

Supplementary data for the article:

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Supporting Information

Hofmann Rearrangement of Carboxamides Mediated by *N*-bromoacetamide

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NMR spectra of the selected precursors (carboxamides) and products (cyclic ureas or carbamates)

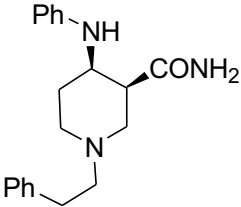
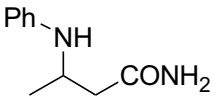
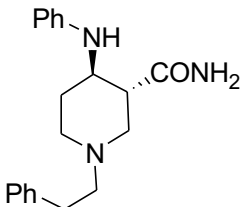
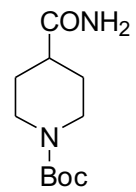
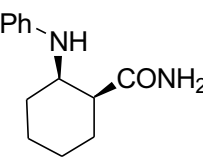
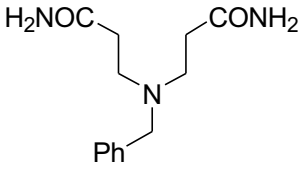
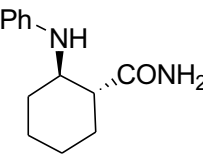
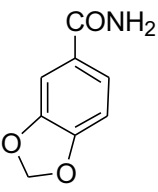
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2.	 <p>1b</p>	¹ H NMR 14 ¹³ C NMR 15 DEPT 16 HSQC 17 NOESY 19-20 3D STRUCTURE 21	6.	 <p>1m</p>	¹ H NMR 41 ¹³ C NMR 42
3.	 <p>1c</p>	¹ H NMR 22 ¹³ C NMR 23 DEPT 24 HSQC 25-26 NOESY 27-28 3D STRUCTURE 29	7.	 <p>1n</p>	¹ H NMR 43 ¹³ C NMR 44 APT 45
4.	 <p>1d</p>	¹ H NMR 30 ¹³ C NMR 31 DEPT 32 HSQC 33-34 NOESY 35-36 3D STRUCTURE 37	8.	 <p>1r</p>	¹ H NMR 46 ¹³ C NMR 47 DEPT 48

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NMR spectra of the selected precursors (carboxamides) and products (cyclic ureas or carbamates)

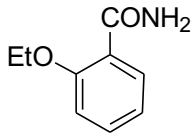
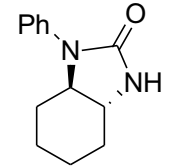
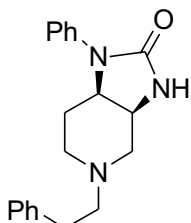
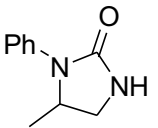
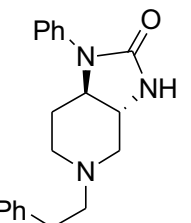
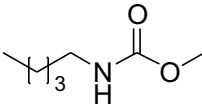
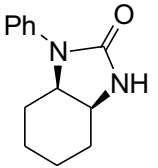
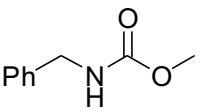
9.	 <p>1t</p>	¹ H NMR 49 ¹³ C NMR 50 APT 51	13.	 <p>2d</p>	¹ H NMR 78 ¹³ C NMR 79 DEPT 80 HSQC 81-82 NOESY 83-84 3D STRUCTURE 2.2a/2.2b 85
10.	 <p>2a</p>	¹ H NMR 52-53 ¹³ C NMR 54 DEPT 55 HSQC 56-57 NOESY 58-59 3D STRUCTURE 60	14.	 <p>2e</p>	¹ H NMR 86 ¹³ C NMR 87 DEPT 88
11.	 <p>2b</p>	¹ H NMR 61-62 ¹³ C NMR 63 DEPT 64 HSQC 65-66 NOESY 67-68 3D STRUCTURE 69	15.	 <p>2f</p>	¹ H NMR 89 ¹³ C NMR 90 APT 91
12.	 <p>2c</p>	¹ H NMR 70-71 ¹³ C NMR 72 DEPT 73 HSQC 74-75 NOESY 76-77	16.	 <p>2g</p>	¹ H NMR 92 ¹³ C NMR 93 APT 94

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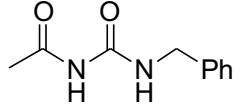
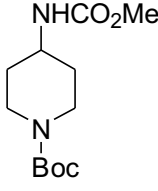
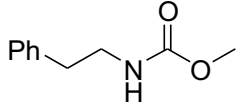
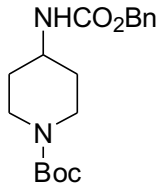
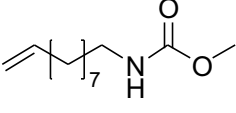
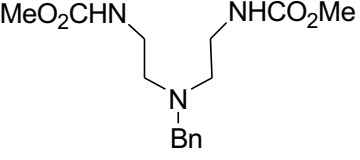
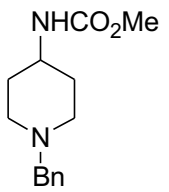

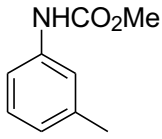
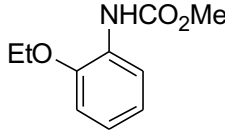
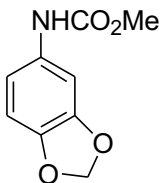
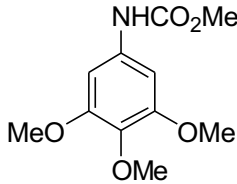
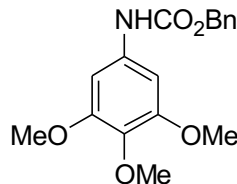
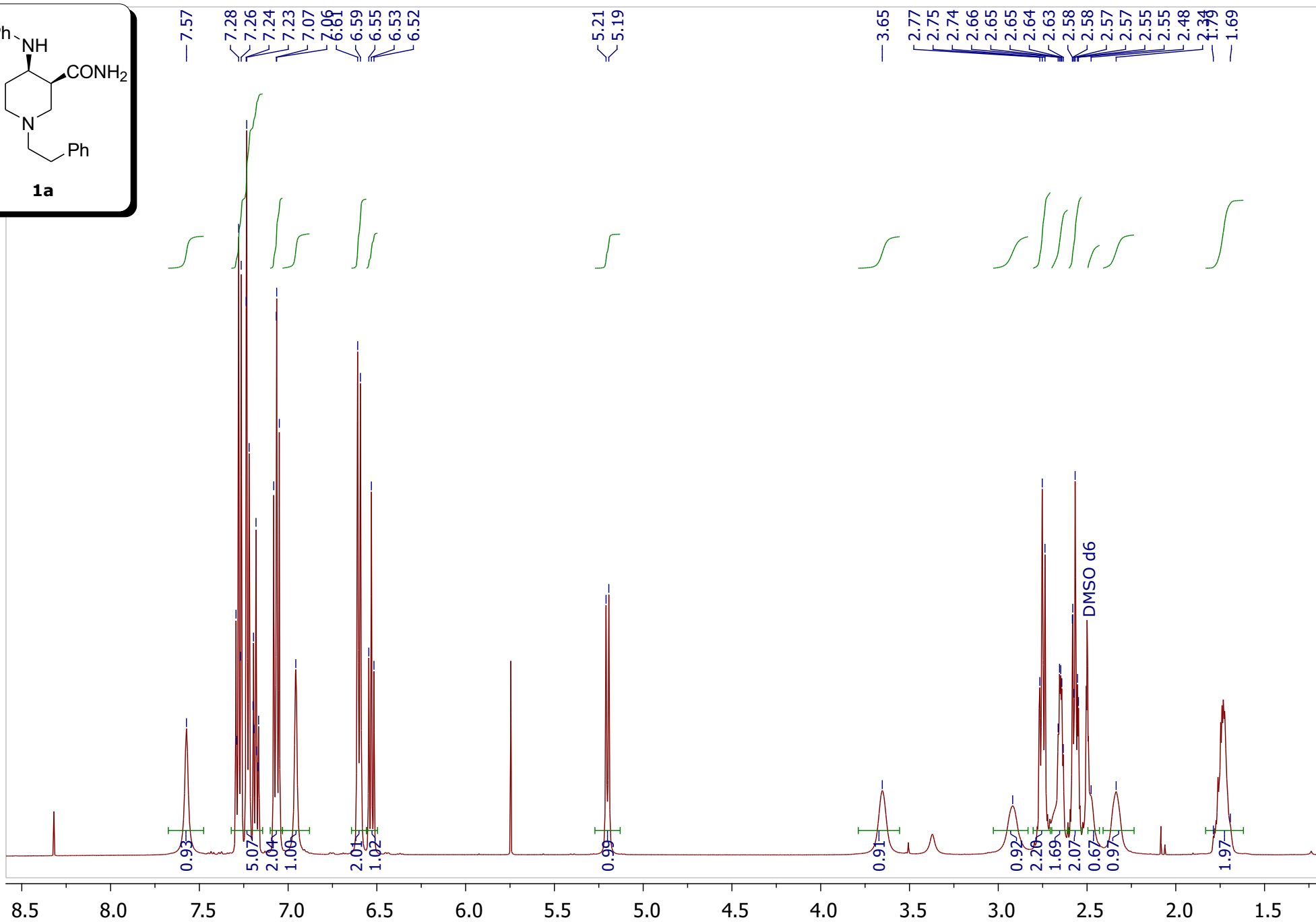
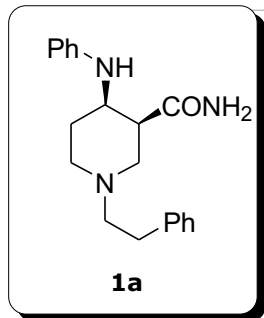
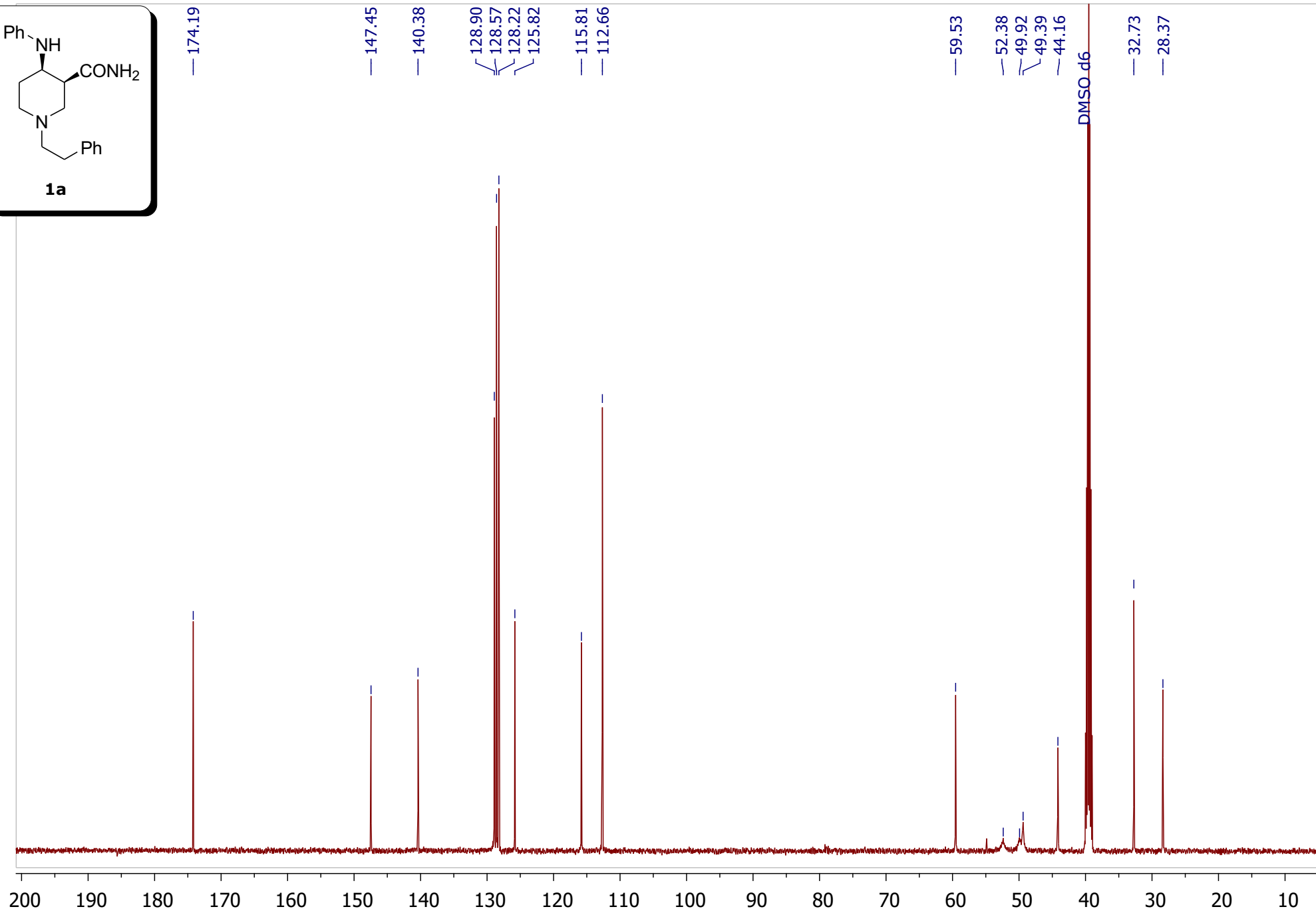
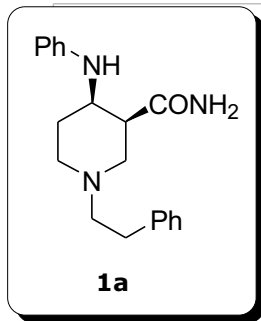
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18.	 <p style="text-align: center;">2j</p>	¹ H NMR 99 ¹³ C NMR 100 APT 101	22.	 <p style="text-align: center;">2n</p>	¹ H NMR 110 ¹³ C NMR 111 DEPT 112 HSQC 113-114 NOESY 115
19.	 <p style="text-align: center;">2k</p>	¹ H NMR 102 ¹³ C NMR 103 APT 104	23.	 <p style="text-align: center;">2o</p>	¹ H NMR 116 ¹³ C NMR 117 APT 118
20.	 <p style="text-align: center;">2l</p>	¹ H NMR 105 ¹³ C NMR 106	24.	 <p style="text-align: center;">2p</p>	¹ H NMR 119 ¹³ C NMR 120 APT 121

