

Supporting Information

Nitrosation of Aryl and Heteroaryltrifluoroborates with Nitrosonium Tetrafluoroborate

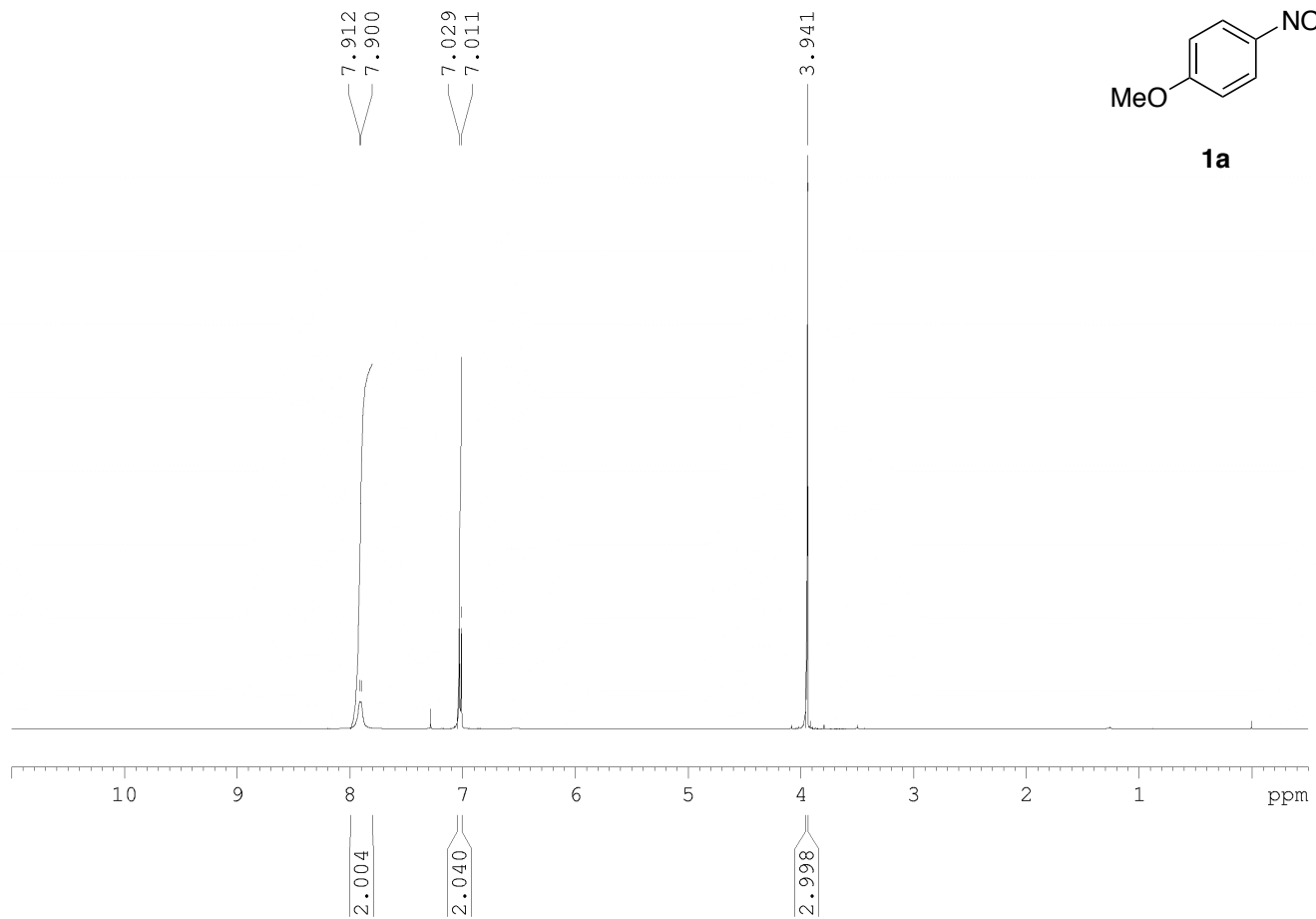
Gary A. Molander* and Livia N. Cavalcanti

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

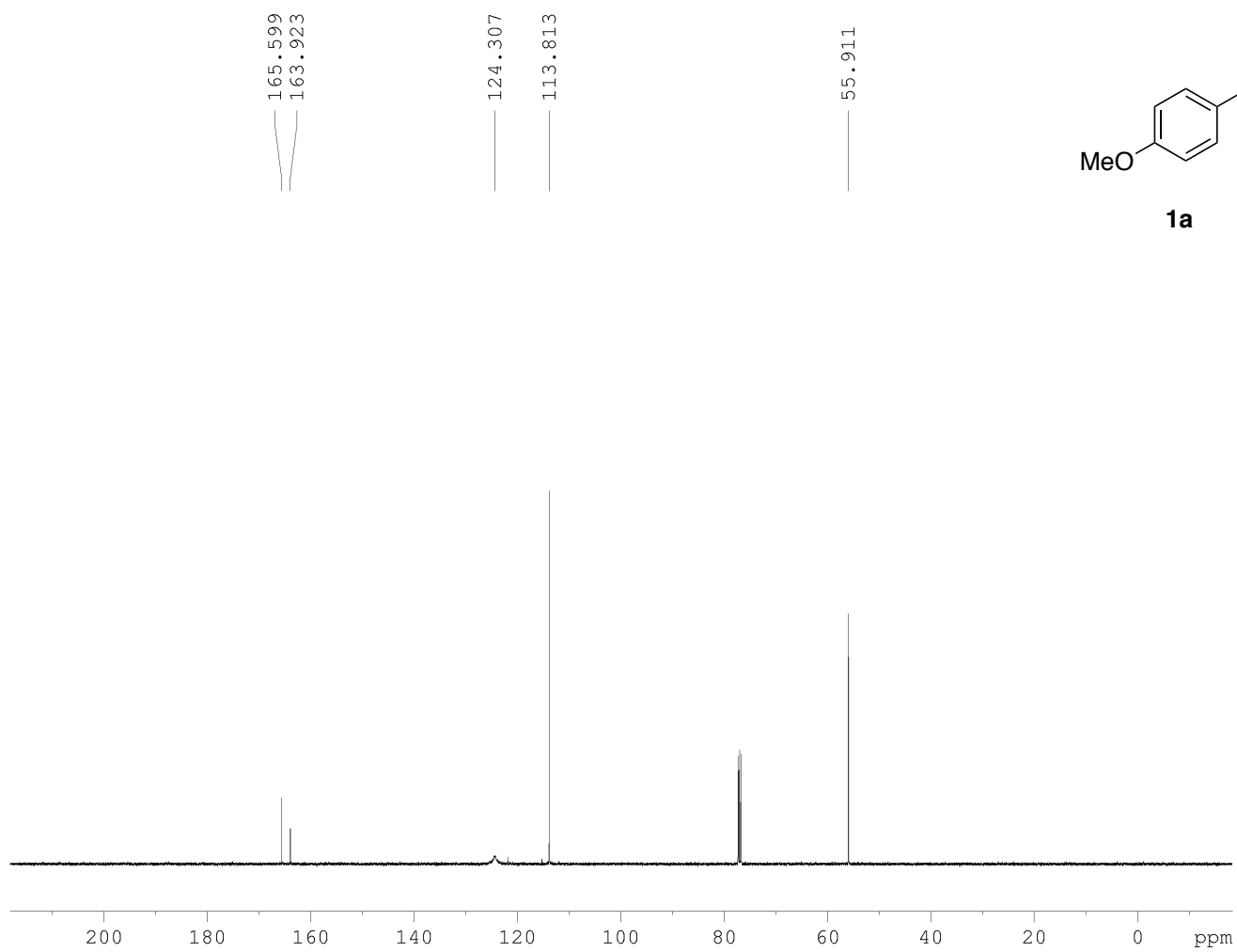
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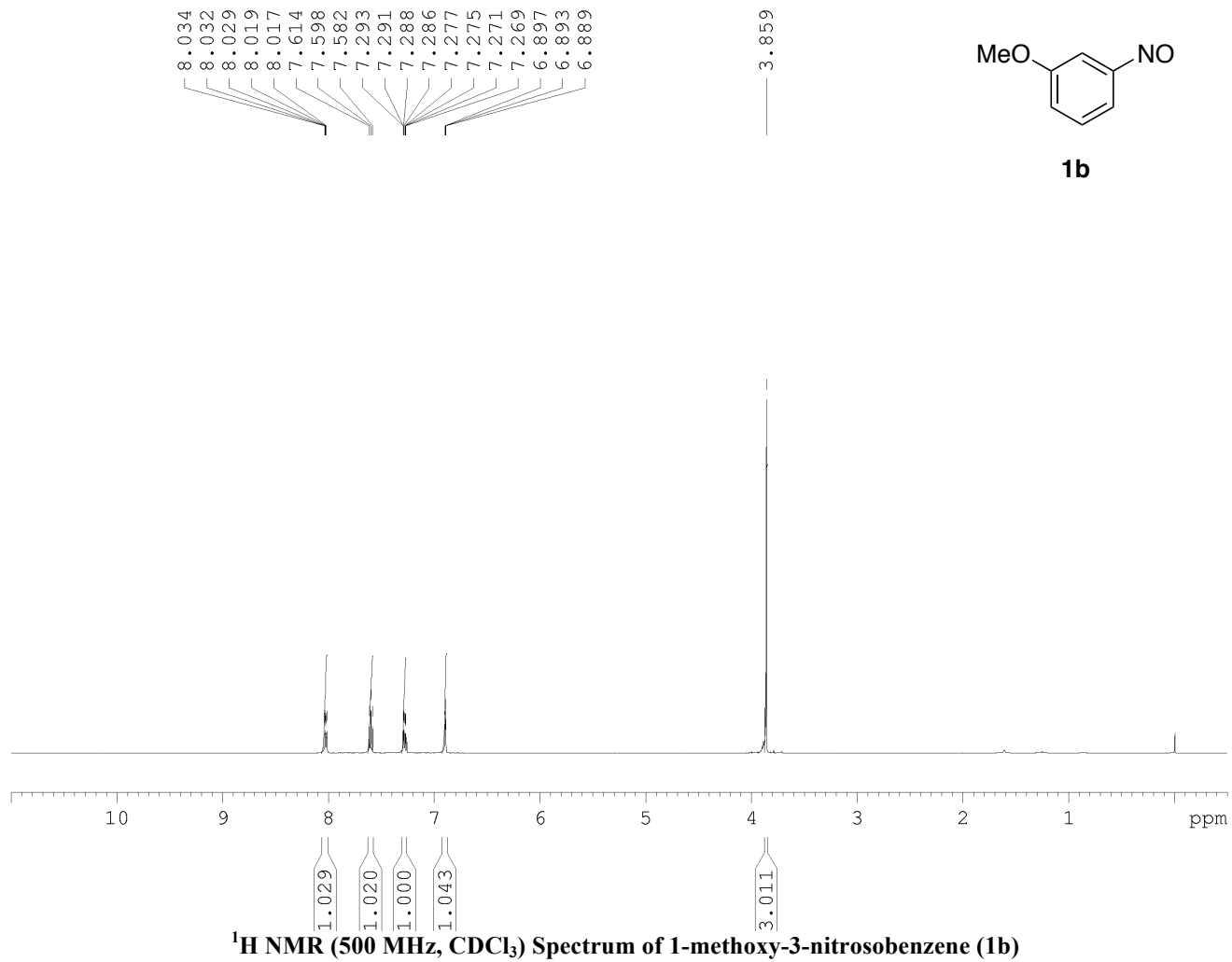
General Considerations: Nitrosonium tetrafluoroborate and HPLC grade acetonitrile, dichloromethane, hexanes and ethyl acetate were used as received. All new compounds were characterized by ^1H , ^{13}C and ^{19}F (when applicable) NMR, IR spectroscopy, high resolution mass spectrometry (HRMS) and melting point determination (for solids). All known compounds were characterized by ^1H and ^{13}C NMR and compared to literature values. ^1H , ^{13}C and ^{19}F spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. Melting points ($^{\circ}\text{C}$) are uncorrected. ^{19}F NMR chemical shifts were referenced to external CFCl_3 (0.0 ppm). HRMS (CI) data were obtained in Pos mode, using methane as the ionizing gas. HRMS (ESI) data were obtained in Pos or Neg mode. All reactions were carried out in an open to air atmosphere.

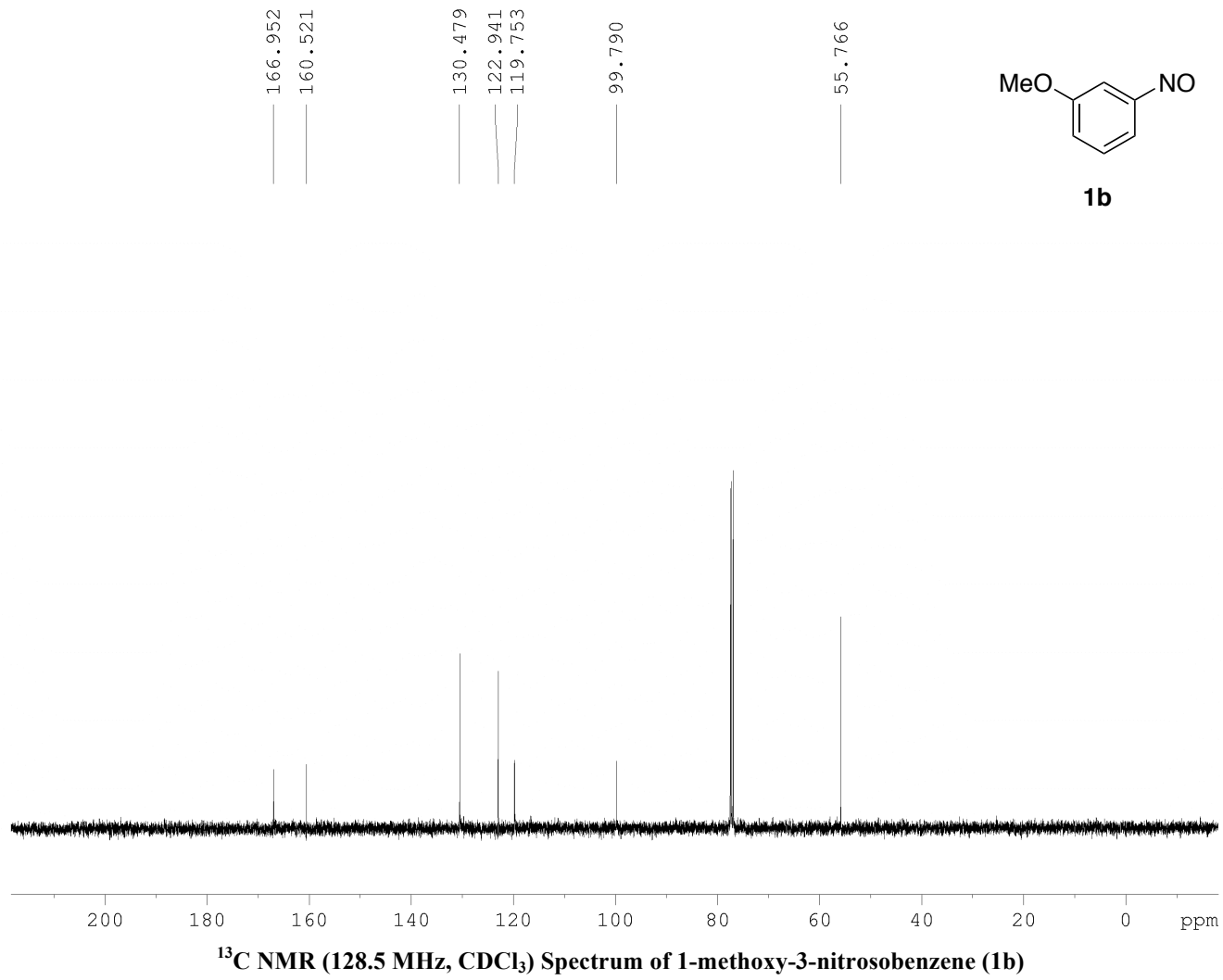


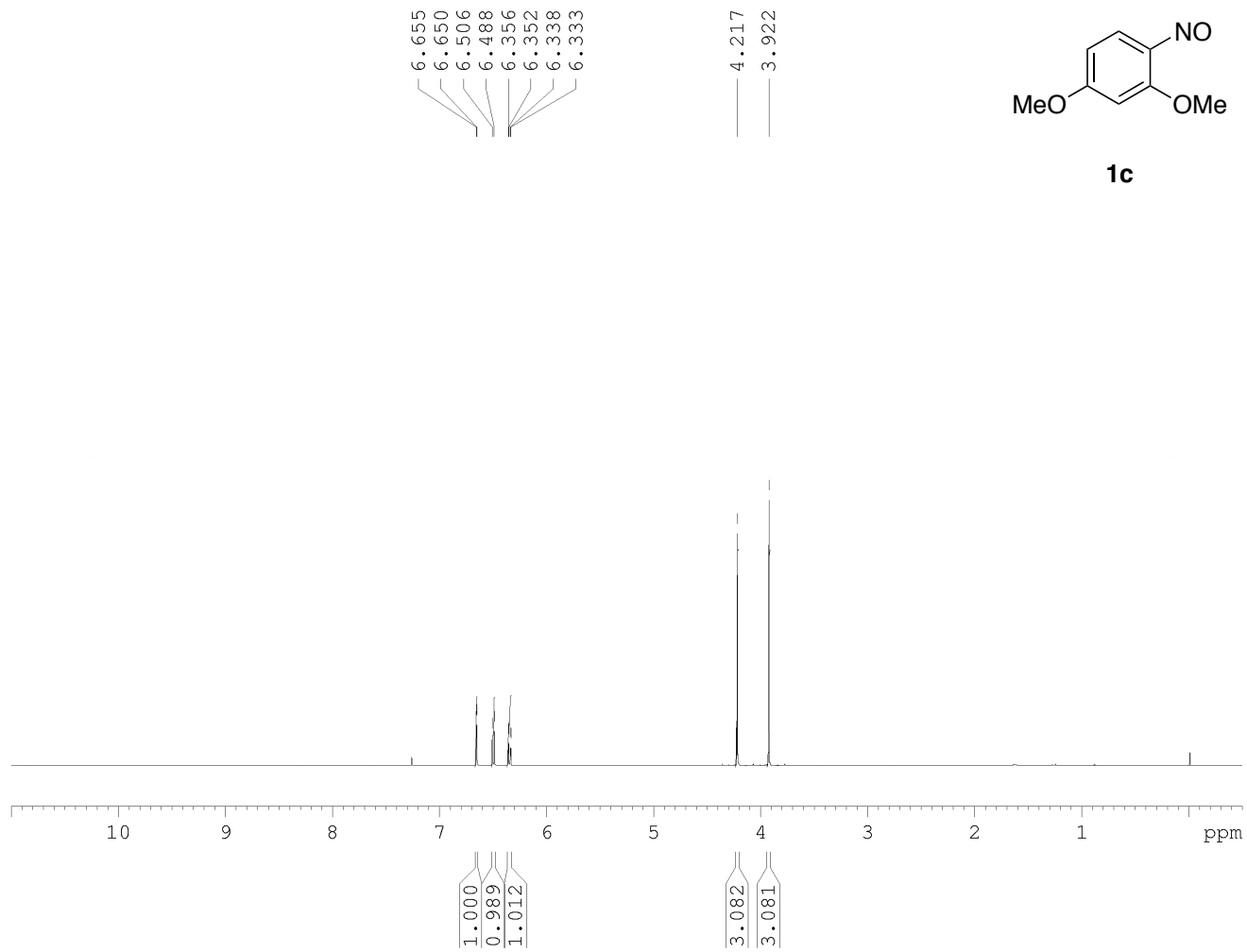
^1H NMR (500 MHz, CDCl_3) Spectrum of 1-methoxy-4-nitrosobenzene (1a)



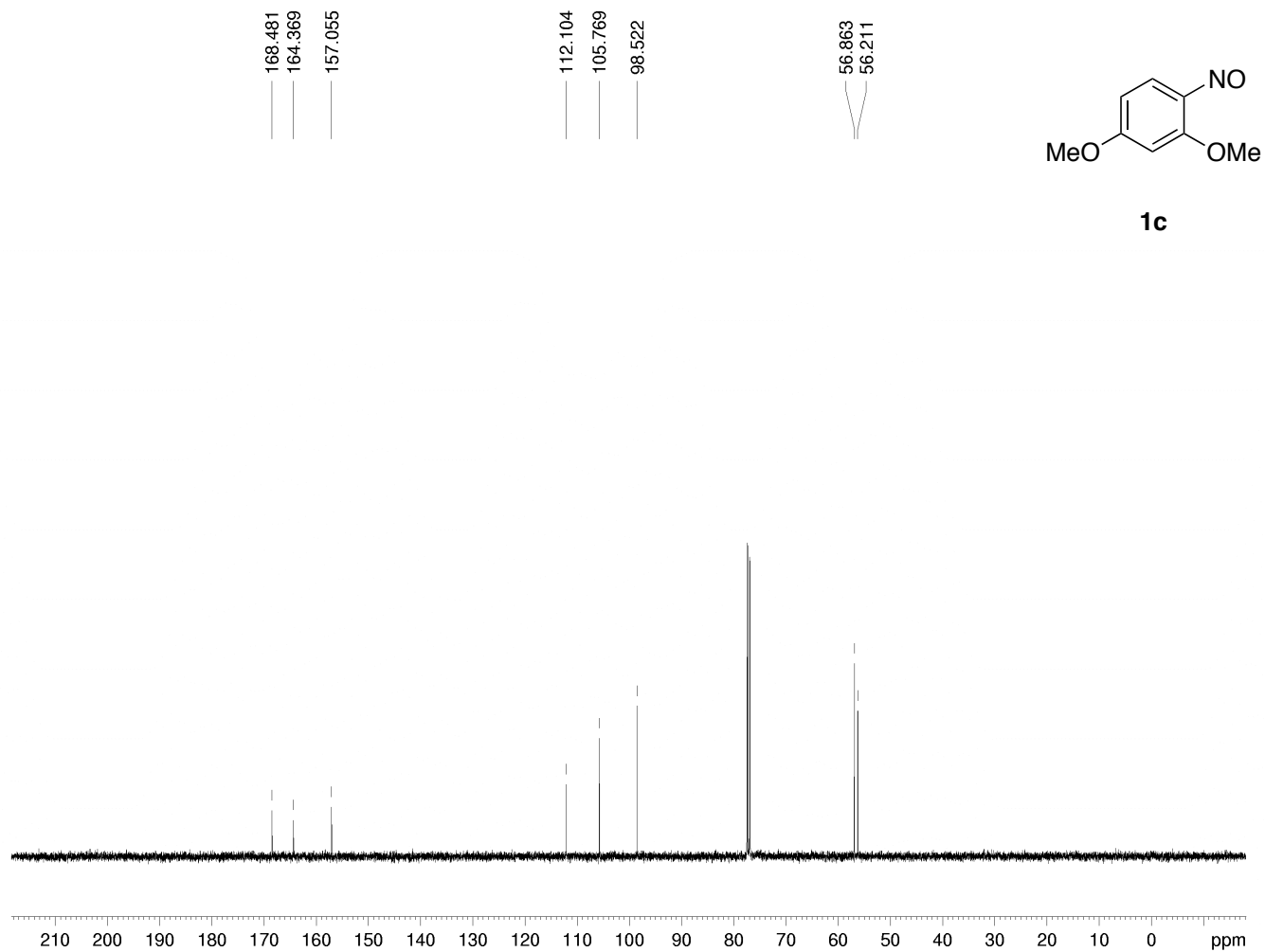
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1-methoxy-4-nitrosobenzene (1a)



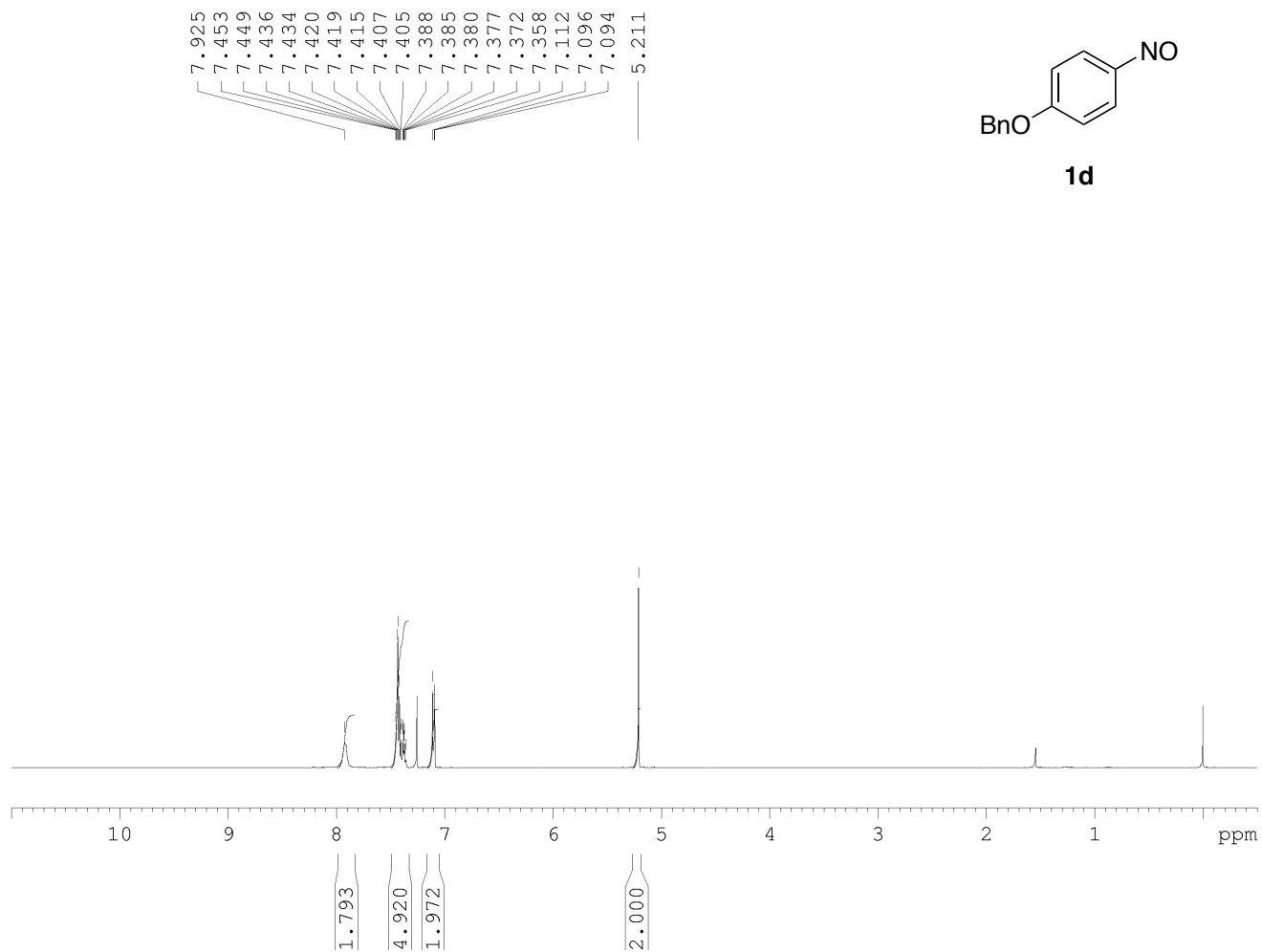




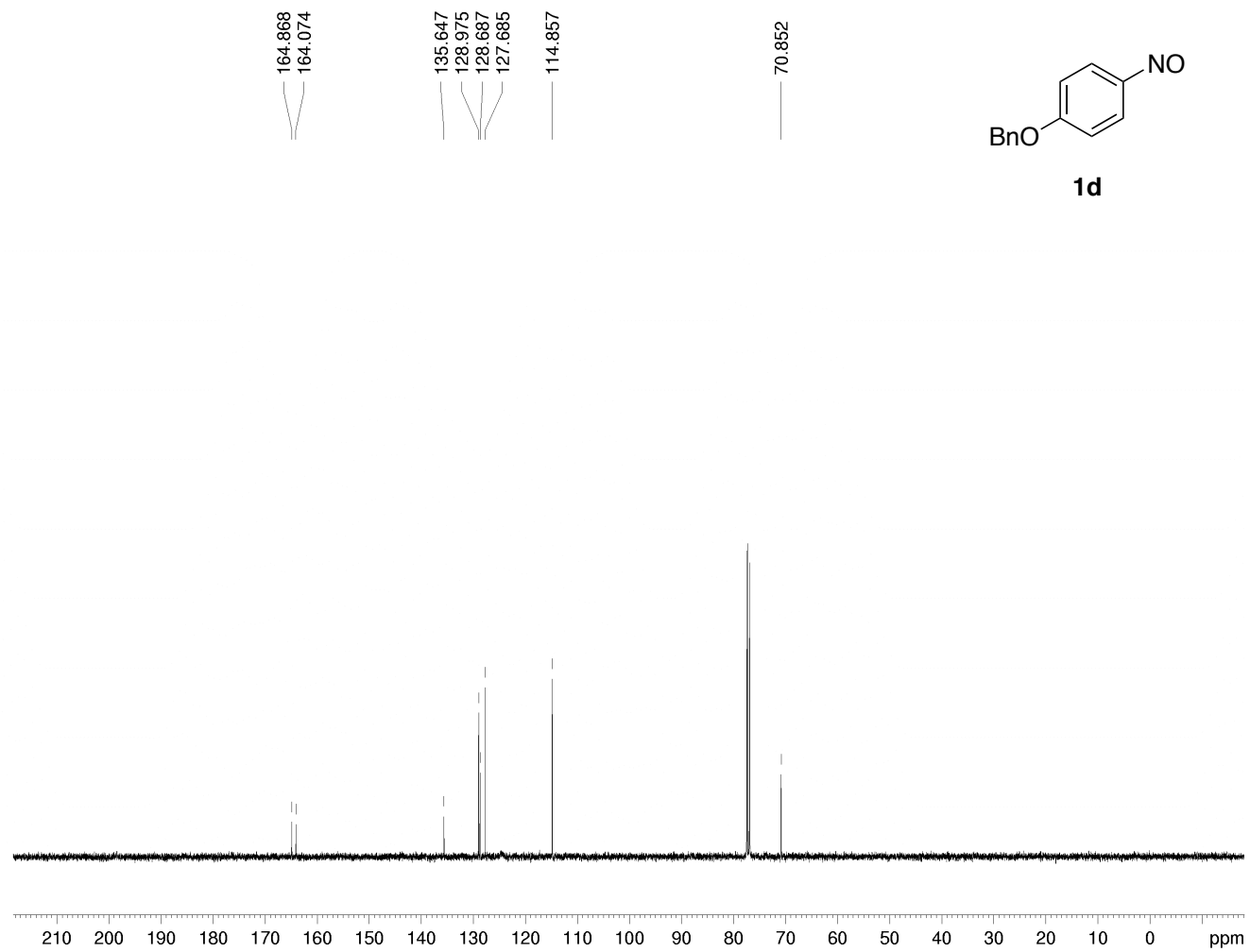
¹H NMR (500 MHz, CDCl₃) Spectrum of 2,4-dimethoxy-1-nitrosobenzene (1c)



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 2,4-dimethoxy-1-nitrosobenzene (1c)



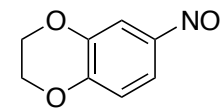
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(benzyloxy)-4-nitrosobenzene (1d)



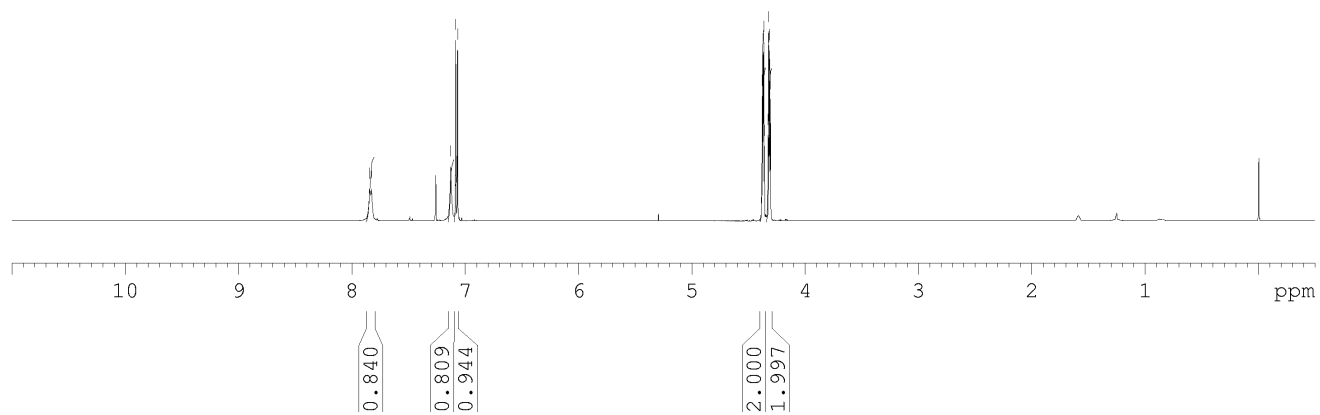
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-(benzyloxy)-4-nitrosobenzene (1d)

7.844
7.828
7.128
7.084
7.067

4.381
4.380
4.375
4.373
4.372
4.368
4.365
4.360
4.327
4.322
4.319
4.315
4.312
4.307

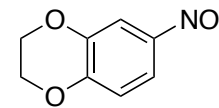


1e

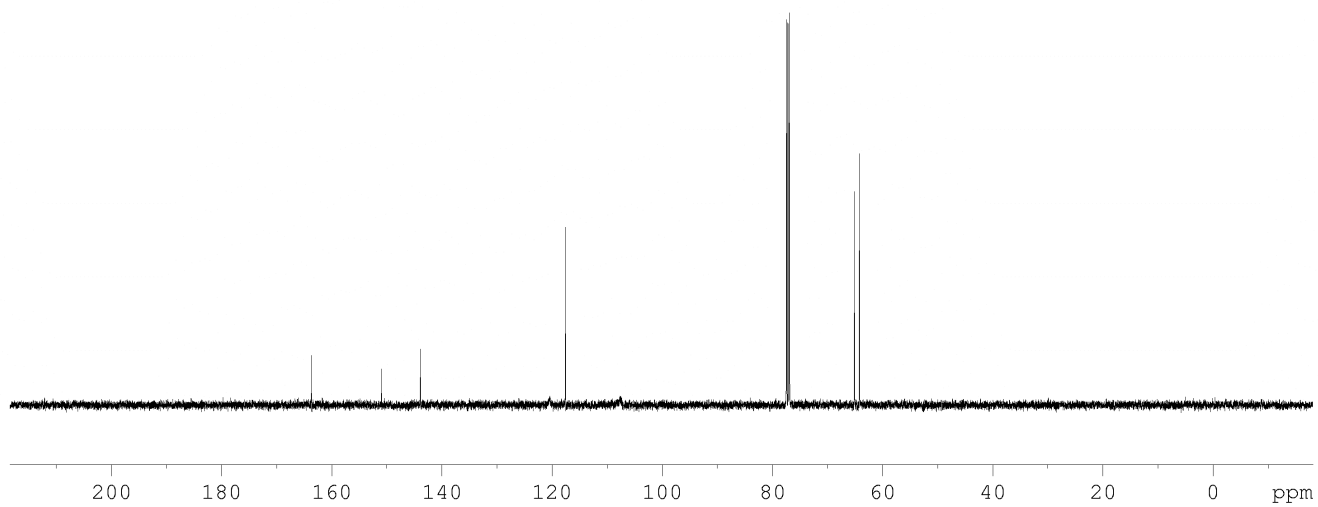


¹H NMR (500 MHz, CDCl₃) Spectrum of 6-nitroso-2,3-dihydrobenzo[b][1,4]dioxine (1e)

