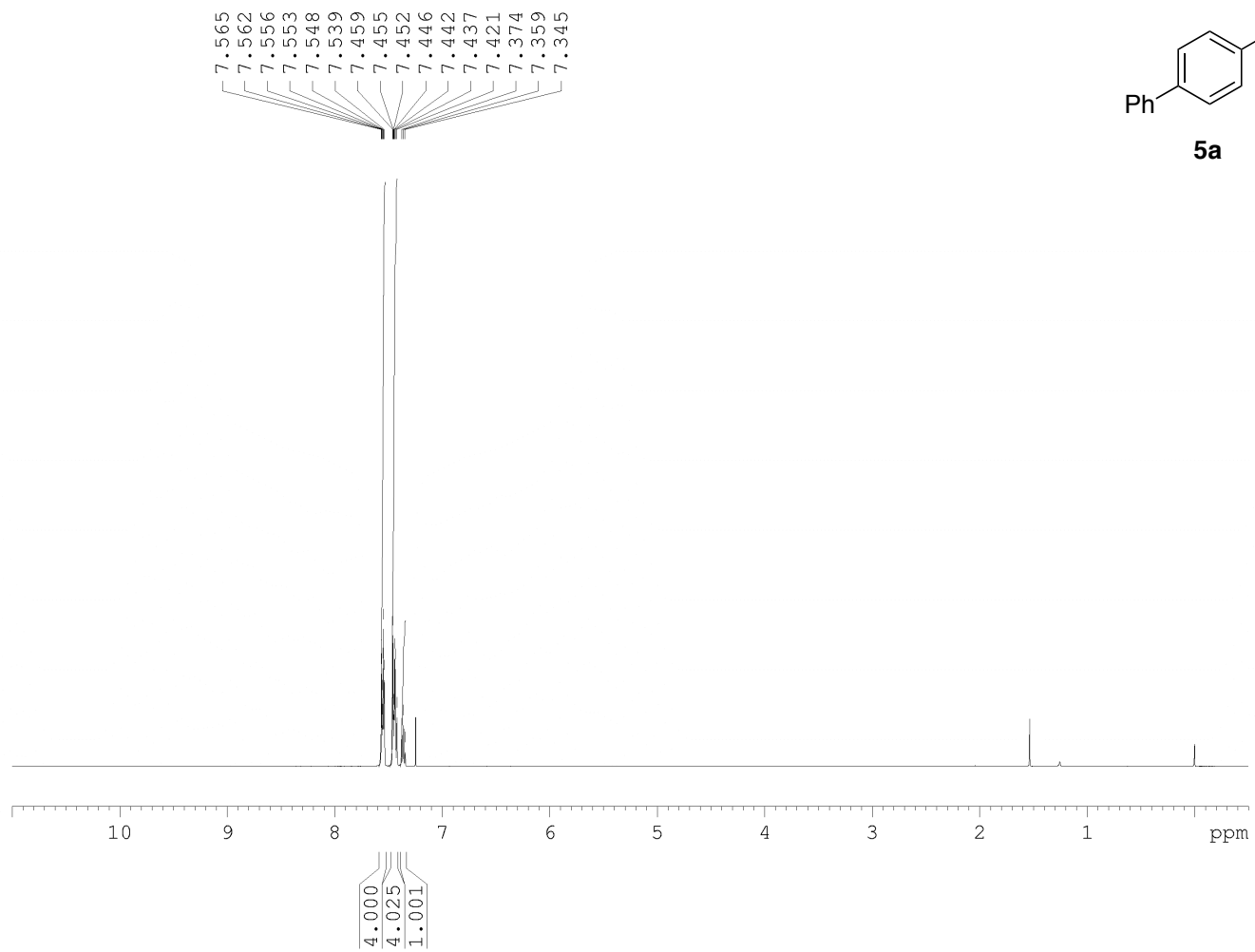
4d



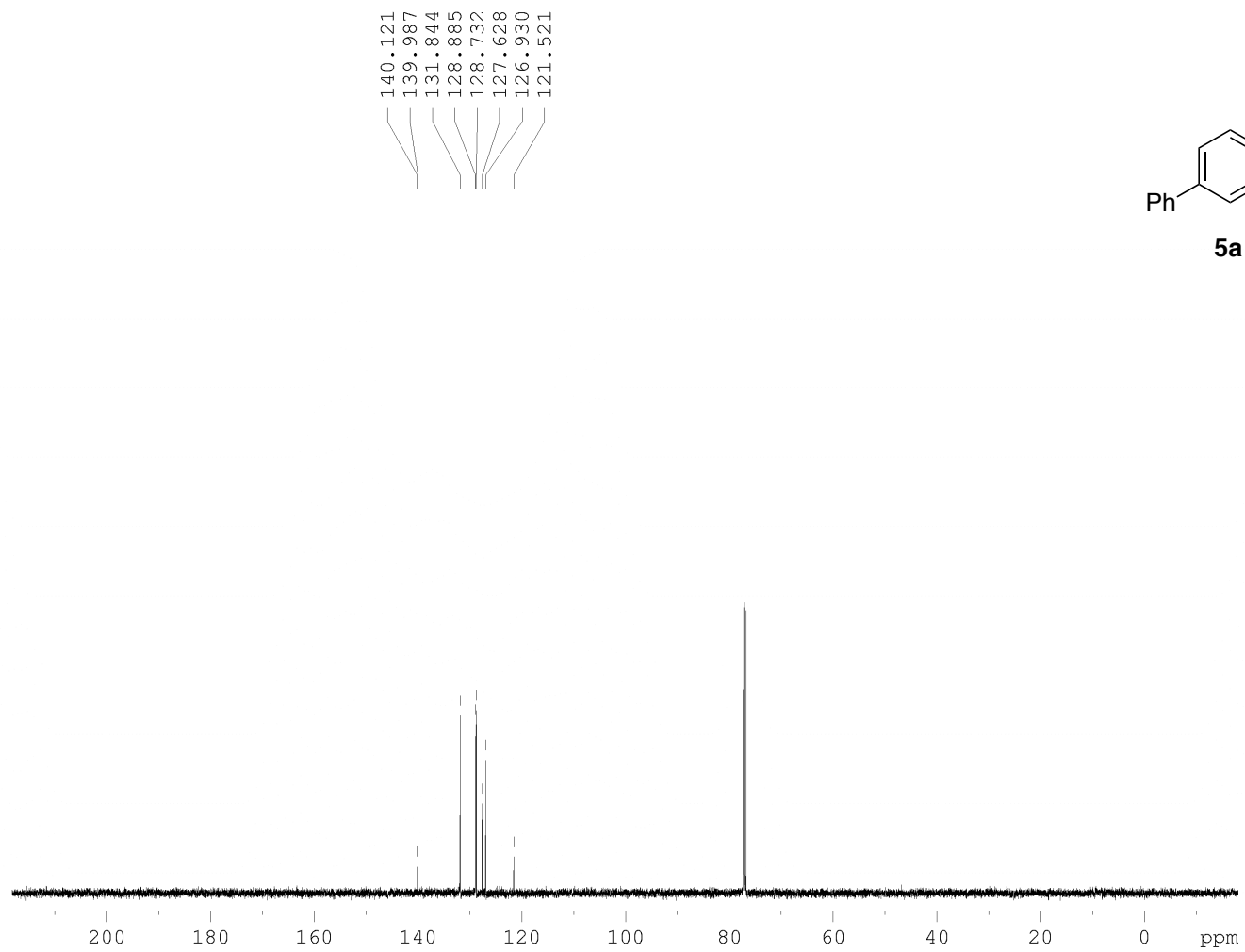
¹H NMR (500 MHz, CDCl₃) Spectrum of 6-chlorohexyl benzoate (4d)



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 6-chlorohexyl benzoate (4d)



¹H NMR (500 MHz, CDCl₃) Spectrum of 4-Bromobiphenyl (5a)



^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-Bromobiphenyl (5a)