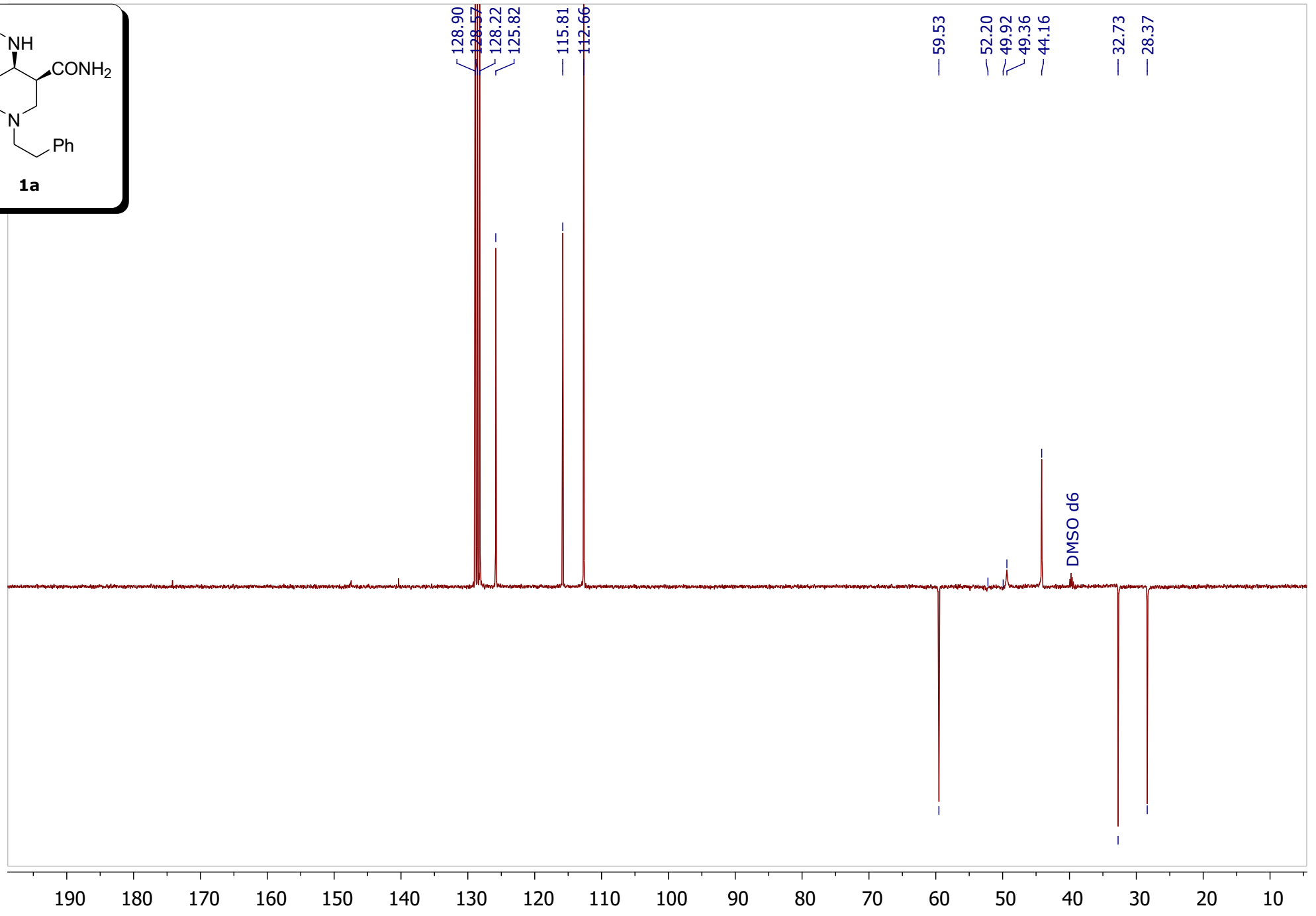
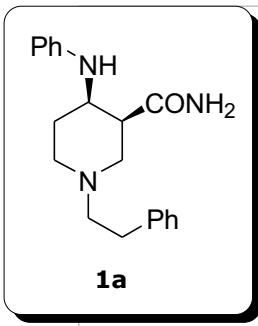
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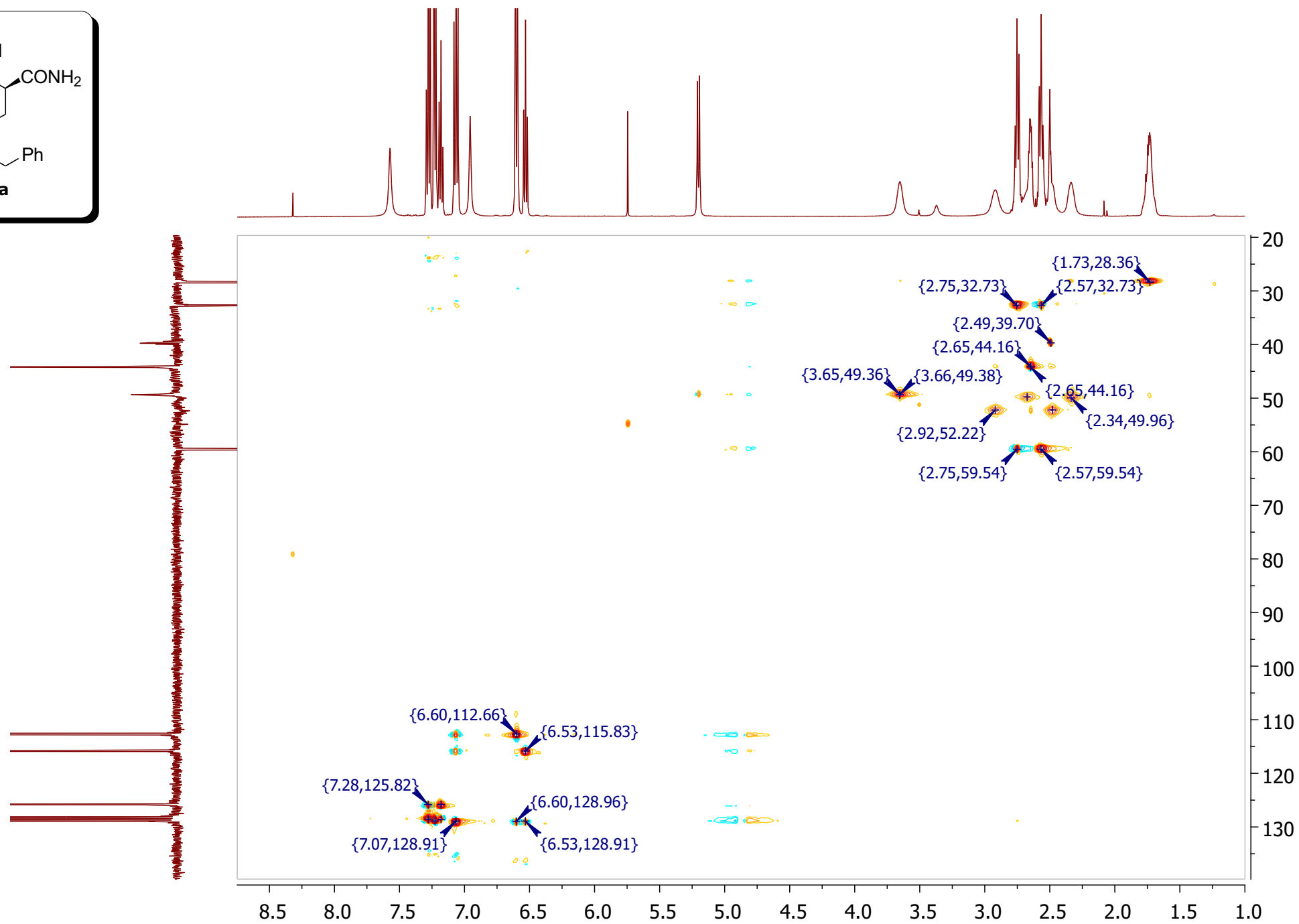
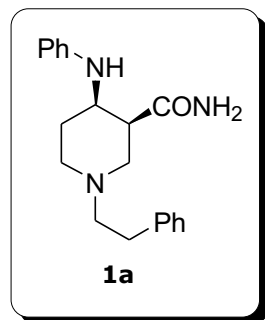
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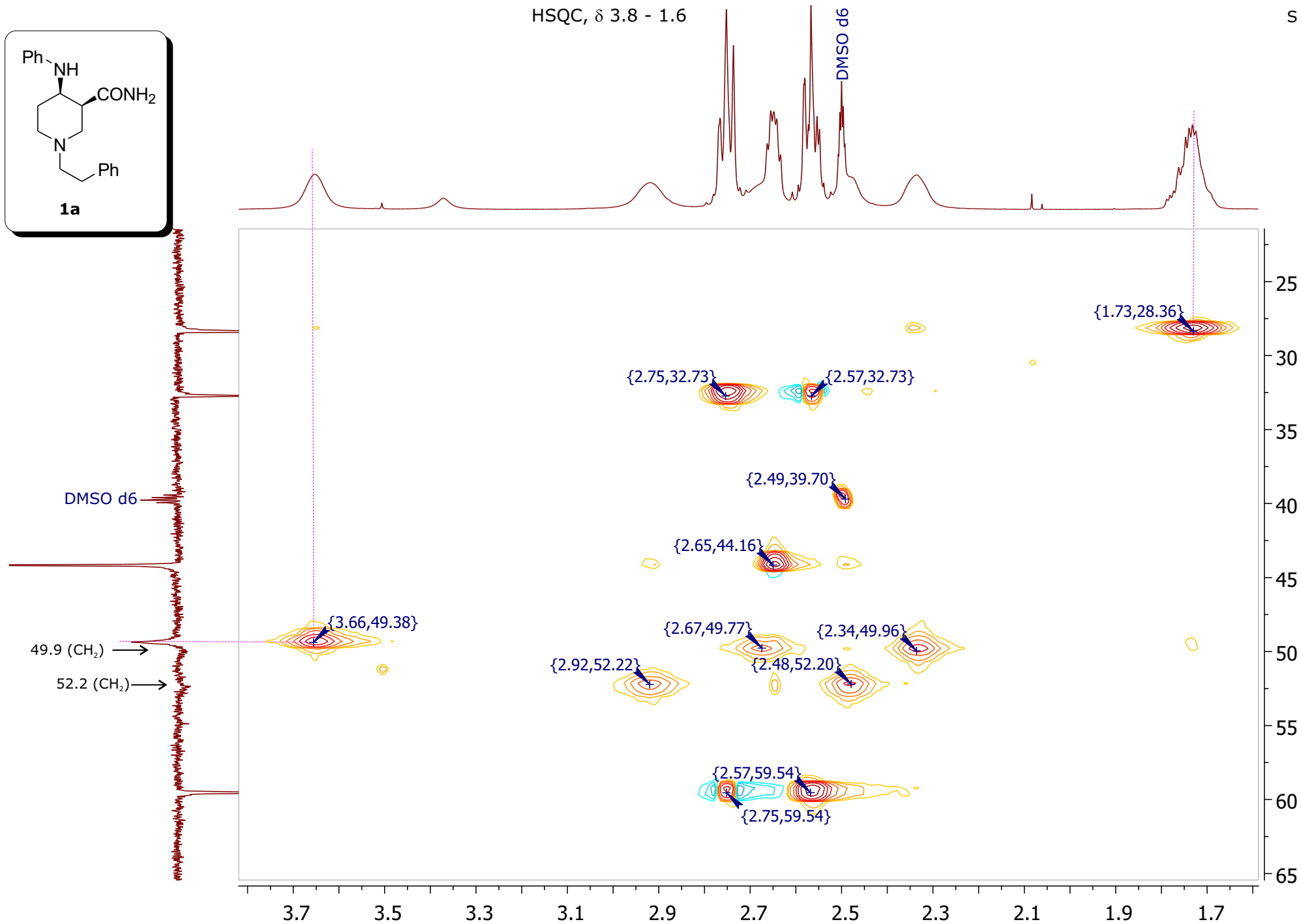
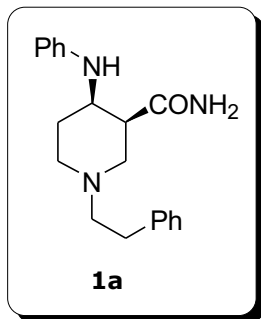
28.	 <p>2q</p>	¹ H NMR 122 ¹³ C NMR 123 DEPT 124	32.	 <p>2u</p>	¹ H NMR 134 ¹³ C NMR 135 APT 136
29.	 <p>2r</p>	¹ H NMR 125 ¹³ C NMR 126 DEPT 127			
30.	 <p>2s</p>	¹ H NMR 128 ¹³ C NMR 129 DEPT 130			
31.	 <p>2t</p>	¹ H NMR 131 ¹³ C NMR 132 APT 133			

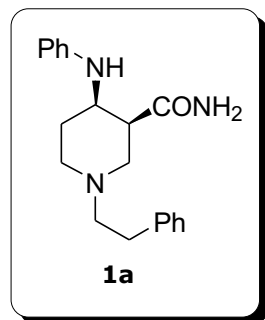




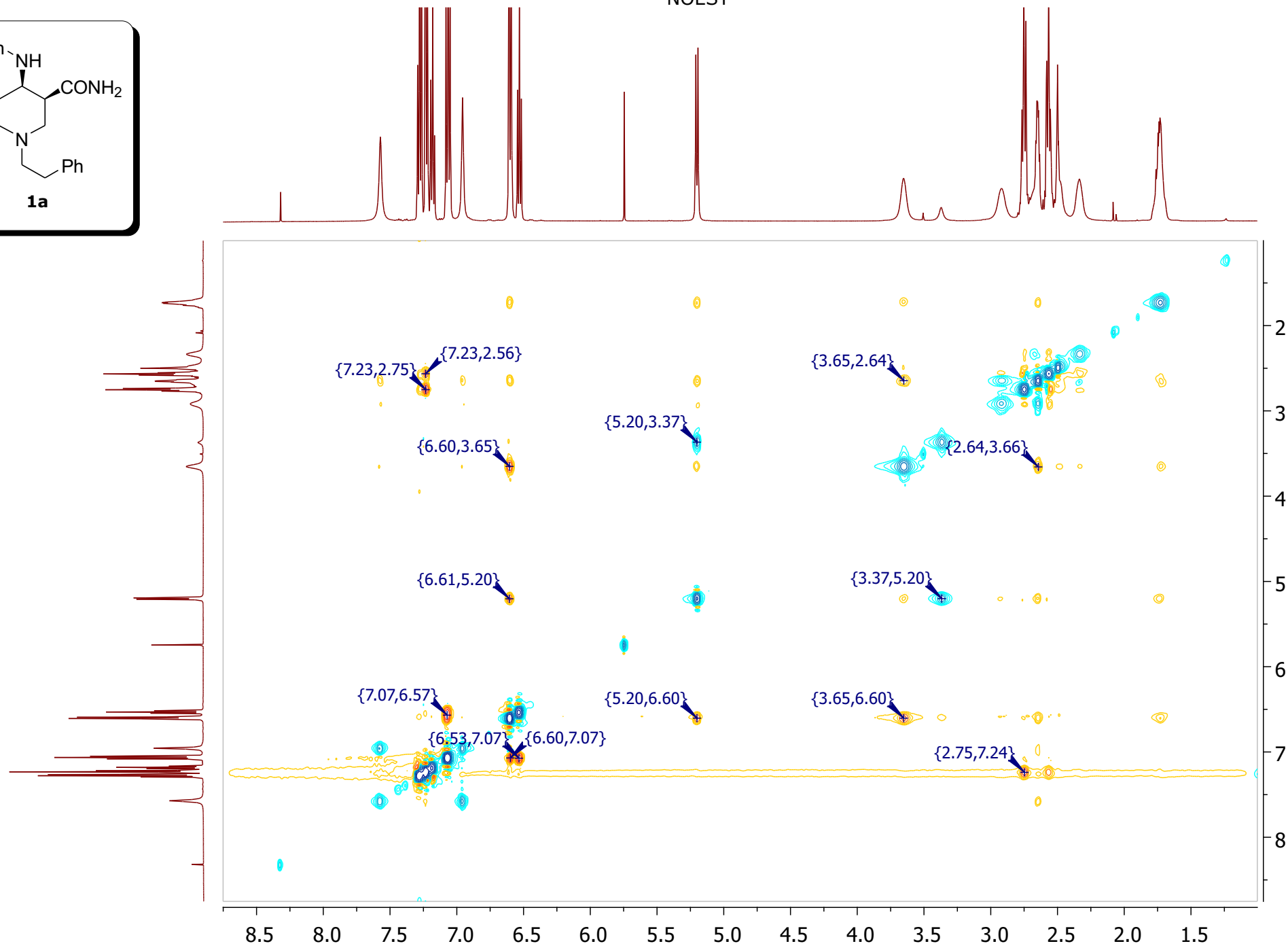


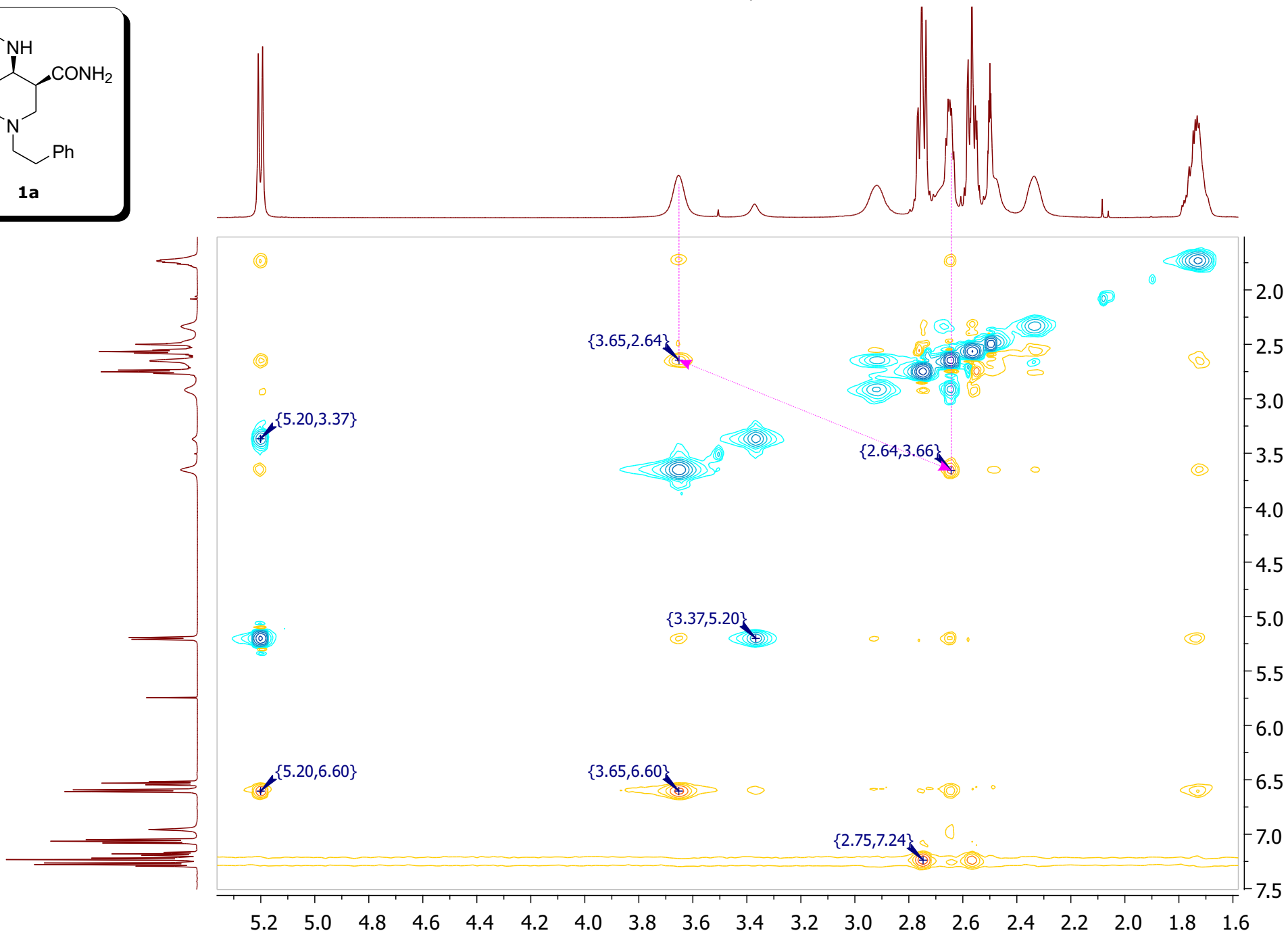
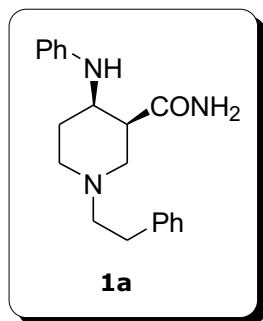