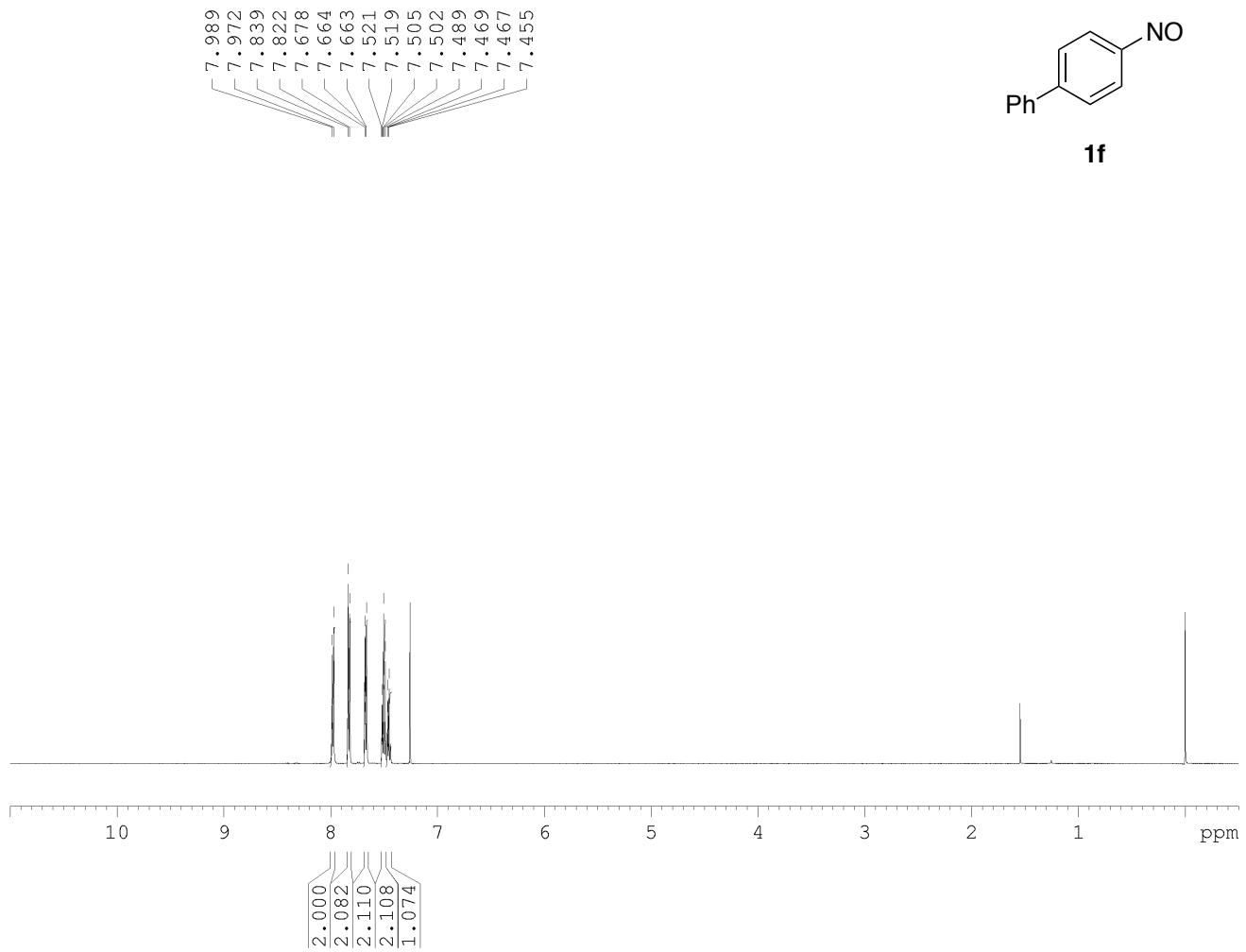
163.633
150.908
143.854
117.584
65.083
64.190



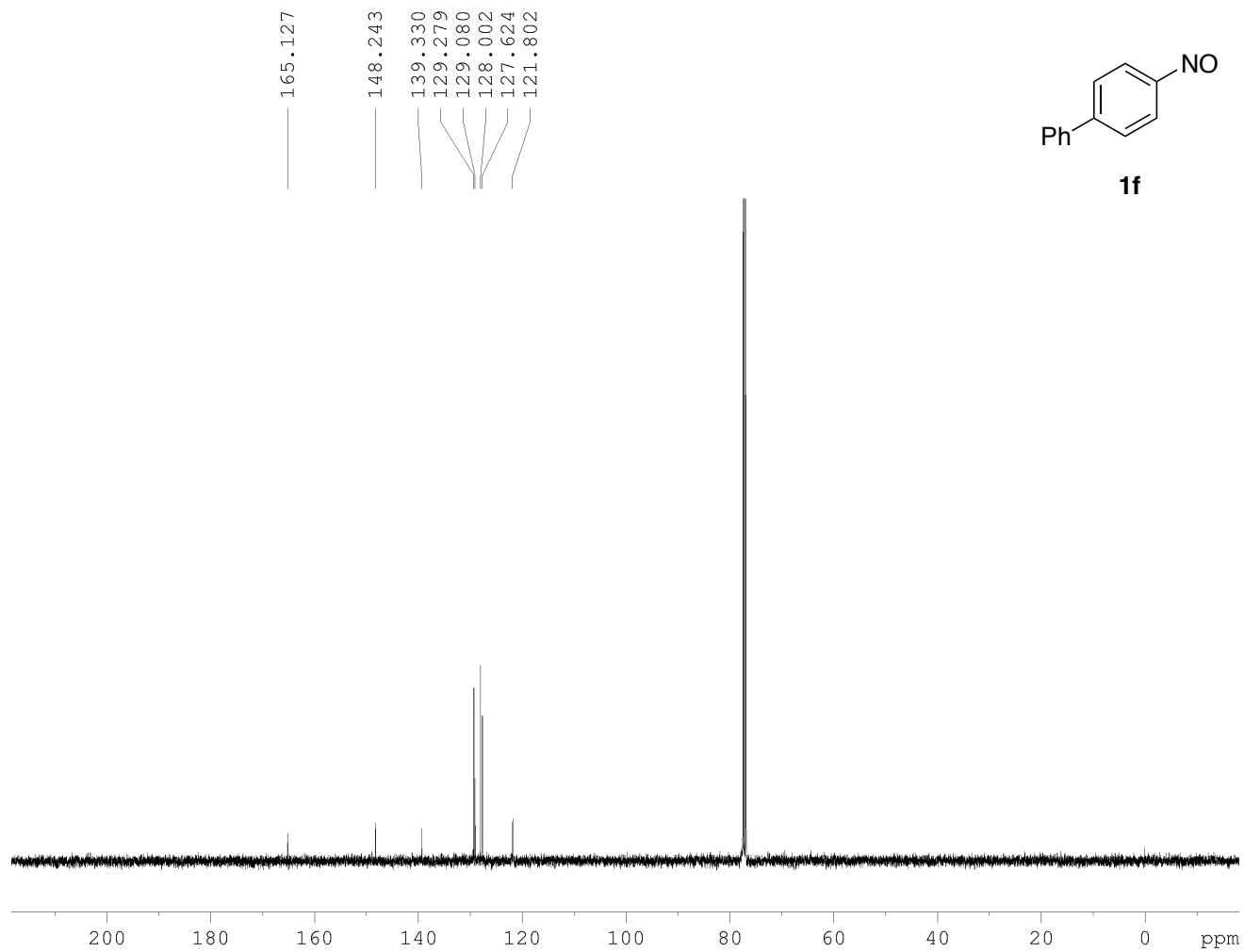
1e



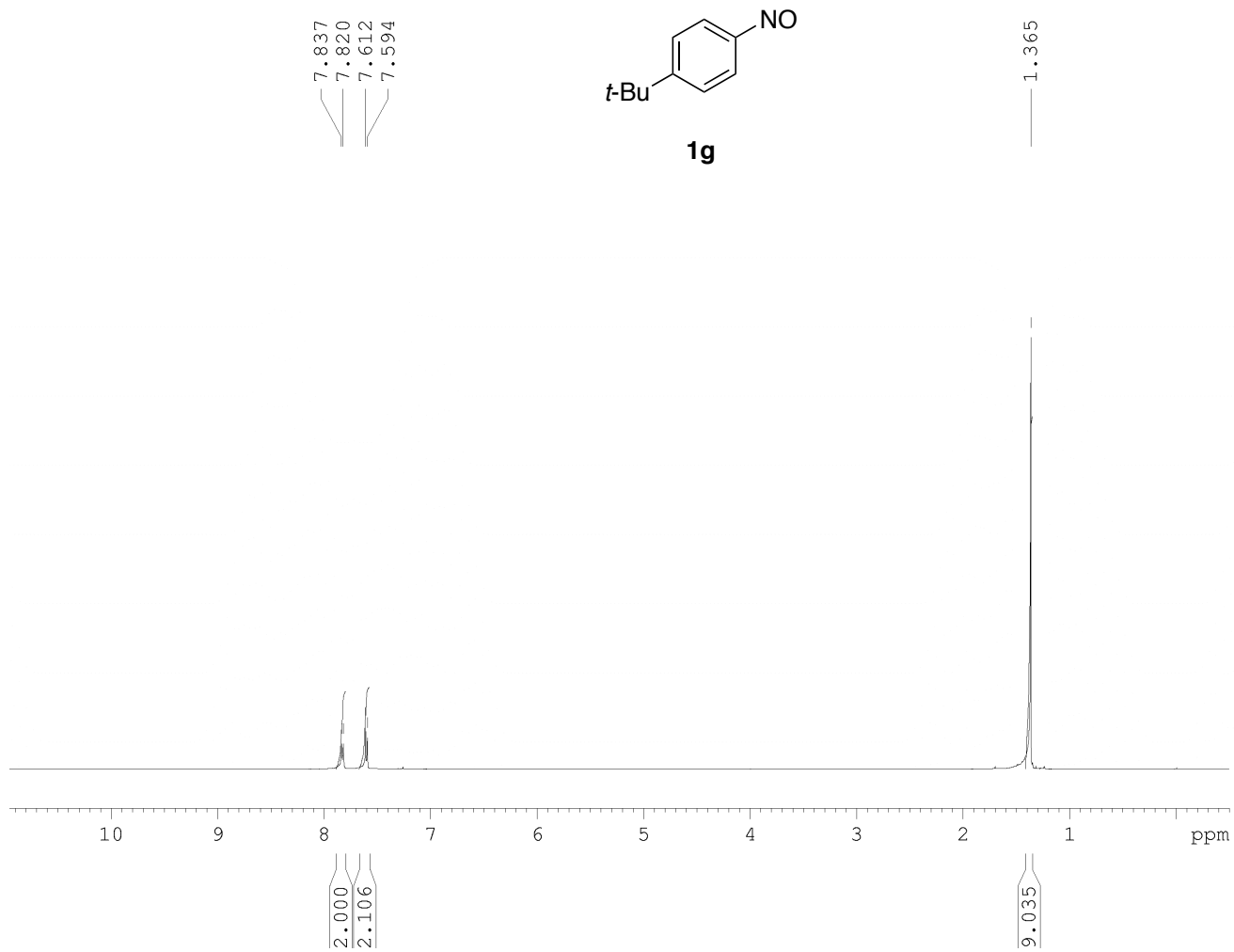
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 6-nitroso-2,3-dihydrobenzo[b][1,4]dioxine (1e)



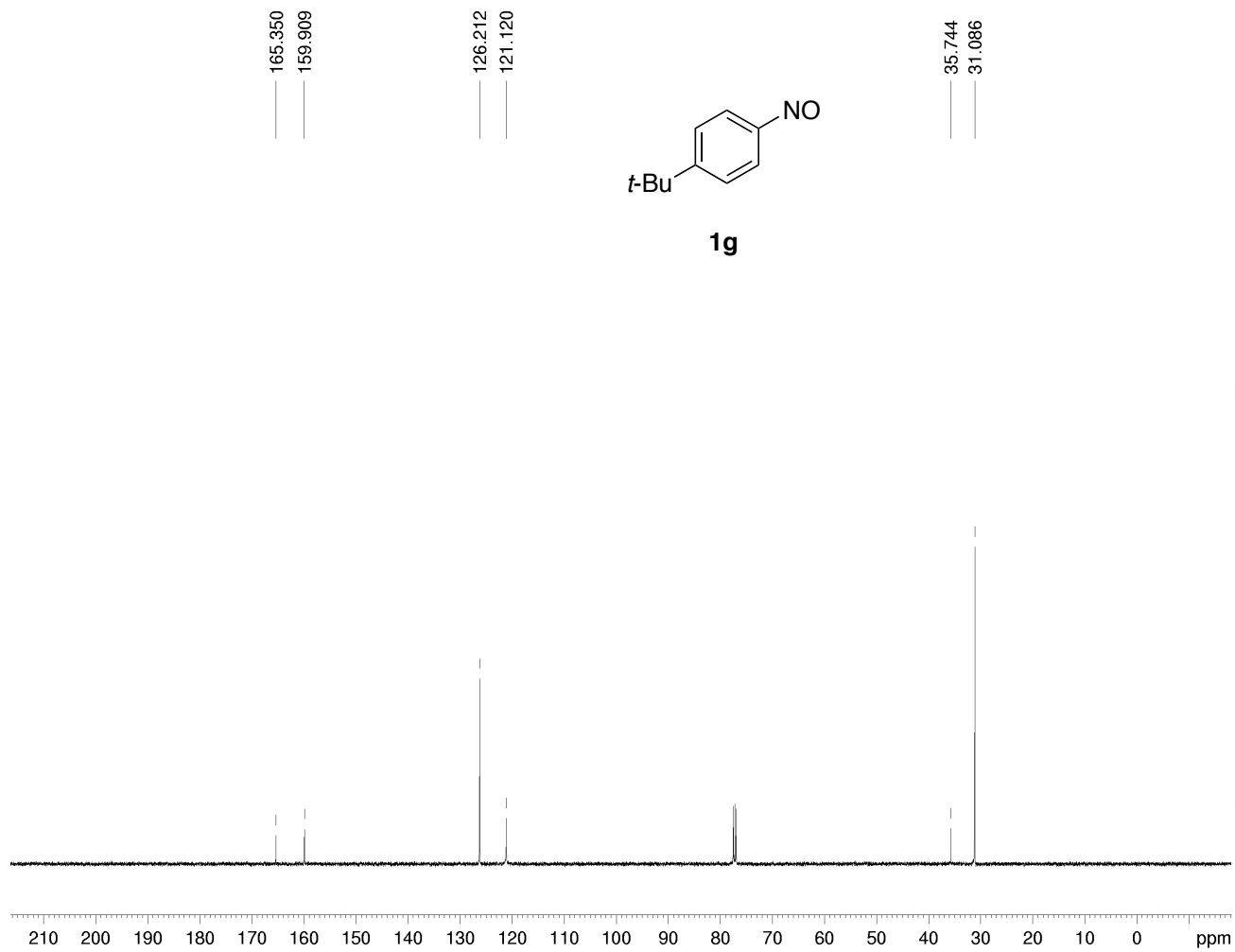
^1H NMR (500 MHz, CDCl_3) Spectrum of 4-nitrosobiphenyl (1f)



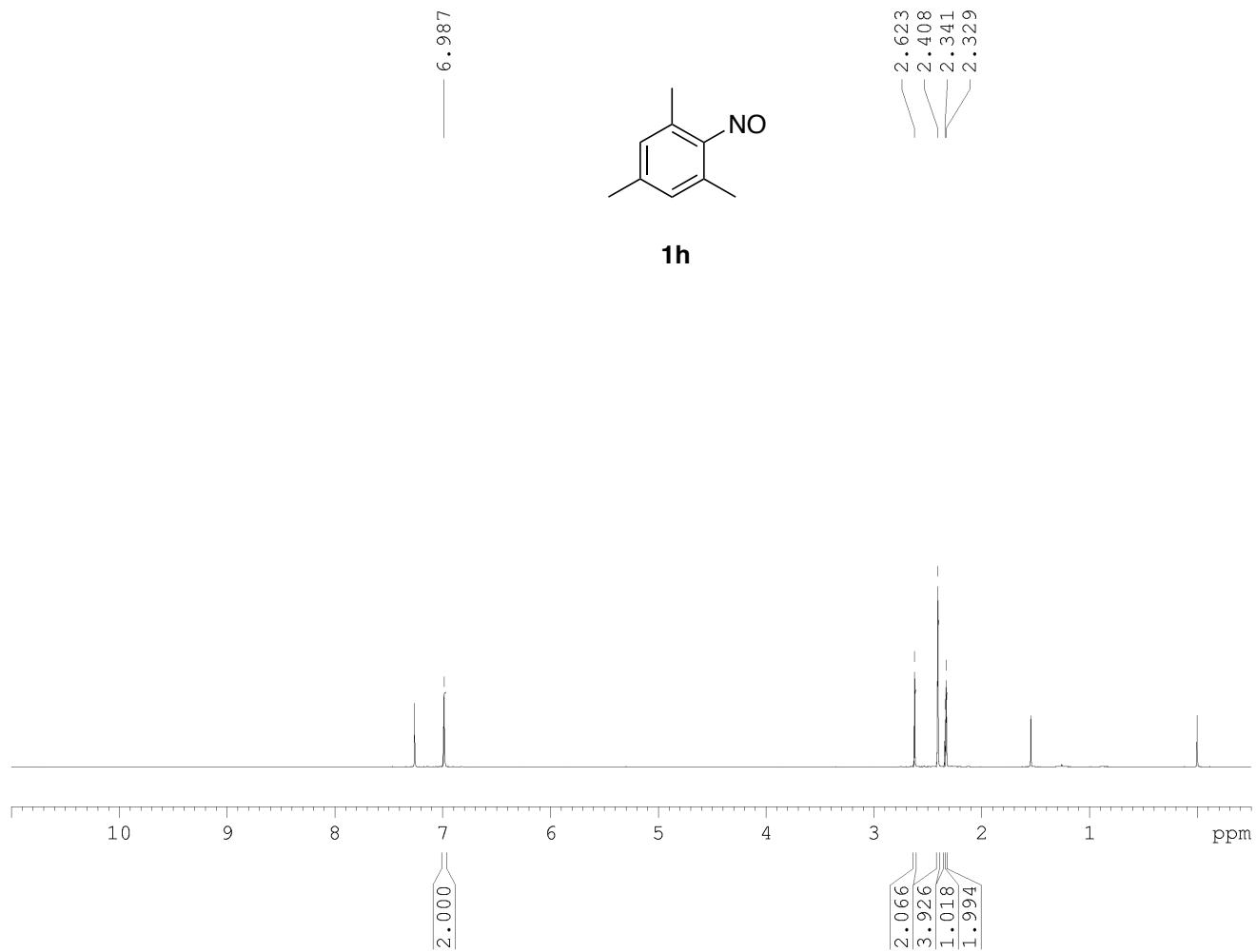
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-nitrosobiphenyl (1f)

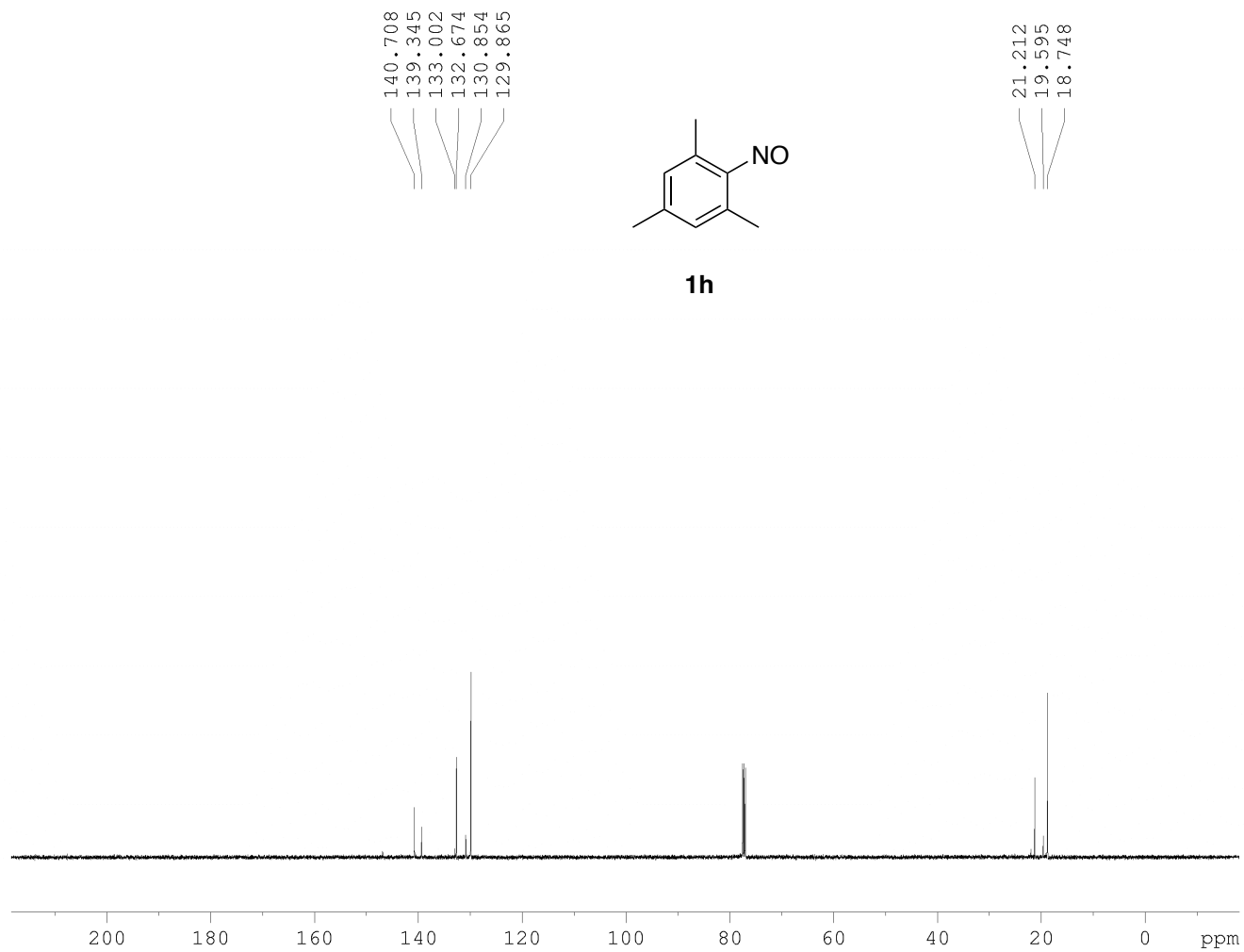


^1H NMR (500 MHz, CDCl_3) Spectrum of 1-tert-butyl-4-nitrosobenzene (1g)

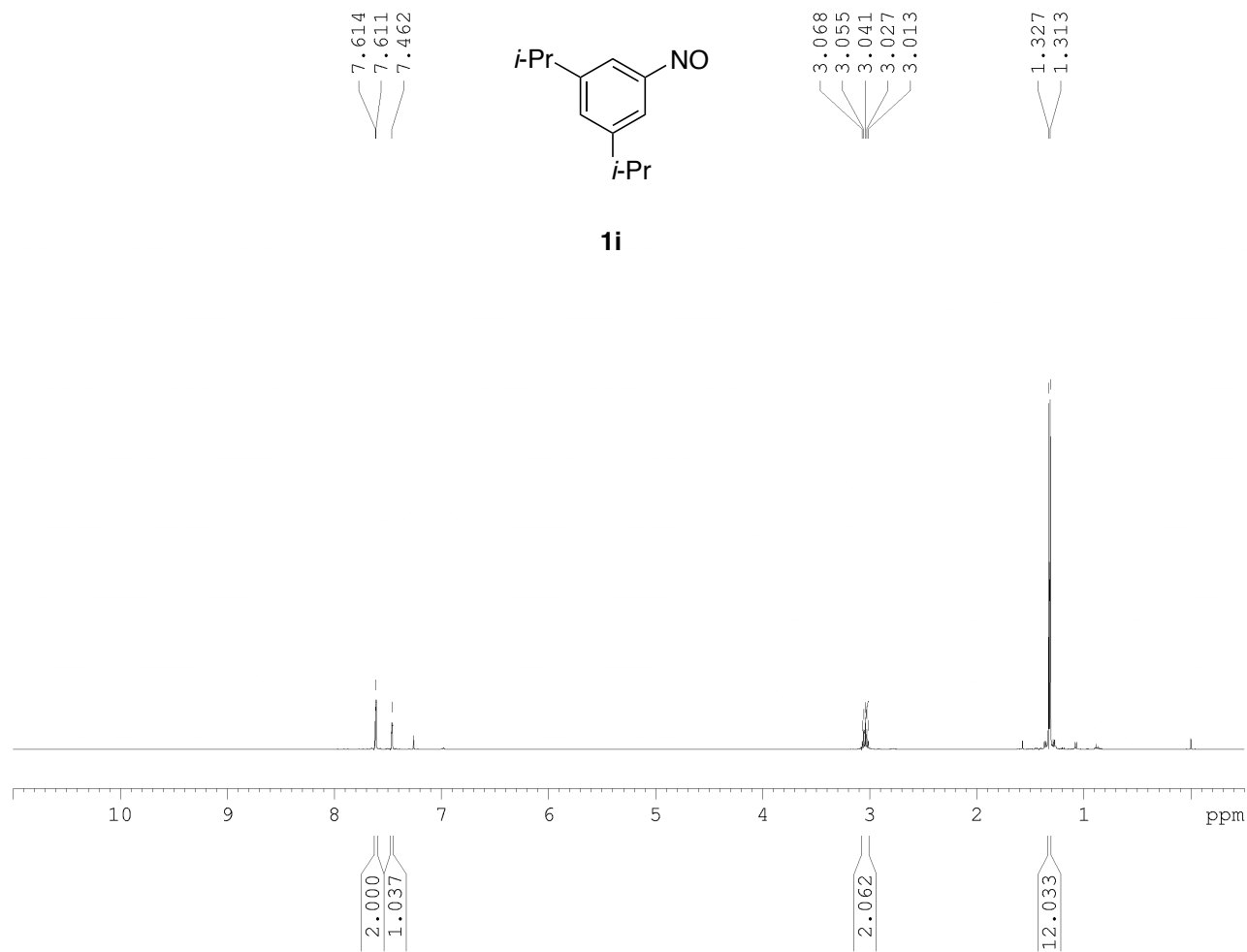


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1-tert-butyl-4-nitrosobenzene (1g)

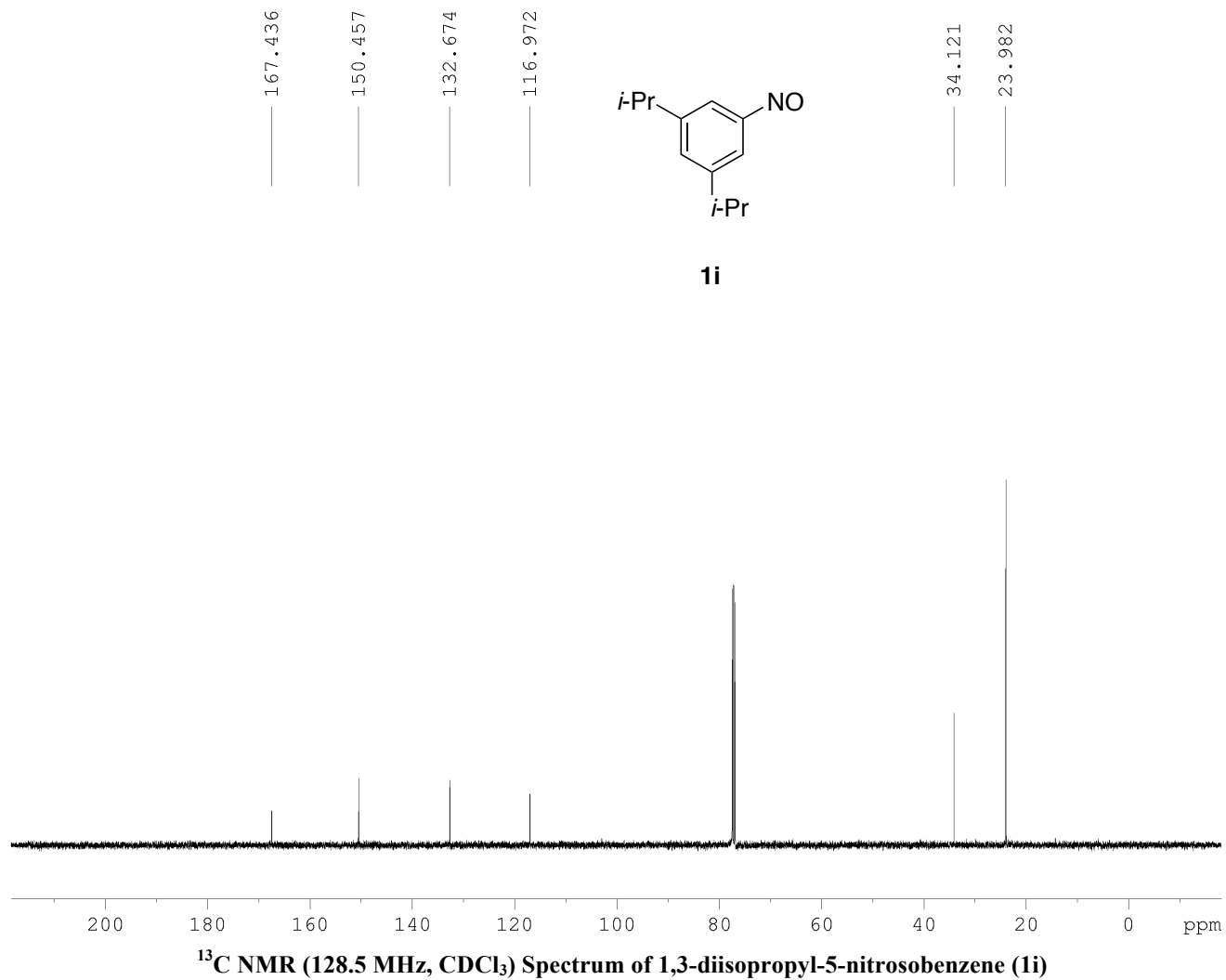




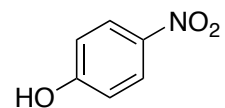
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1,3,5-trimethyl-2-nitrosobenzene (1h)



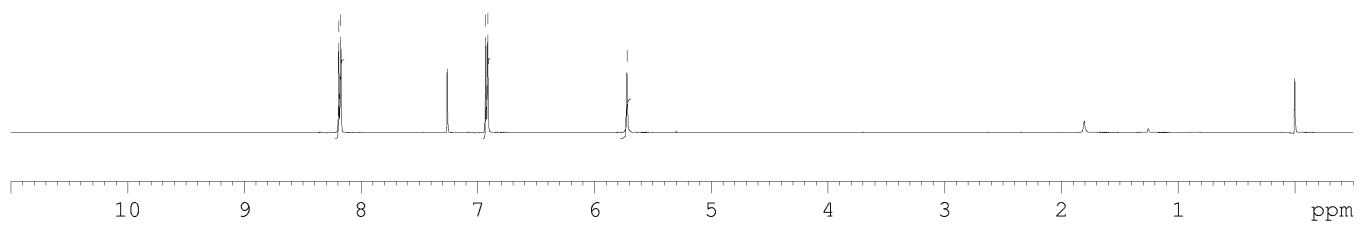
¹H NMR (500 MHz, CDCl₃) Spectrum of 1,3-diisopropyl-5-nitrosobenzene (**1i**)