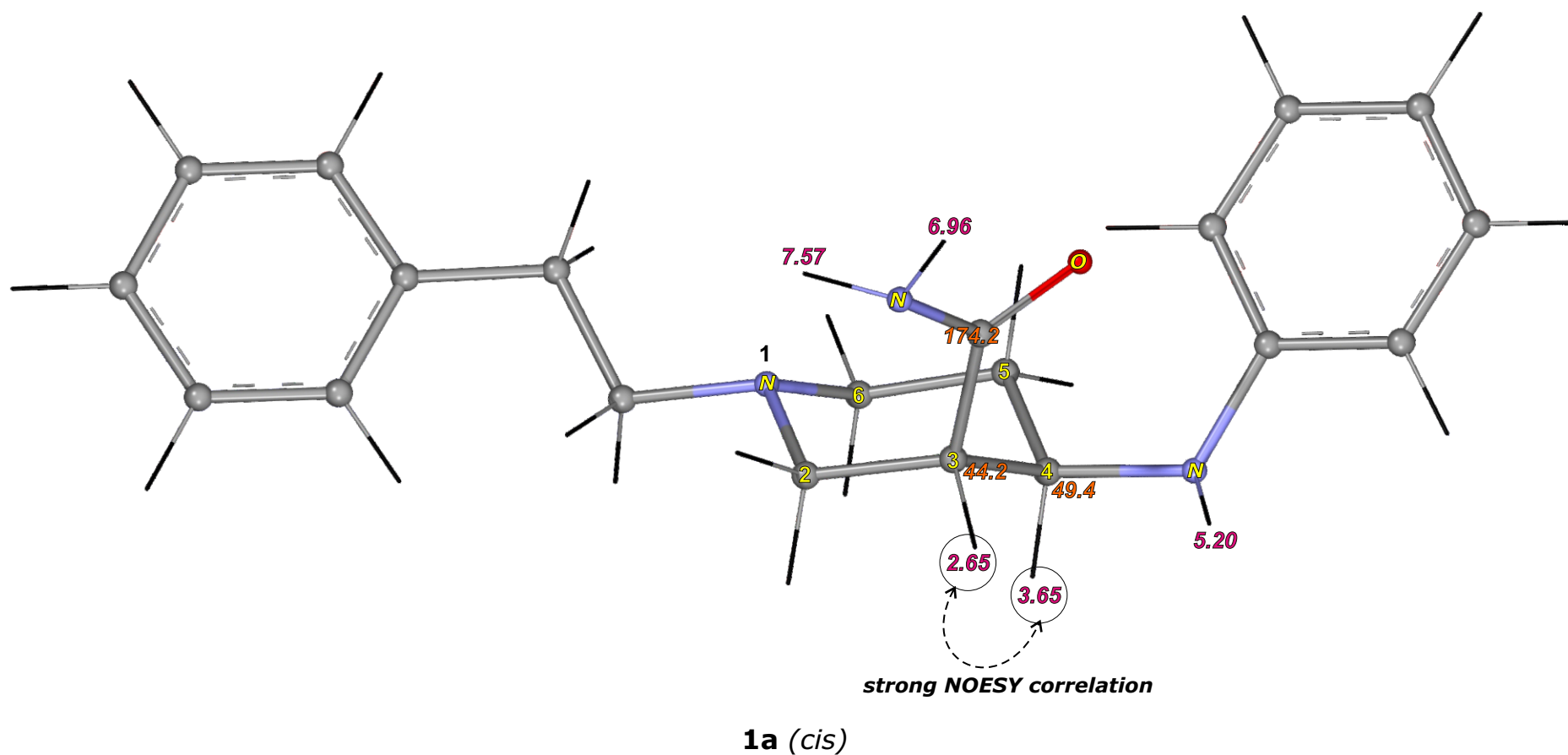


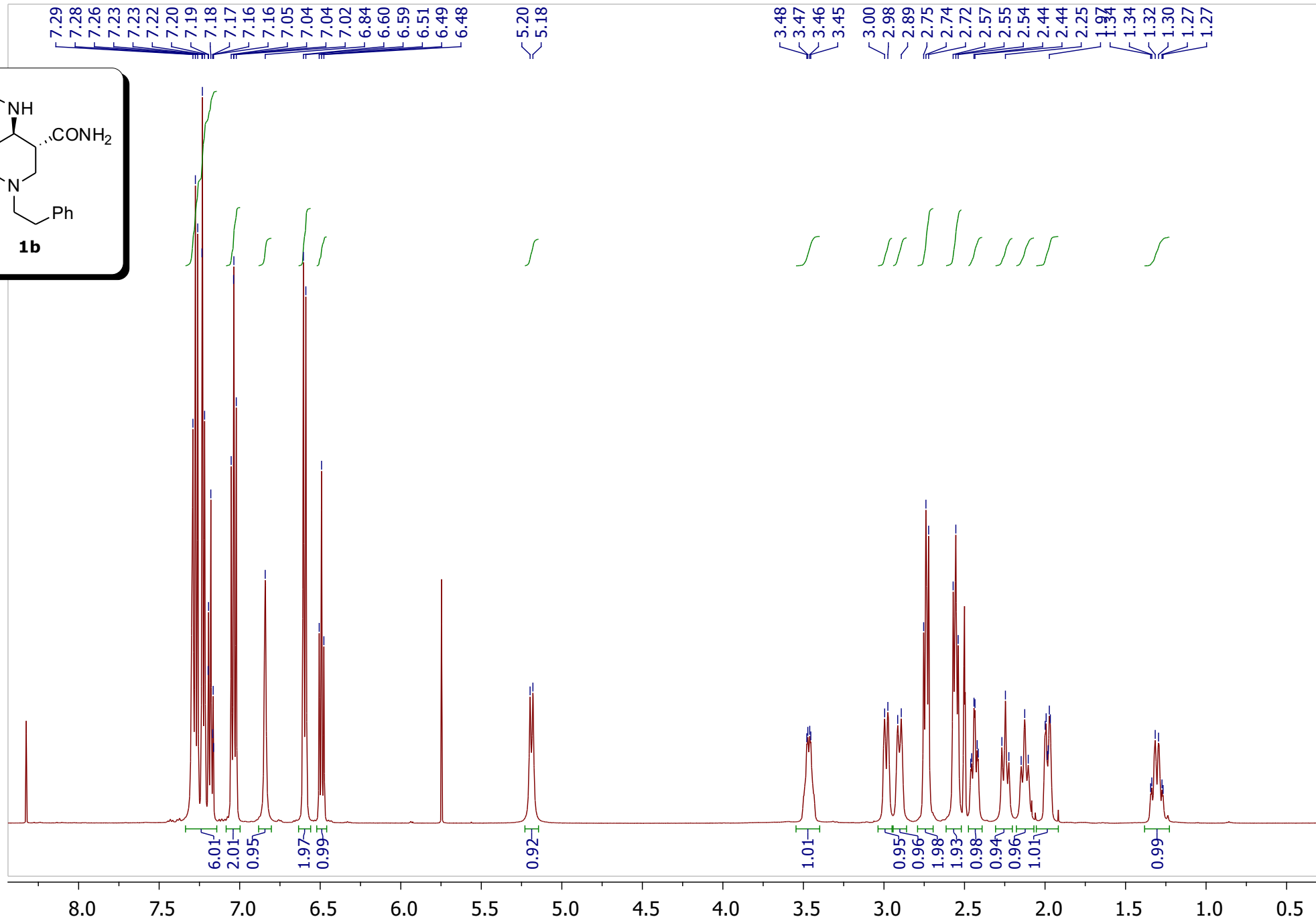
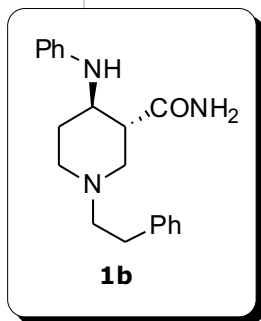
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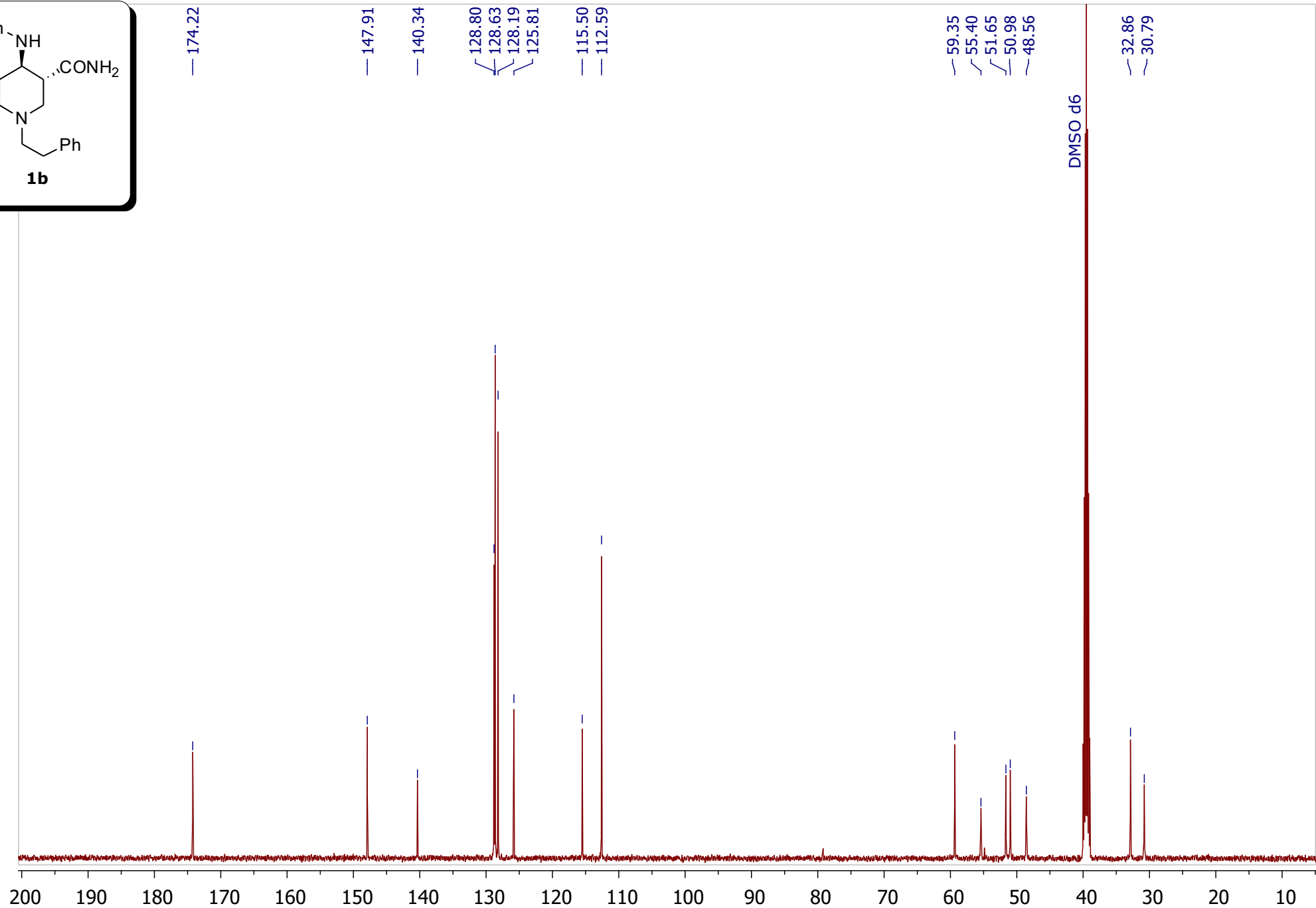
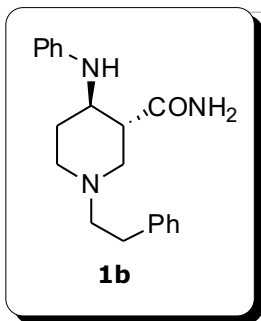


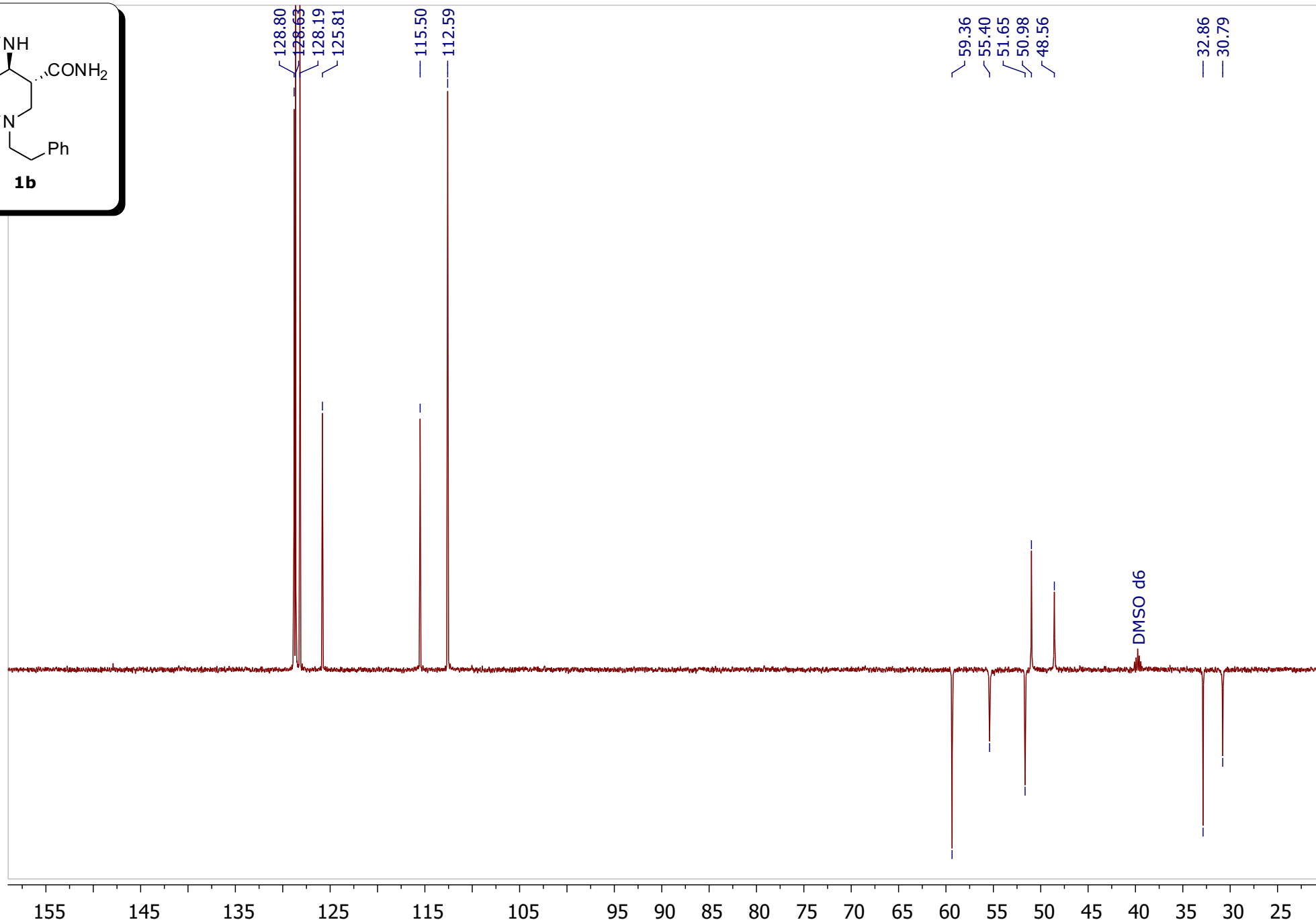
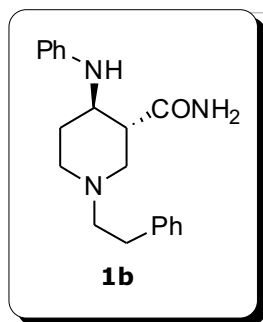


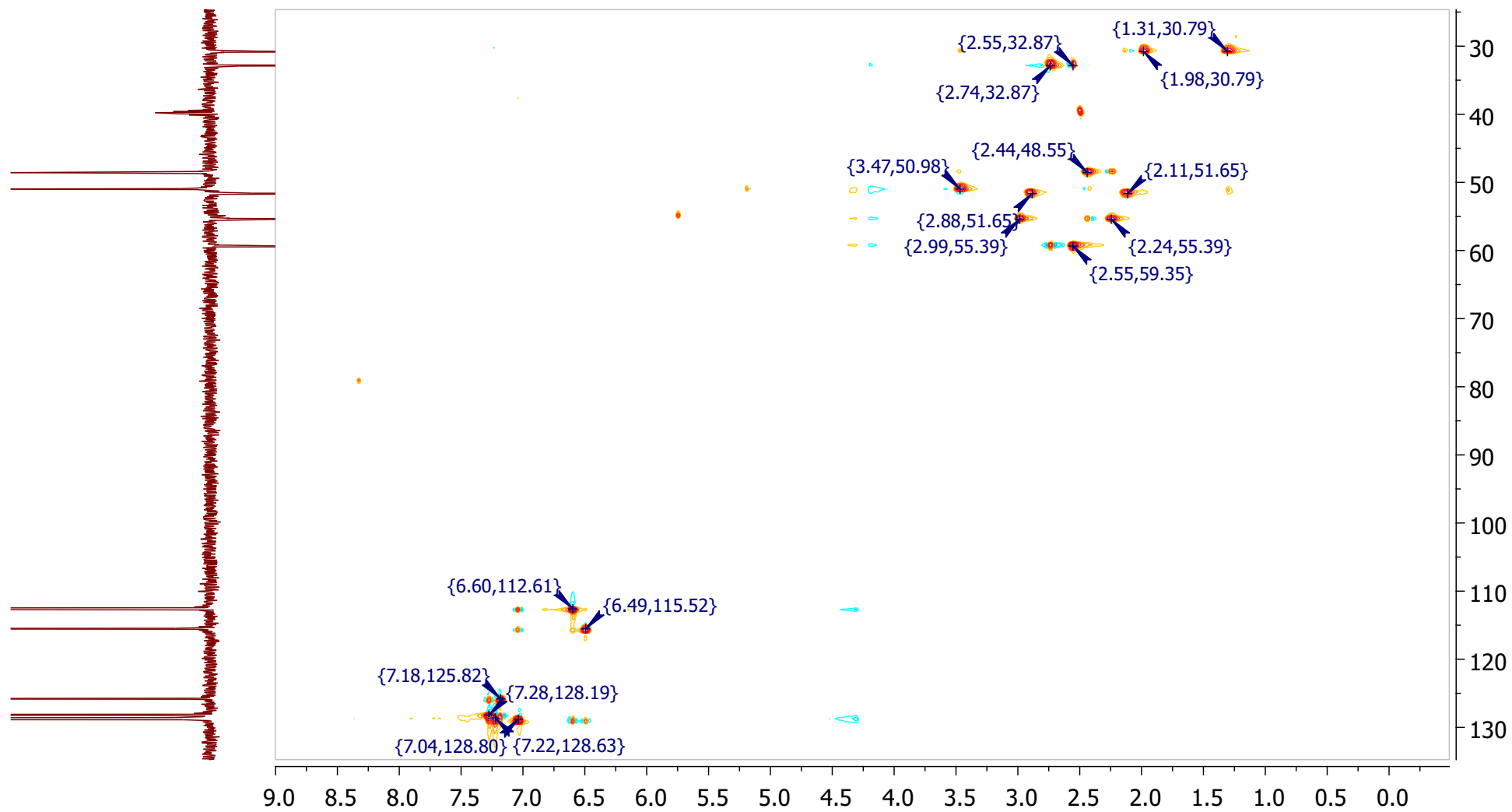
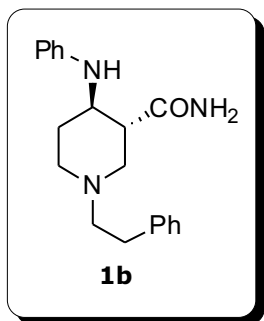
Approximate 3D model of amide **1a**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*cis*) is strongly corroborated by spectral data of amide **1a**, amide **1b** (*trans*), urea **2a** (*cis*) and urea **2b** (*trans*).

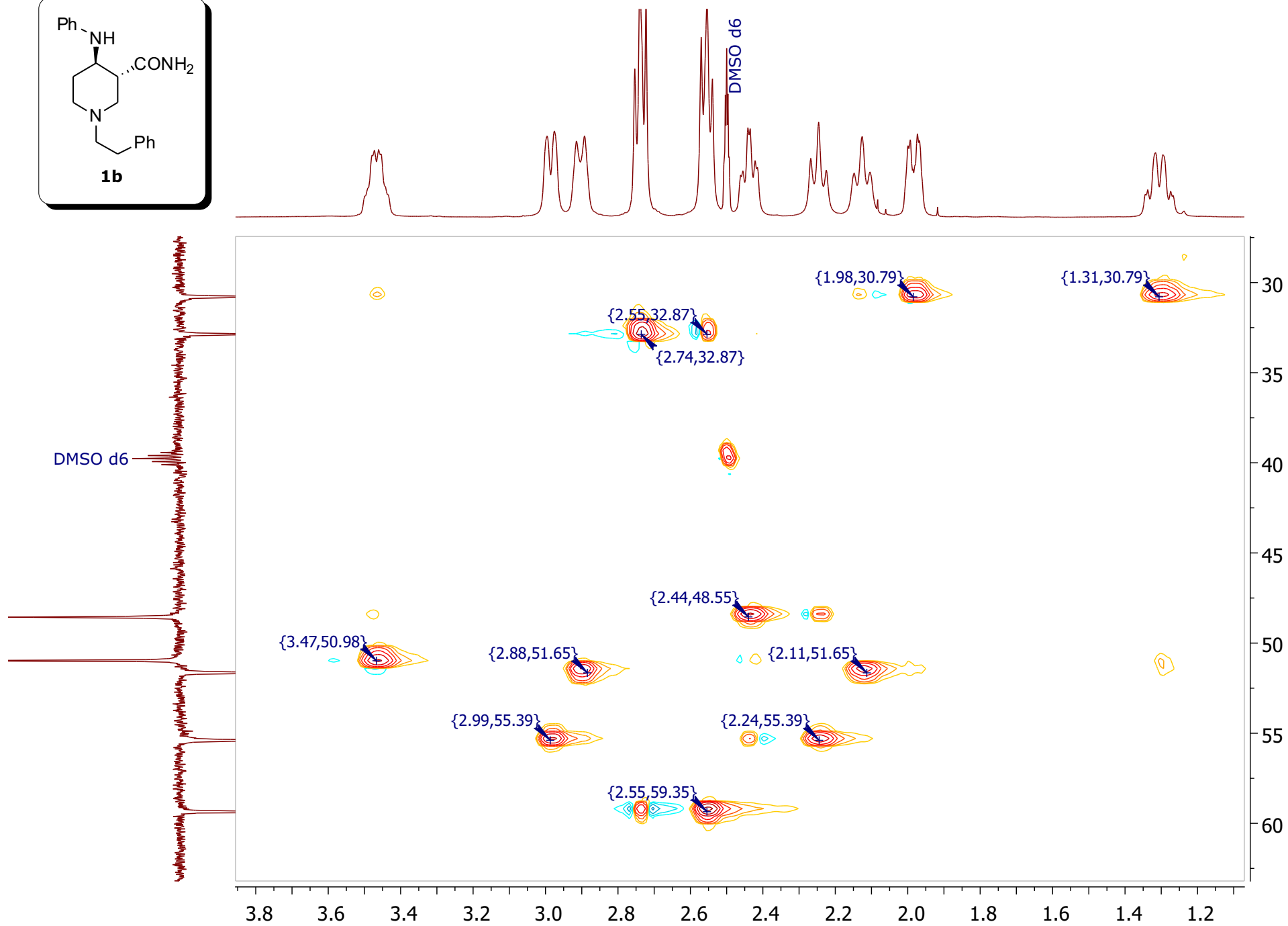
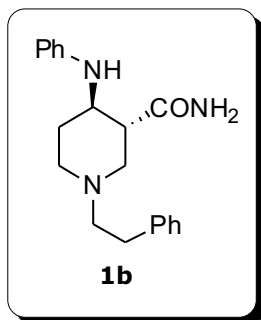