8.193
8.174
6.933
6.915
5.723

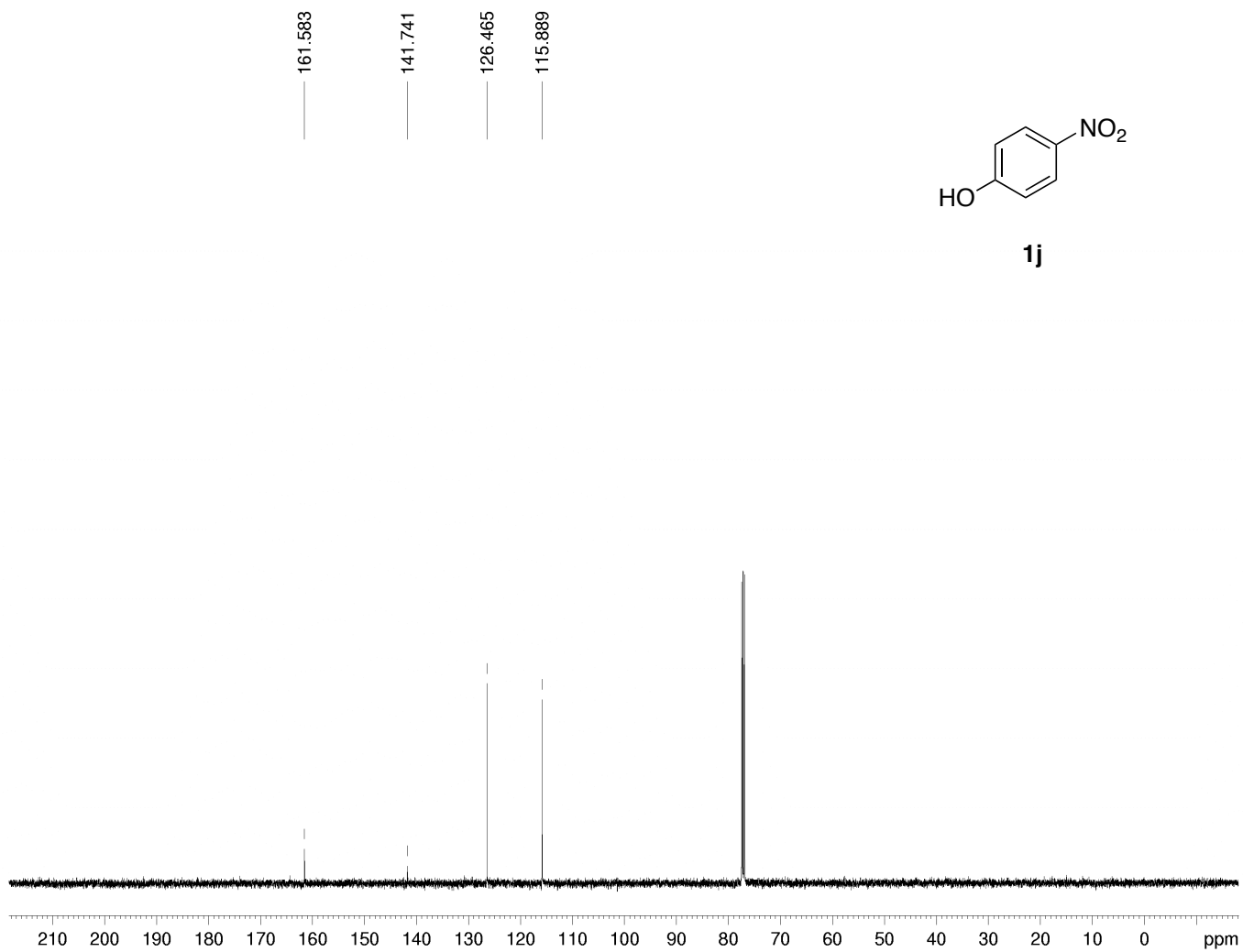


1j

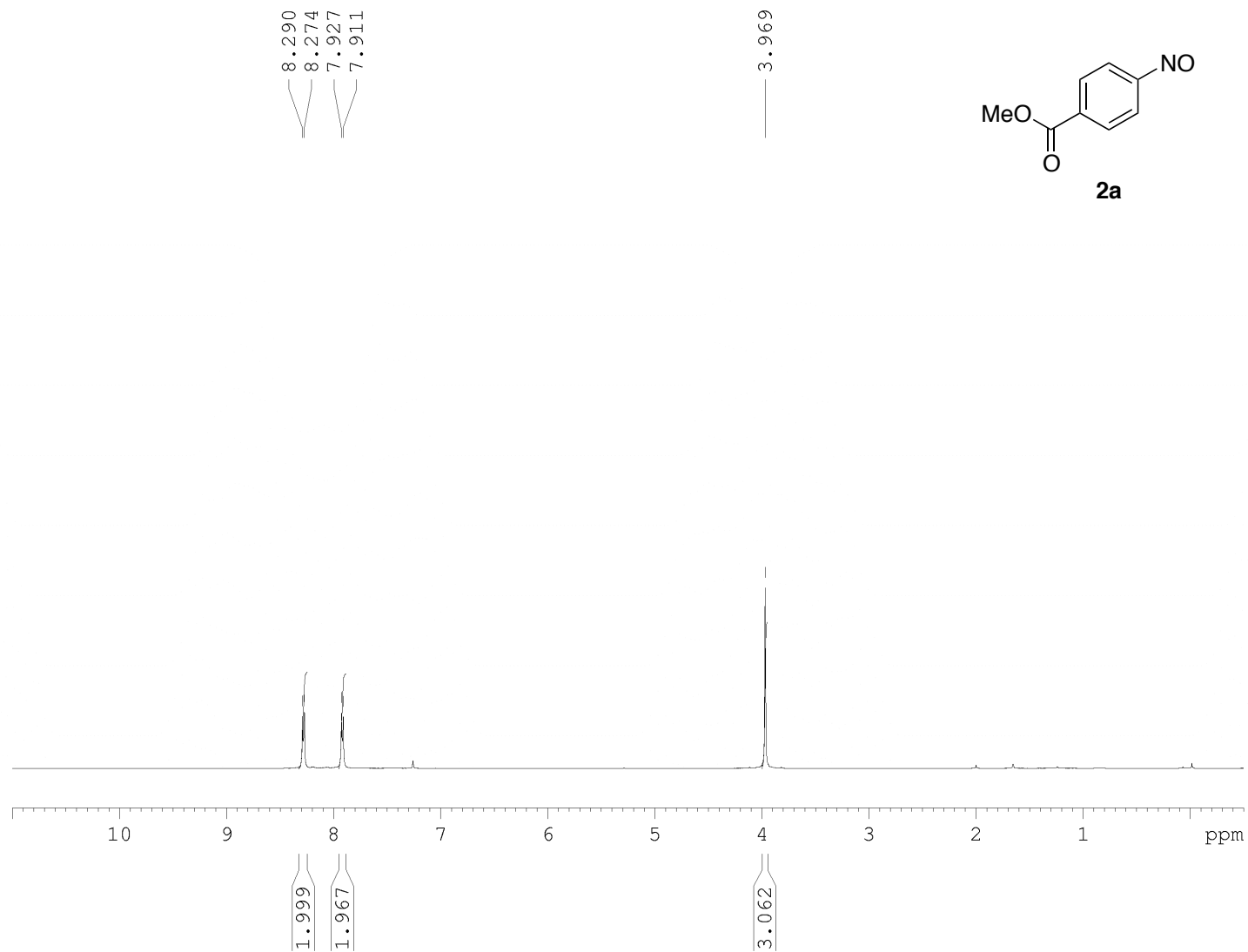


1.961
1.999
0.985

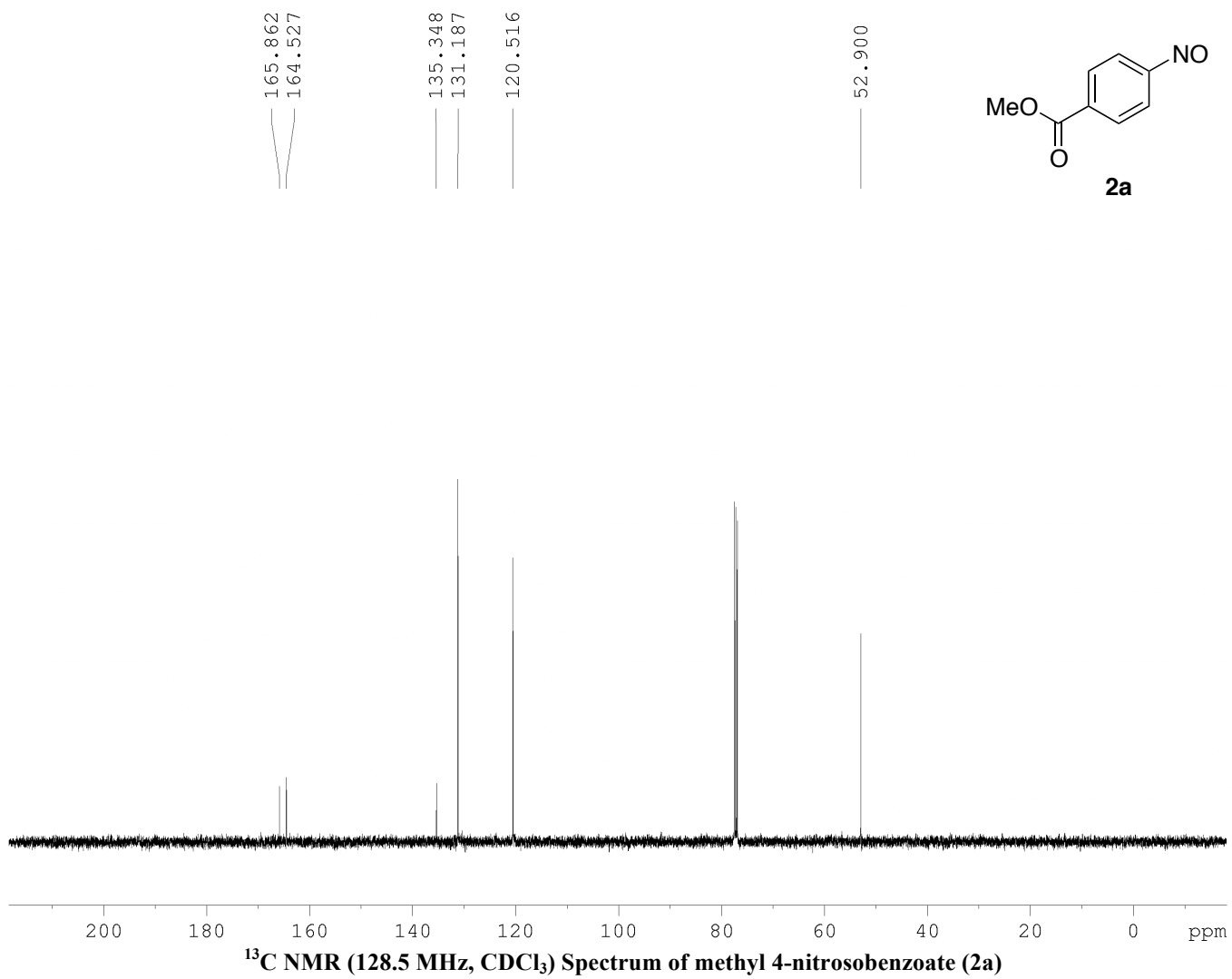
¹H NMR (500 MHz, CDCl₃) Spectrum of 4-nitrophenol (1j)

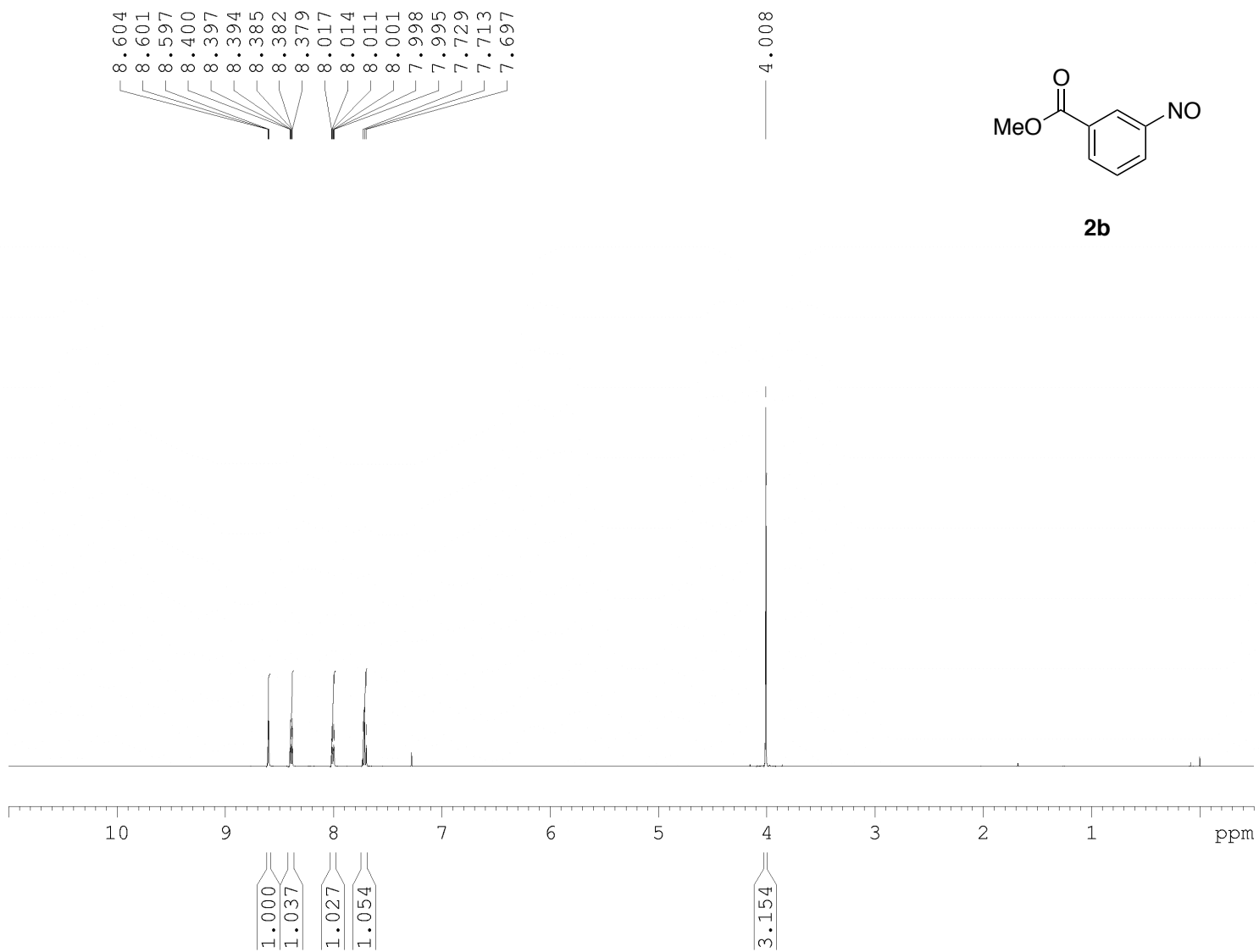


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 4-nitrophenol (1j)

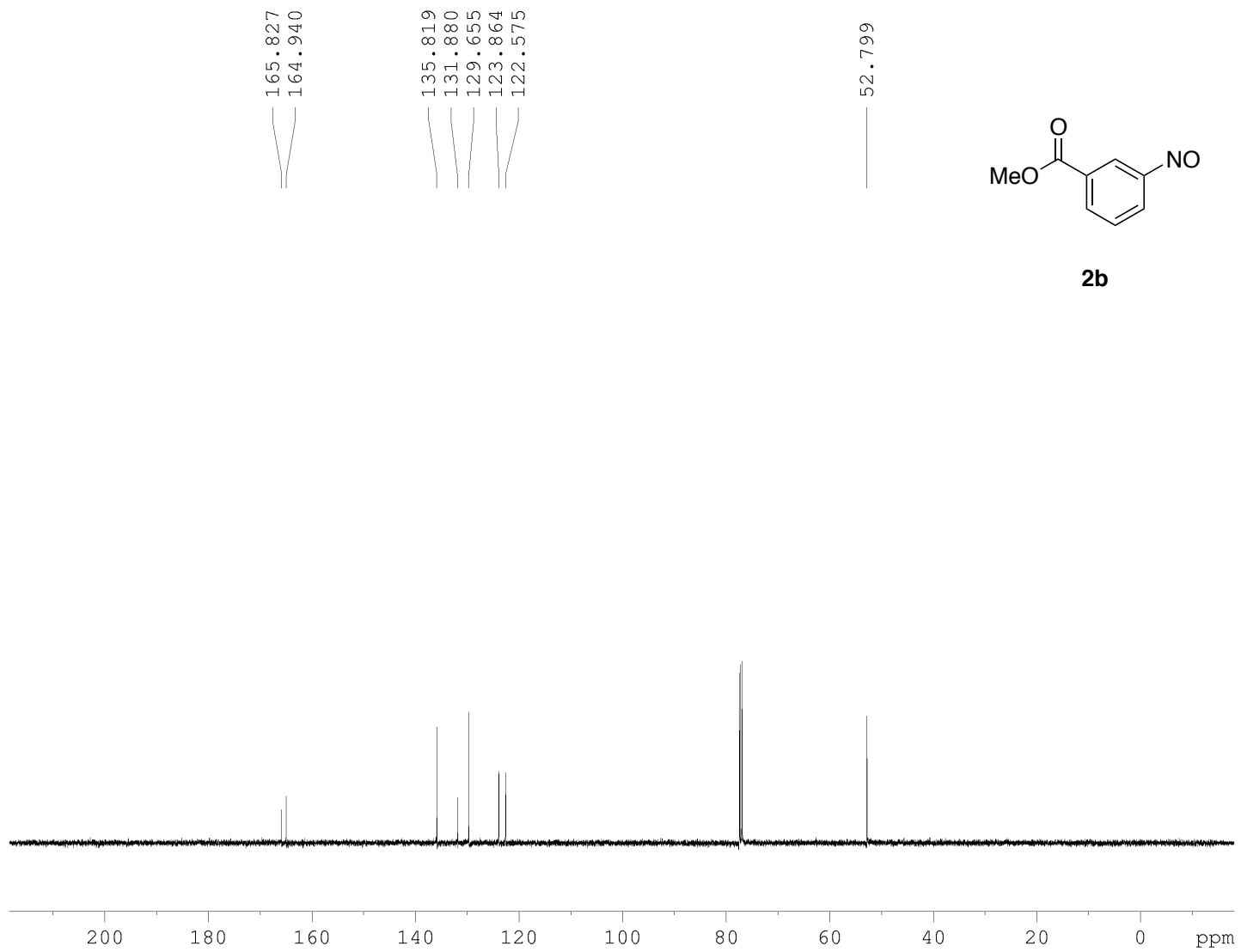


¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 4-nitrobenzoate (2a)

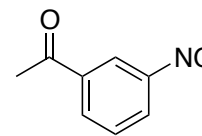
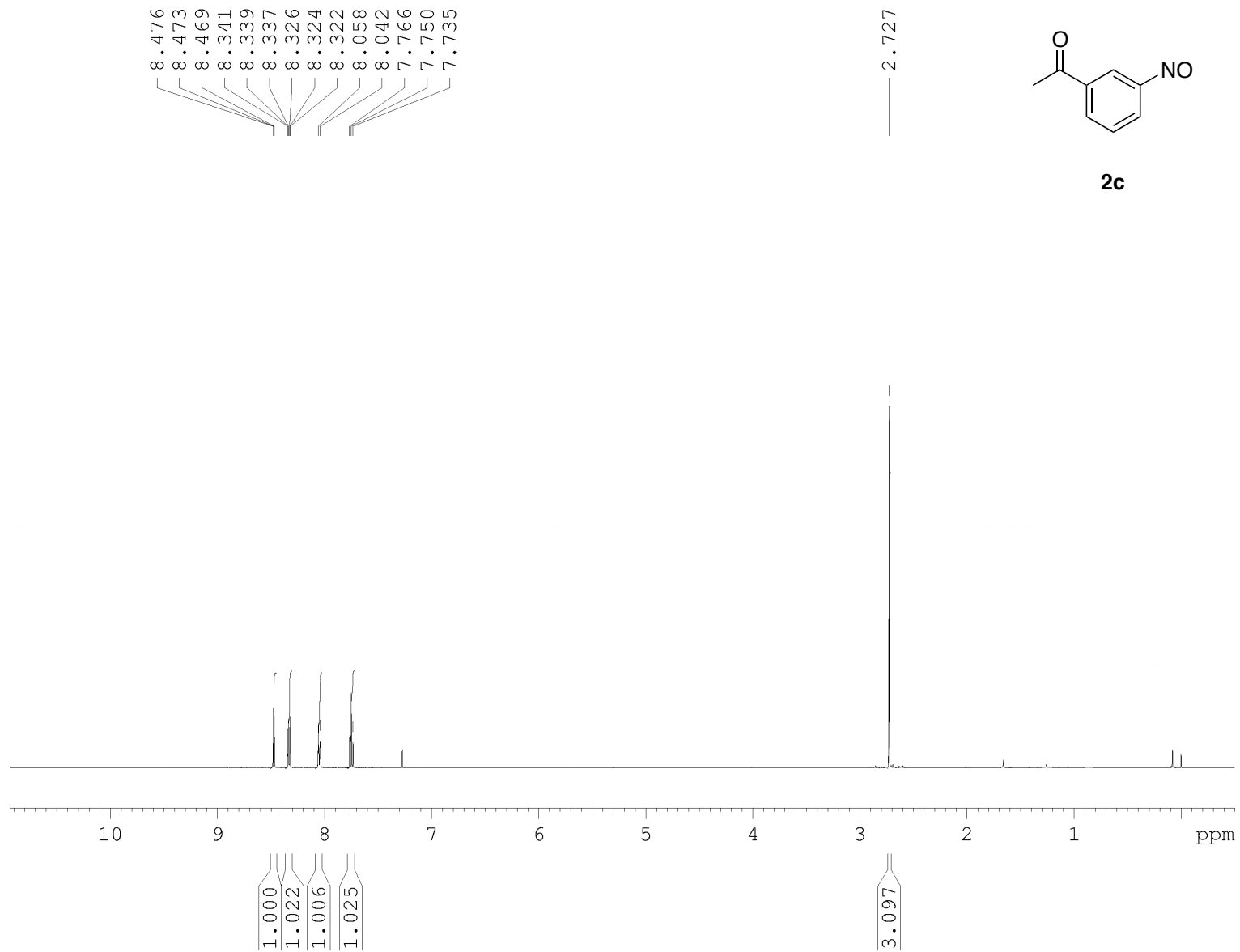




¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 3-nitrosobenzoate (2b)

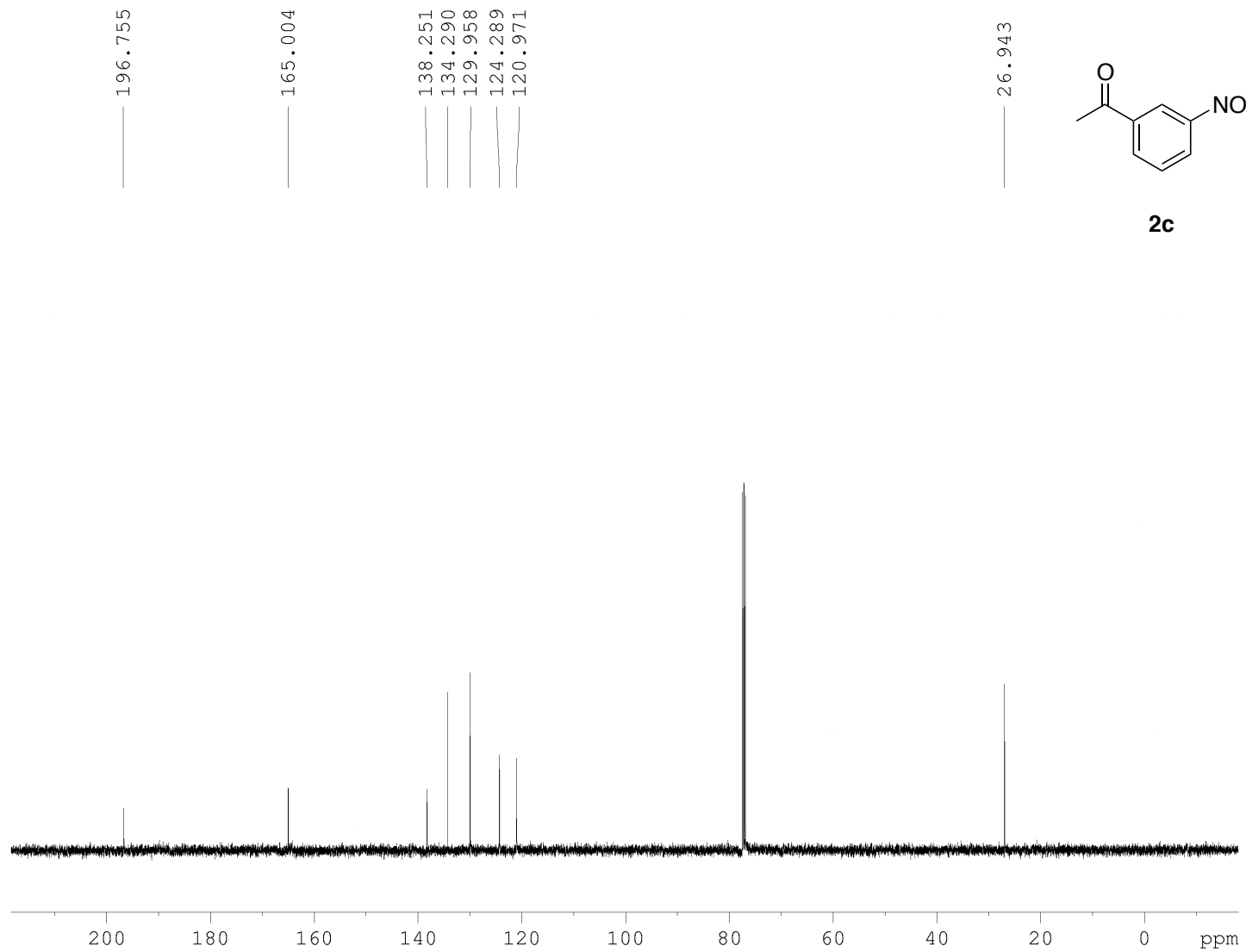


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of methyl 3-nitrosobenzoate (2b)

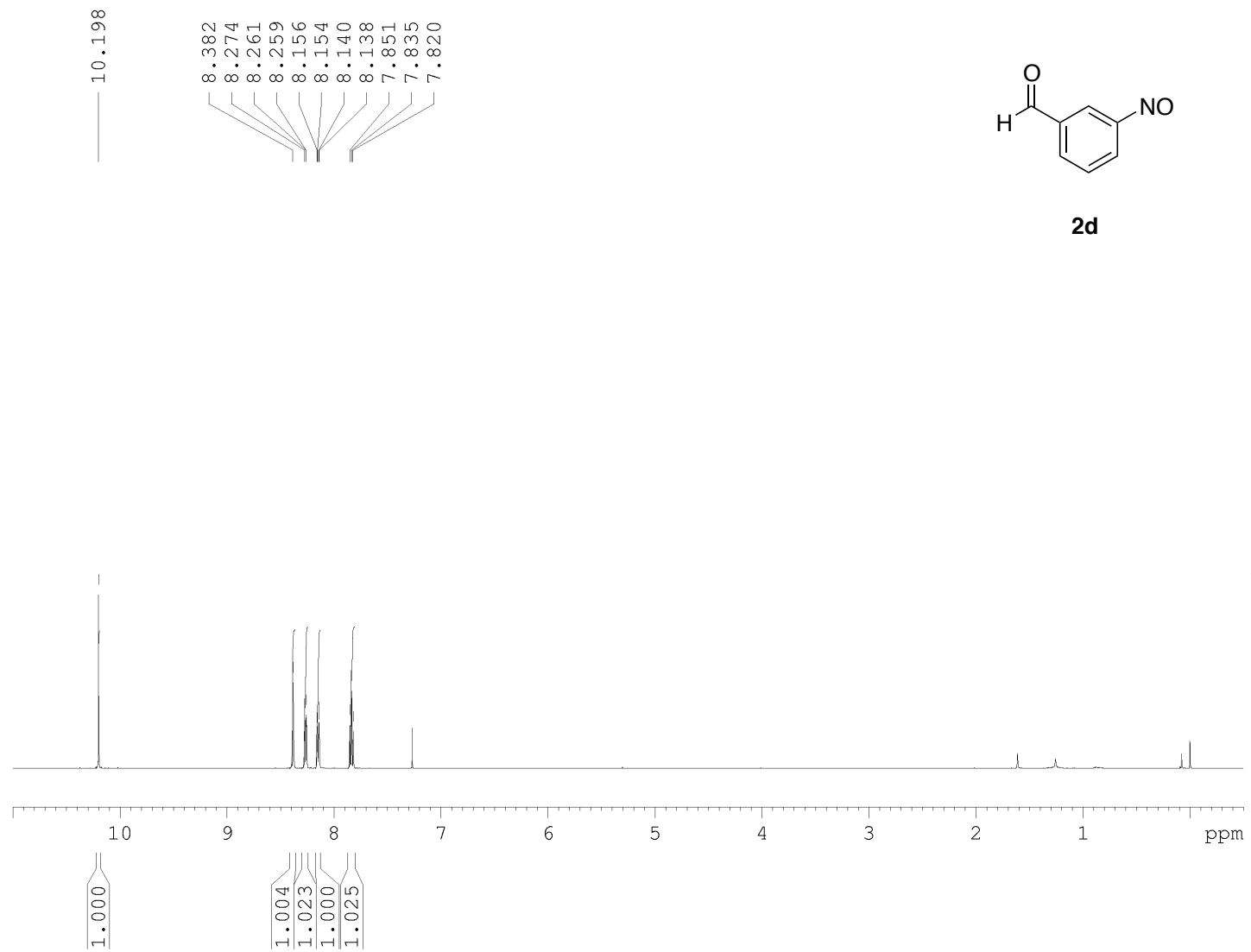


2c

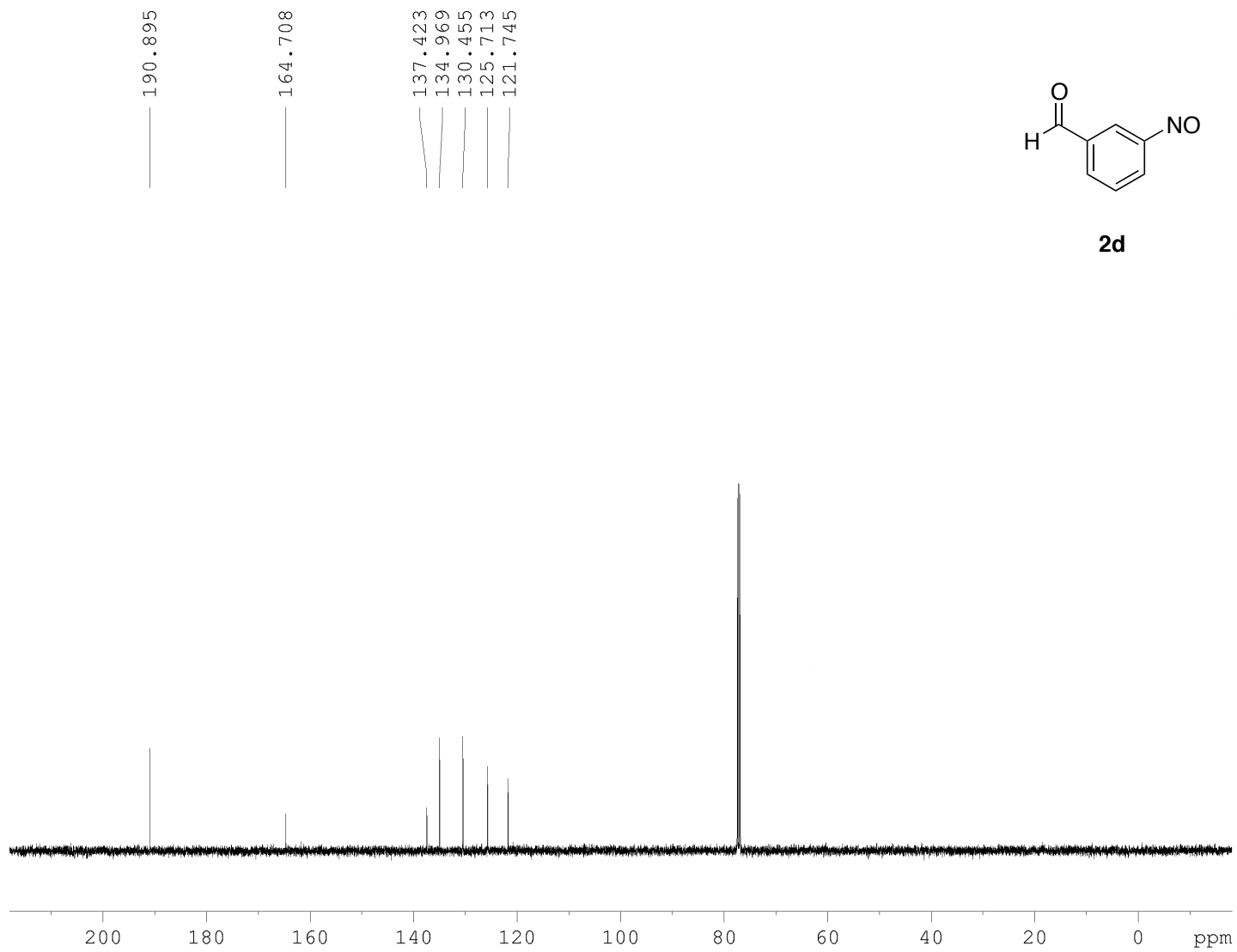
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-(3-nitrosophenyl)ethanone (2c)



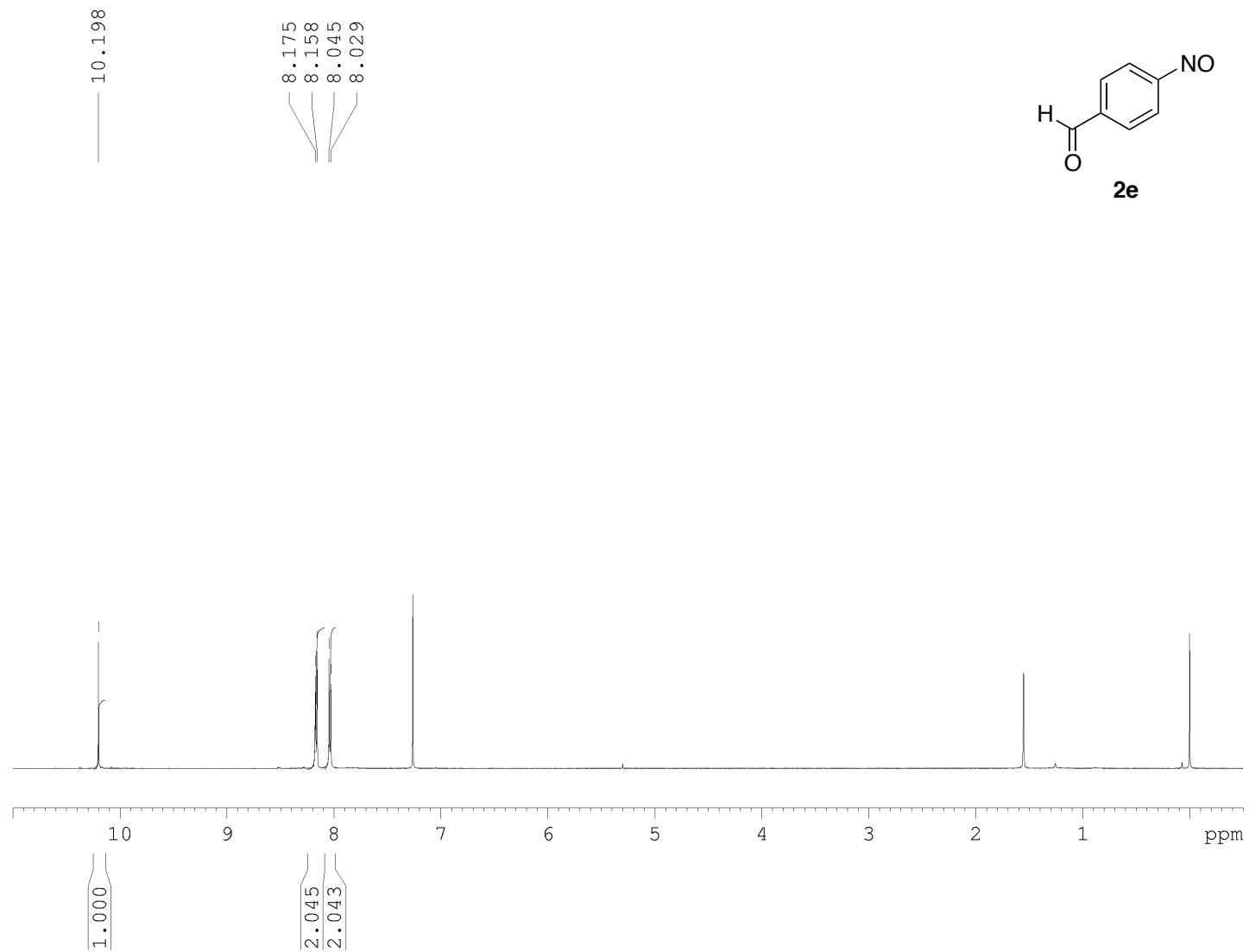
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-(3-nitrosophenyl)ethanone (2c)



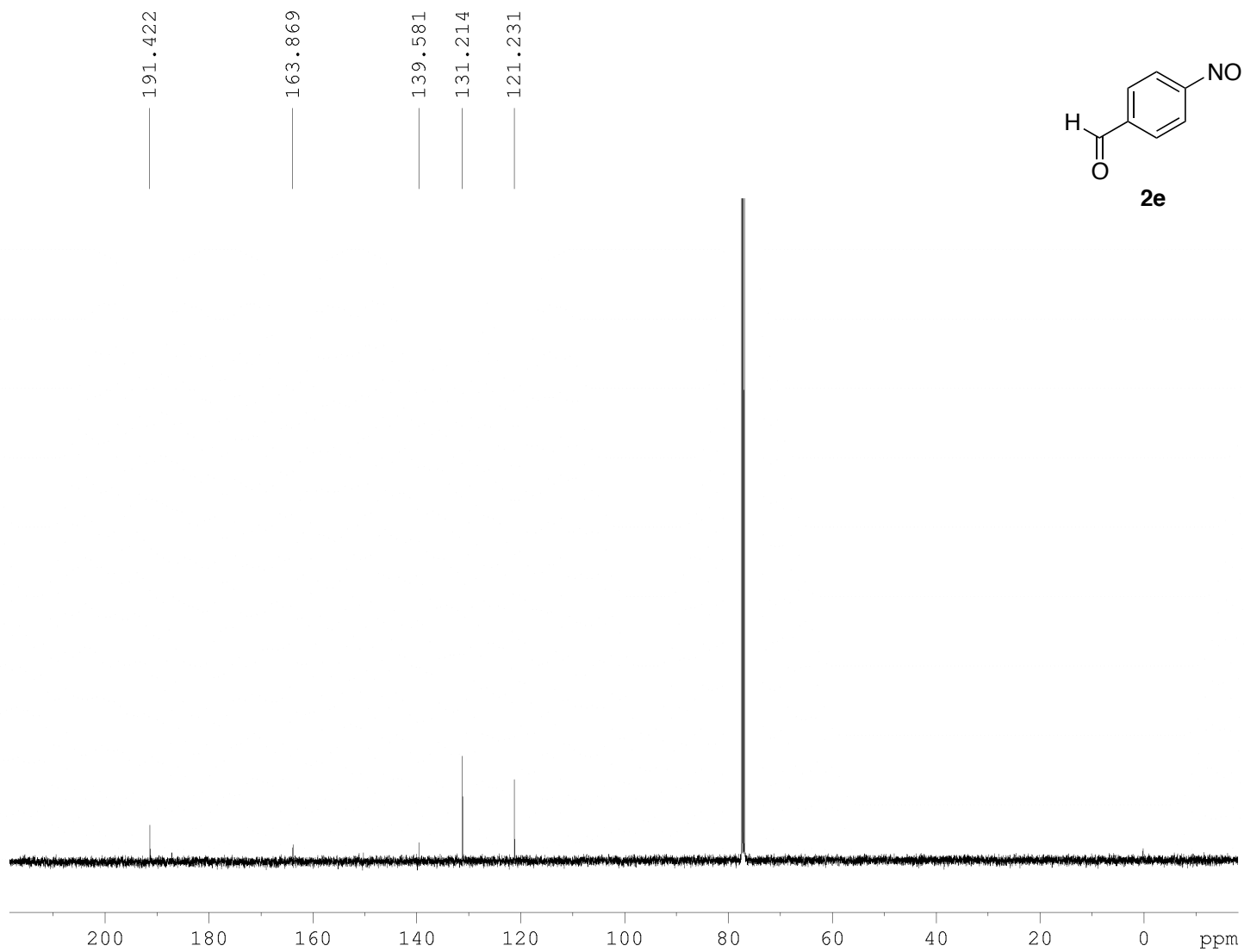
¹H NMR (500 MHz, CDCl₃) Spectrum of 3-nitrosobenzaldehyde (2d)



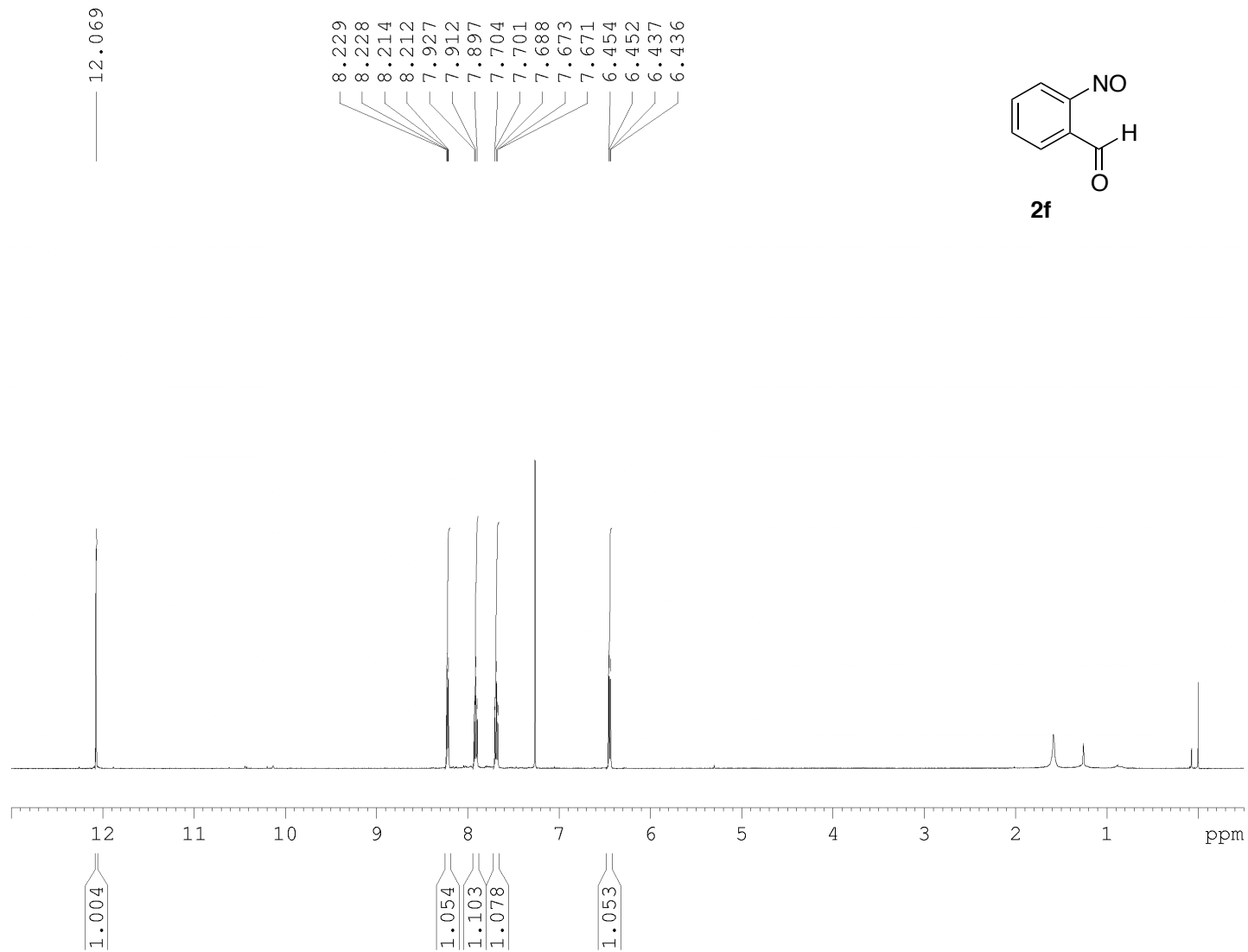
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 3-nitrosobenzaldehyde (2d)



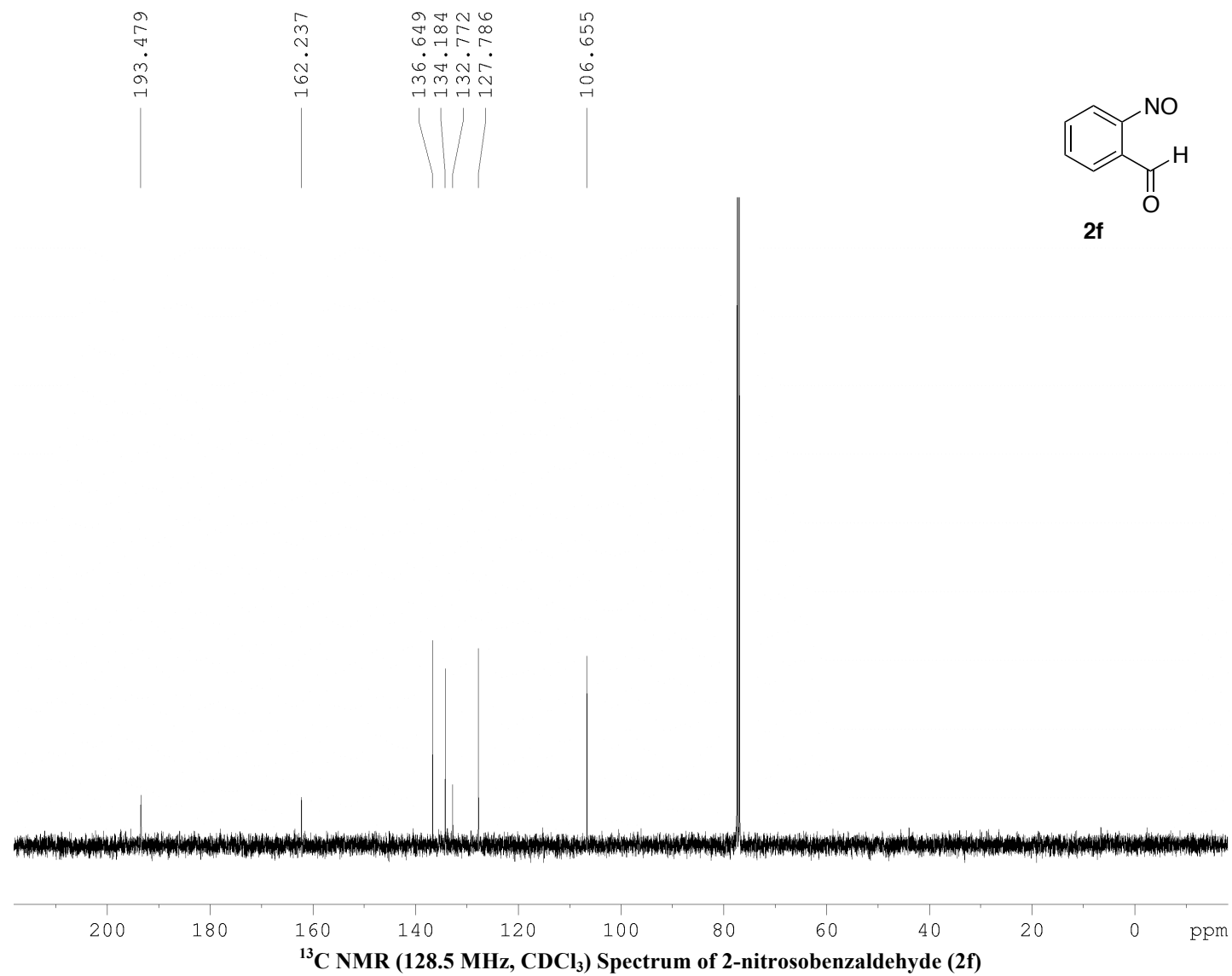
¹H NMR (500 MHz, CDCl₃) Spectrum of 4-nitrosobenzaldehyde (2e)



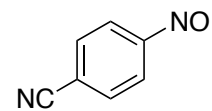
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-nitrosobenzaldehyde (2e)



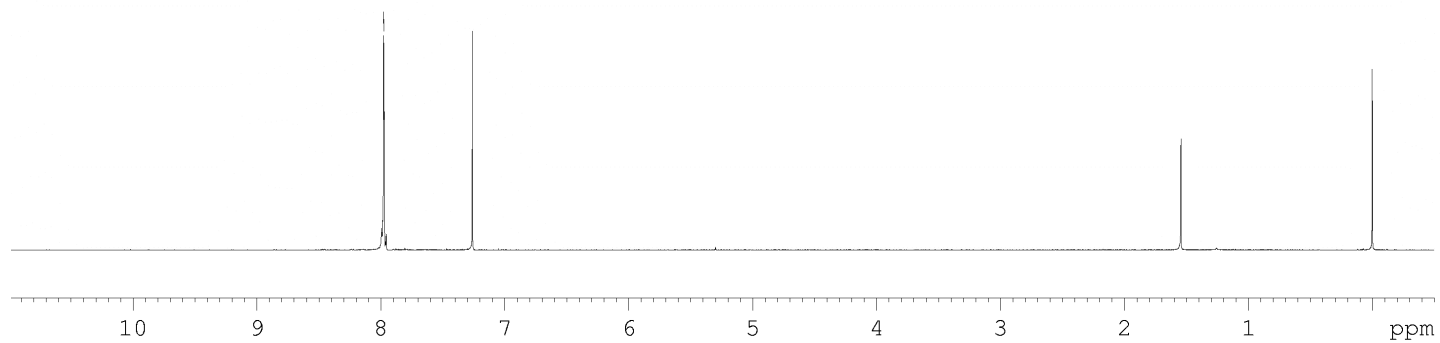
^1H NMR (500 MHz, CDCl_3) Spectrum of 2-nitrosobenzaldehyde (2f)



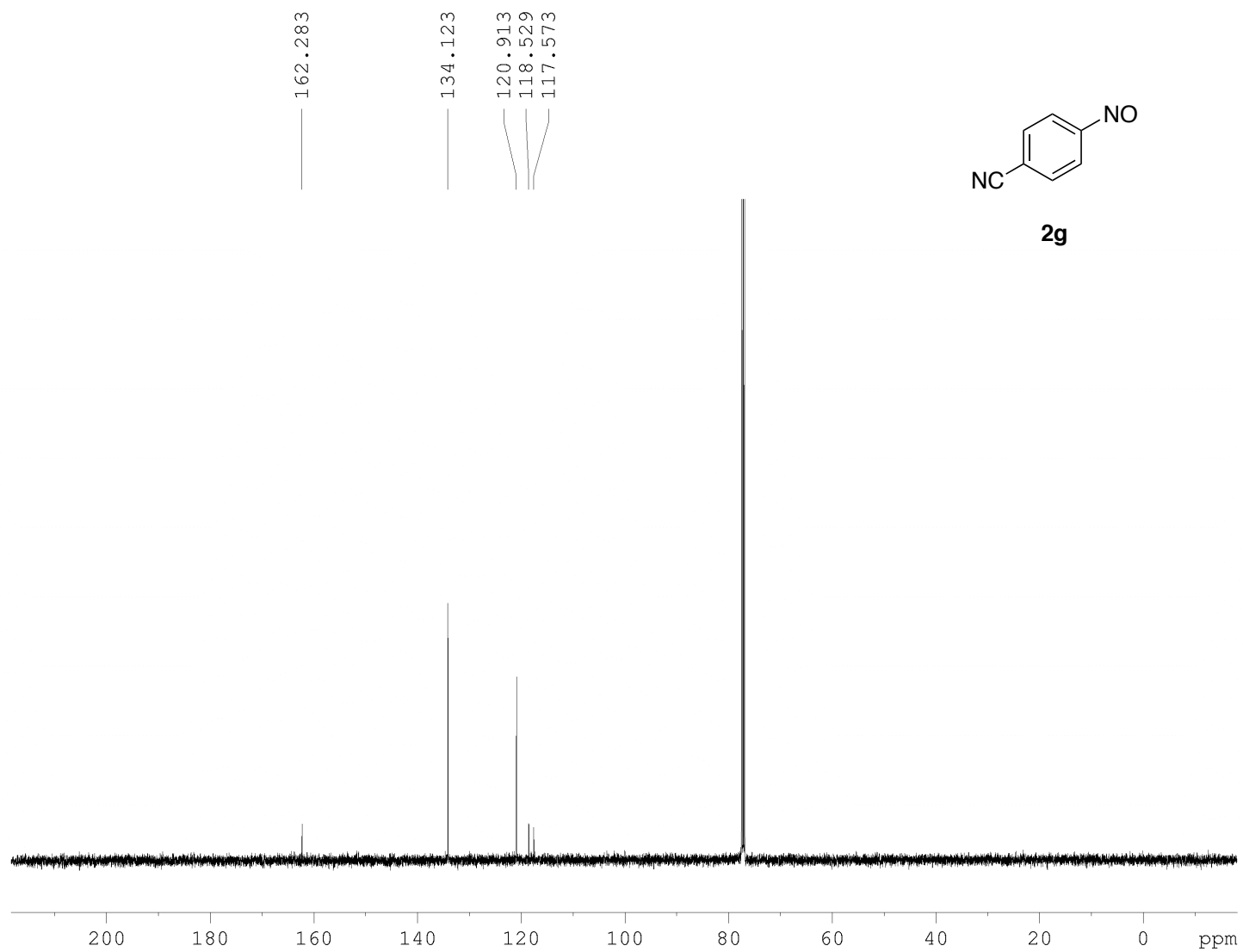
7.978
7.975



2g

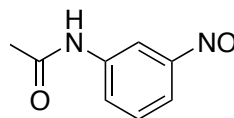


¹H NMR (500 MHz, CDCl₃) Spectrum of 4-nitrosobenzonitrile (2g)



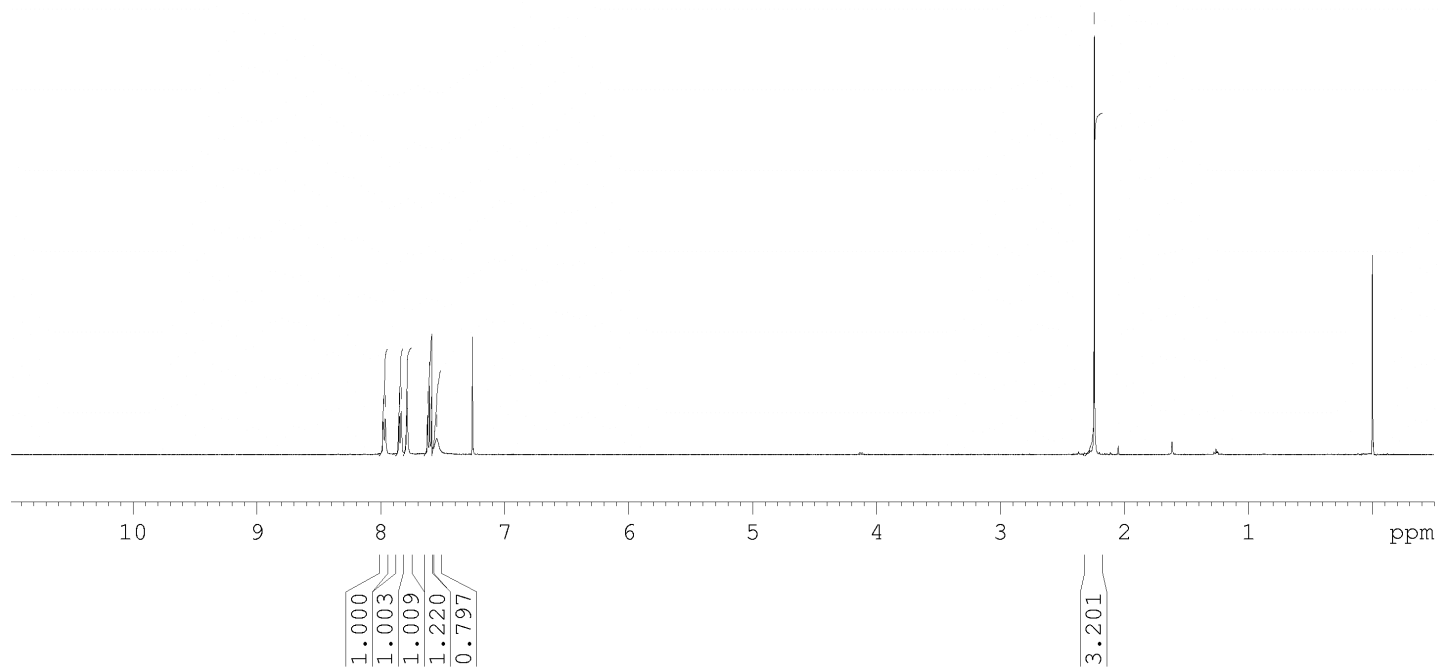
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-nitrosobenzonitrile (2g)

7.980
7.964
7.852
7.836
7.788
7.622
7.607
7.591
7.550

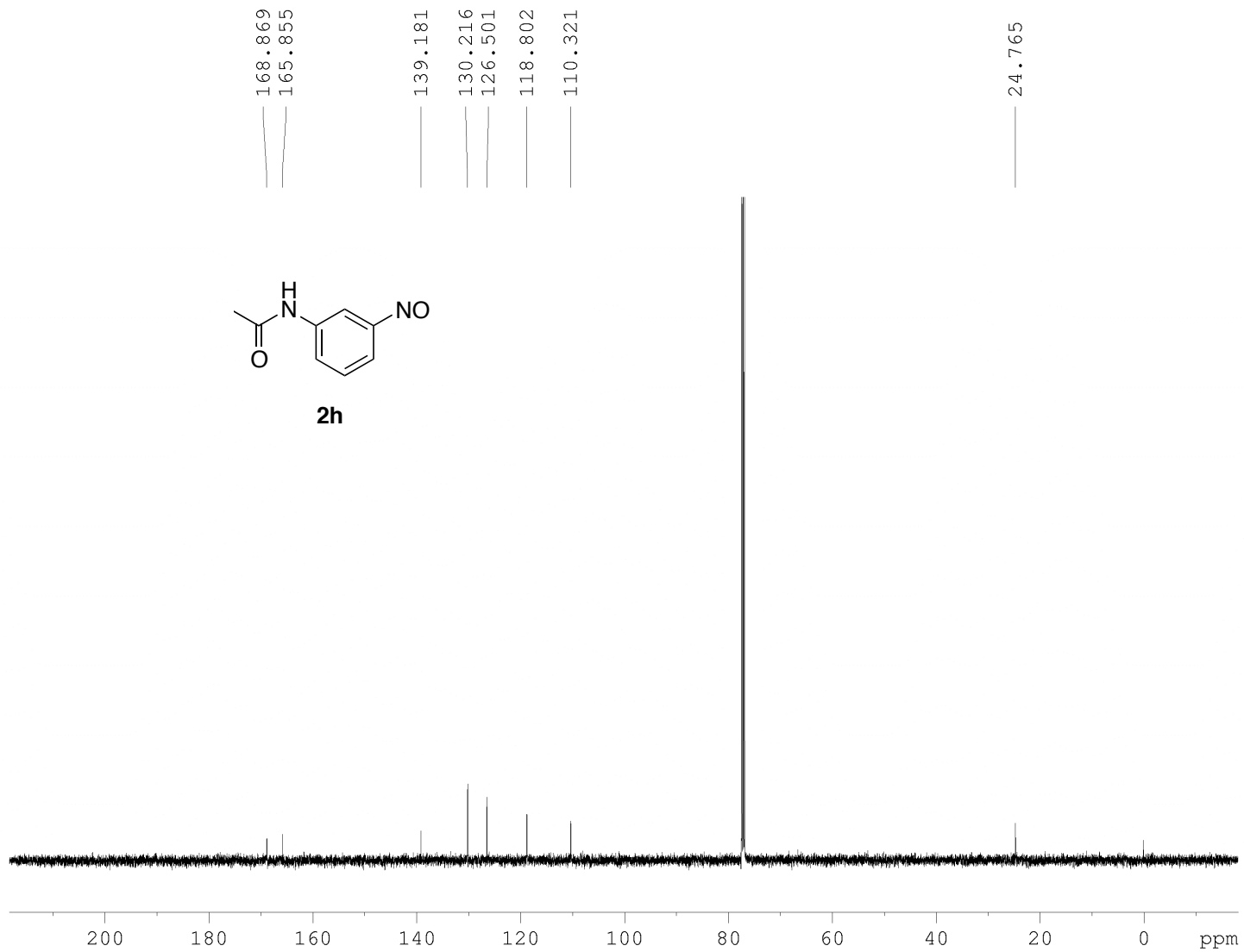


2h

2.243

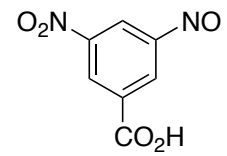


¹H NMR (500 MHz, CDCl₃) Spectrum of *N*-(3-nitrosophenyl)acetamide (2h)

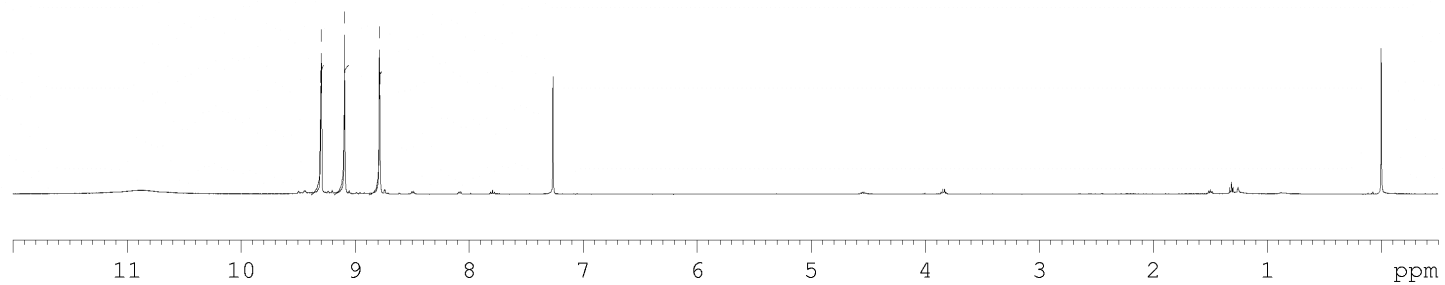


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of *N*-(3-nitrosophenyl)acetamide (2h)

9.301
9.297
9.294
9.093
8.790
8.786
8.783

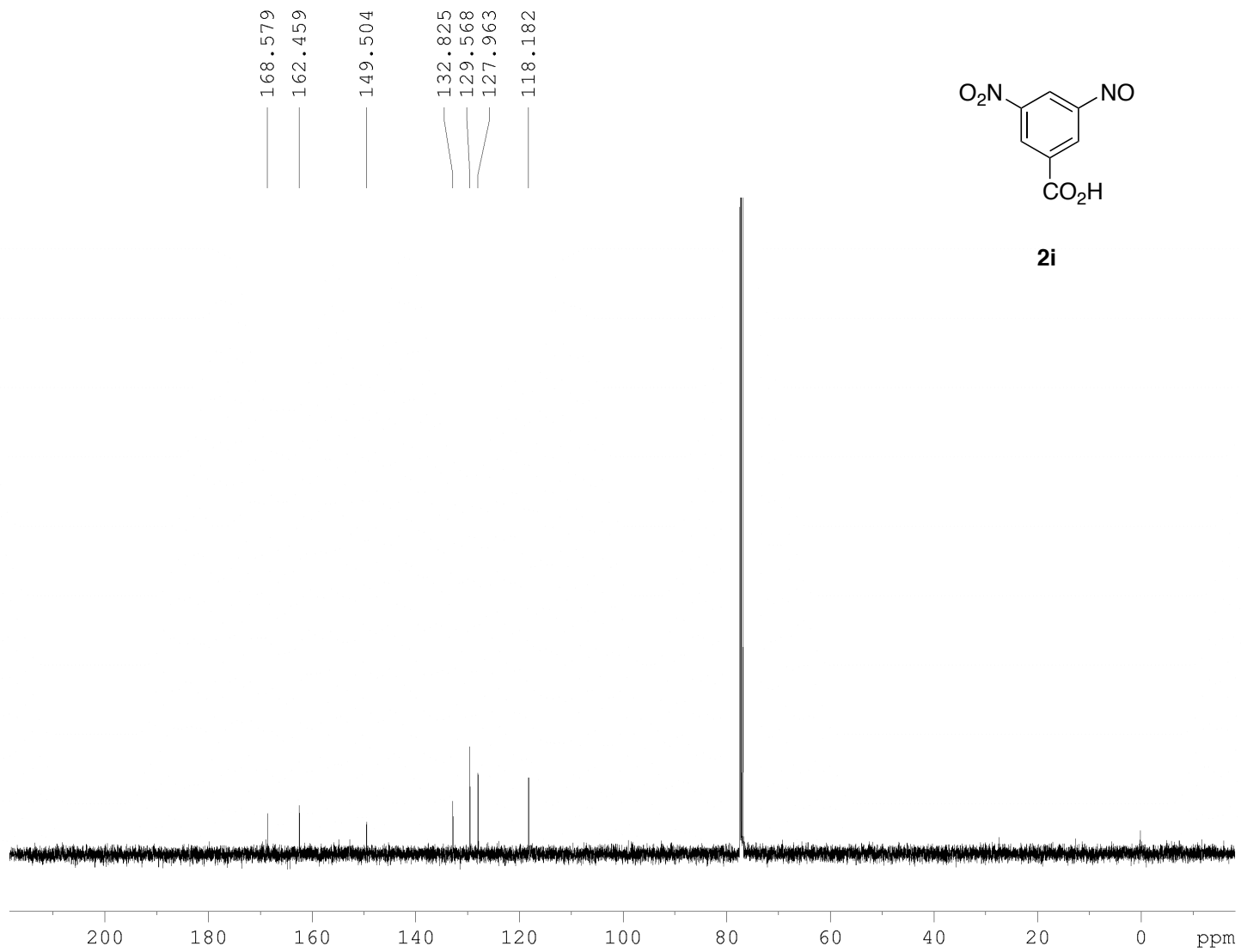


2i

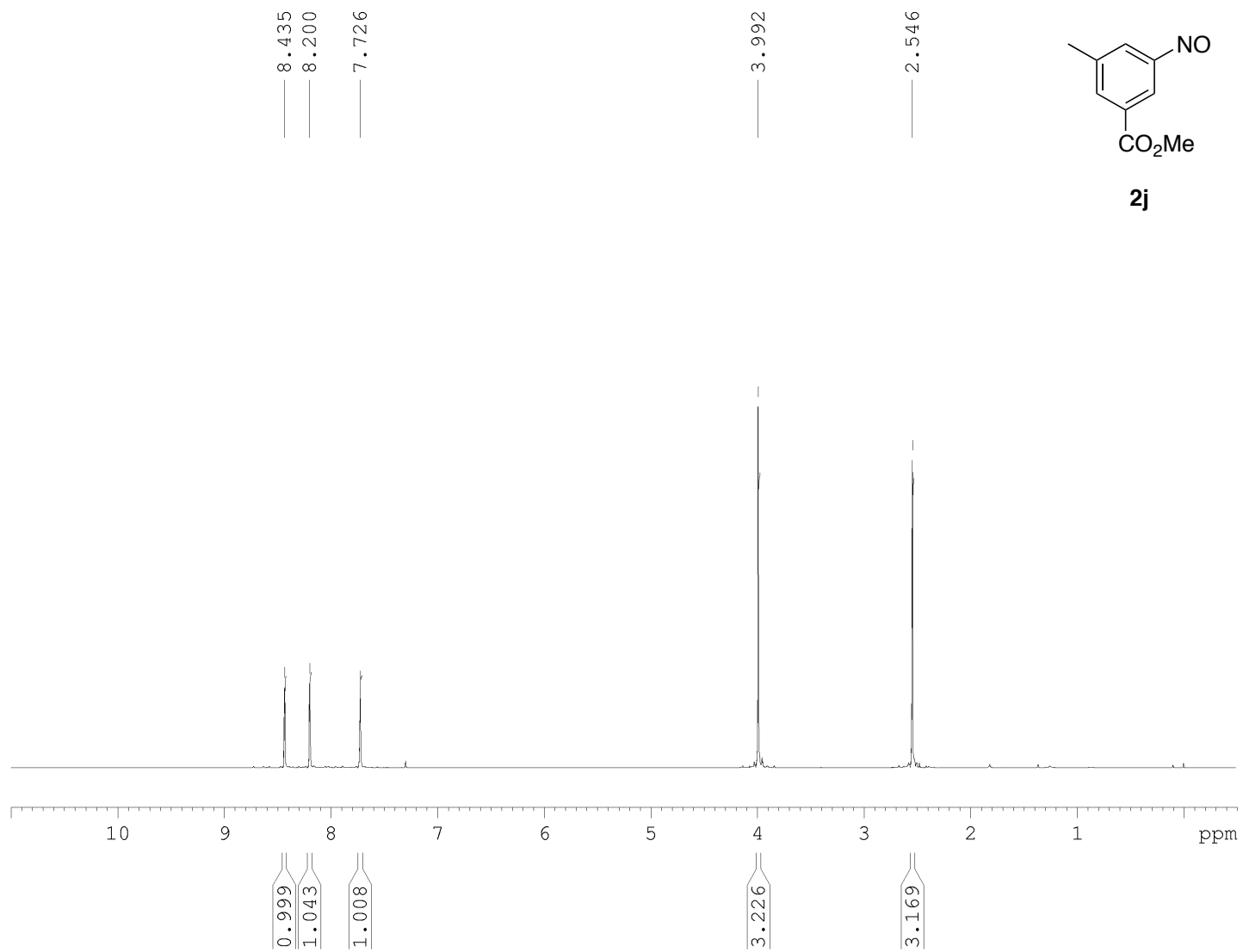


1.000
1.005
0.953

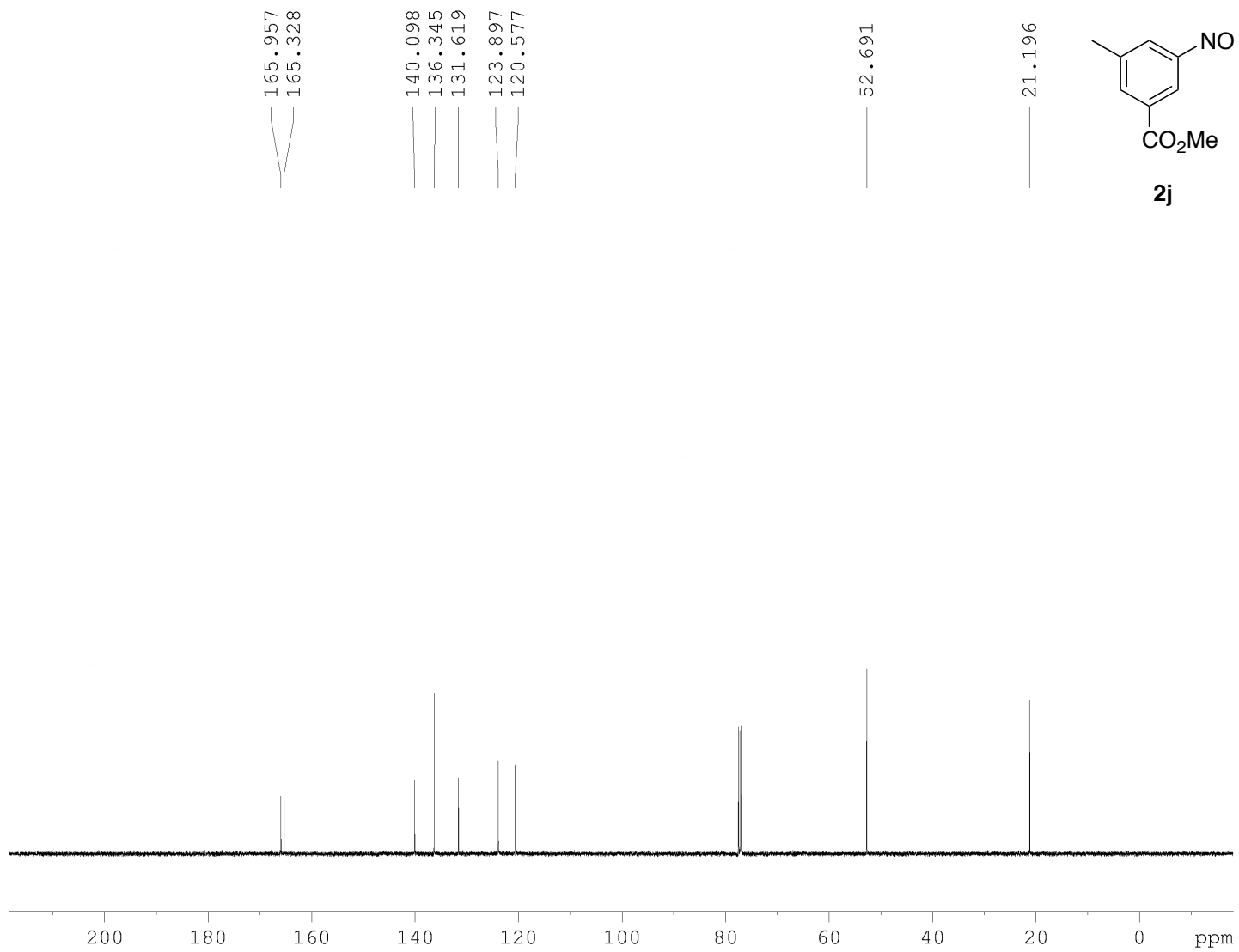
¹H NMR (500 MHz, CDCl₃) Spectrum of 3-nitro-5-nitrosobenzoic acid (2i)