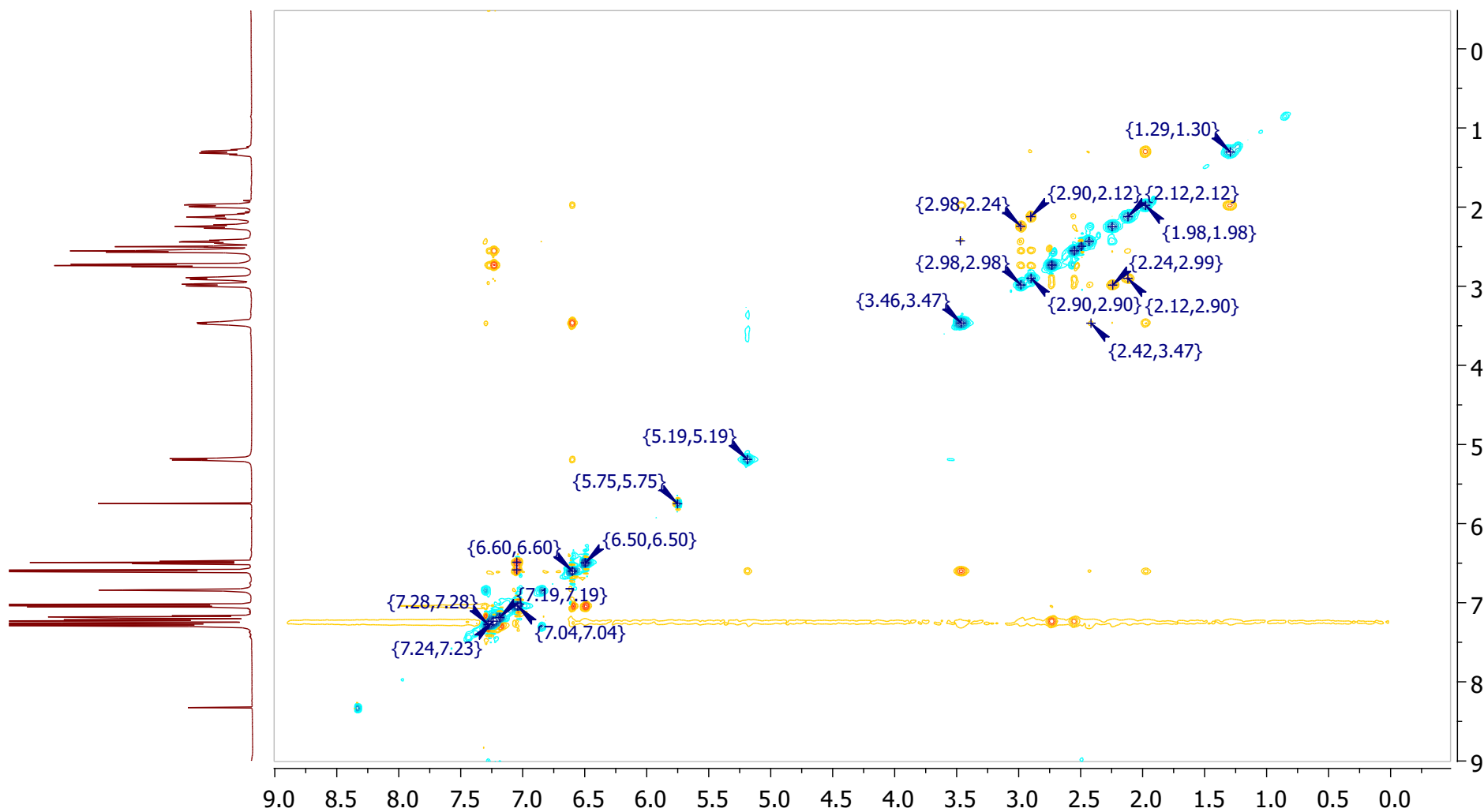
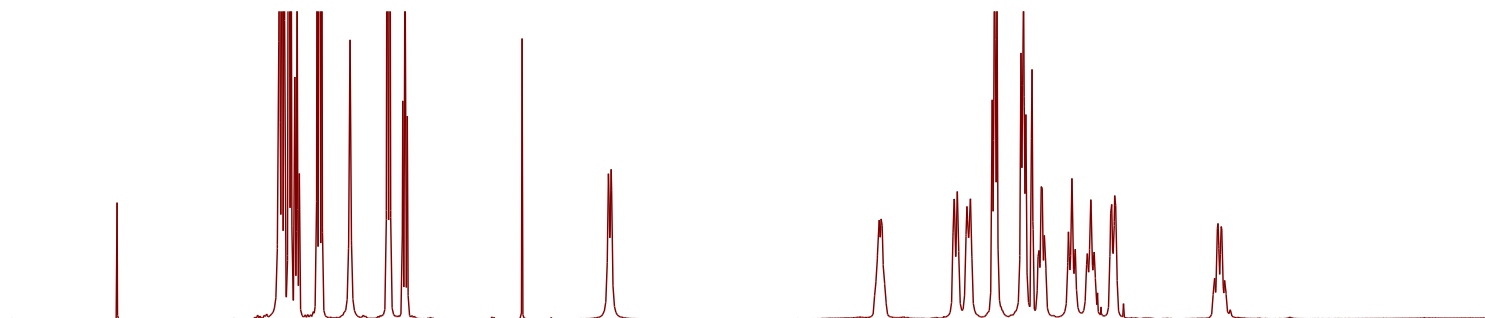
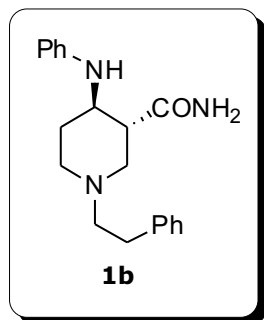


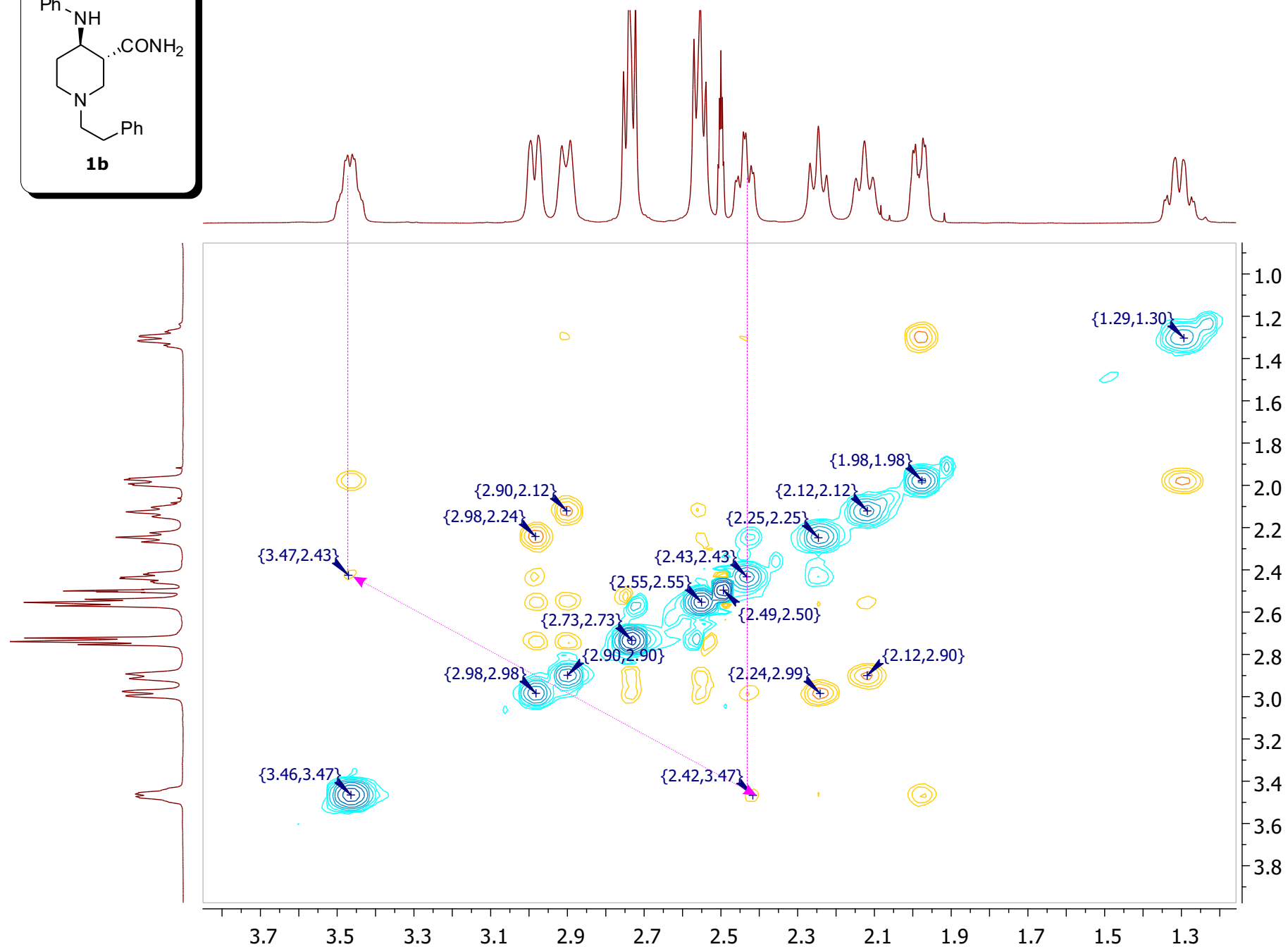
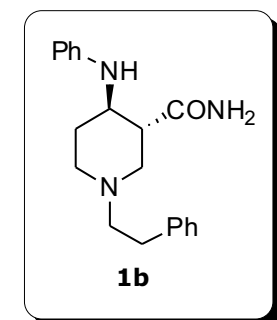




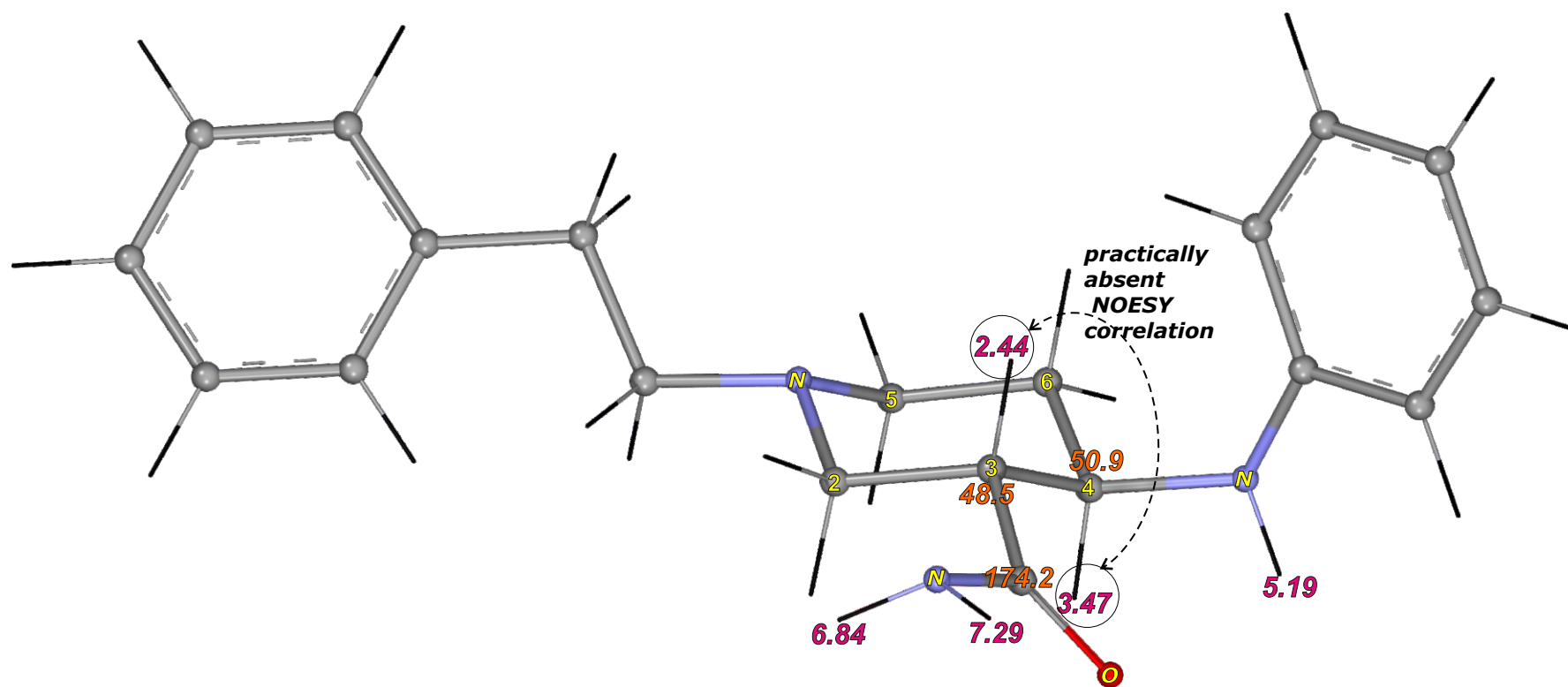


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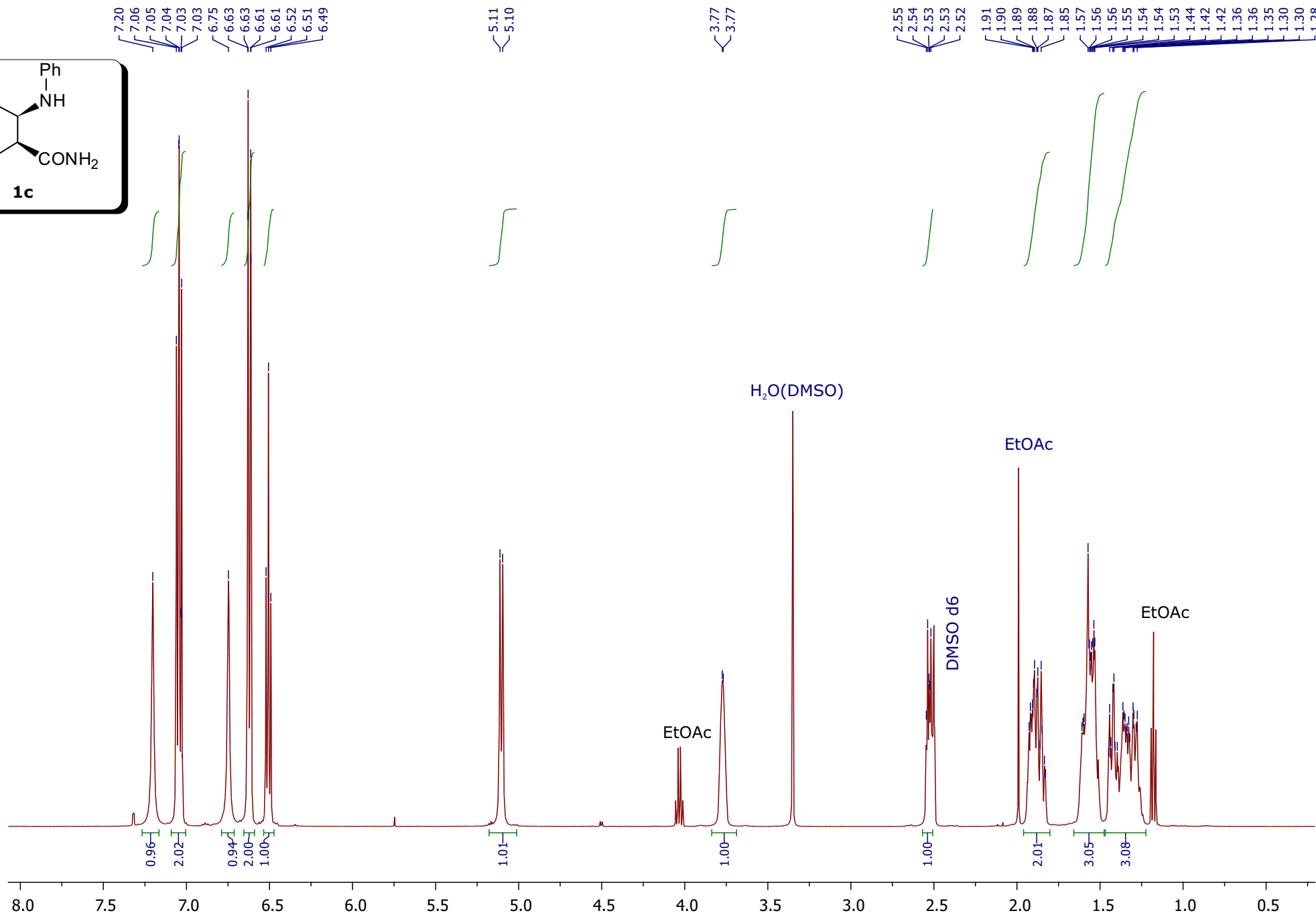
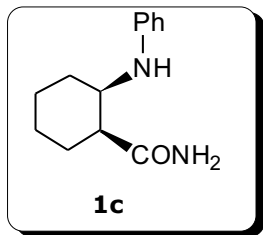


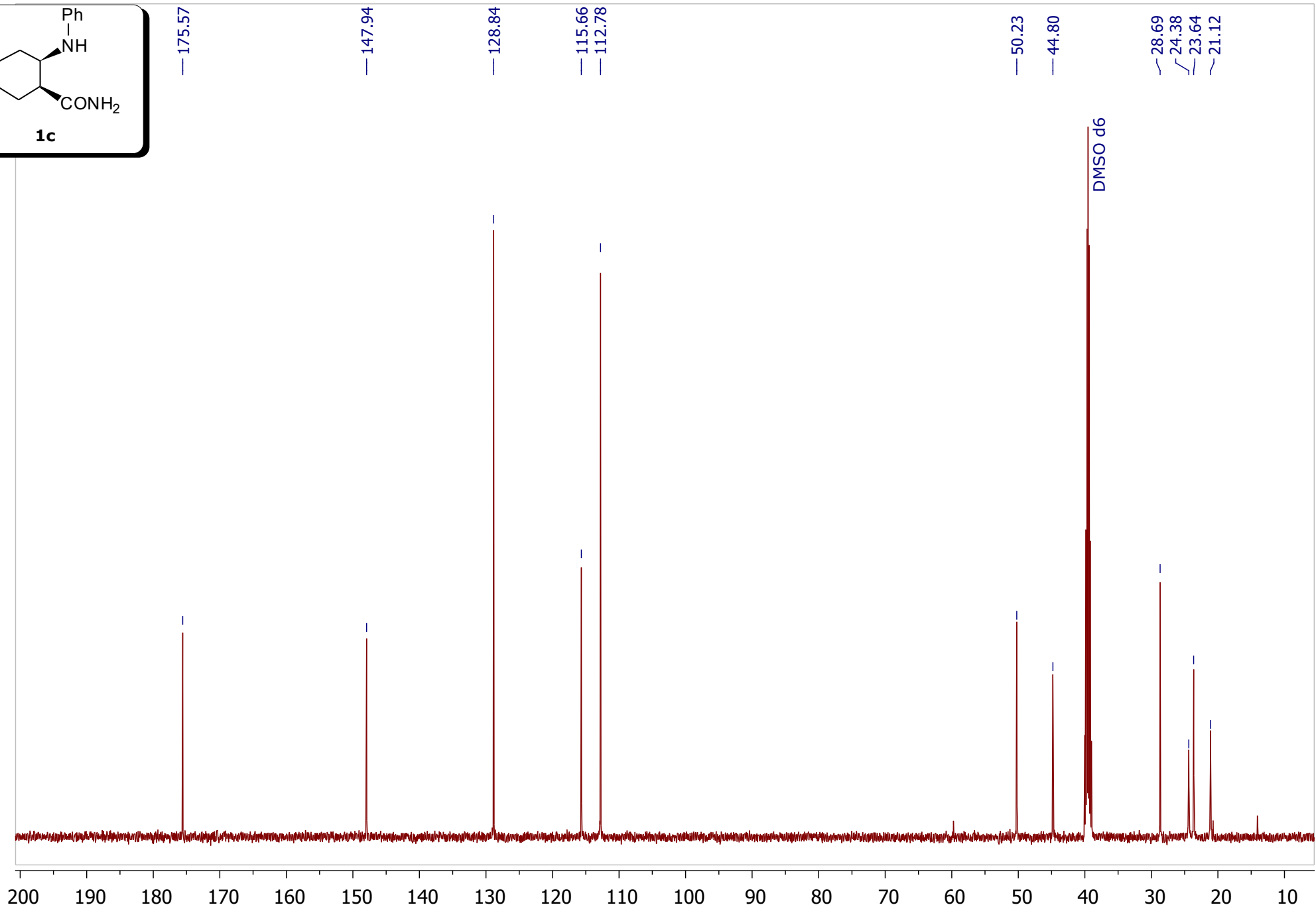
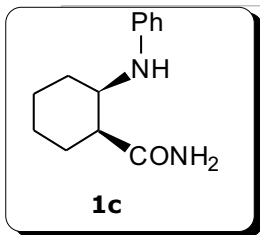


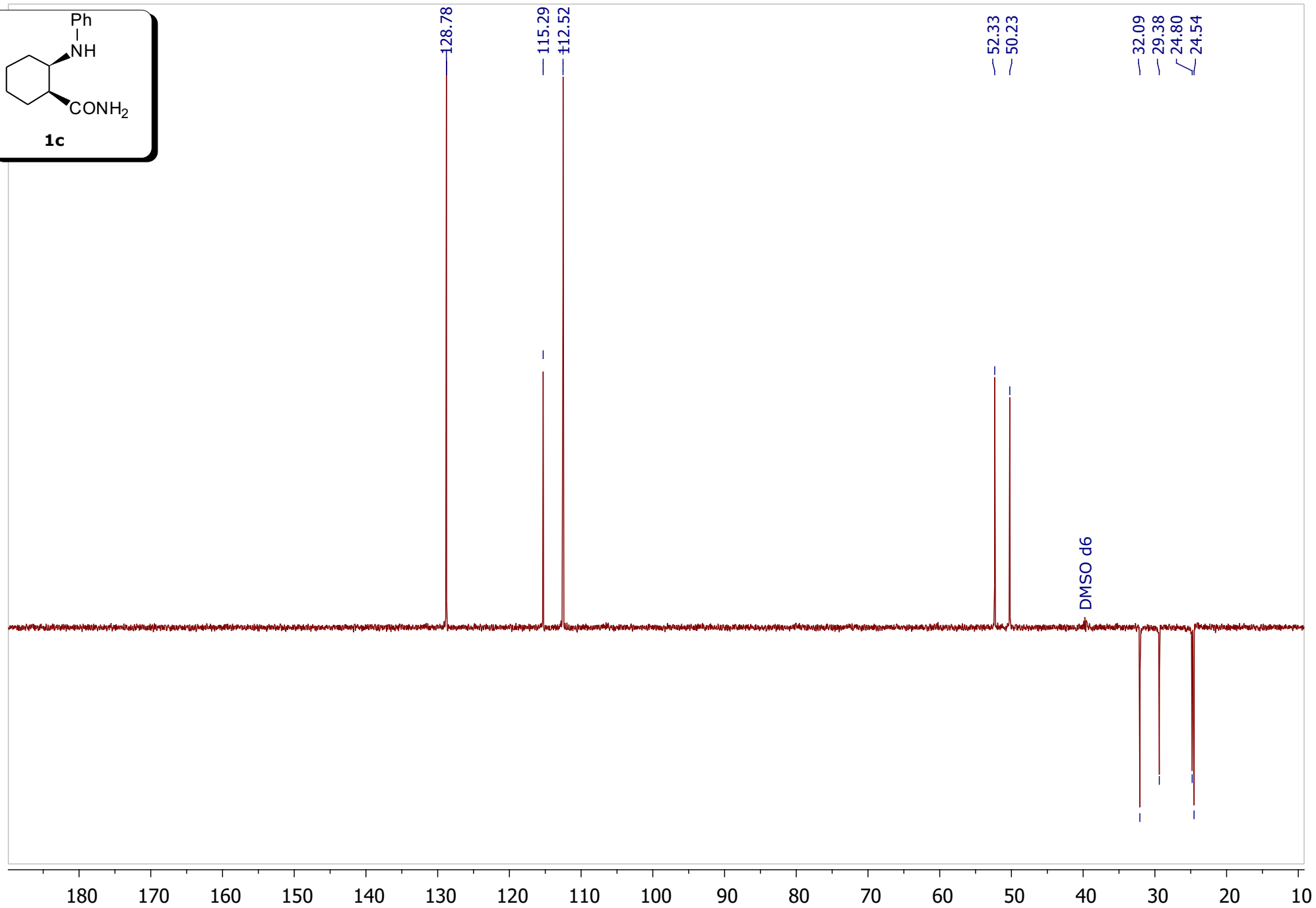
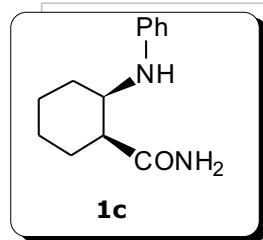
Approximate 3D model of amide **1b**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*trans*) is strongly corroborated by spectral data of amide **1a** (*cis*), amide **1b** (*trans*), urea **2a** (*cis*) and urea **2b** (*trans*).

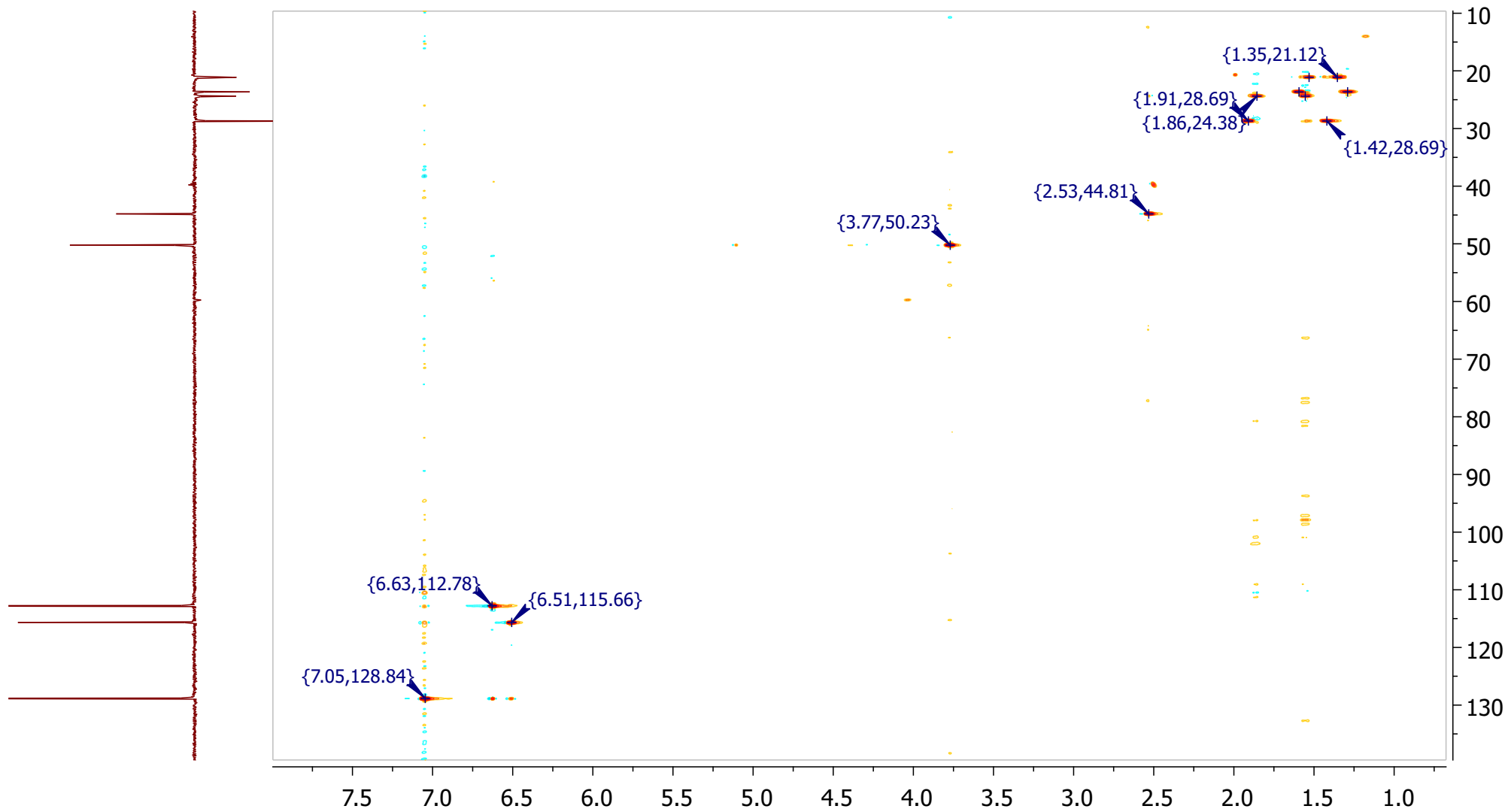
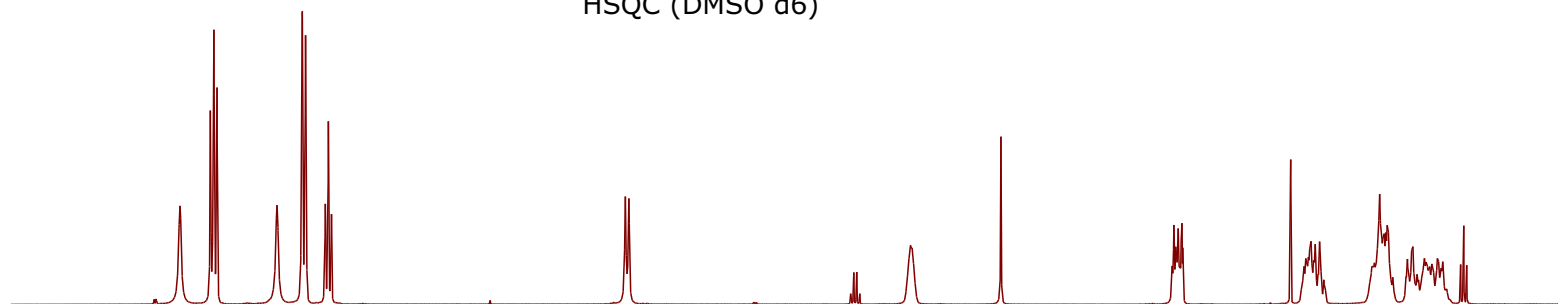
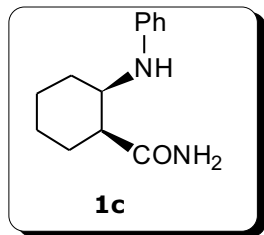


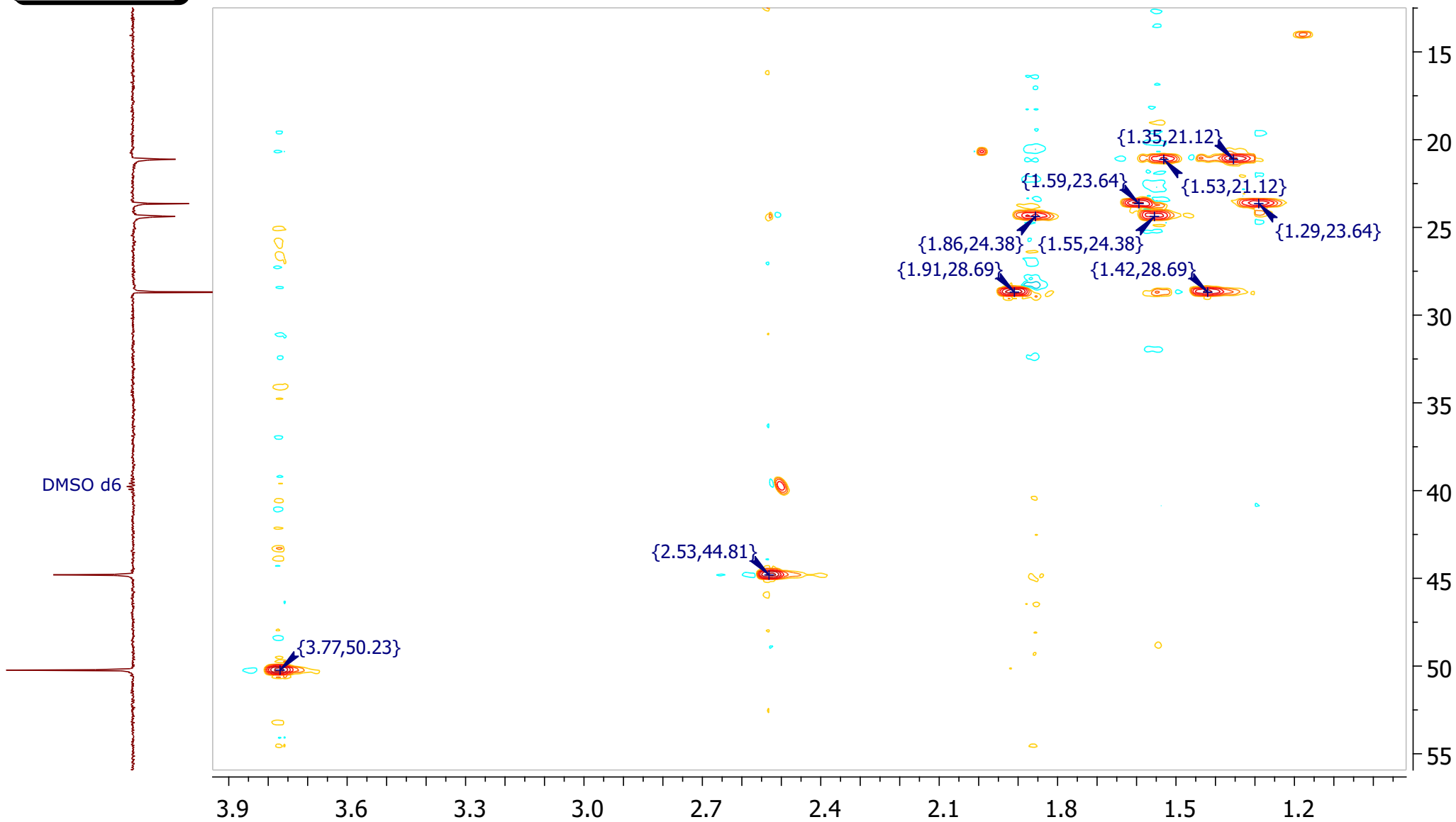
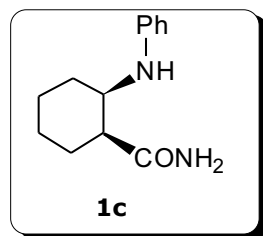
1b (*trans*)

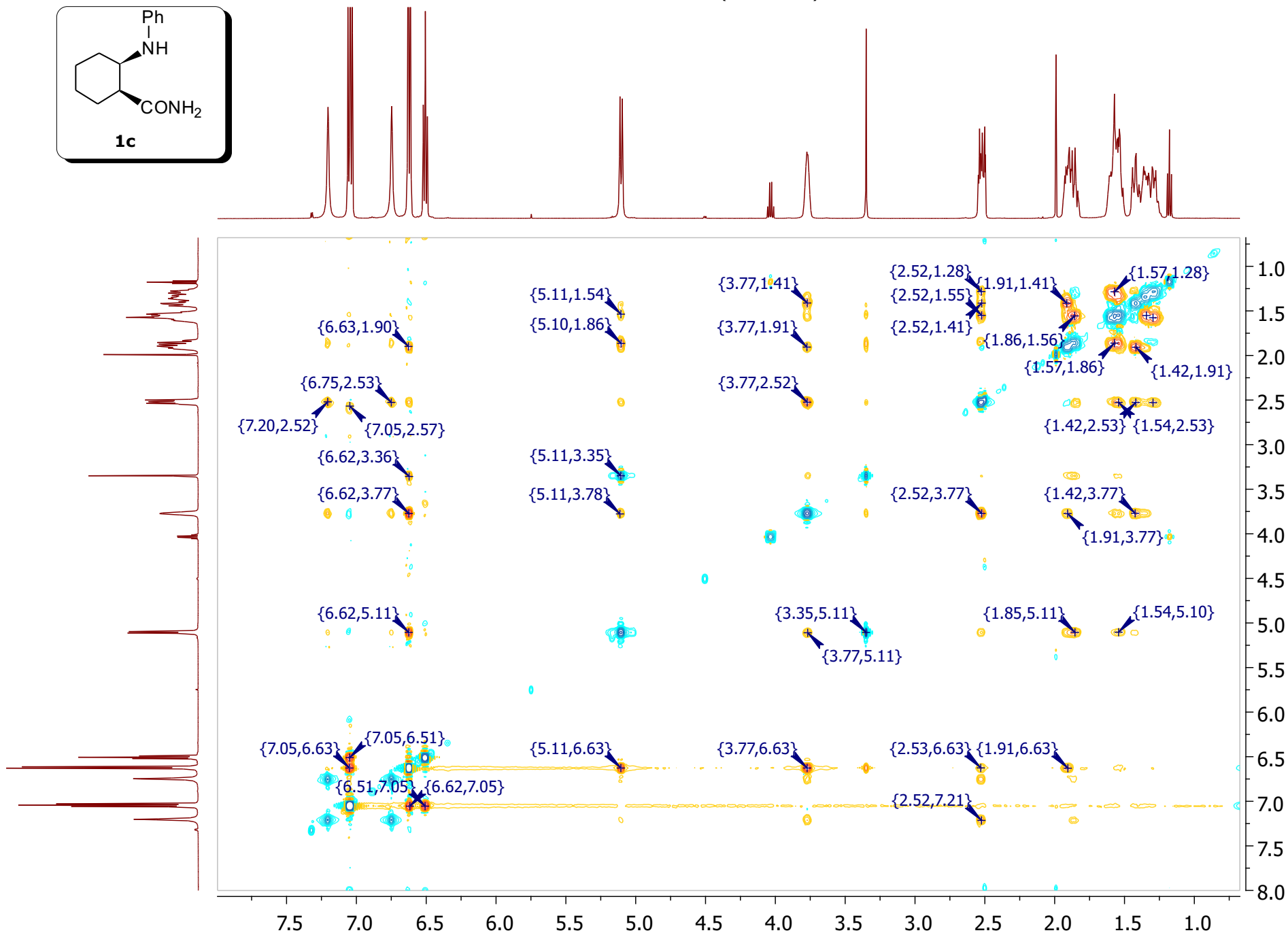
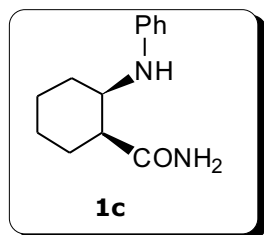


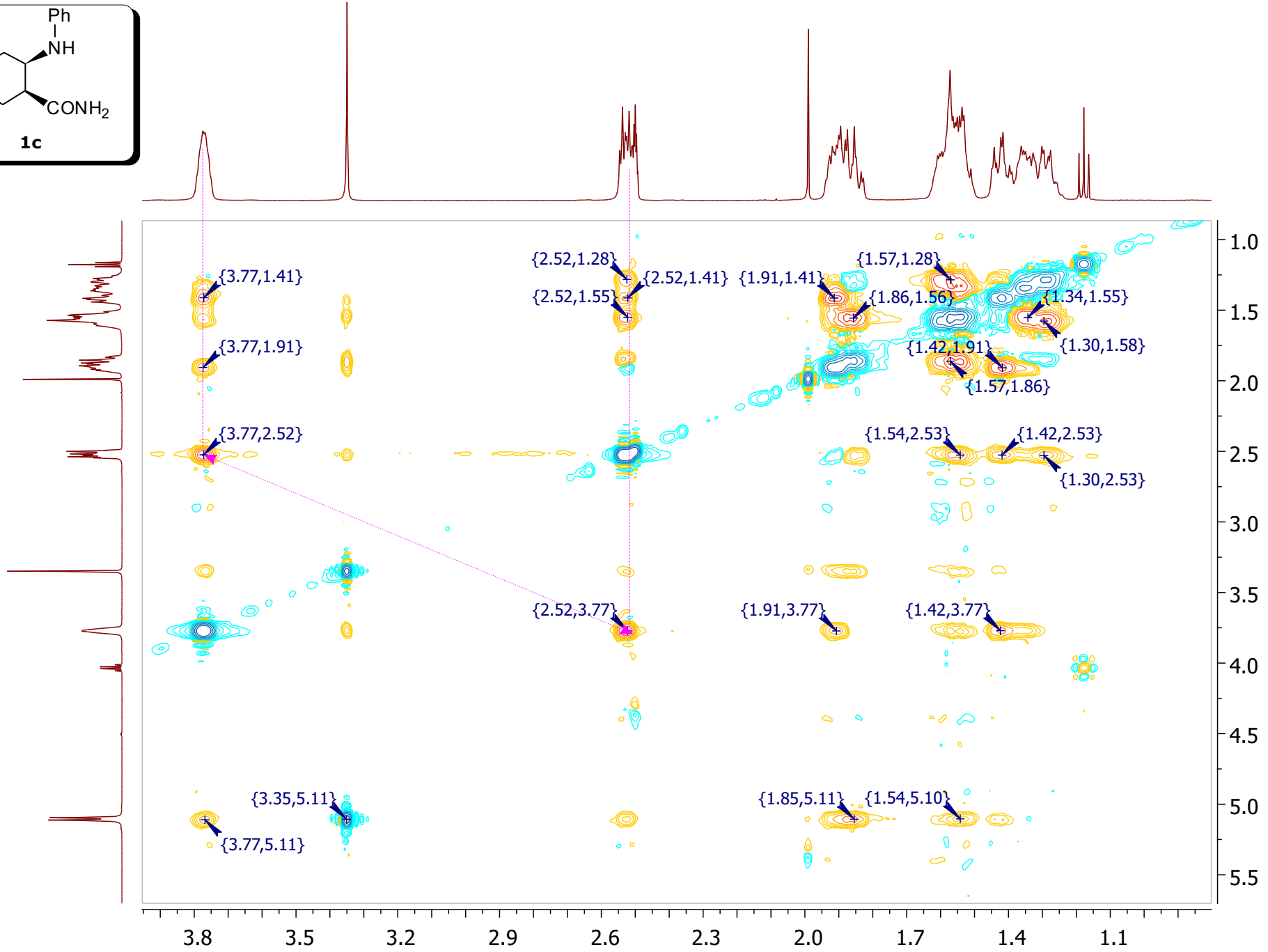
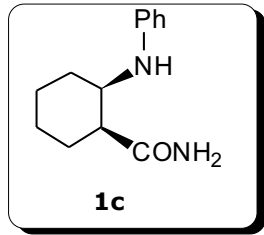