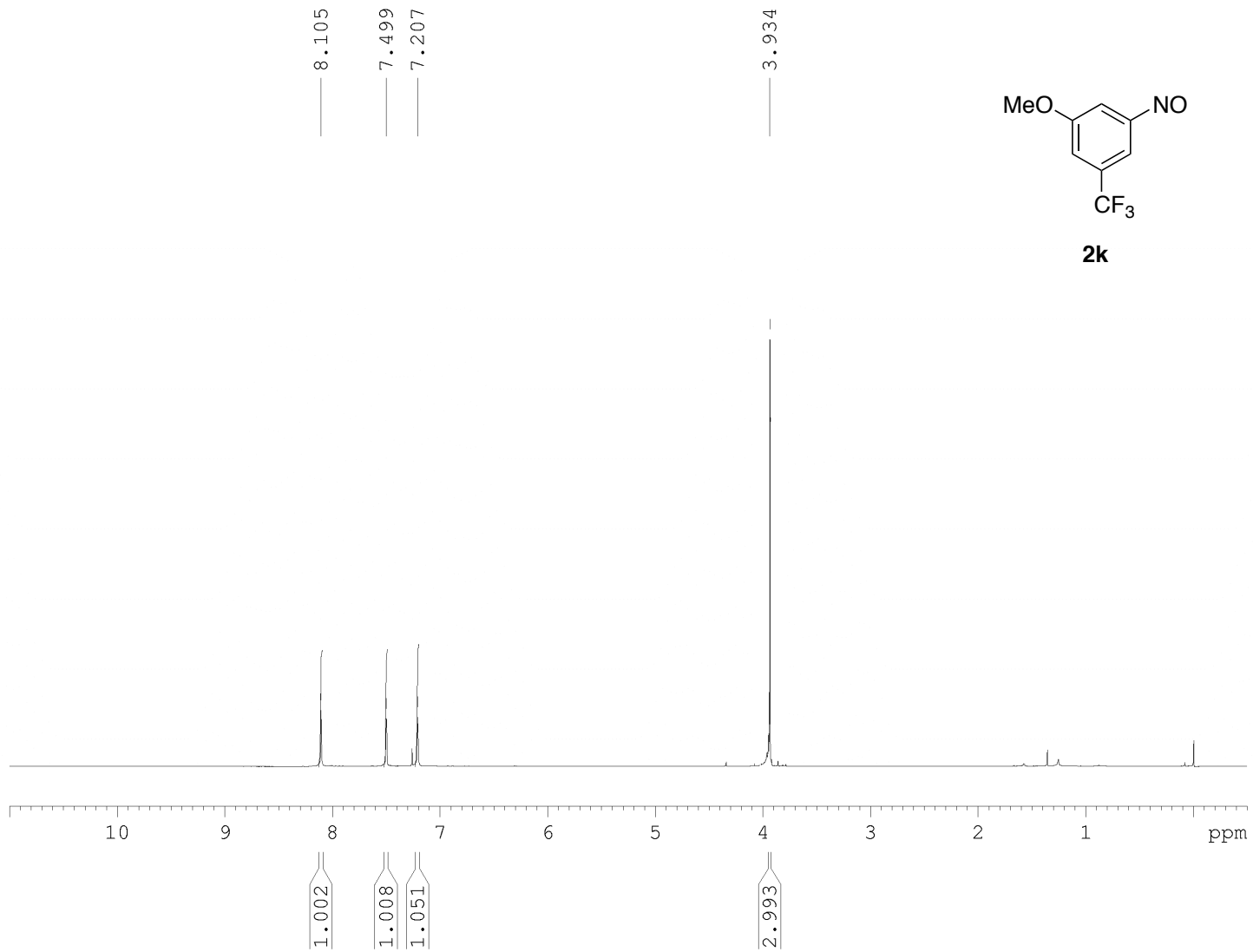
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 3-nitro-5-nitrosobenzoic acid (2i)



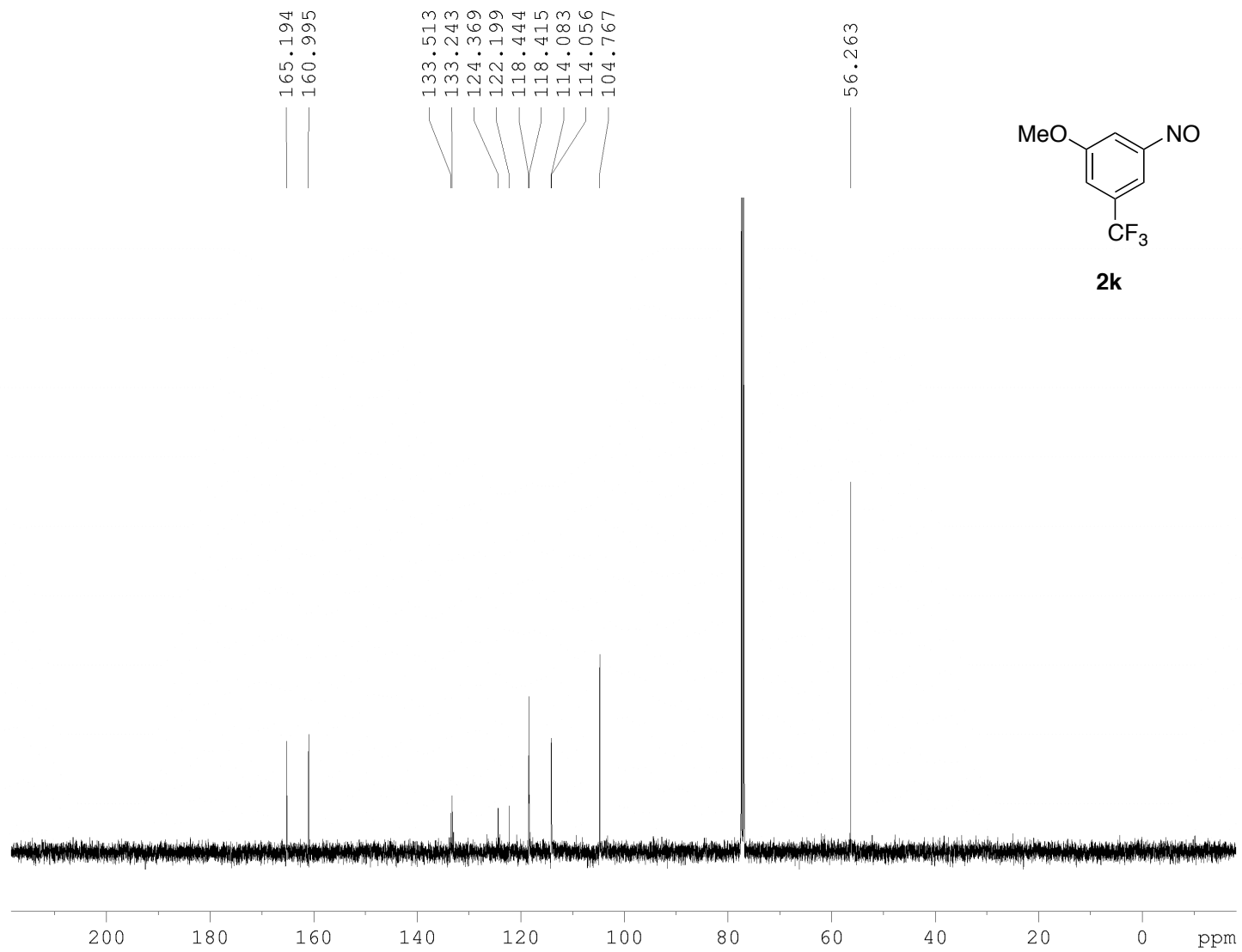
¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 3-methyl-5-nitrosobenzoate (2j)

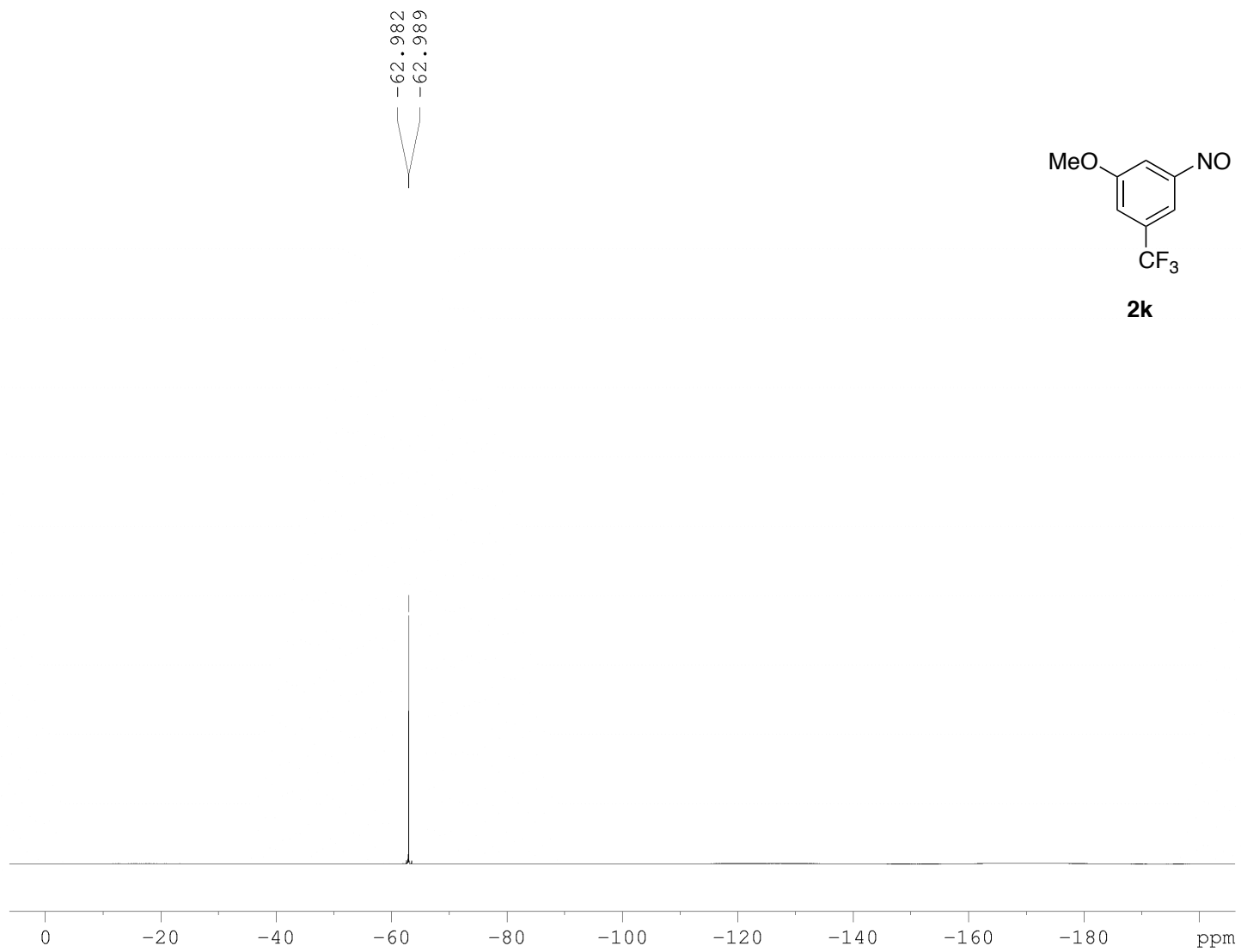


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of methyl 3-methyl-5-nitrosobenzoate (2j)

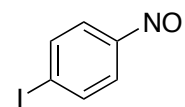


¹H NMR (500 MHz, CDCl₃) Spectrum of 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene (2k)

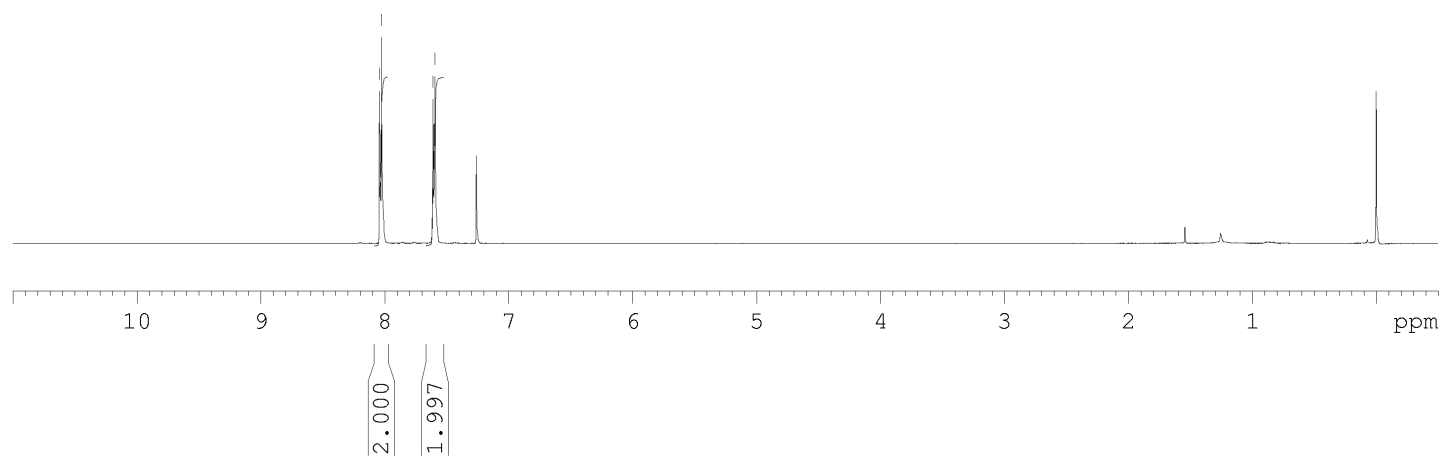




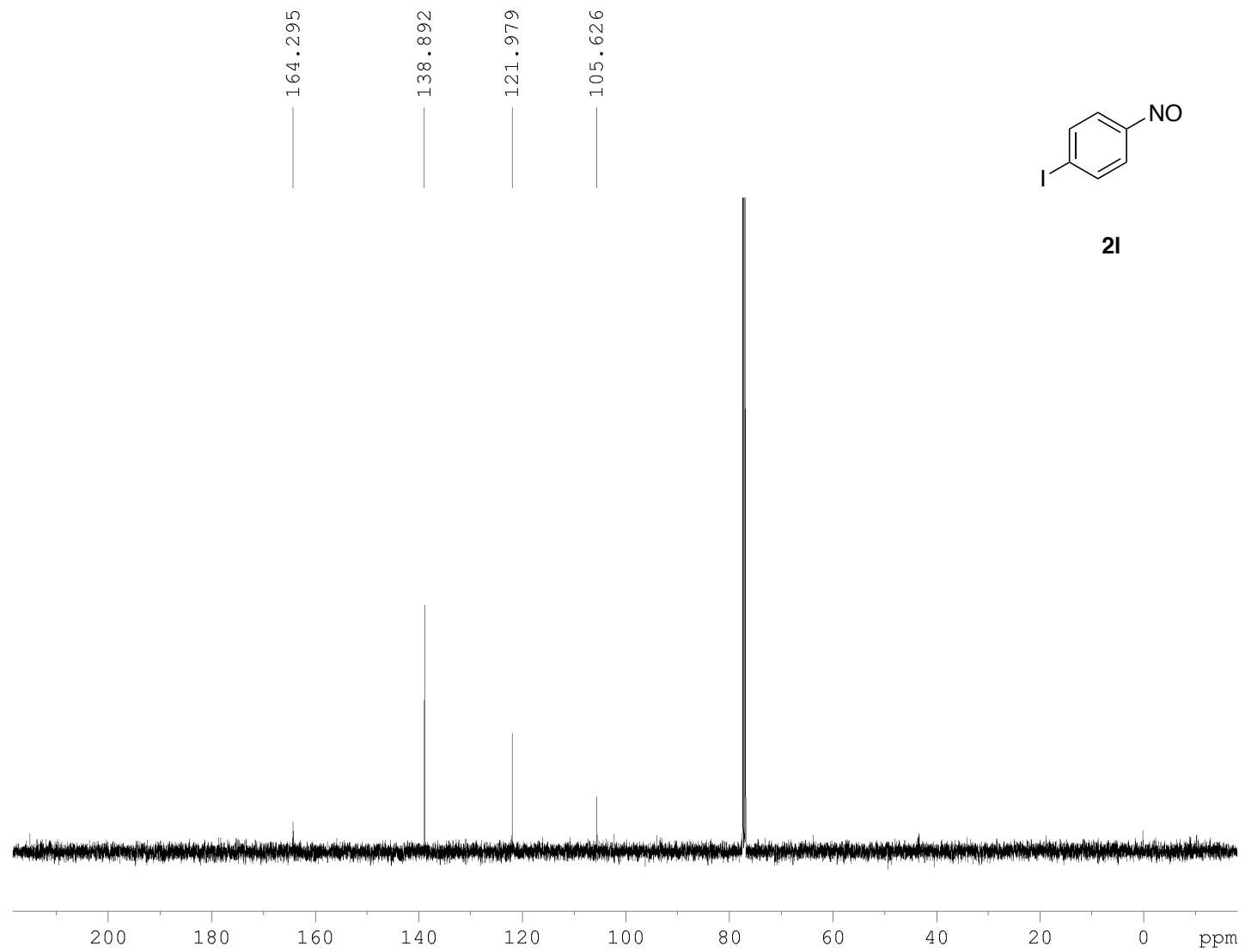
8.043
8.026
7.613
7.596



21

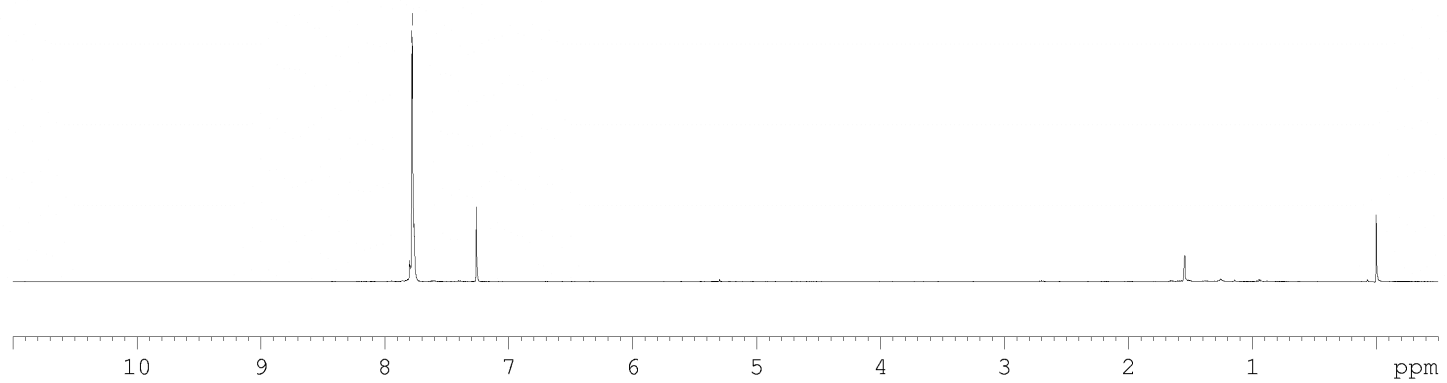
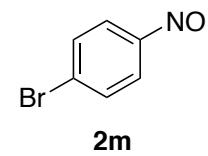


¹H NMR (500 MHz, CDCl₃) Spectrum of 1-iodo-4-nitrosobenzene (21)

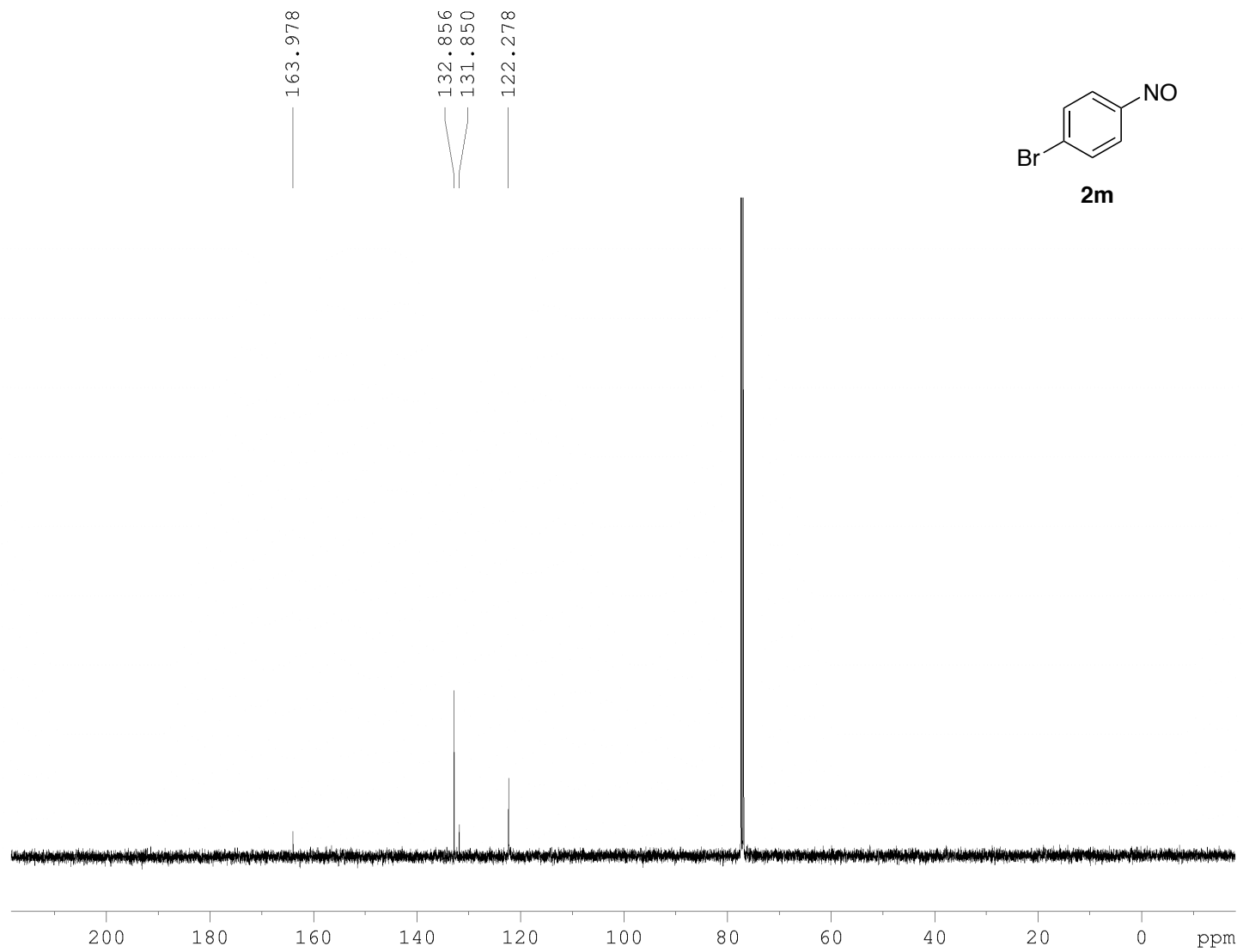


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-iodo-4-nitrosobenzene (21).

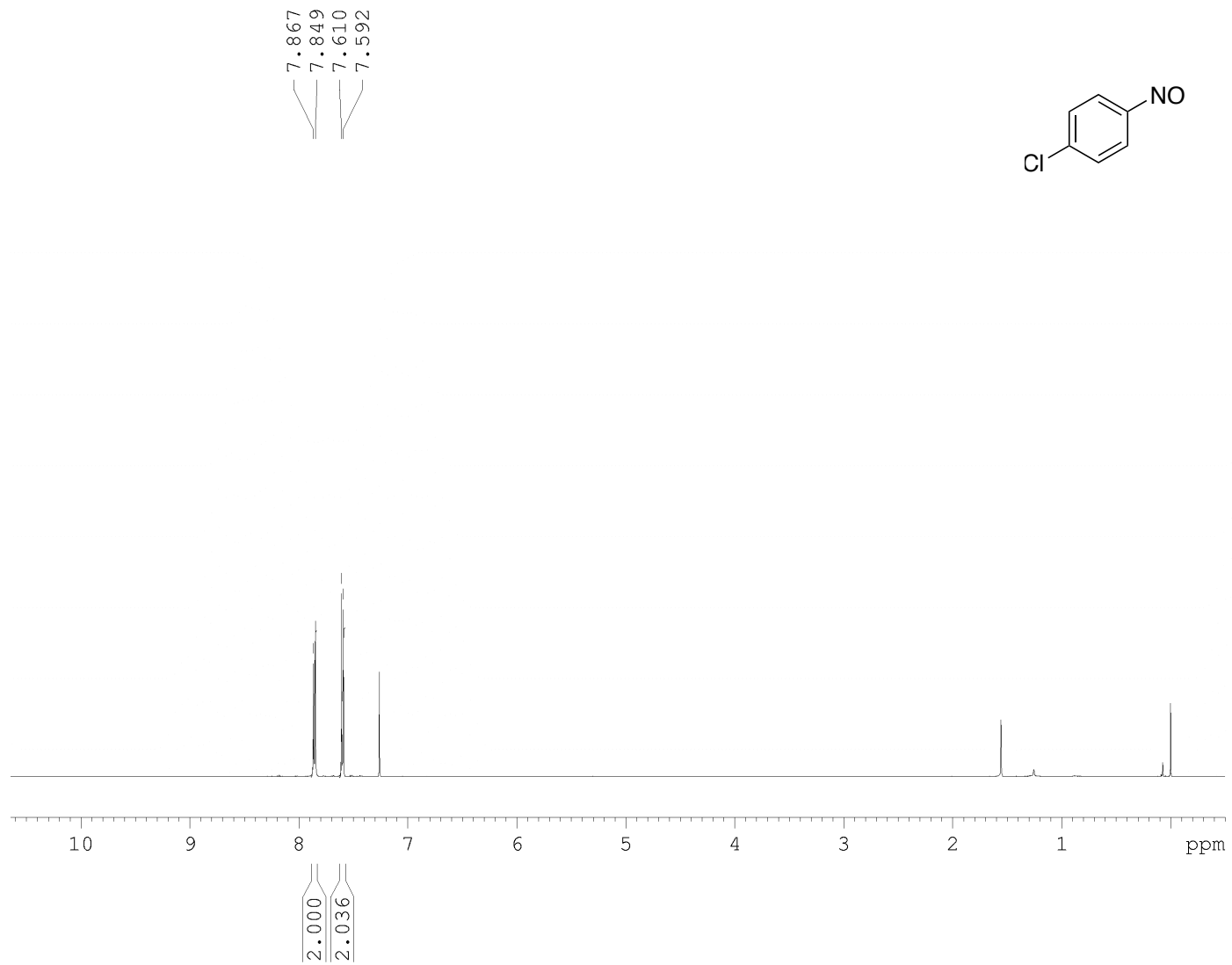
7.782
7.778



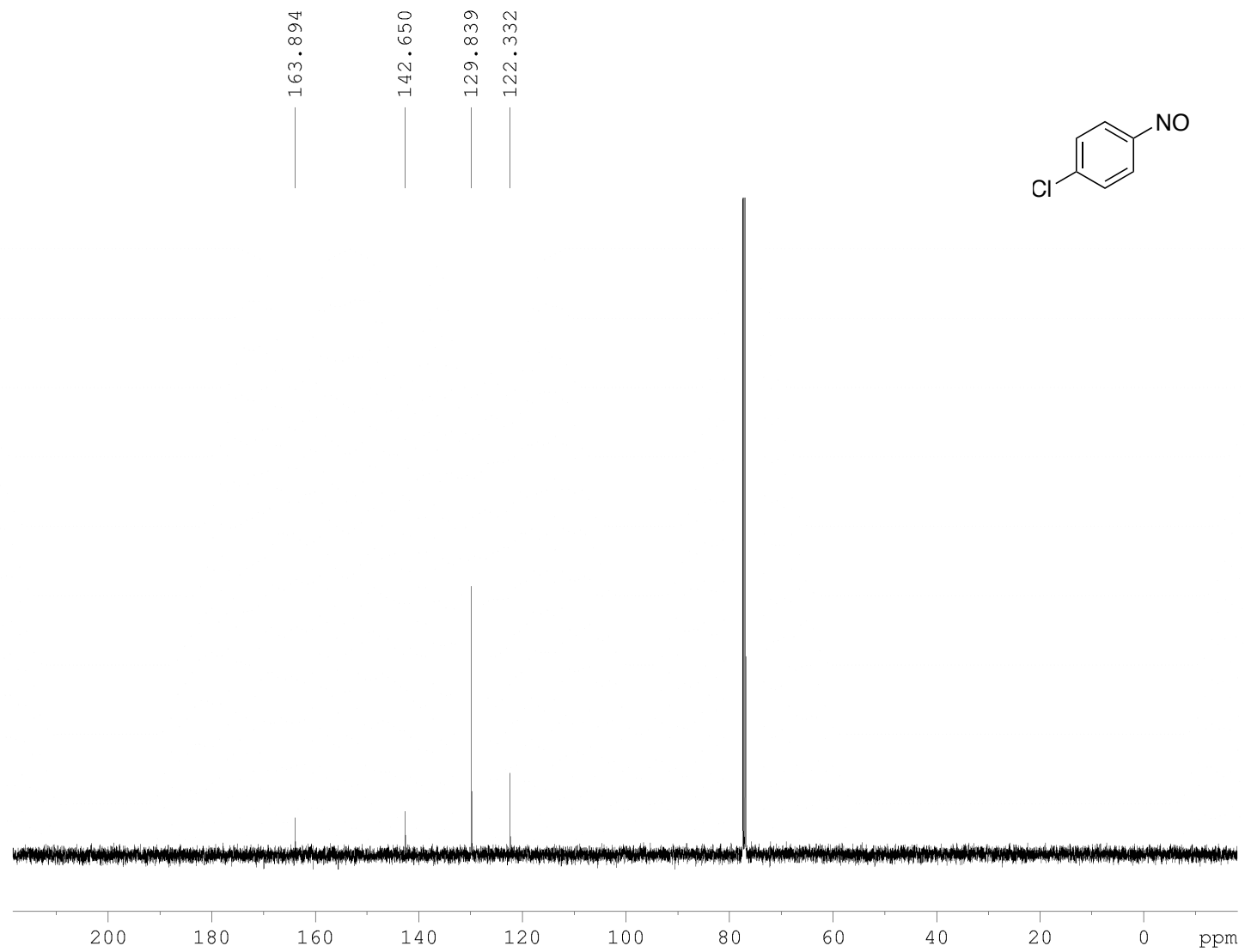
¹H NMR (500 MHz, CDCl₃) Spectrum of 1-bromo-4-nitrosobenzene (2m)



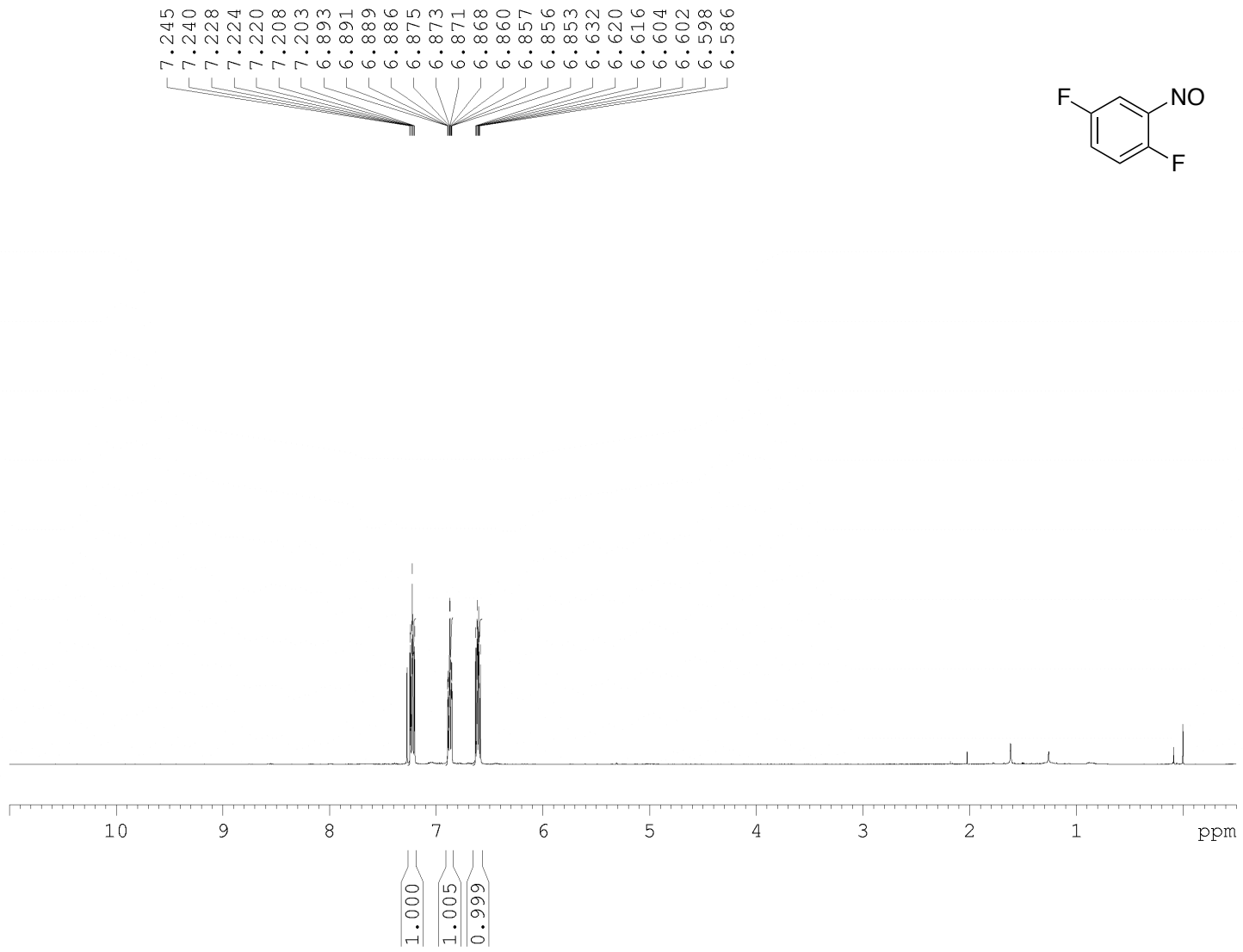
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-bromo-4-nitrosobenzene (2m)