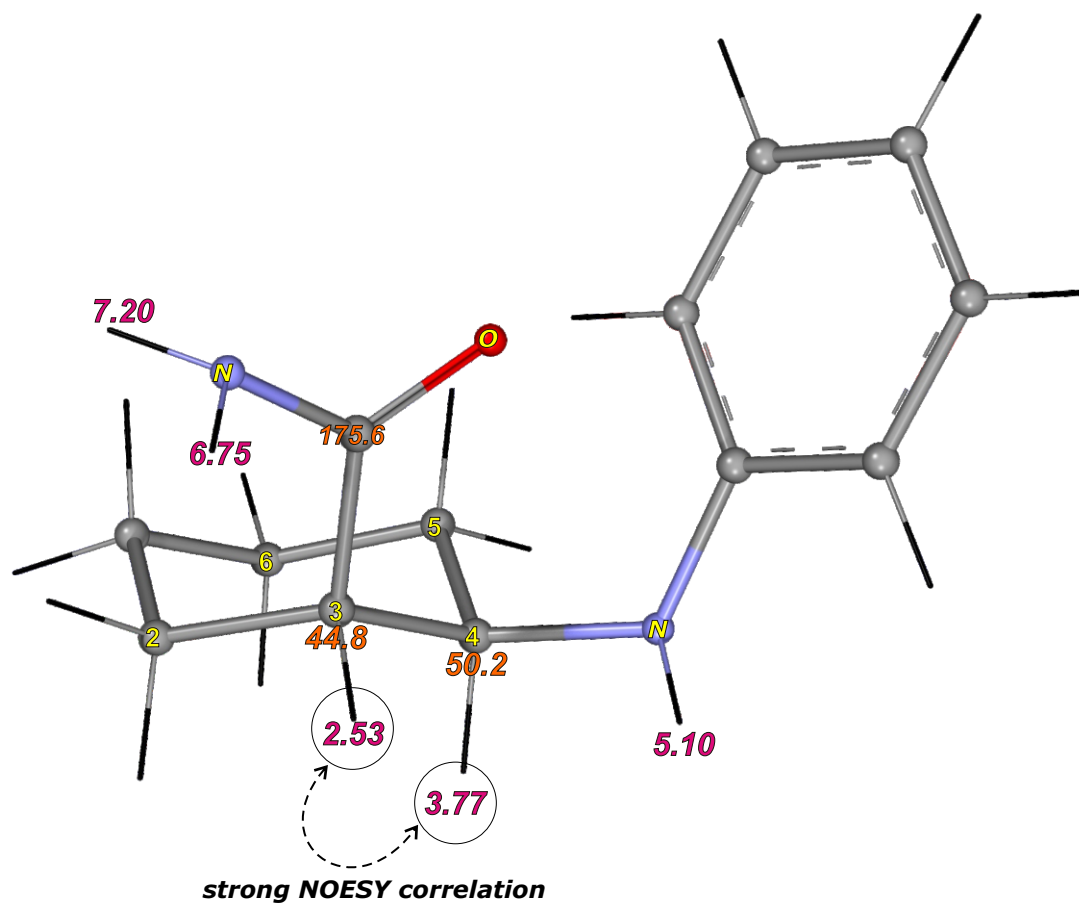




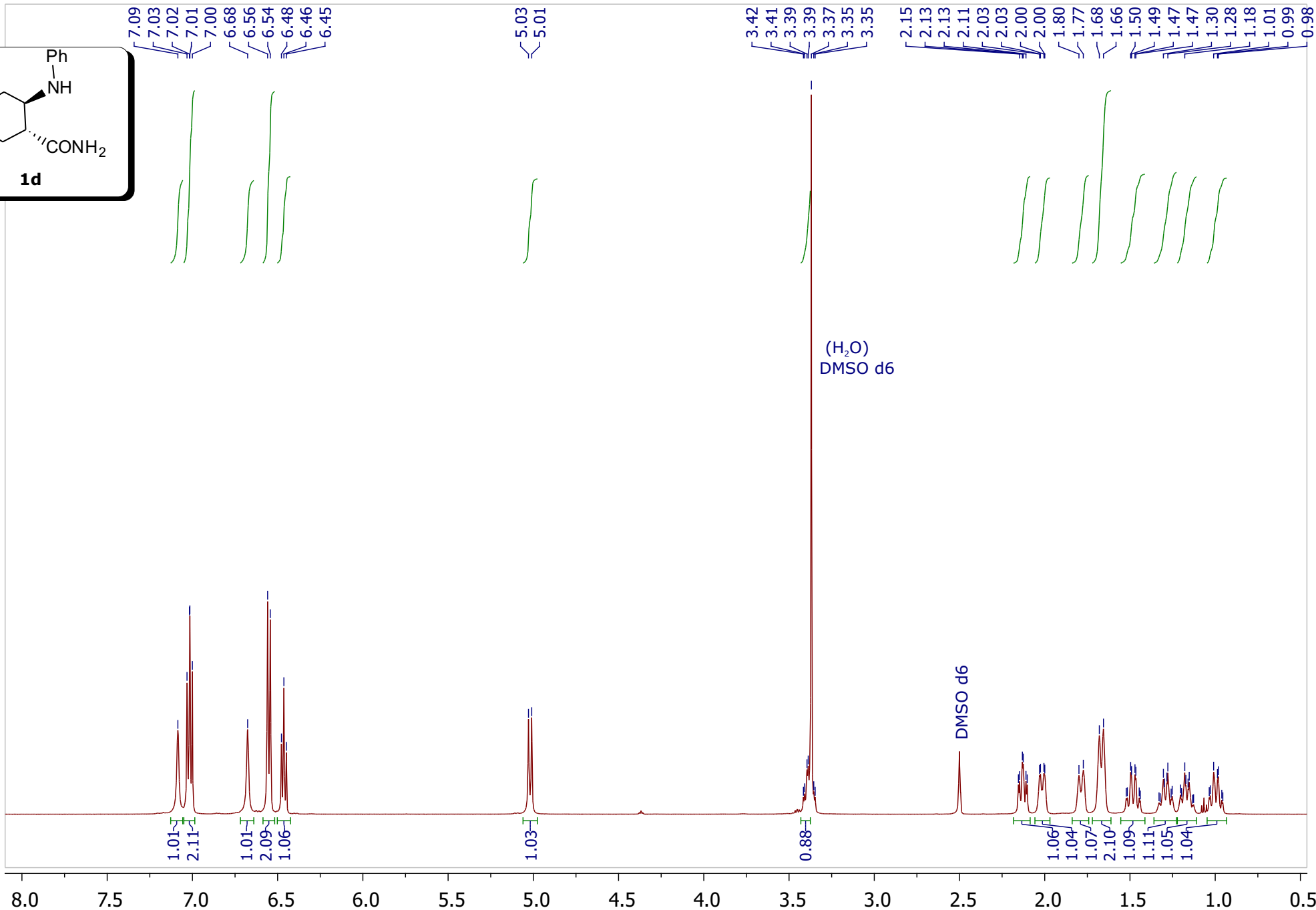
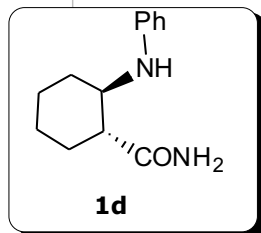


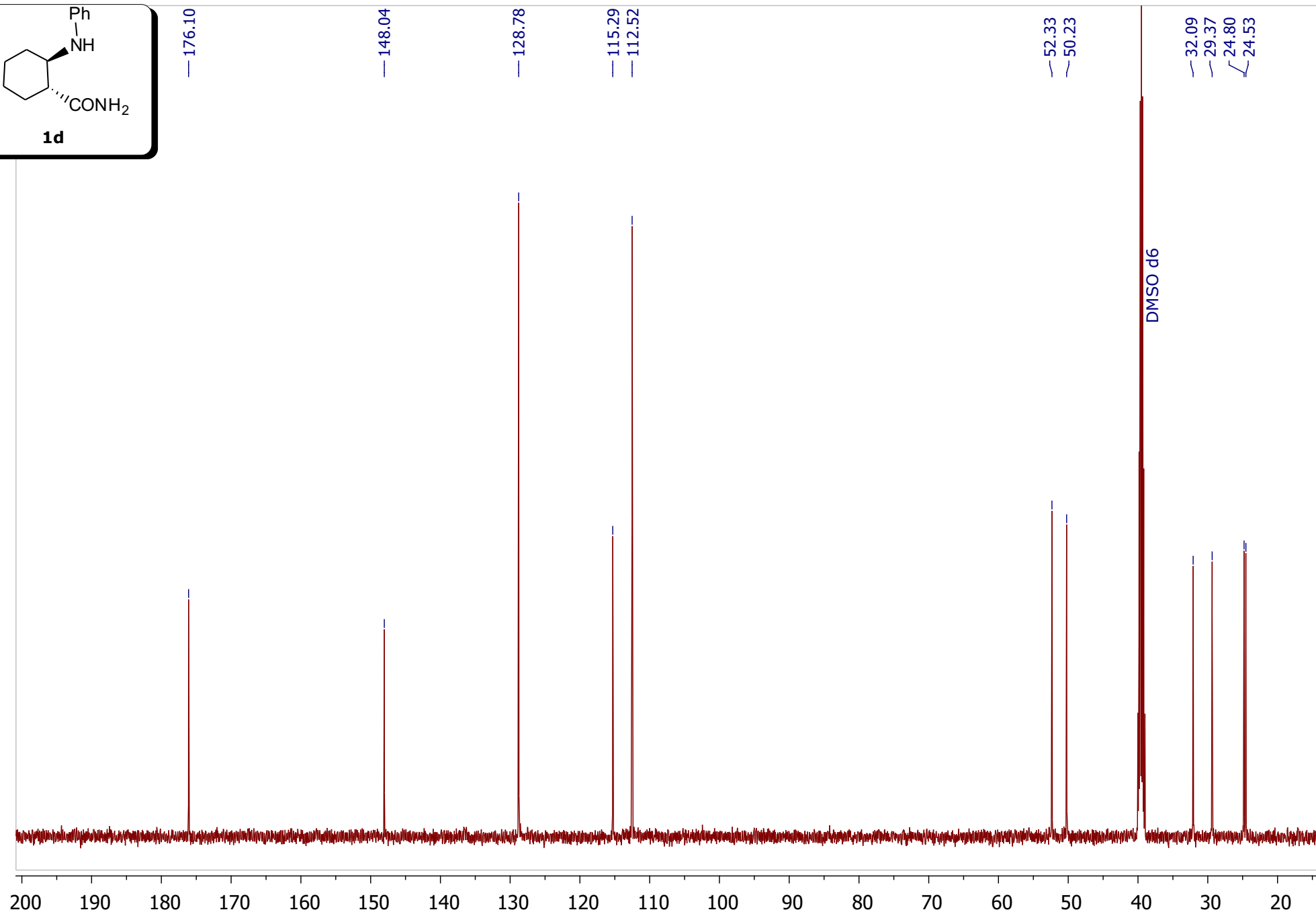
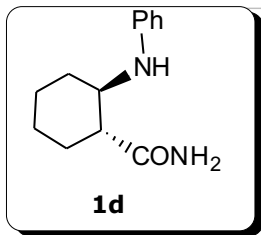


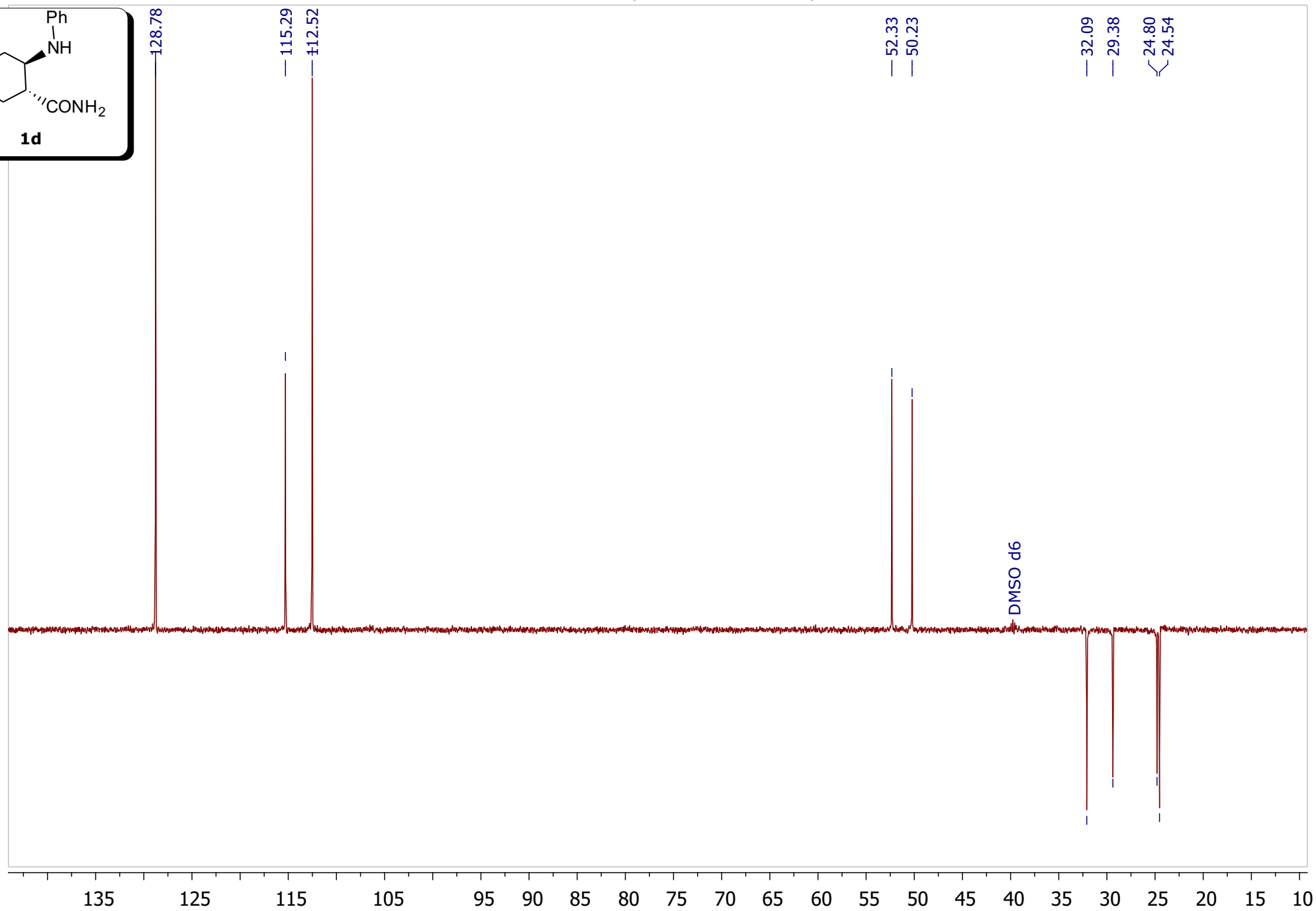
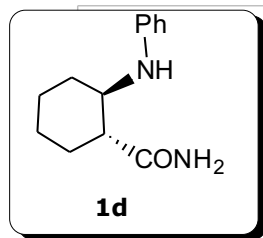
Approximate 3D model of amide **1c**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*cis*) is strongly corroborated by spectral data of amide **1c** (*cis*), amide **1d** (*trans*), urea **2c** (*cis*) and urea **2d** (*trans*).

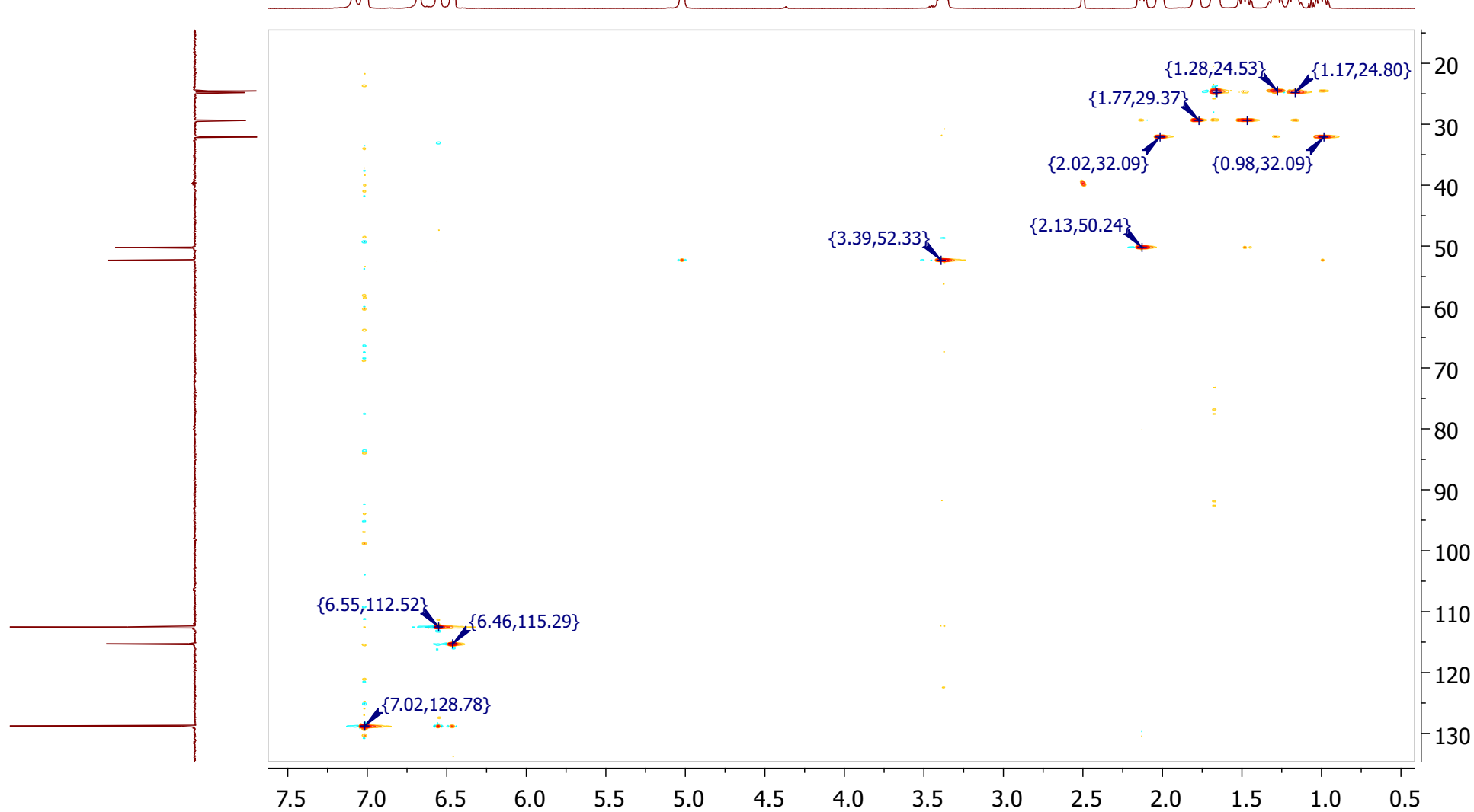
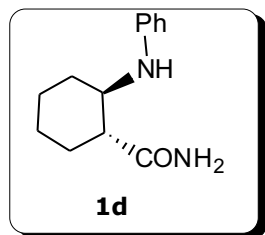


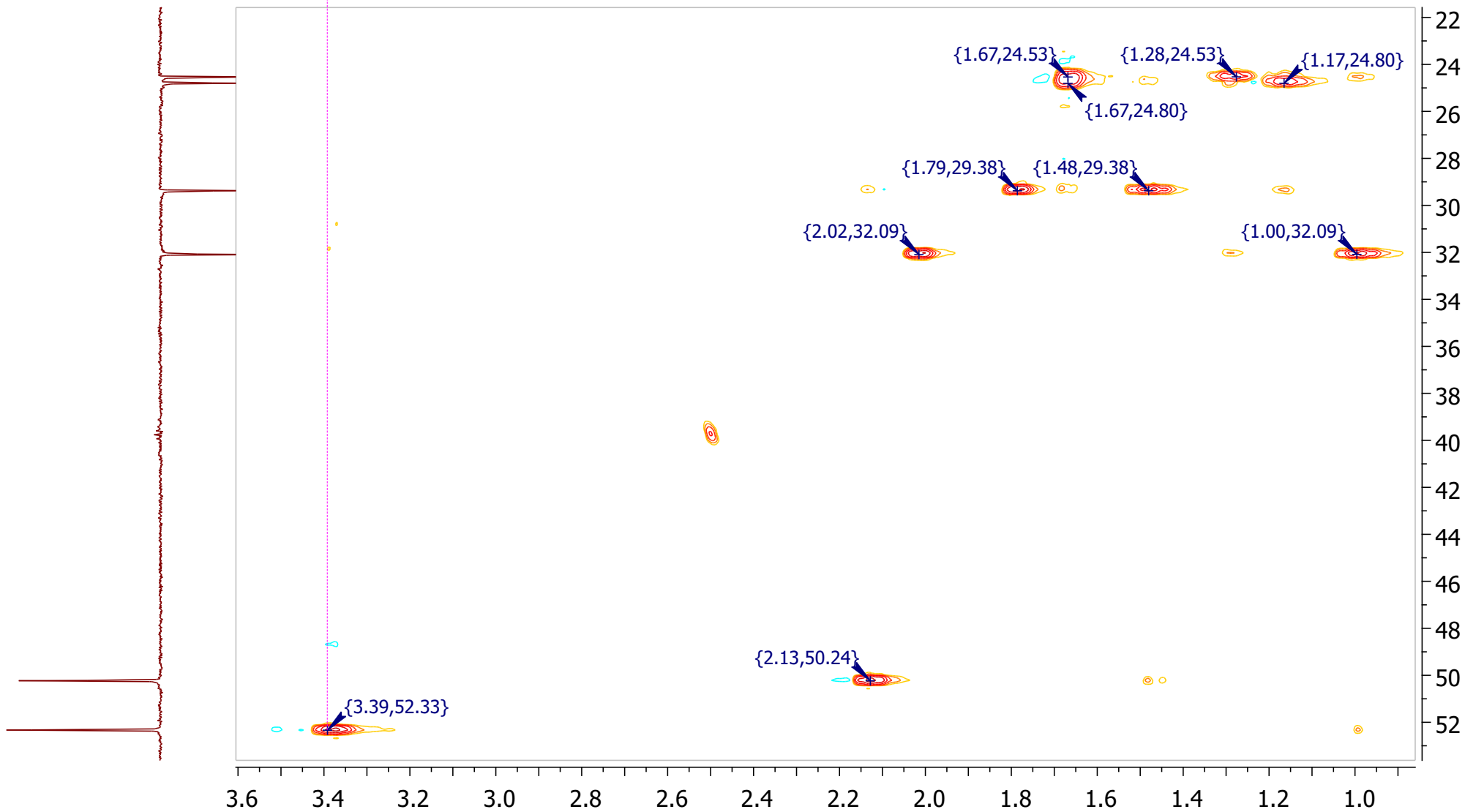
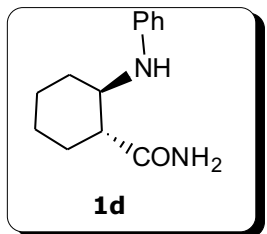
1c (*cis*)

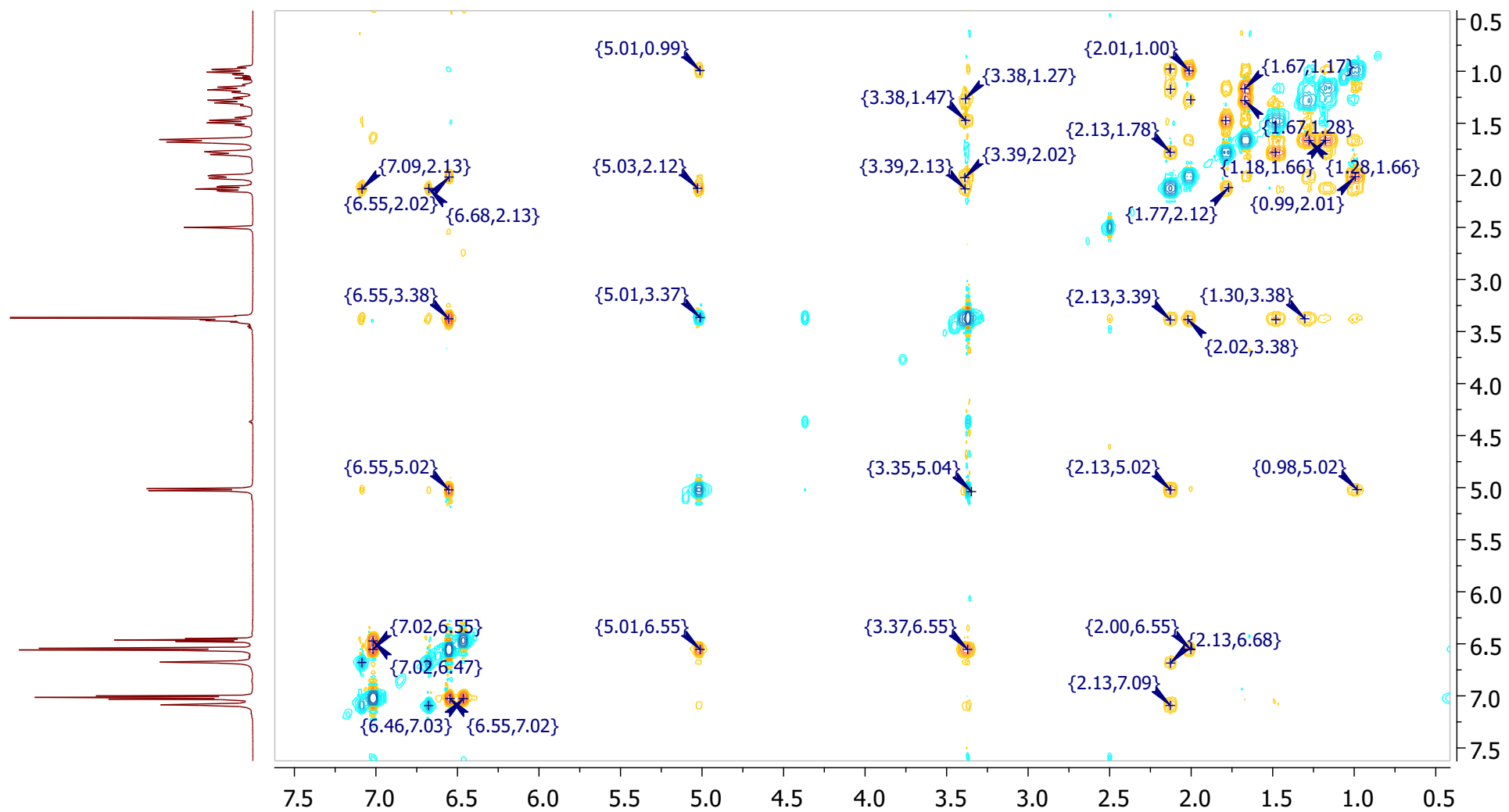
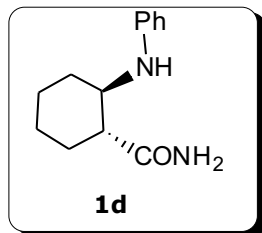


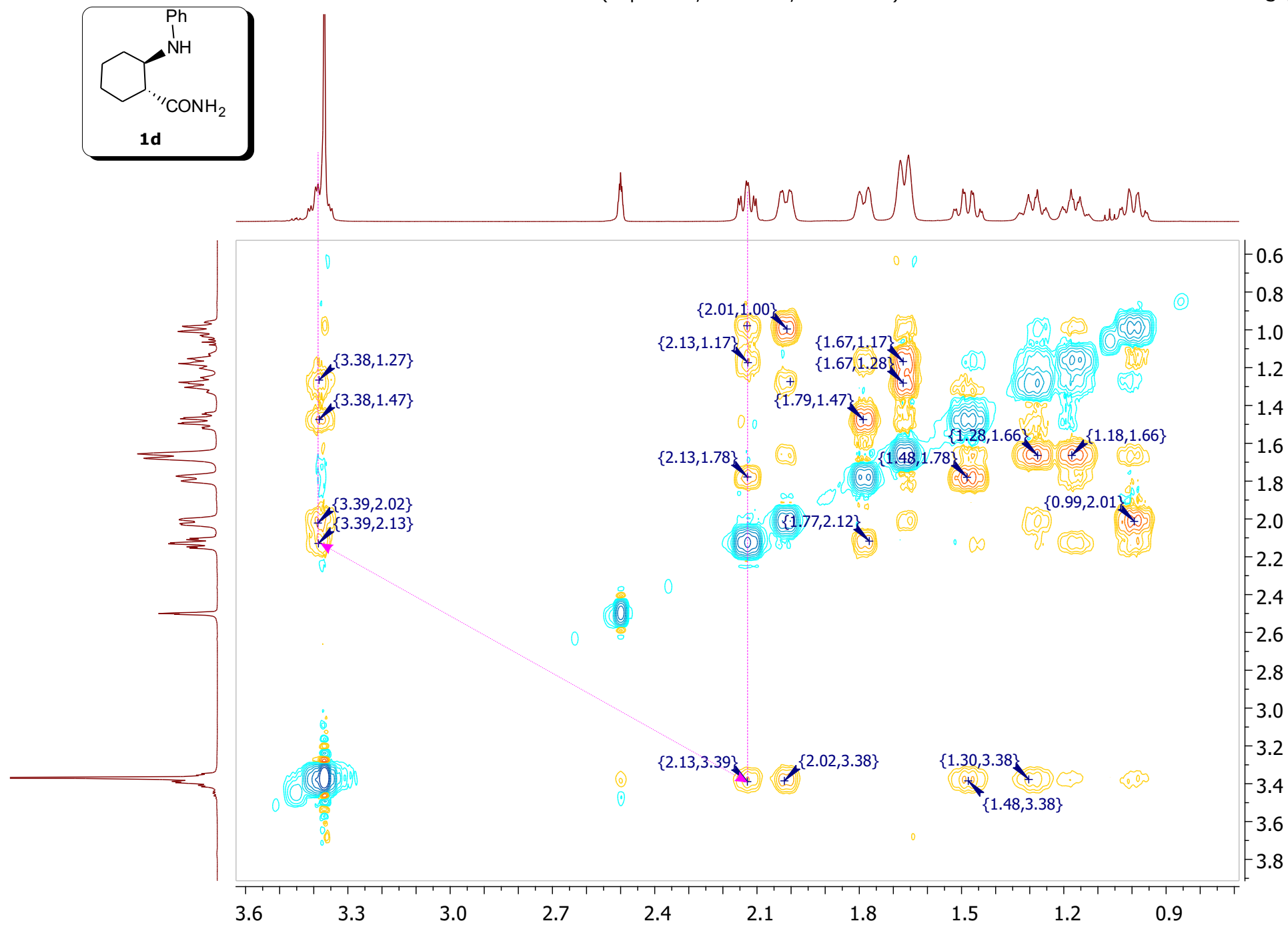
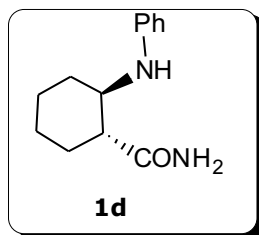




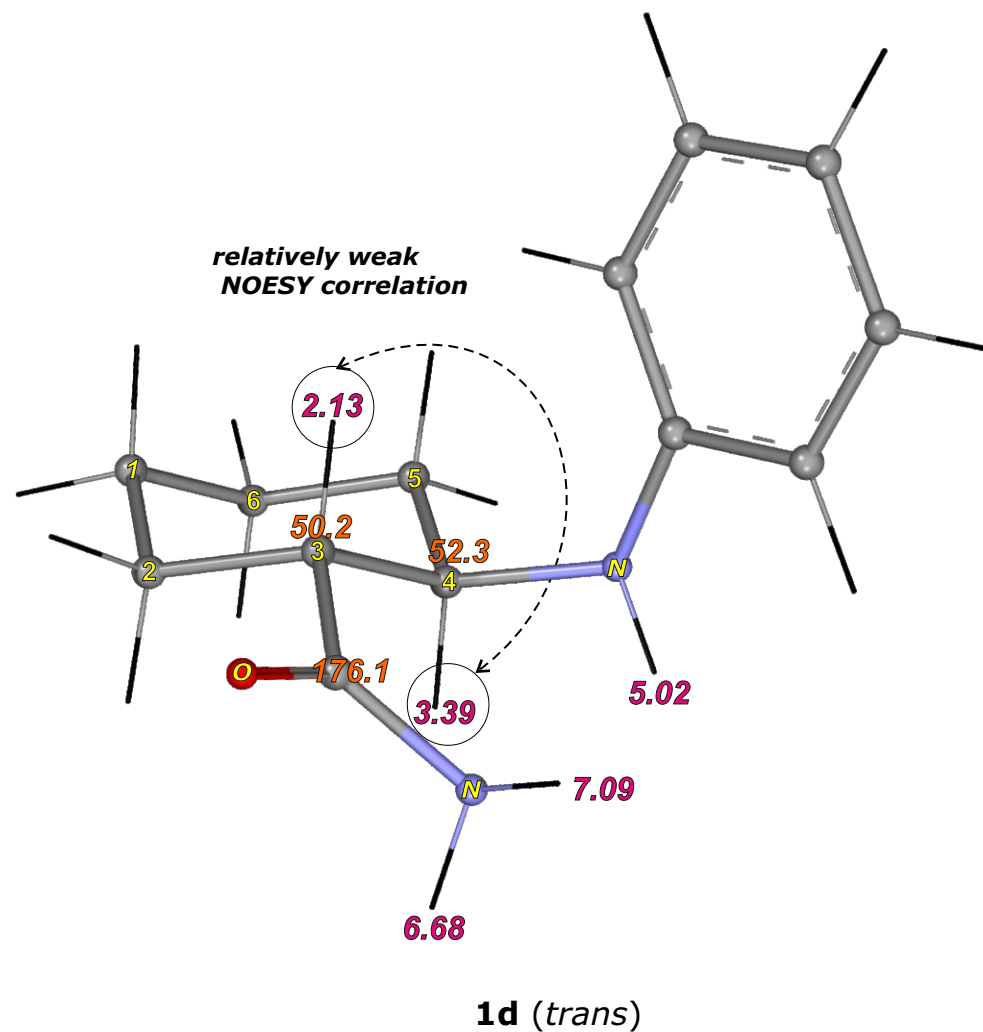


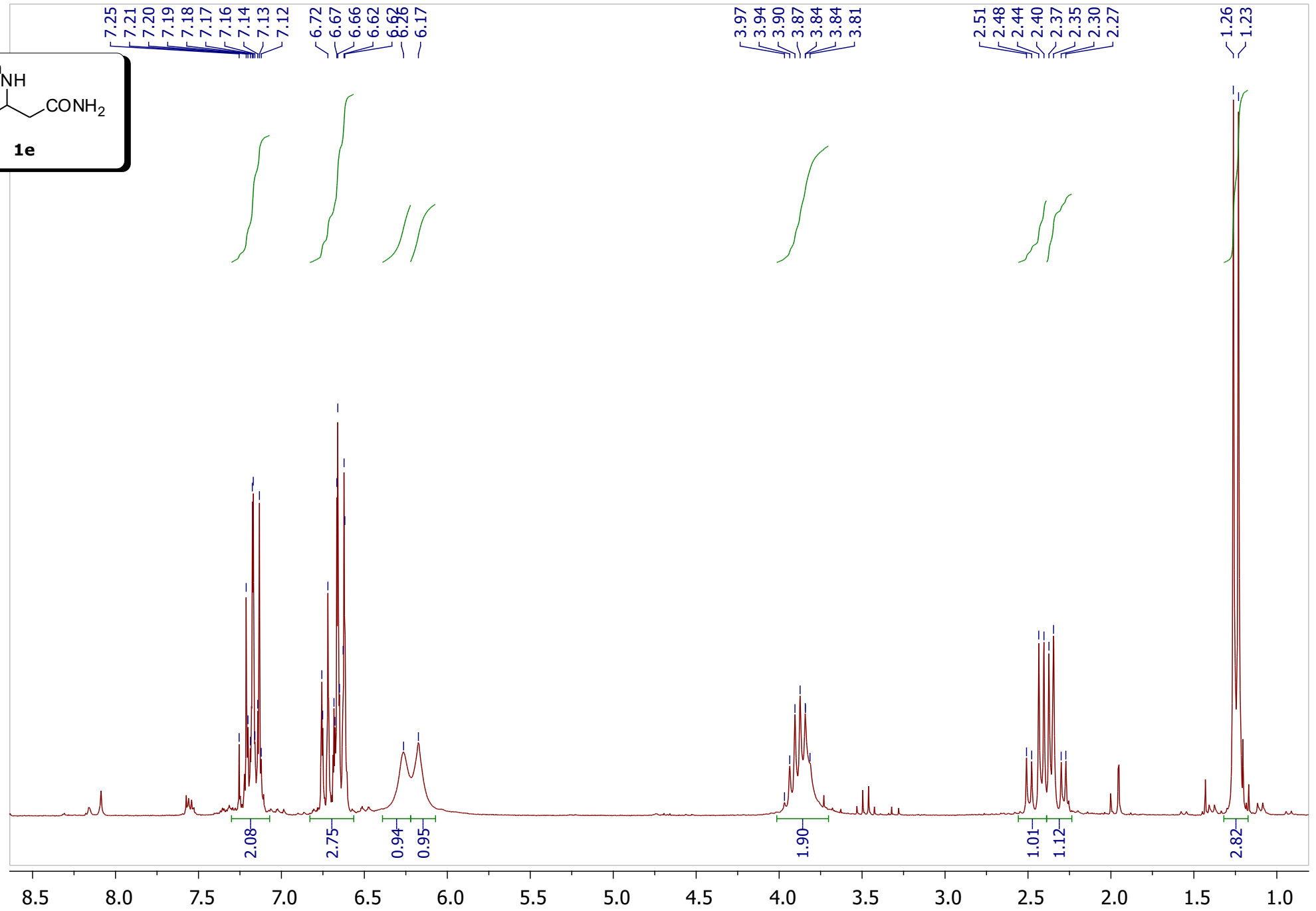
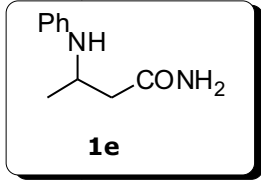


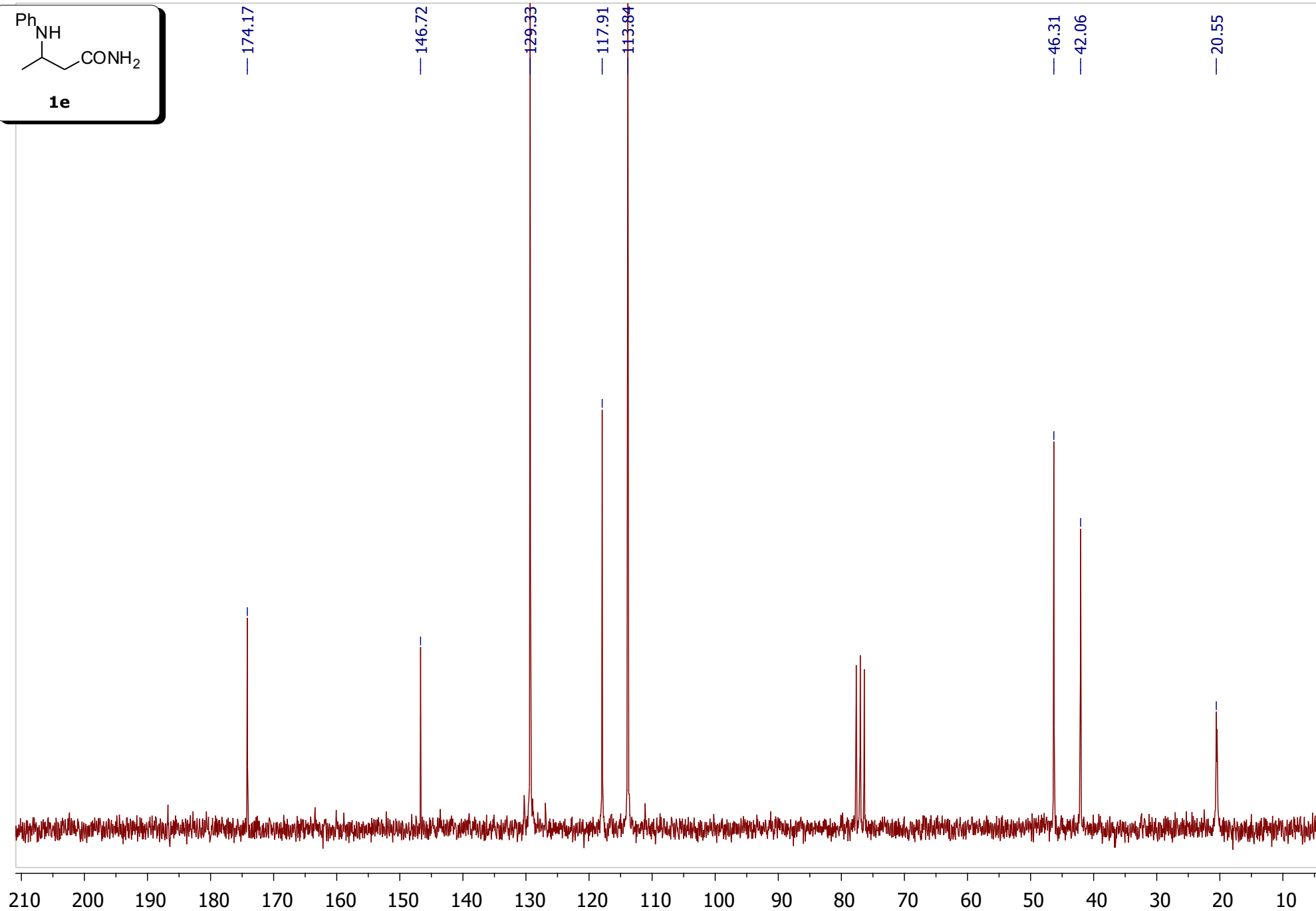
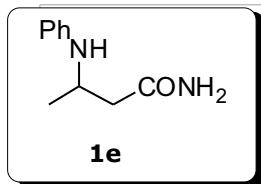