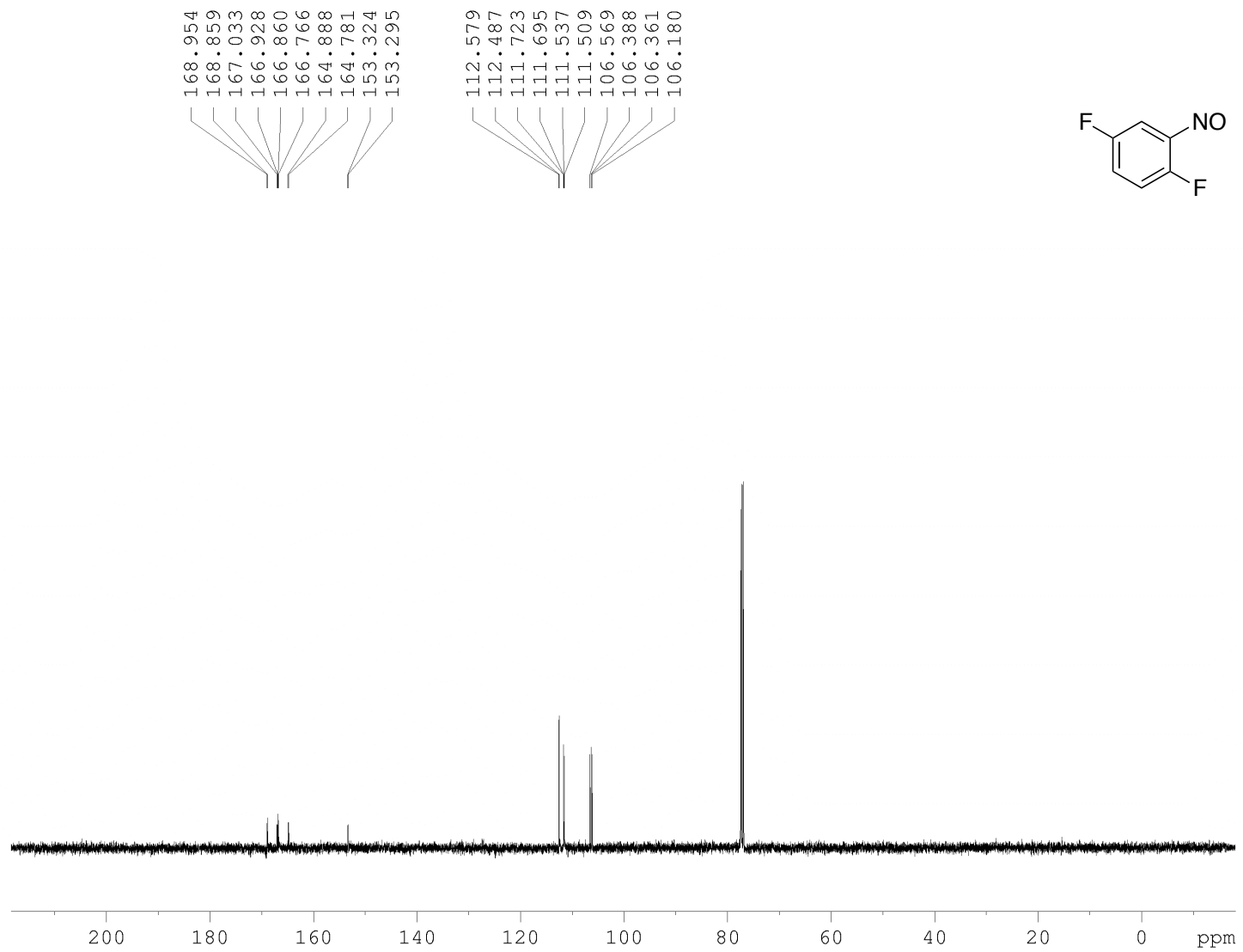
^1H NMR (500 MHz, CDCl_3) Spectrum of 1-chloro-4-nitrosobenzene (2n)



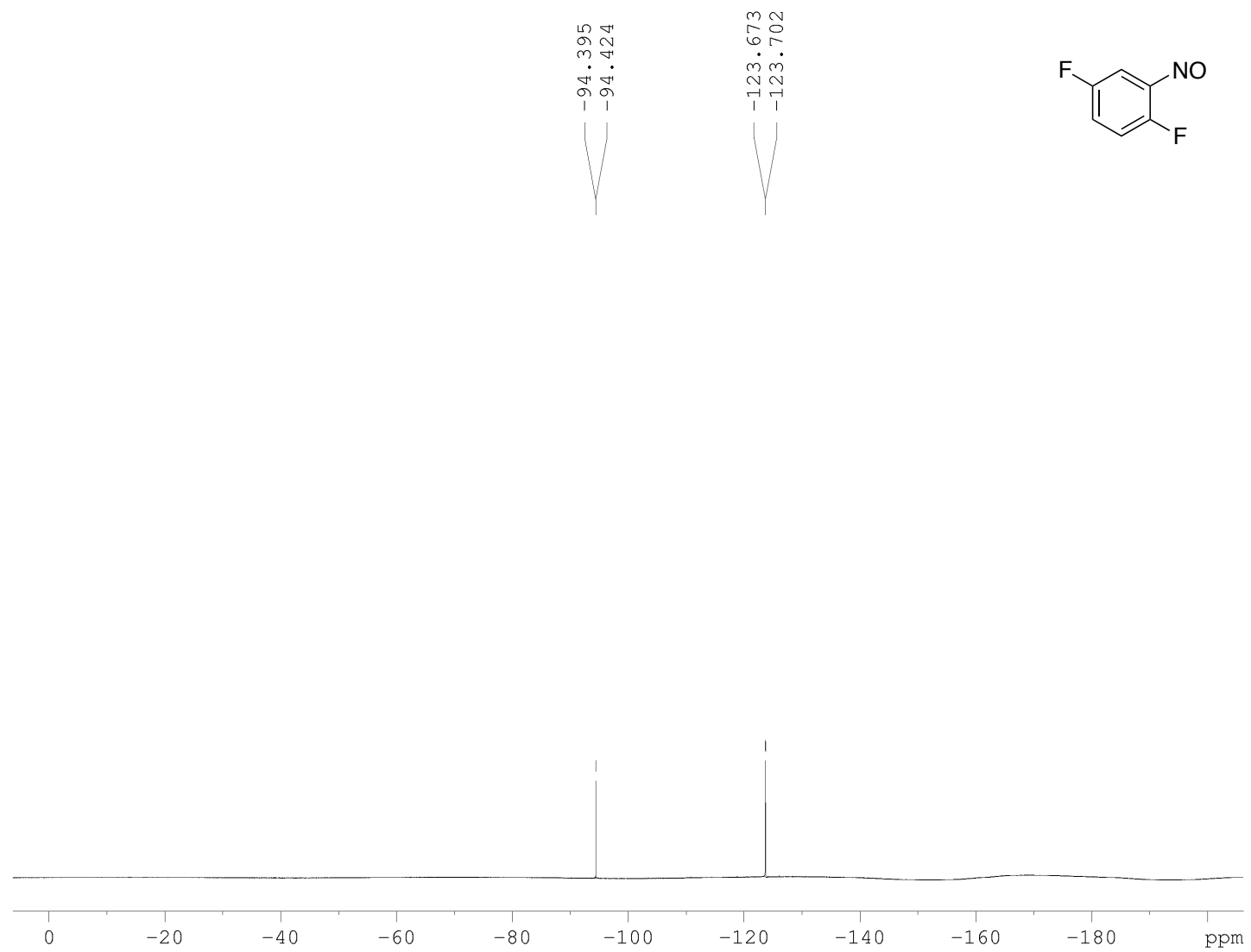
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1-chloro-4-nitrosobenzene (2n)



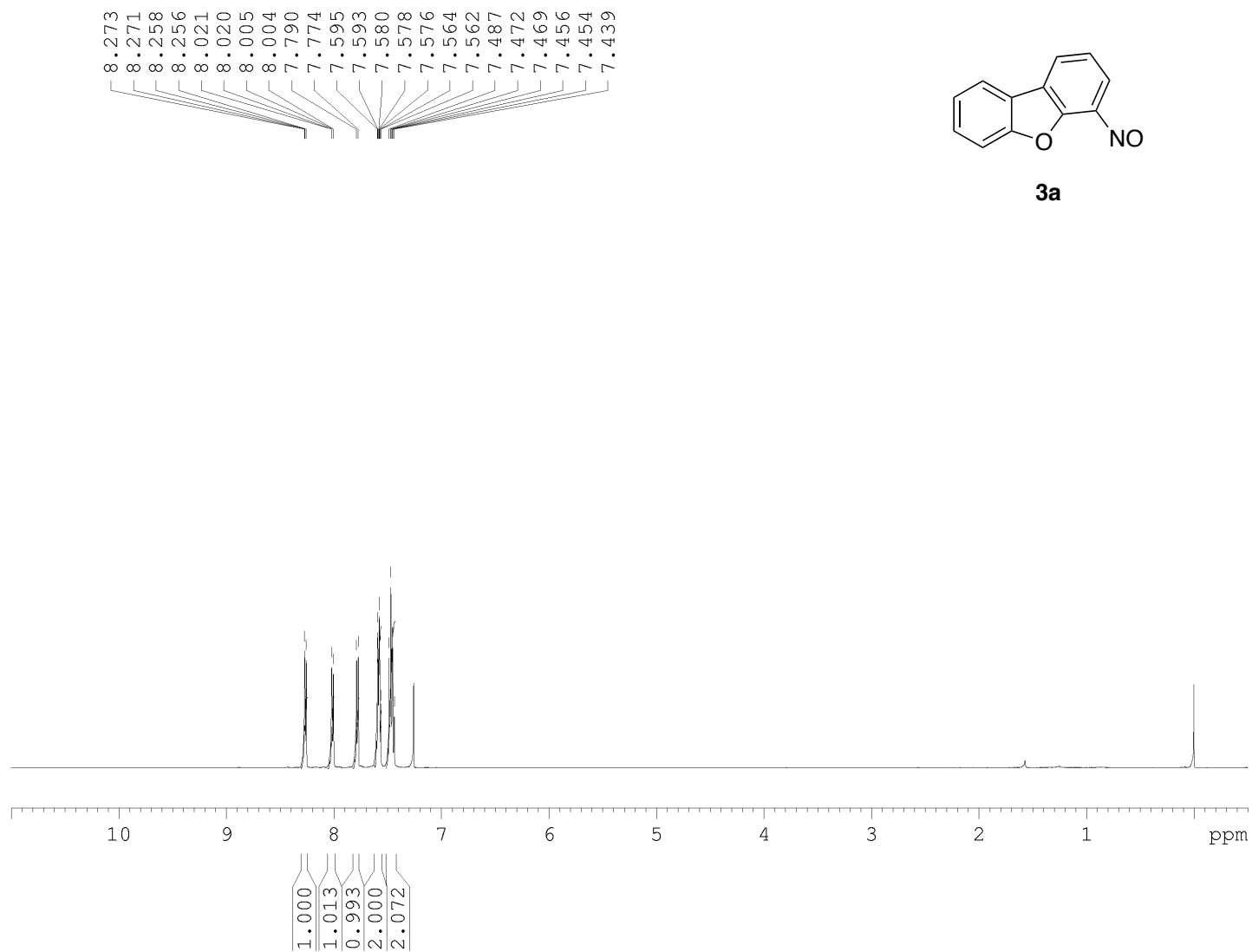
¹H NMR (500 MHz, CDCl₃) Spectrum of 1,4-difluoro-2-nitrosobenzene (2o)



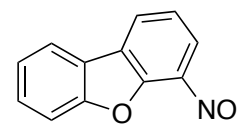
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 1,4-difluoro-2-nitrosobenzene (2o)



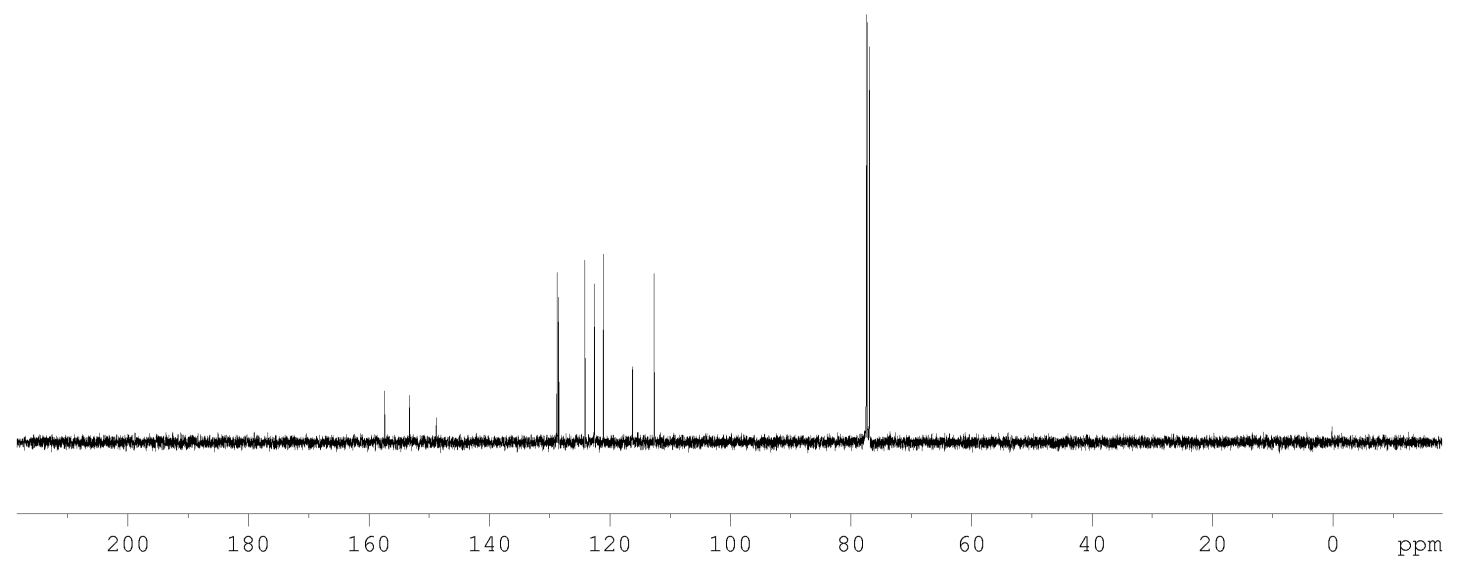
^{19}F NMR (470.8 MHz, CDCl_3) Spectrum of 1,4-difluoro-2-nitrosobenzene (2o)



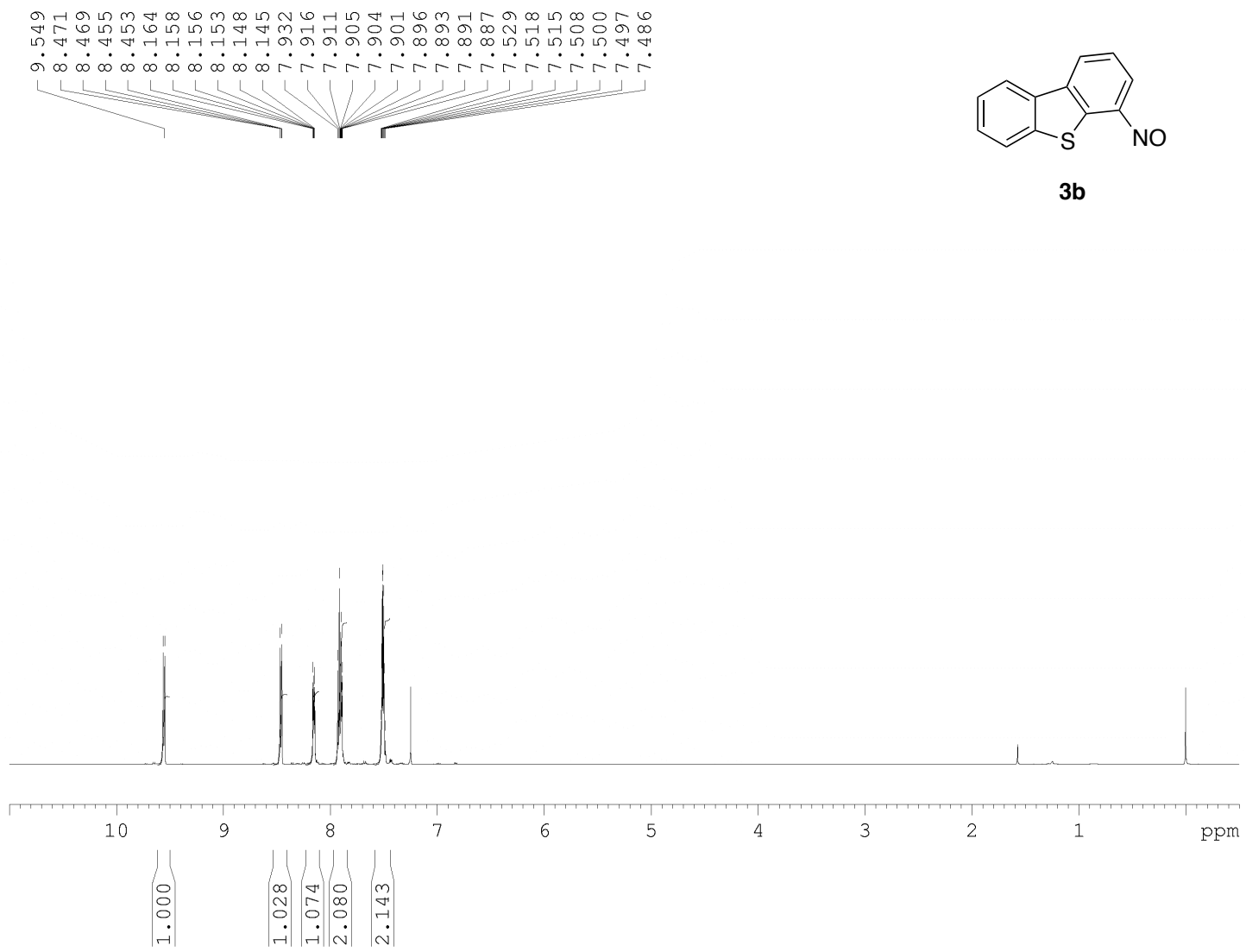
157.384
153.265
148.813
128.760
128.554
128.421
124.148
122.580
122.534
121.051
116.263
112.669



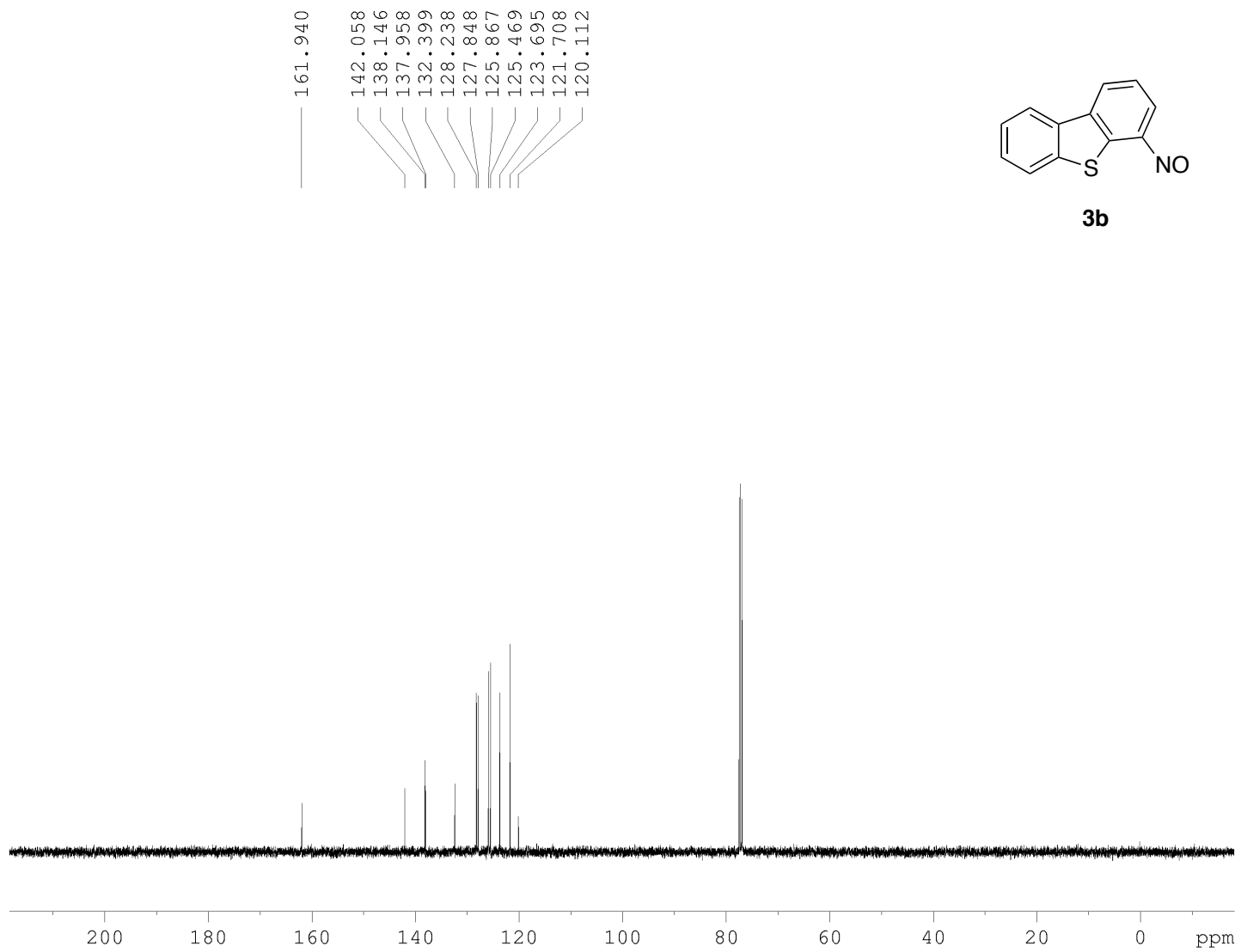
3a

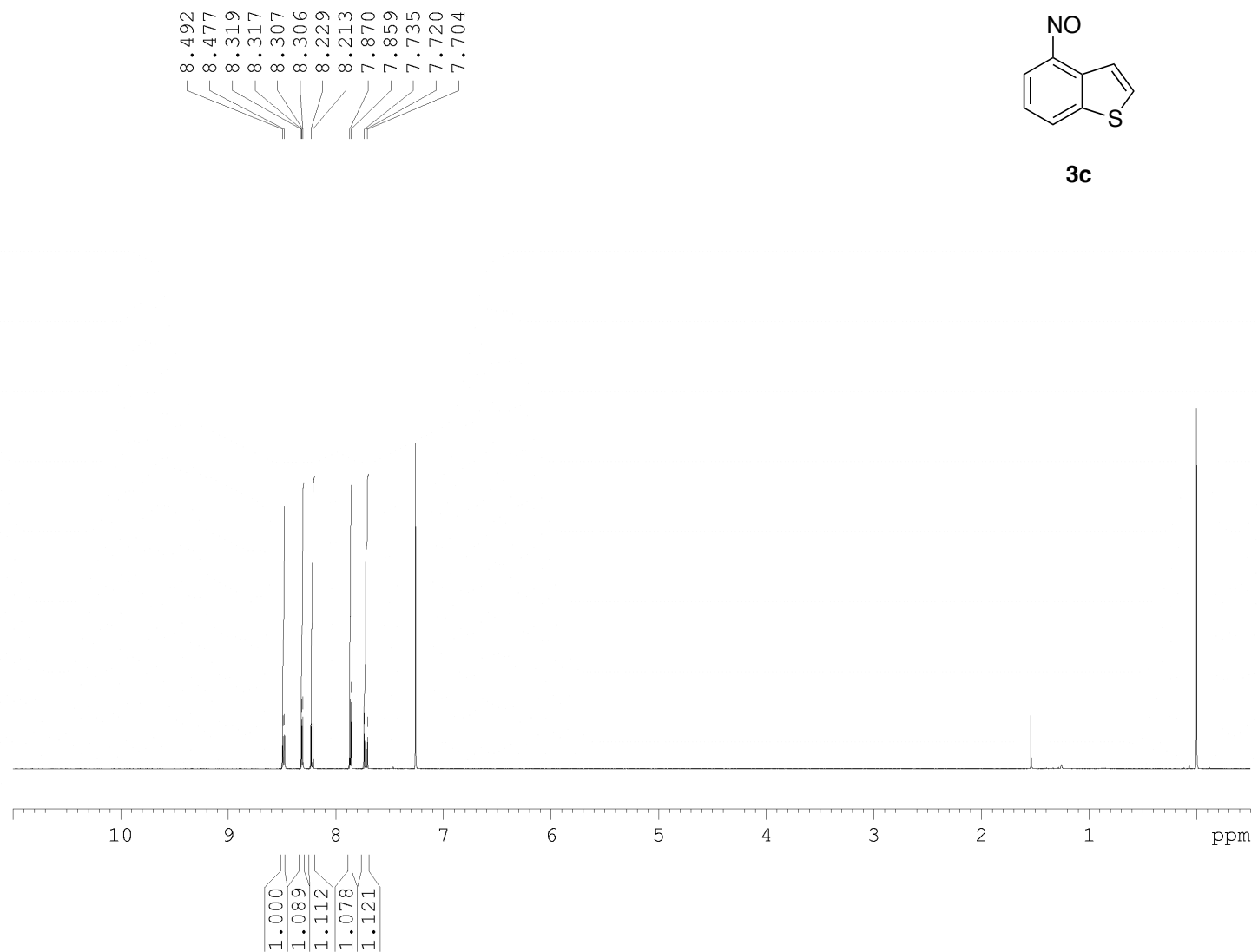


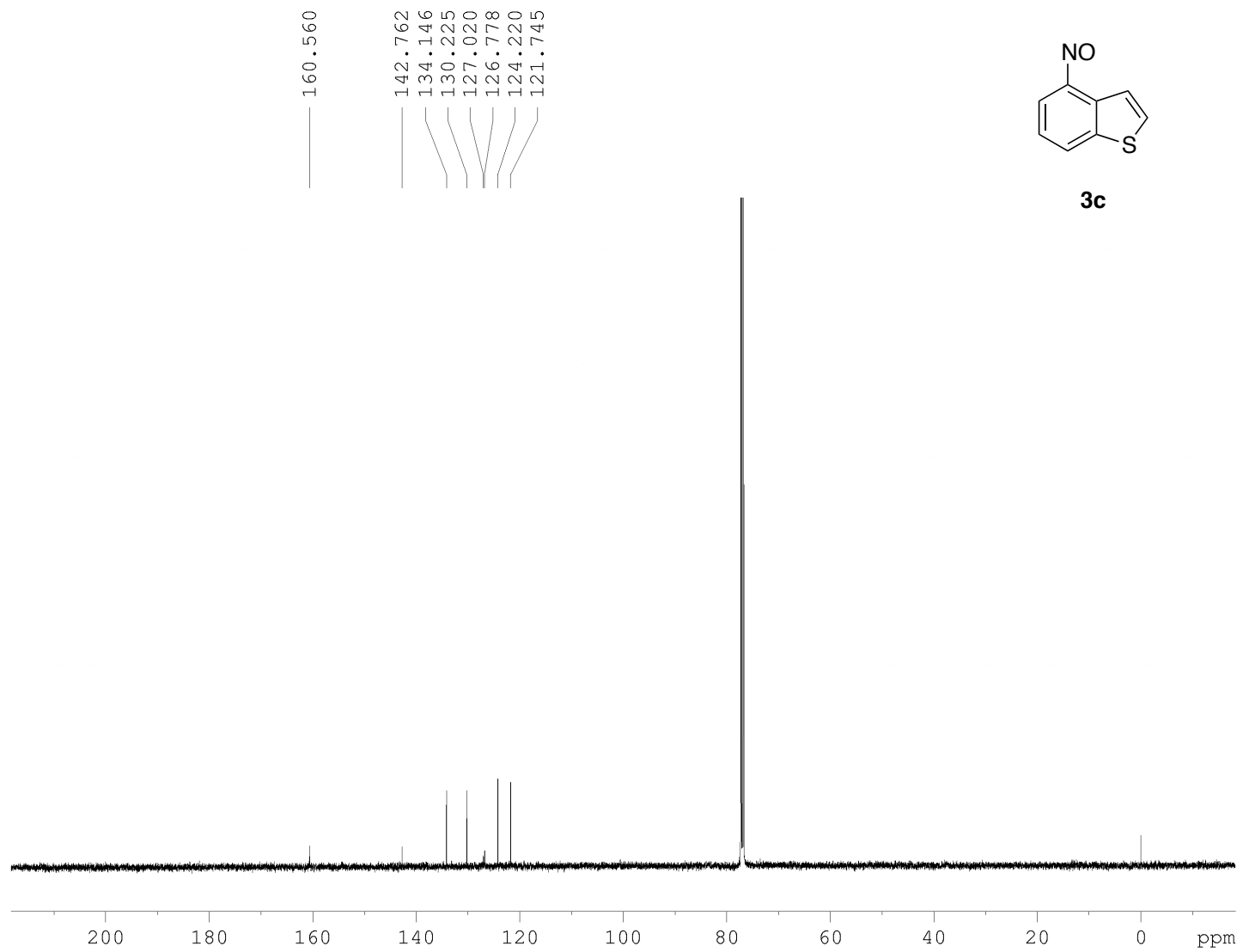
¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 4-nitrosodibenzo[*b,d*]furan (3a)



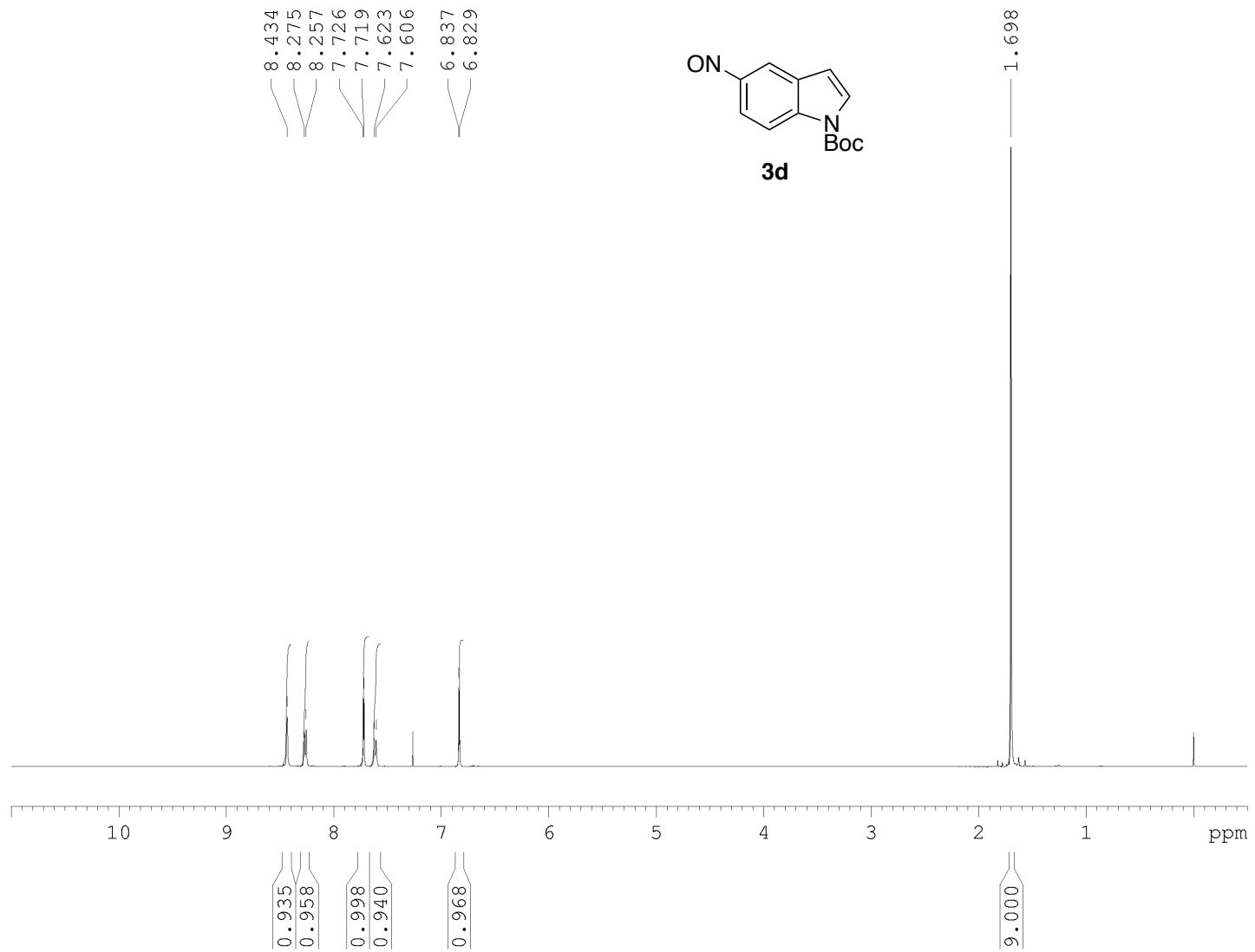
¹H NMR (500 MHz, CDCl₃) Spectrum of 4-nitrosodibenzo[*b,d*]thiophene (3b)



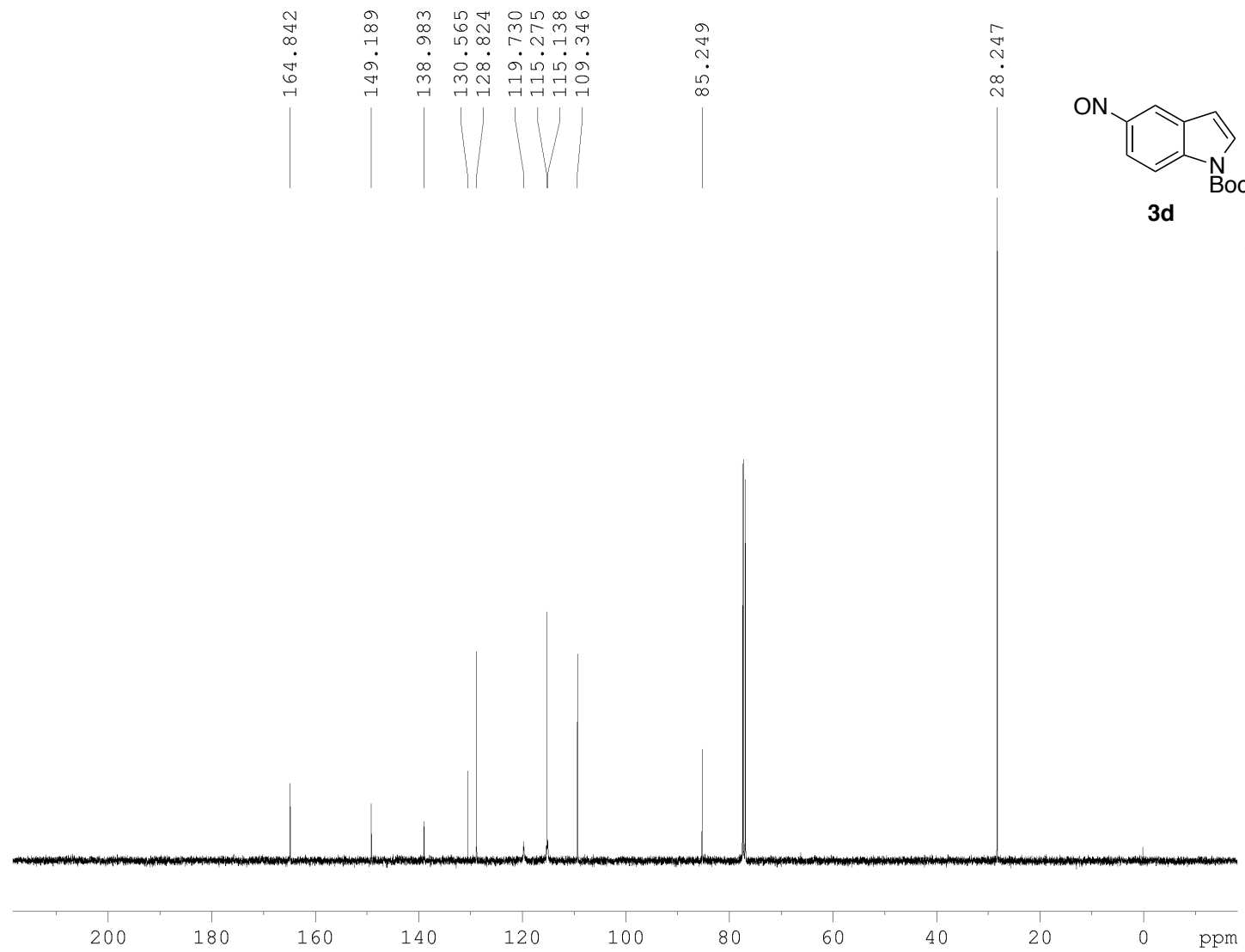


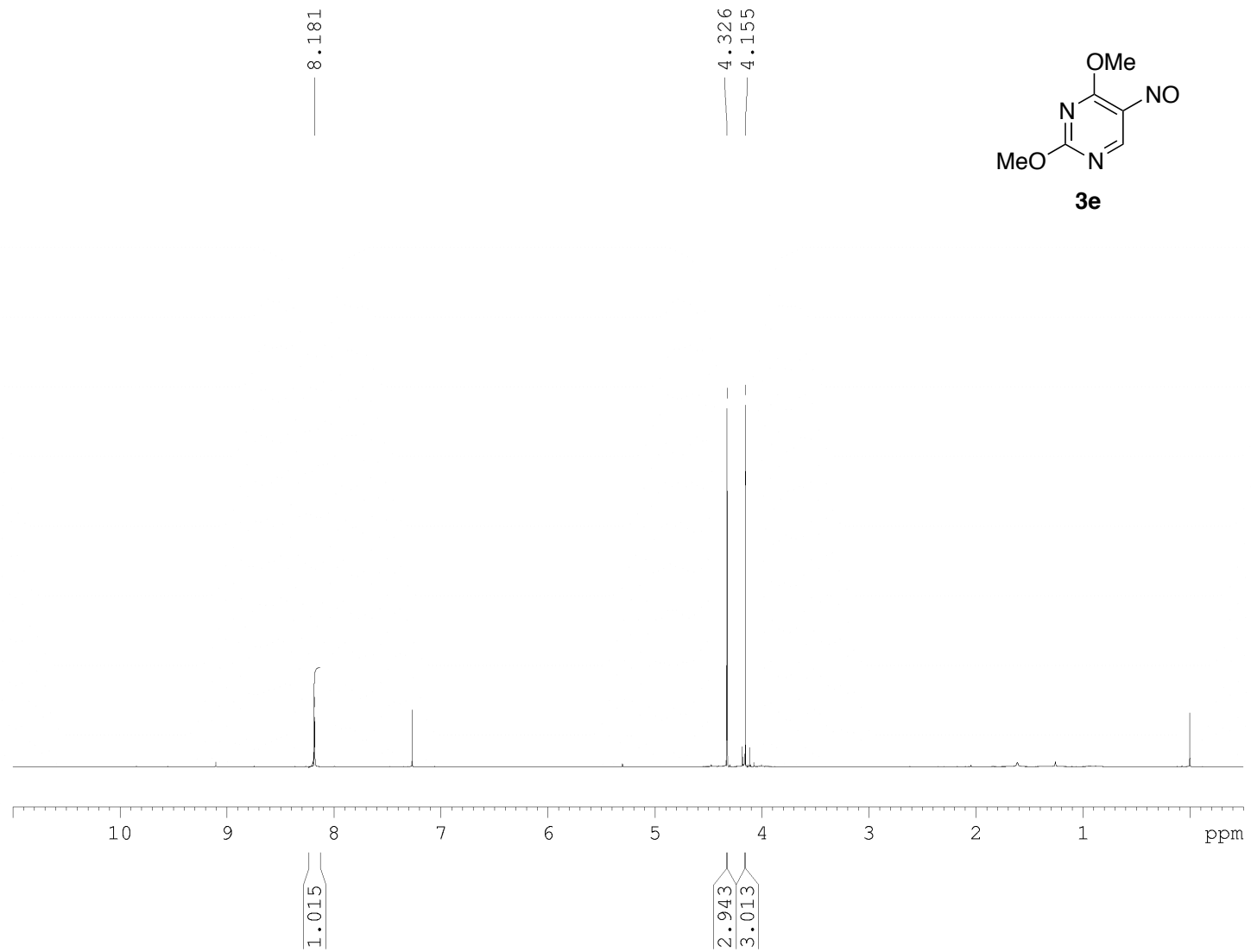


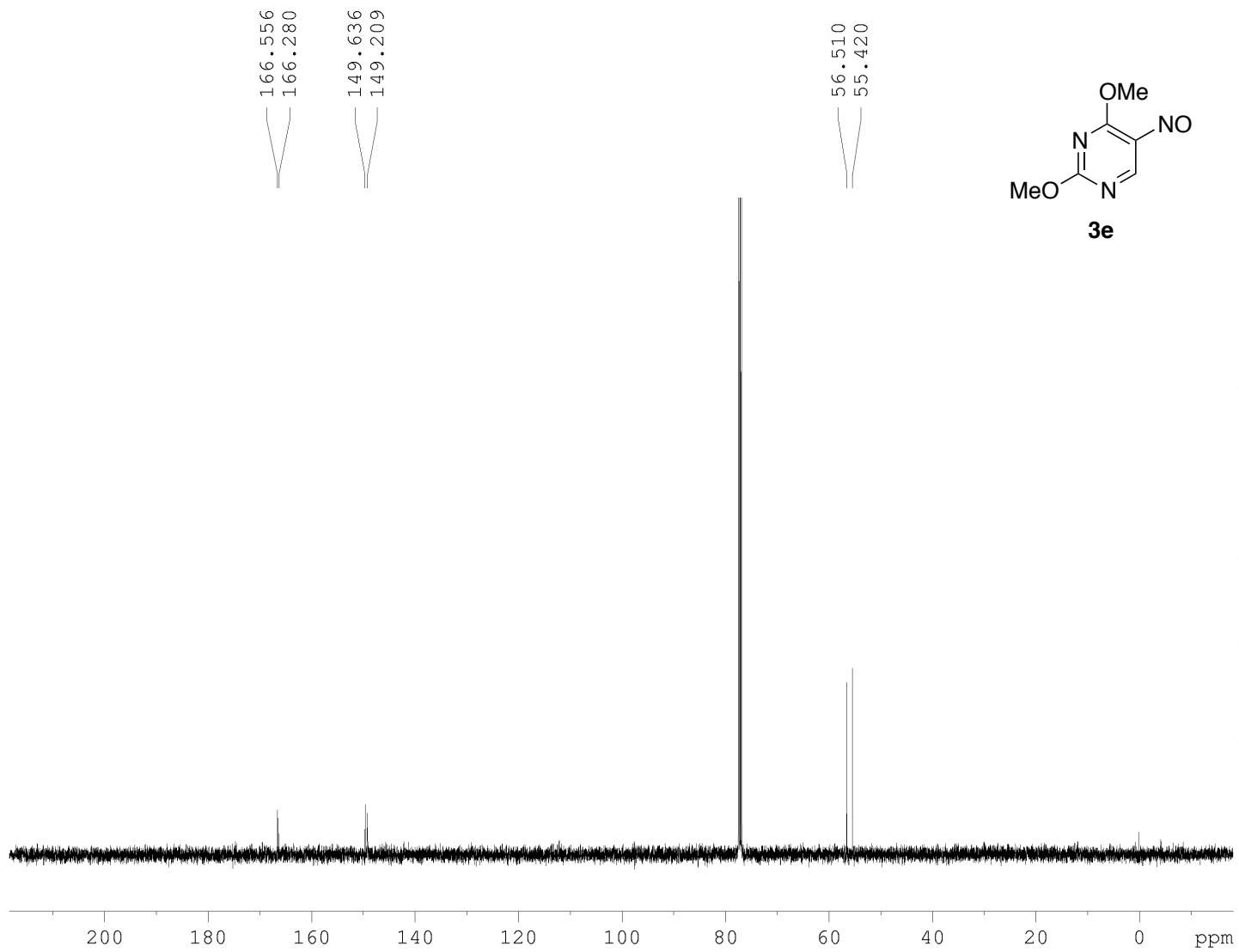
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 4-nitrosobenzo[*b*]thiophene (3c)



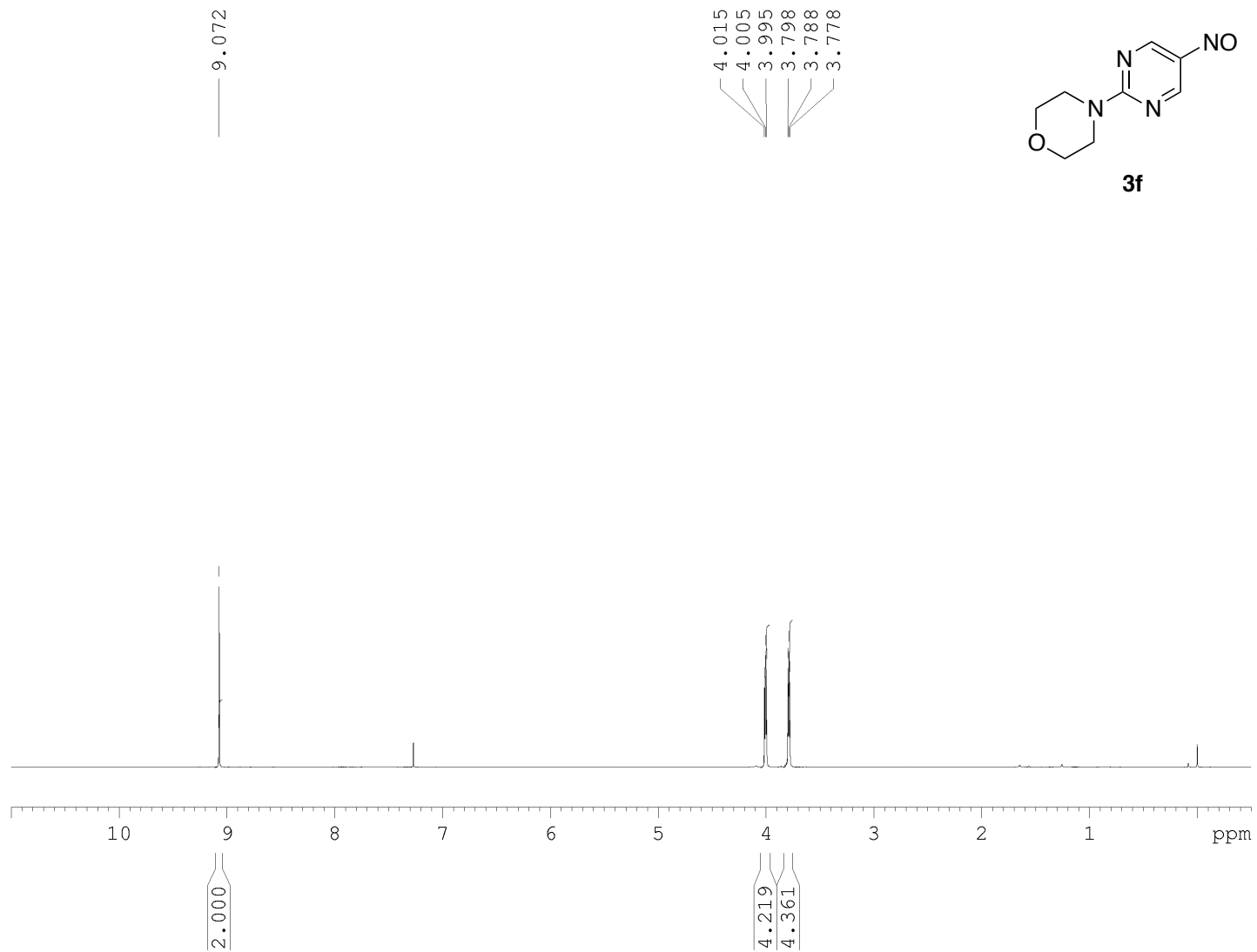
¹H NMR (500 MHz, CDCl₃) Spectrum of *tert*-butyl 5-nitroso-1*H*-indole-1-carboxylate (3d)



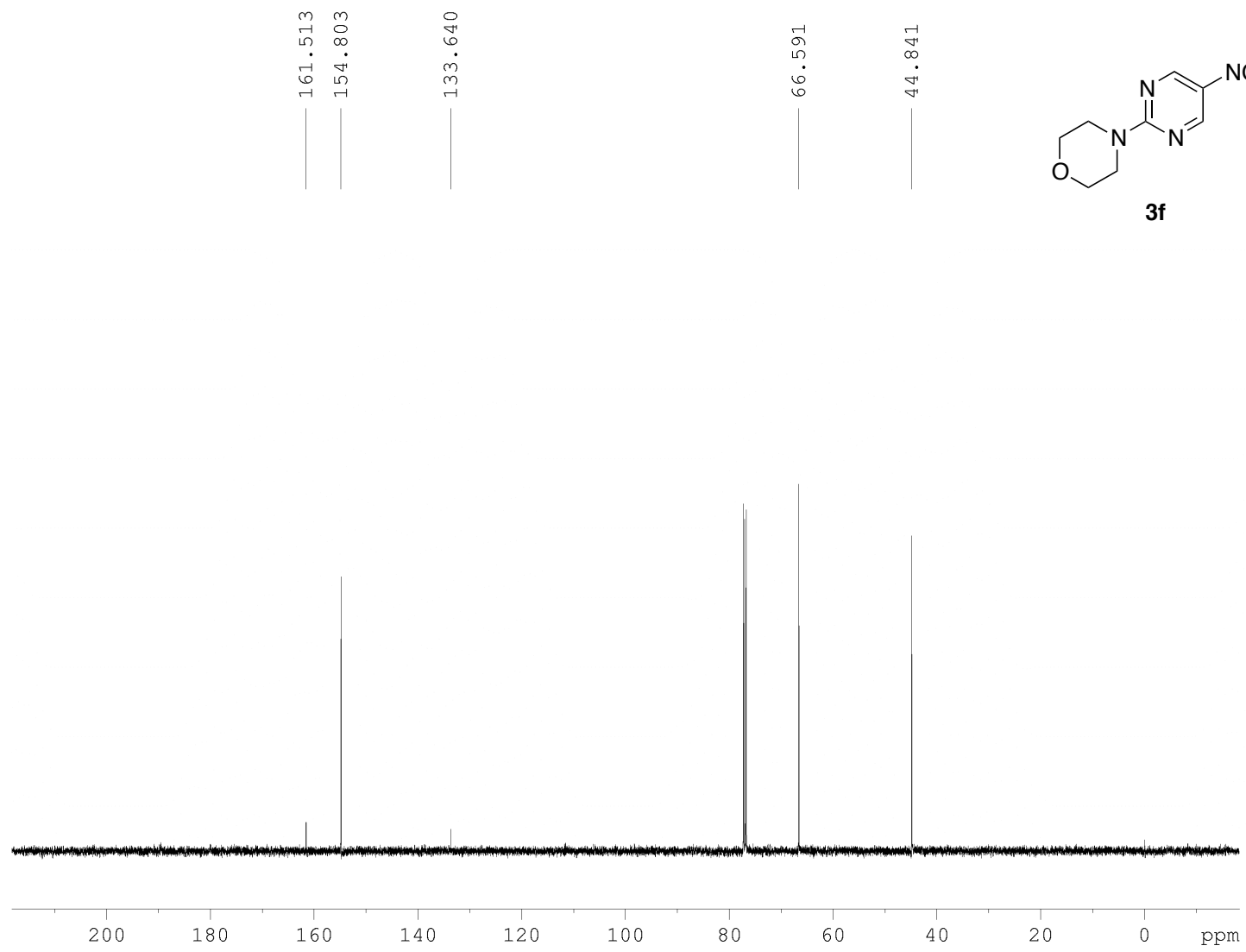


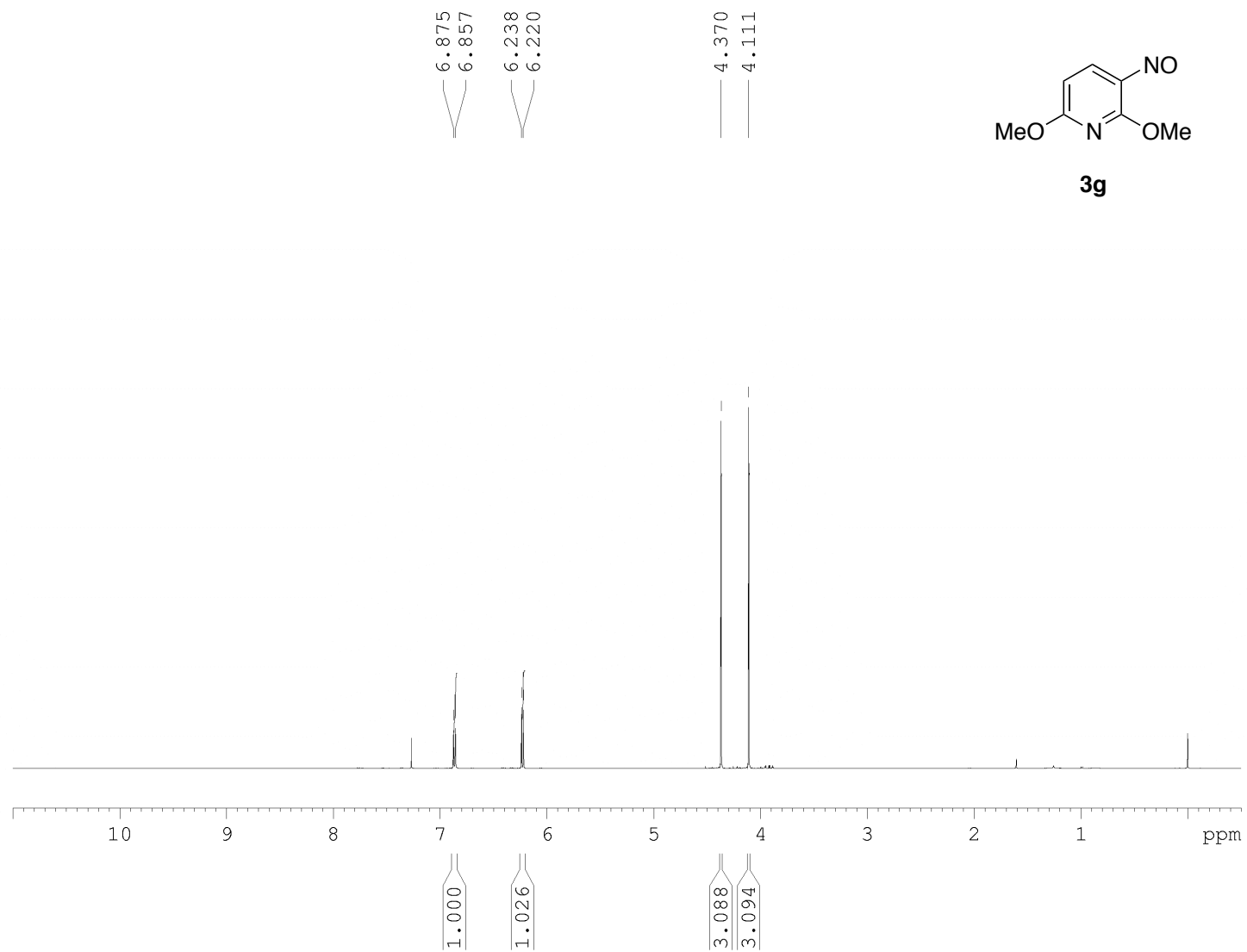


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 2,4-dimethoxy-5-nitrosopyrimidine (3e)

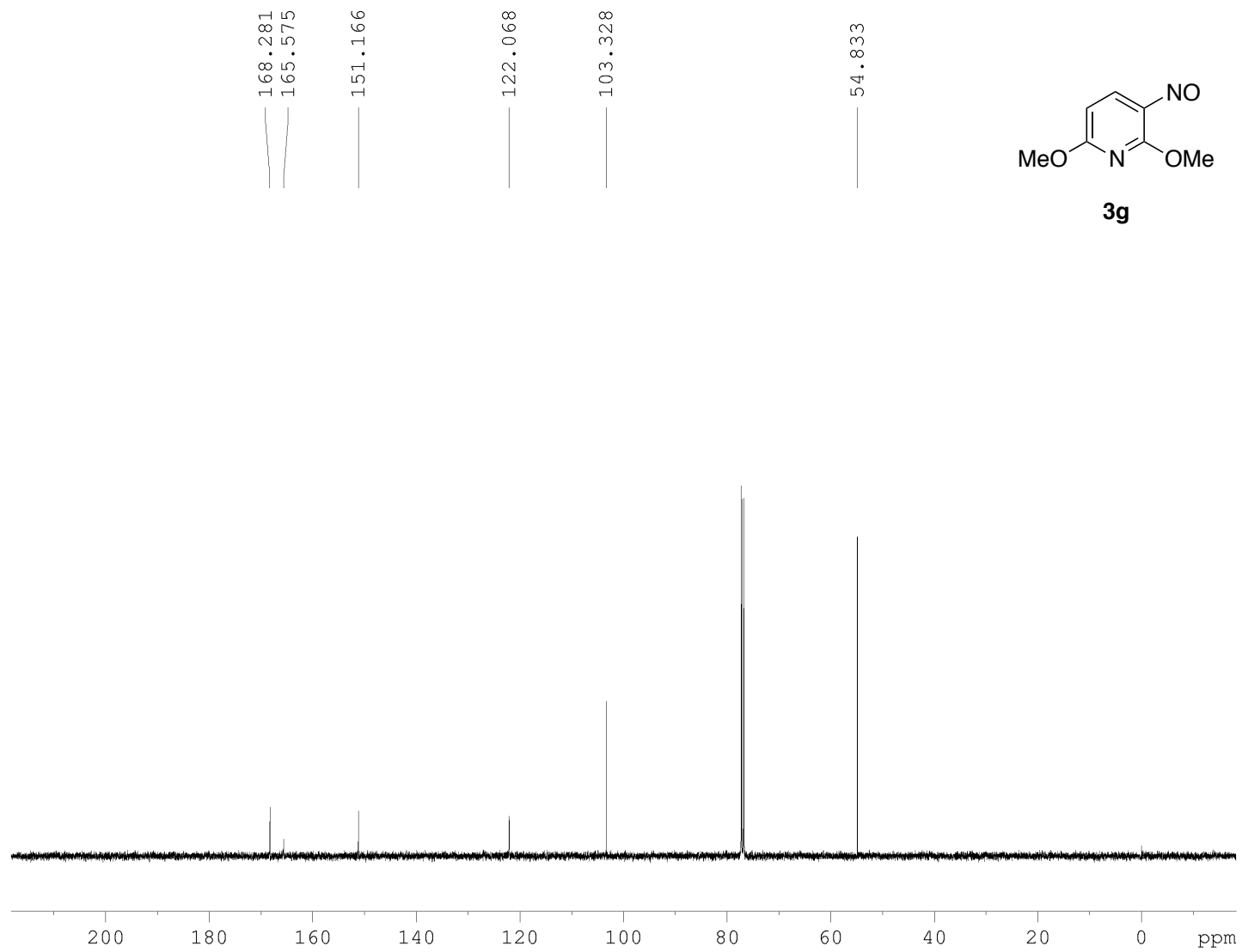


¹H NMR (500 MHz, CDCl₃) Spectrum of 4-(5-nitrosopyrimidin-2-yl)morpholine (**3f**)



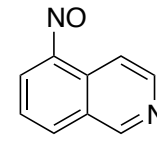


¹H NMR (500 MHz, CDCl₃) Spectrum of 2,6-dimethoxy-3-nitrosopyridine (3g)

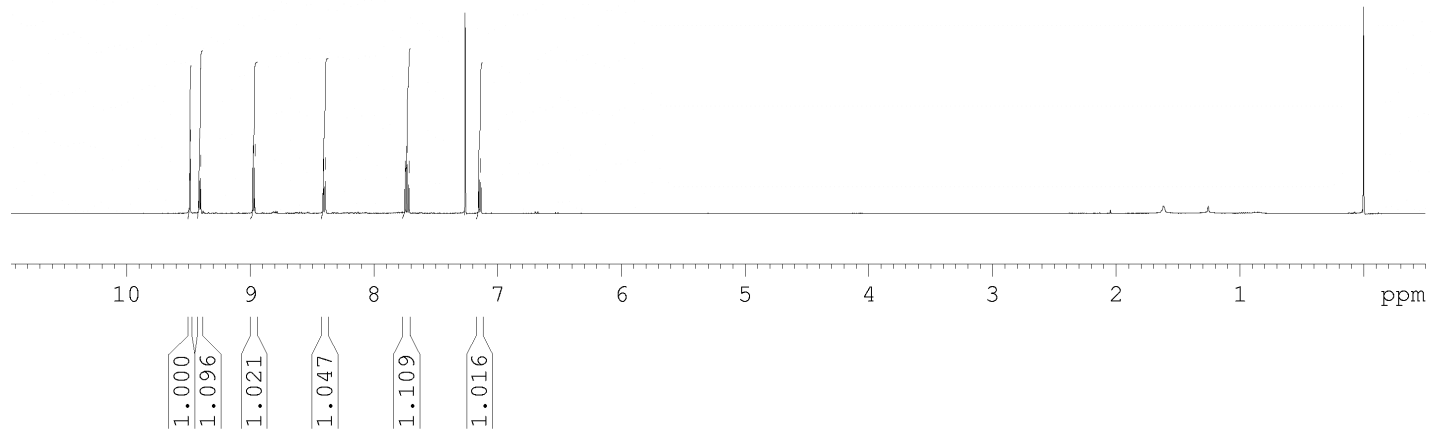


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 2,6-dimethoxy-3-nitrosopyridine (3g)

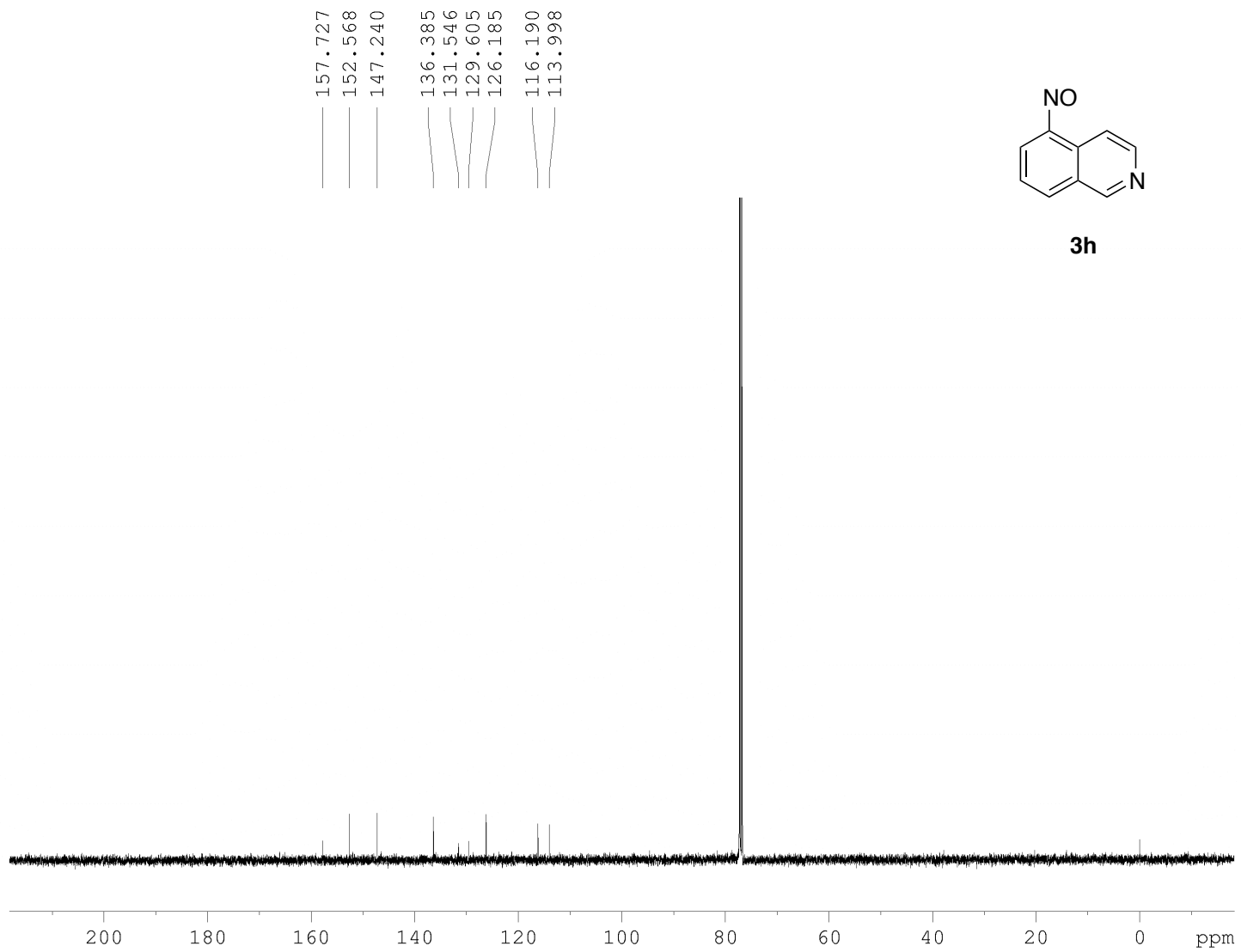
9.485
9.412
9.400
8.975
8.963
8.408
8.392
7.746
7.731
7.715
7.154
7.152
7.139
7.137



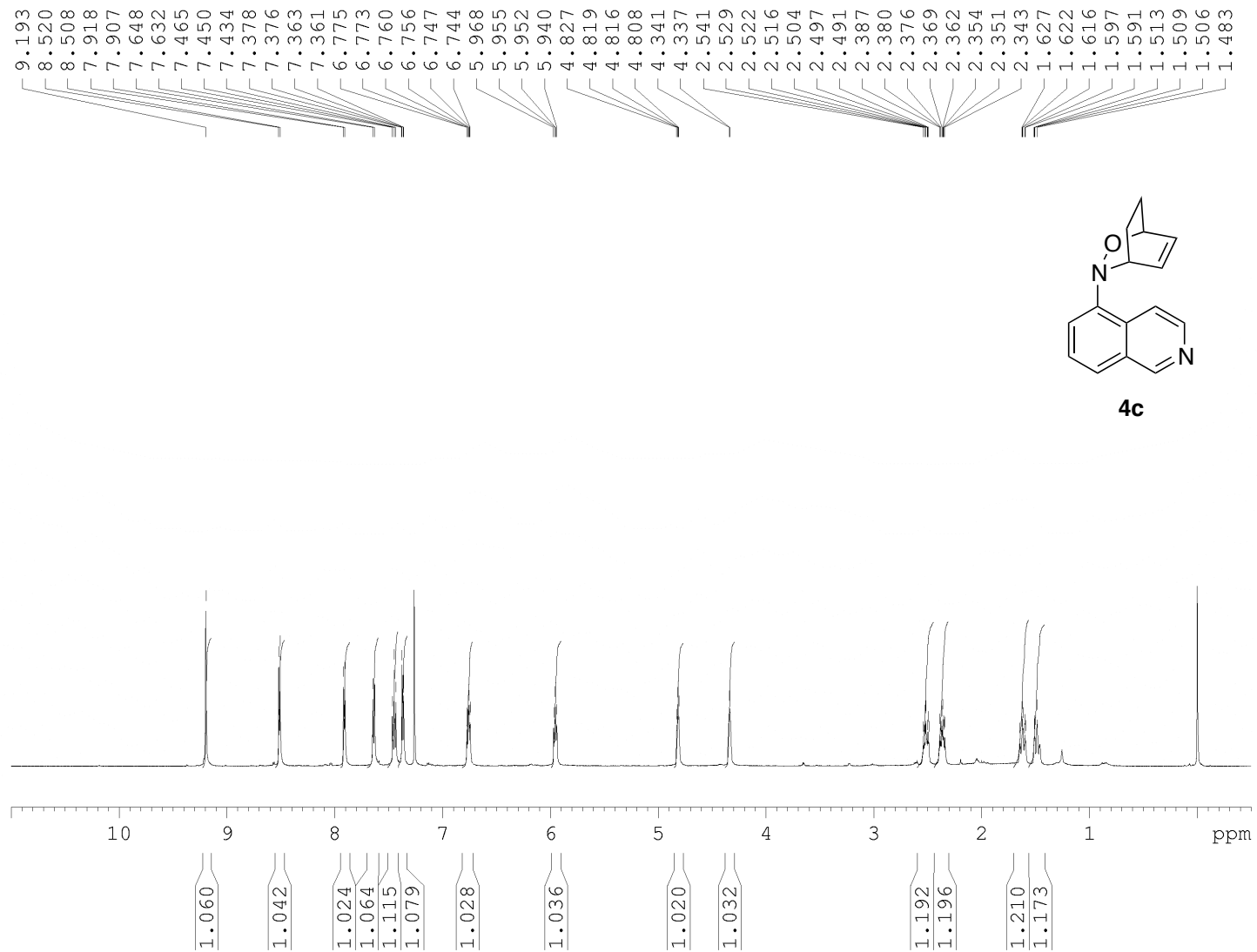
3h

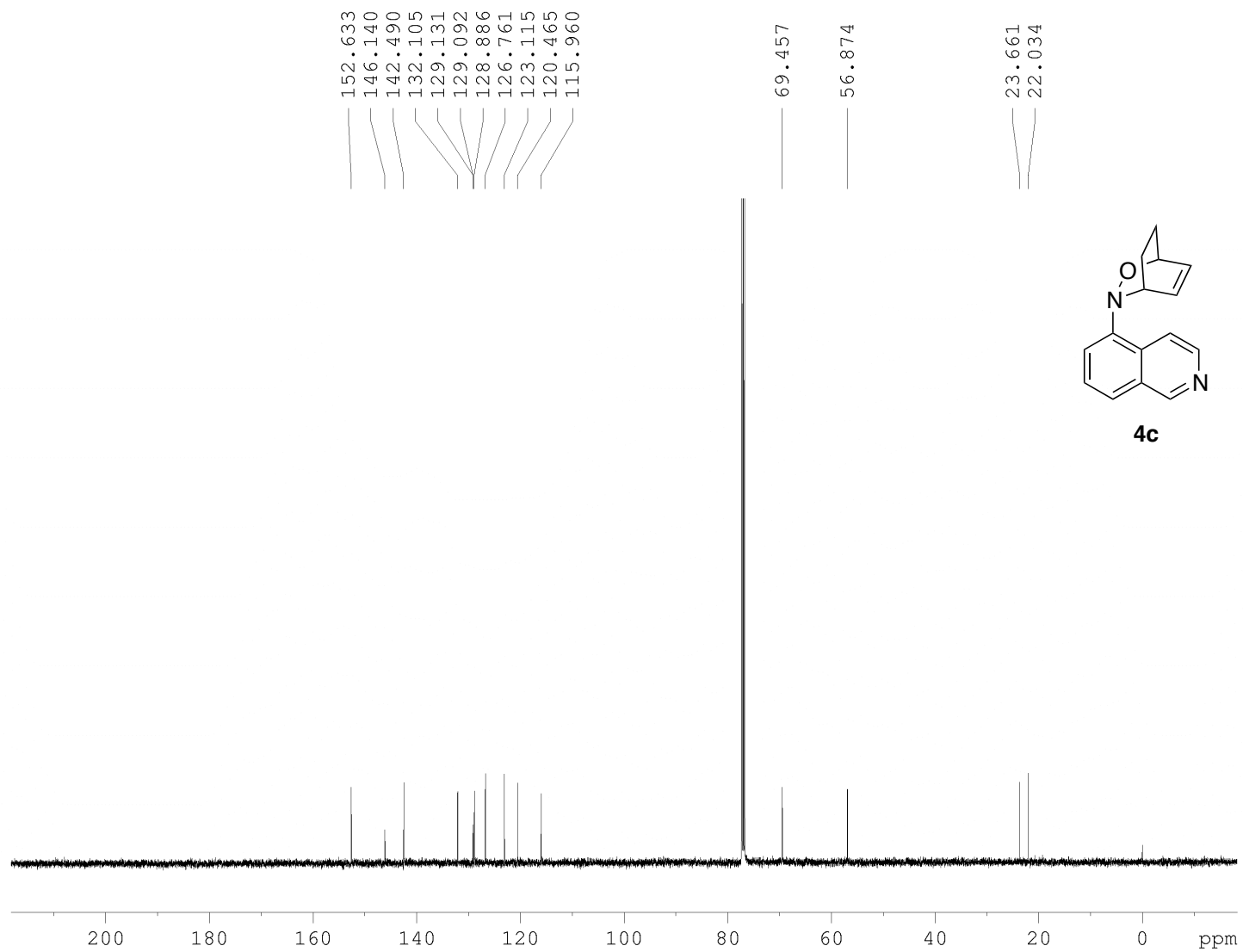


¹H NMR (500 MHz, CDCl₃) Spectrum of 5-nitrosoisoquinoline (3h)

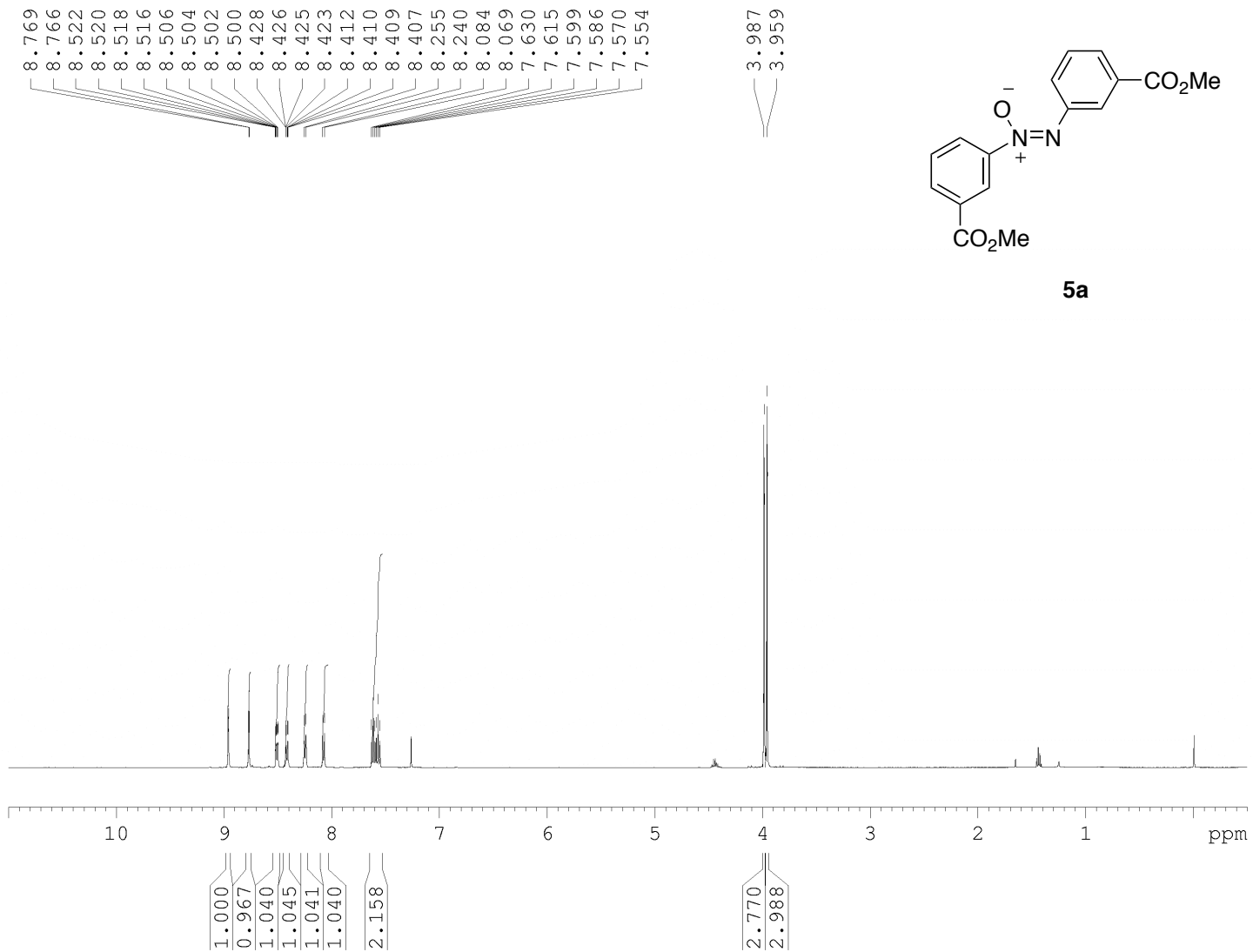


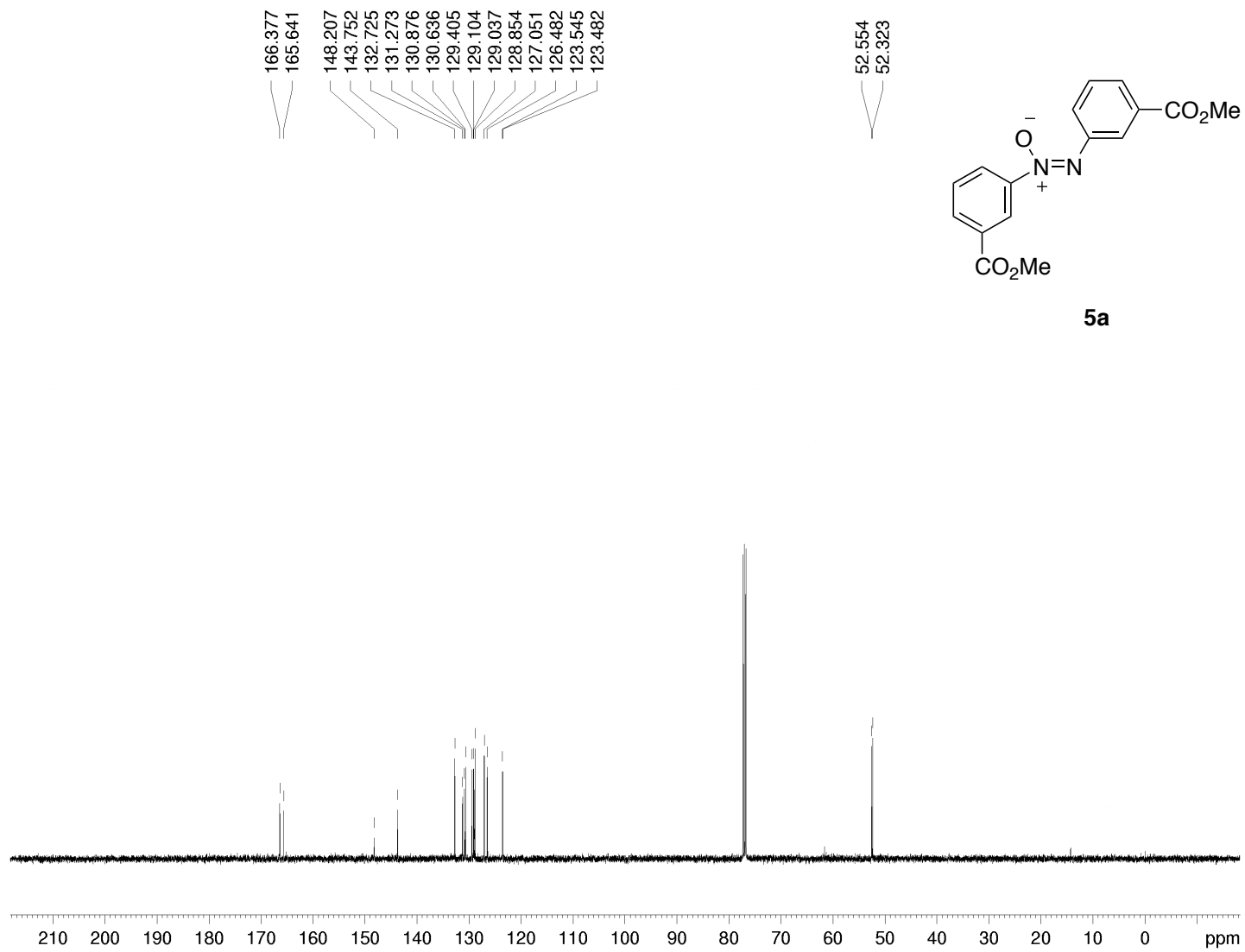
^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of 5-nitrosoisoquinoline (3h)



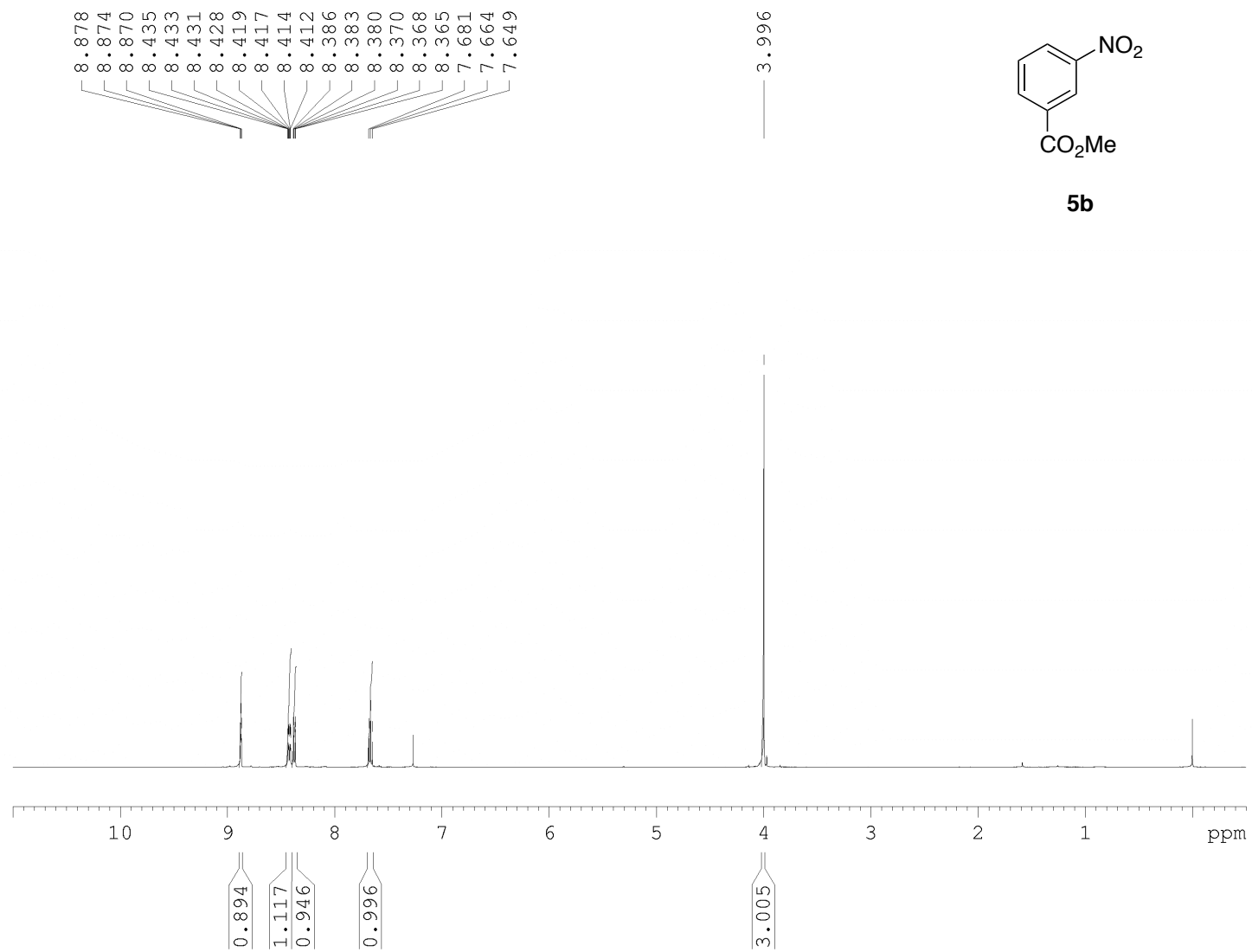


¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 3-(isoquinolin-5-yl)-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (**4c**)

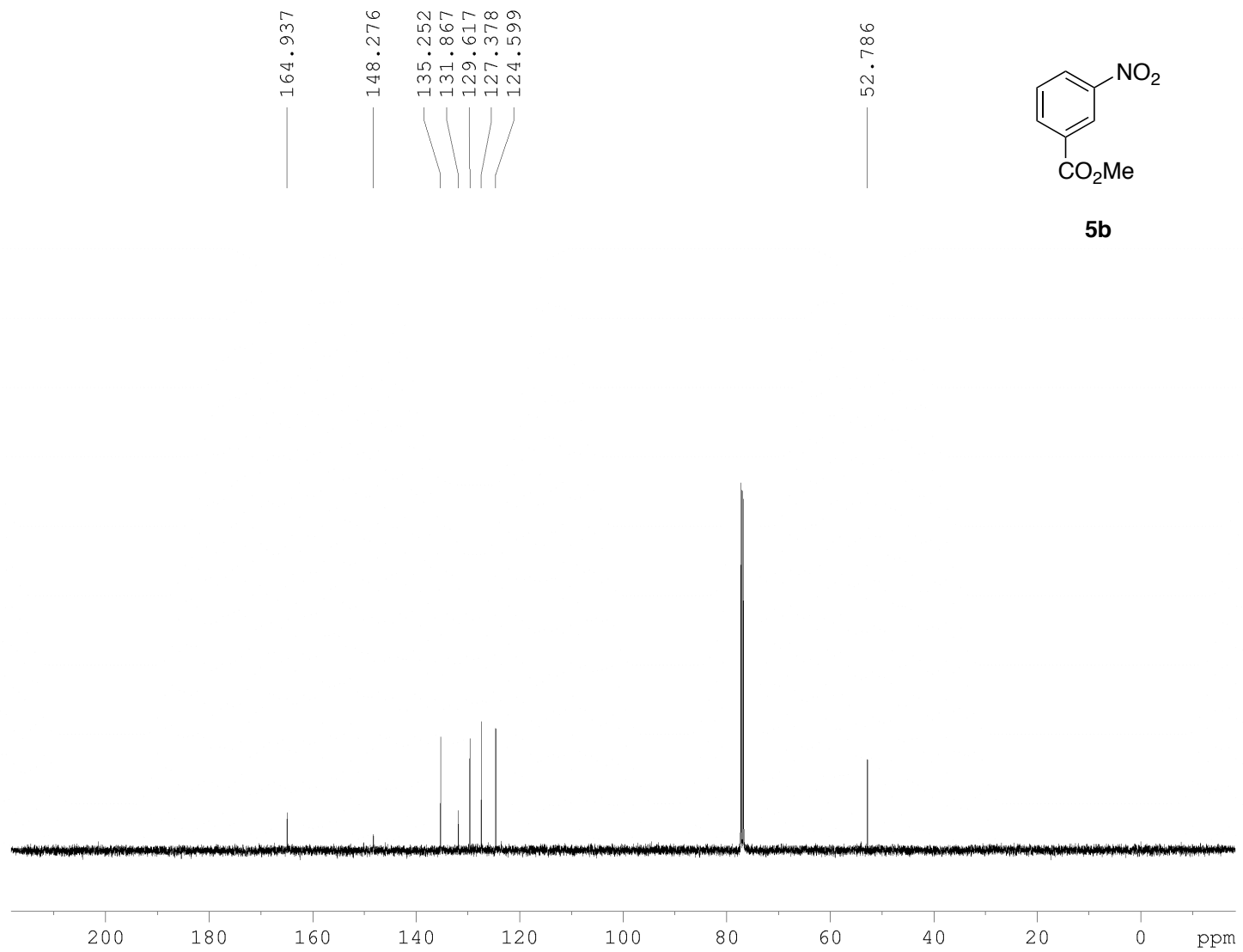




¹³C NMR (128.5 MHz, CDCl₃) Spectrum of 1,2-bis(3-(methoxycarbonyl)phenyl)diazene oxide (5a)

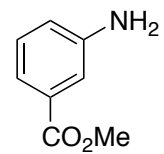


¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 3-nitrobenzoate (5b)

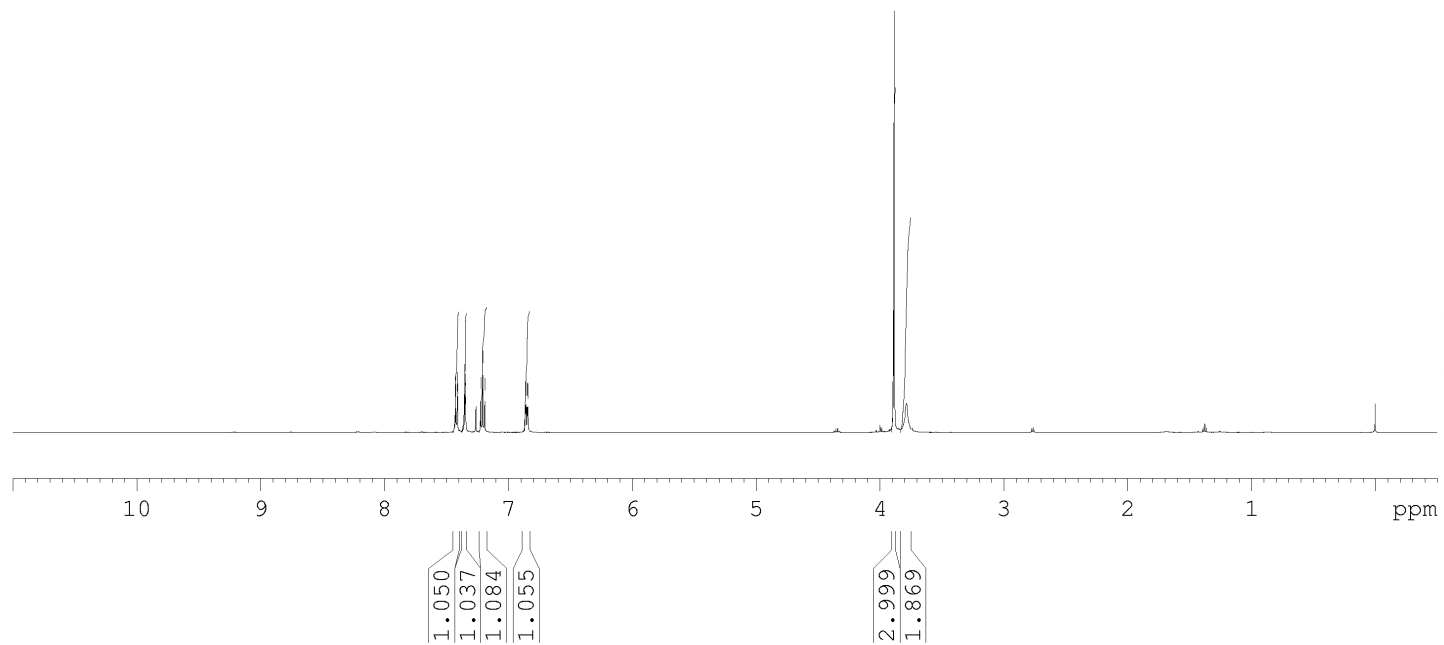


^{13}C NMR (128.5 MHz, CDCl_3) Spectrum of methyl 3-nitrobenzoate (5b)

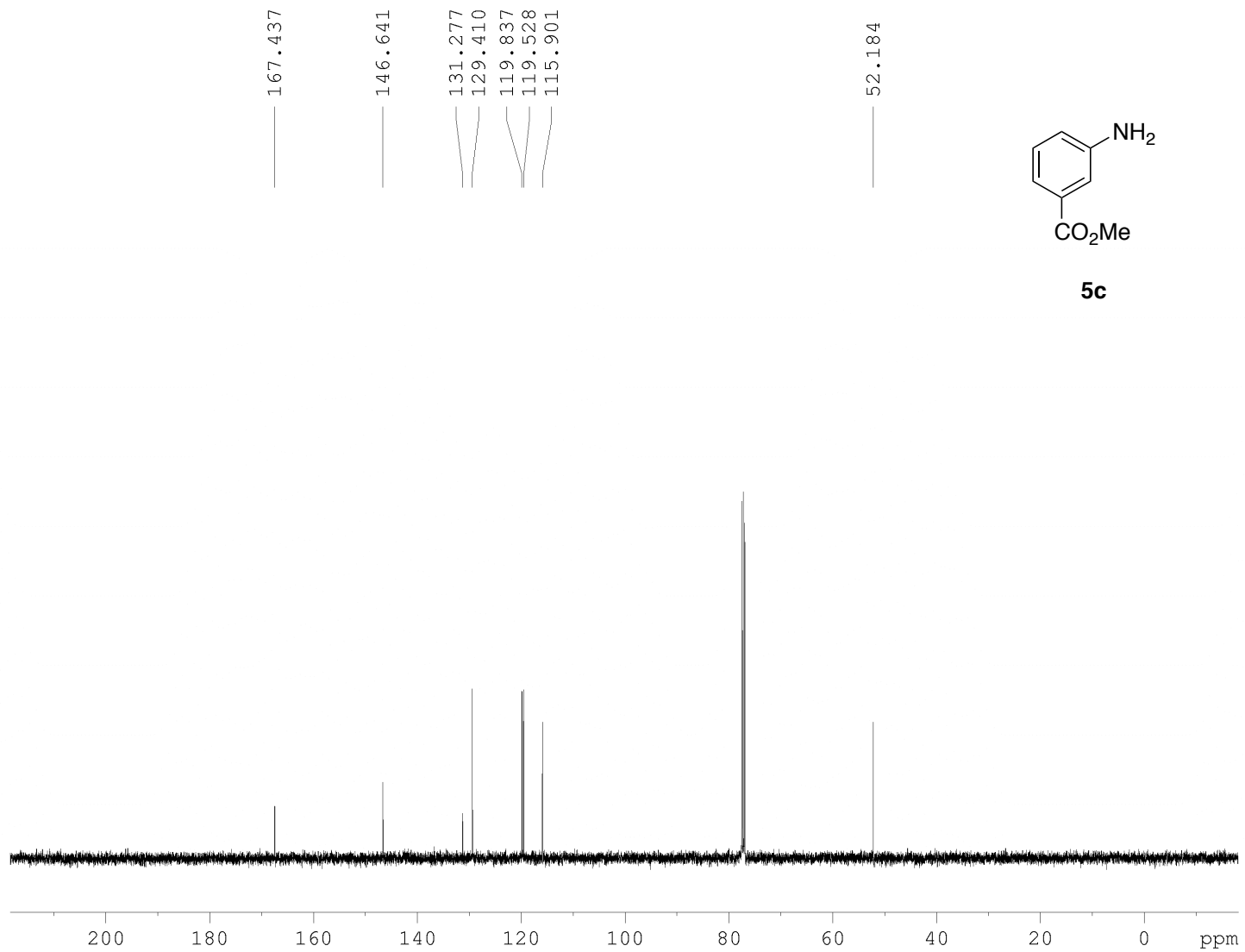
7.429
7.427
7.424
7.414
7.412
7.409
7.352
7.348
7.344
7.222
7.207
7.191
6.863
6.861
6.858
6.857
6.847
6.846
6.842
6.841



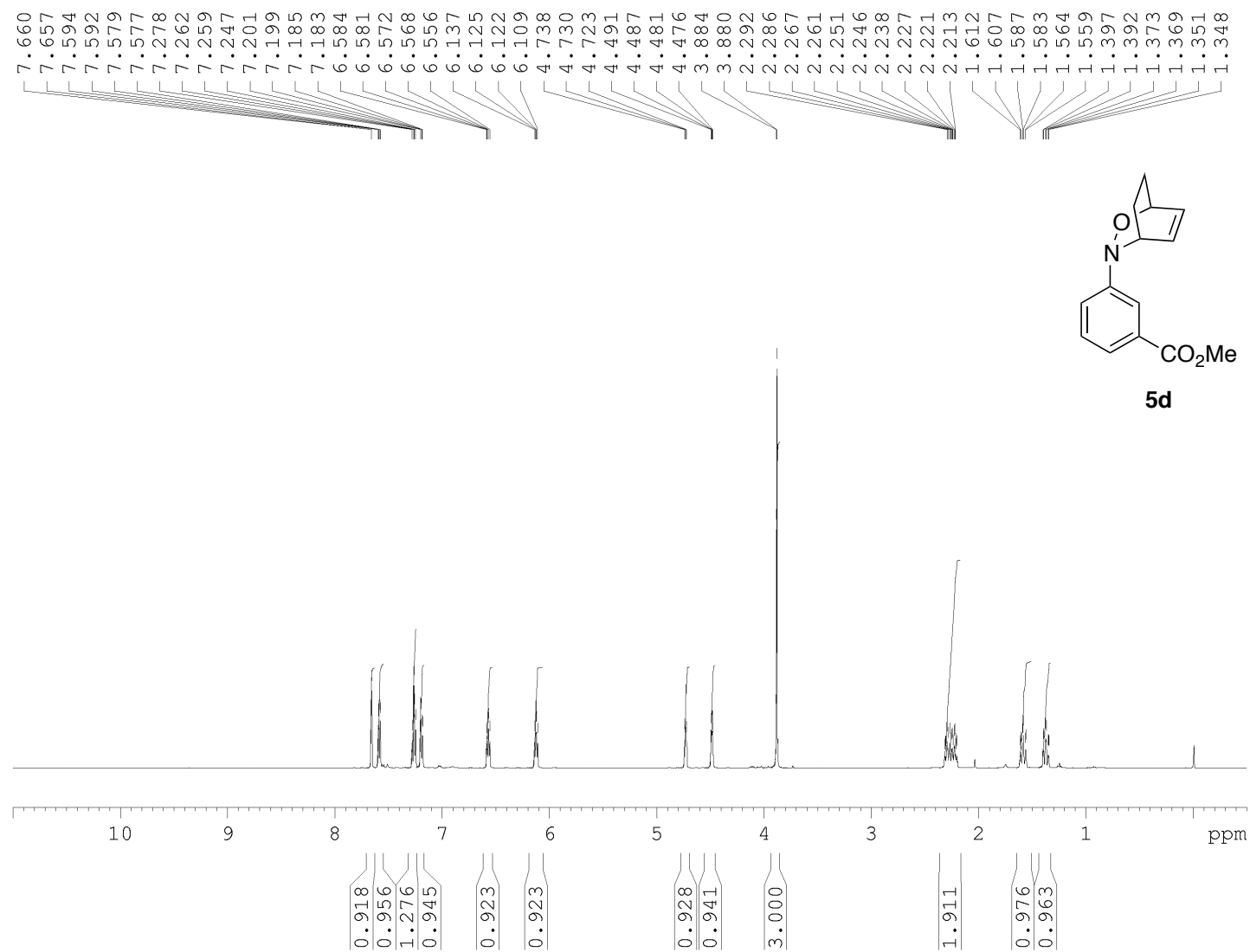
5c

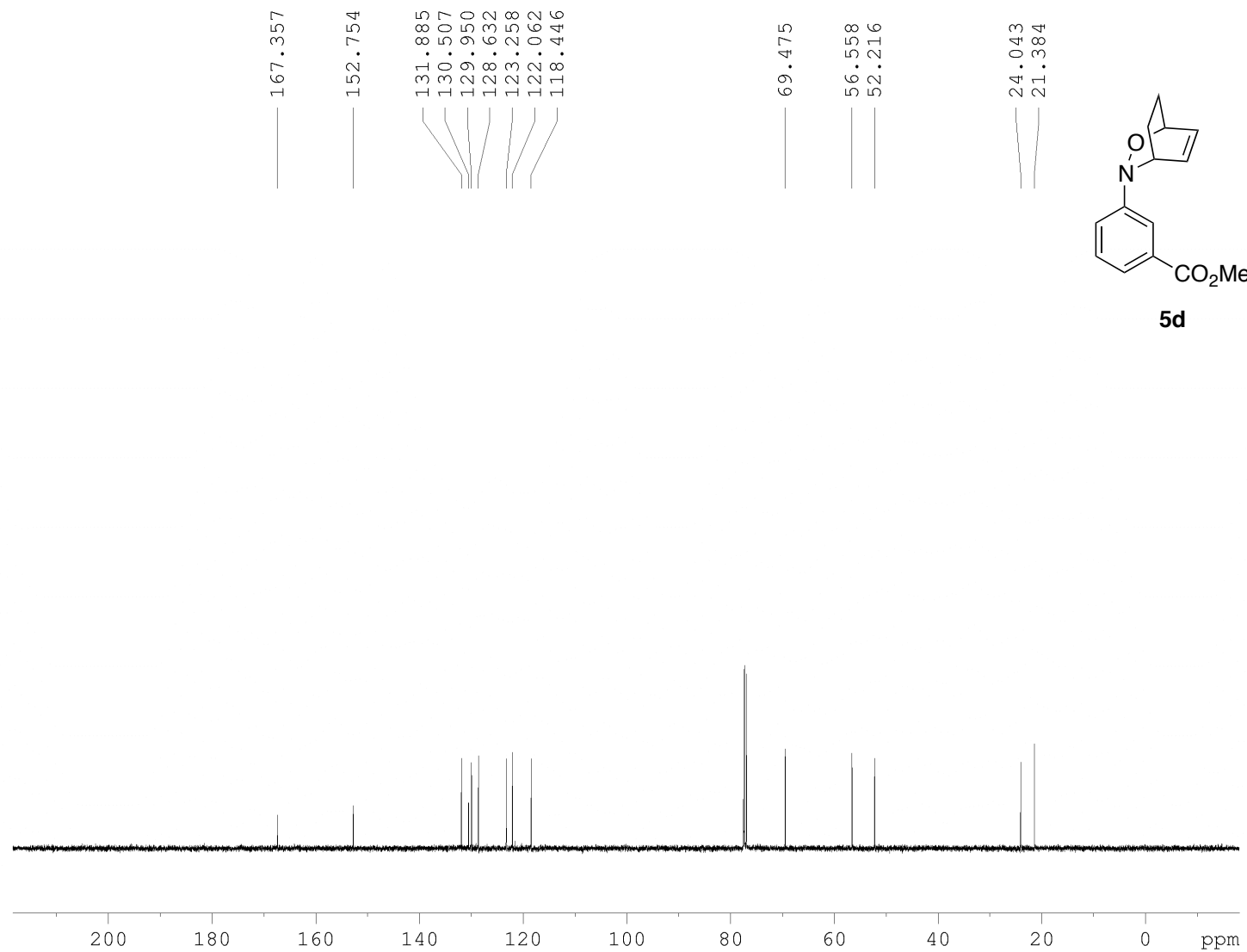


¹H NMR (500 MHz, CDCl₃) Spectrum of methyl 3-aminobenzoate (5c)



¹³C NMR (128.5 MHz, CDCl₃) Spectrum of methyl 3-aminobenzoate (5c)





¹³C NMR (128.5 MHz, CDCl₃) Spectrum of methyl 3-(2-oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)benzoate (5d)