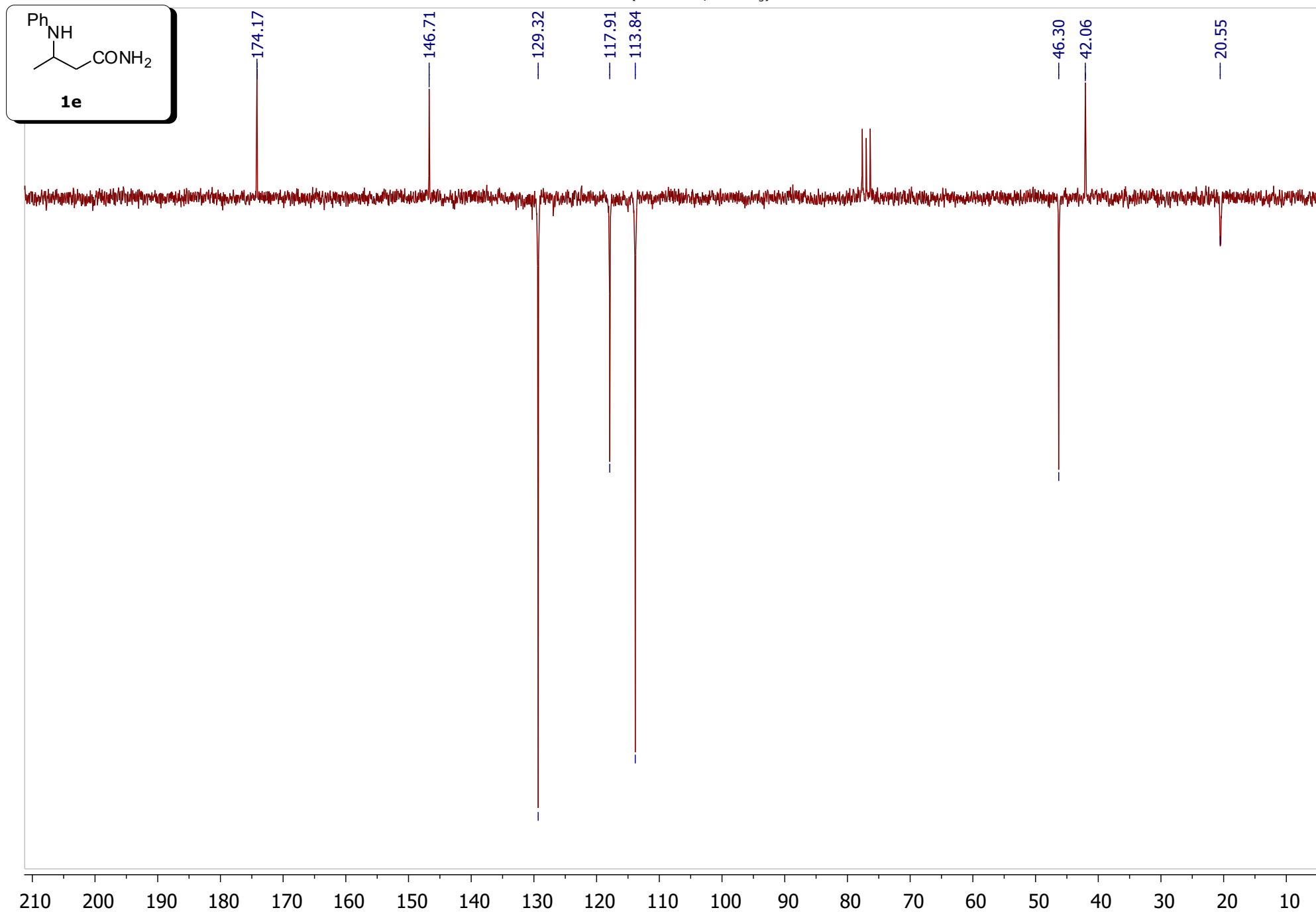


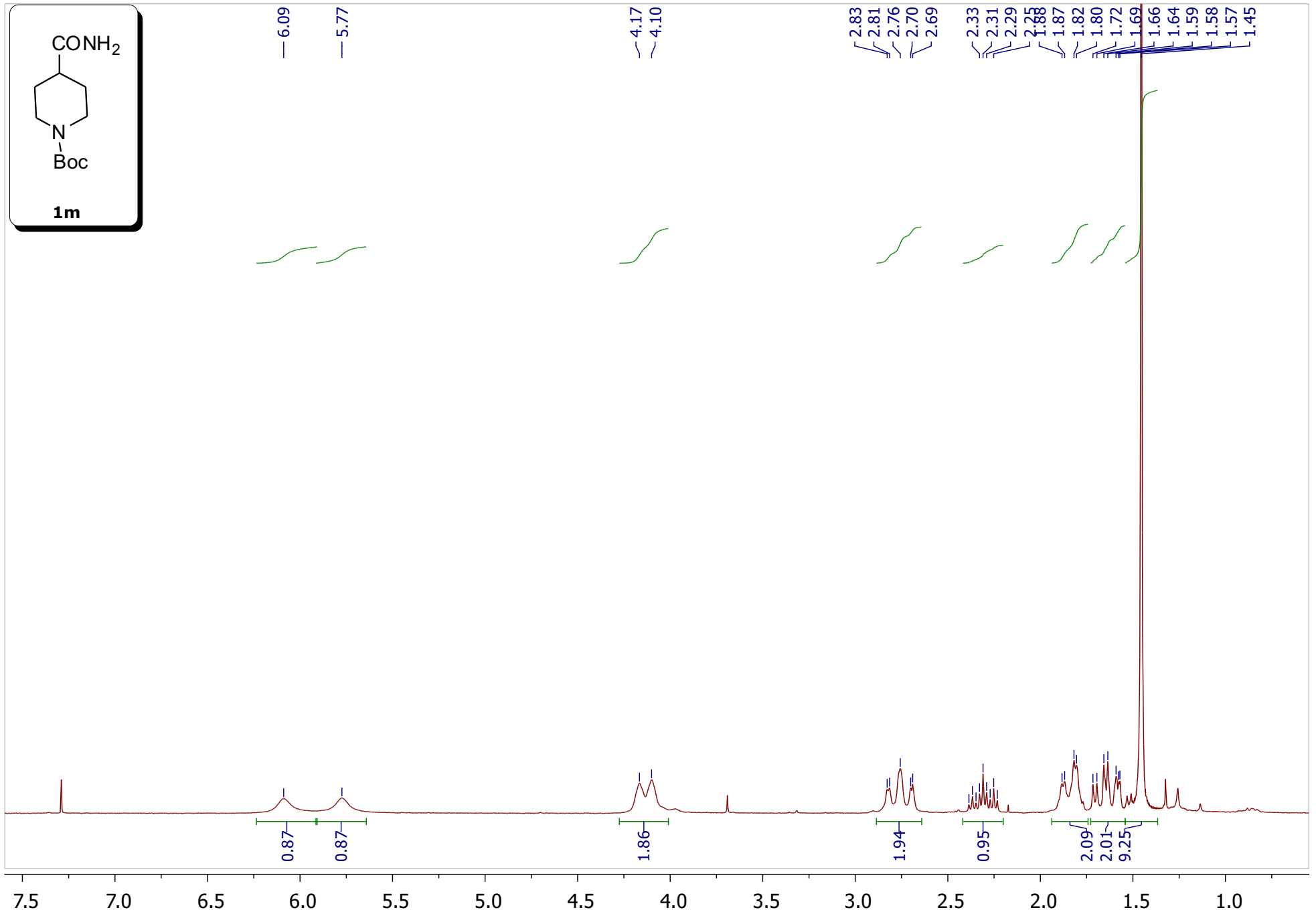
Approximate 3D model of amide **1d**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*trans*) is corroborated by spectral data of amide **1c** (*cis*), amide **1d** (*trans*), urea **2c** (*cis*) and urea **2d** (*trans*).

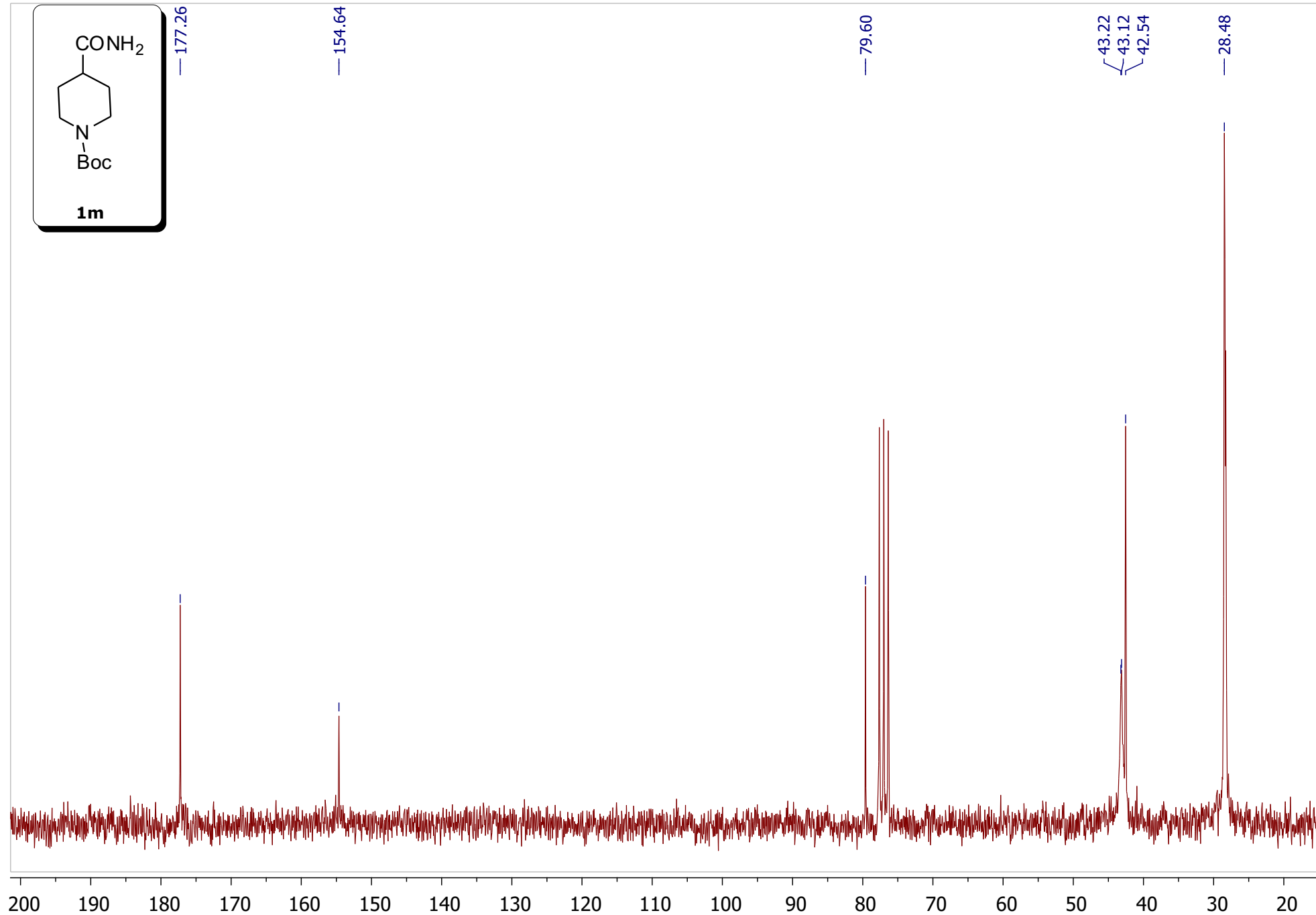
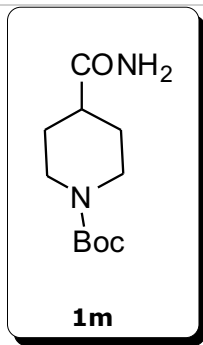


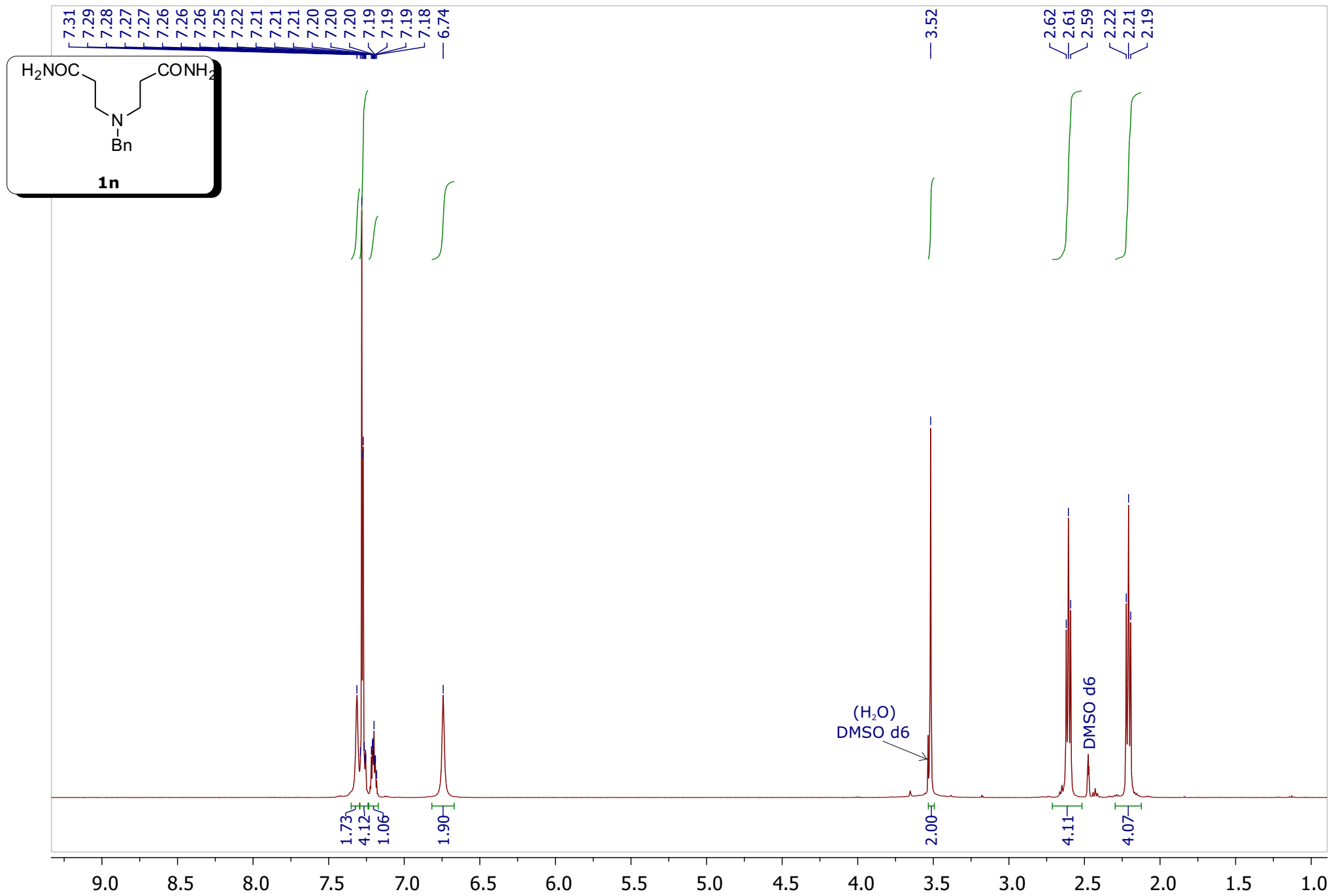


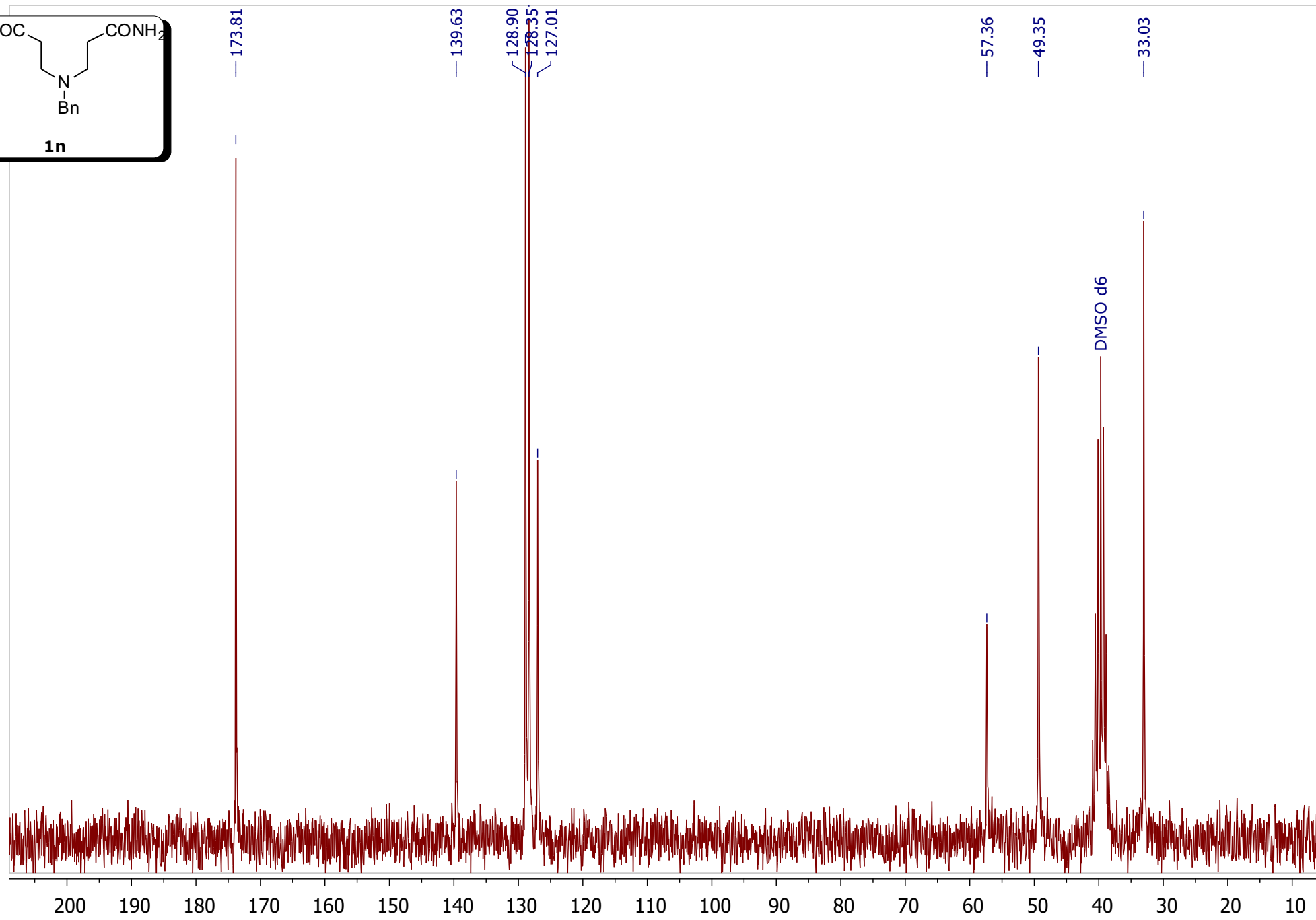
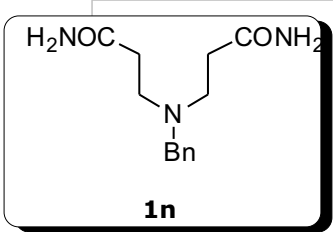


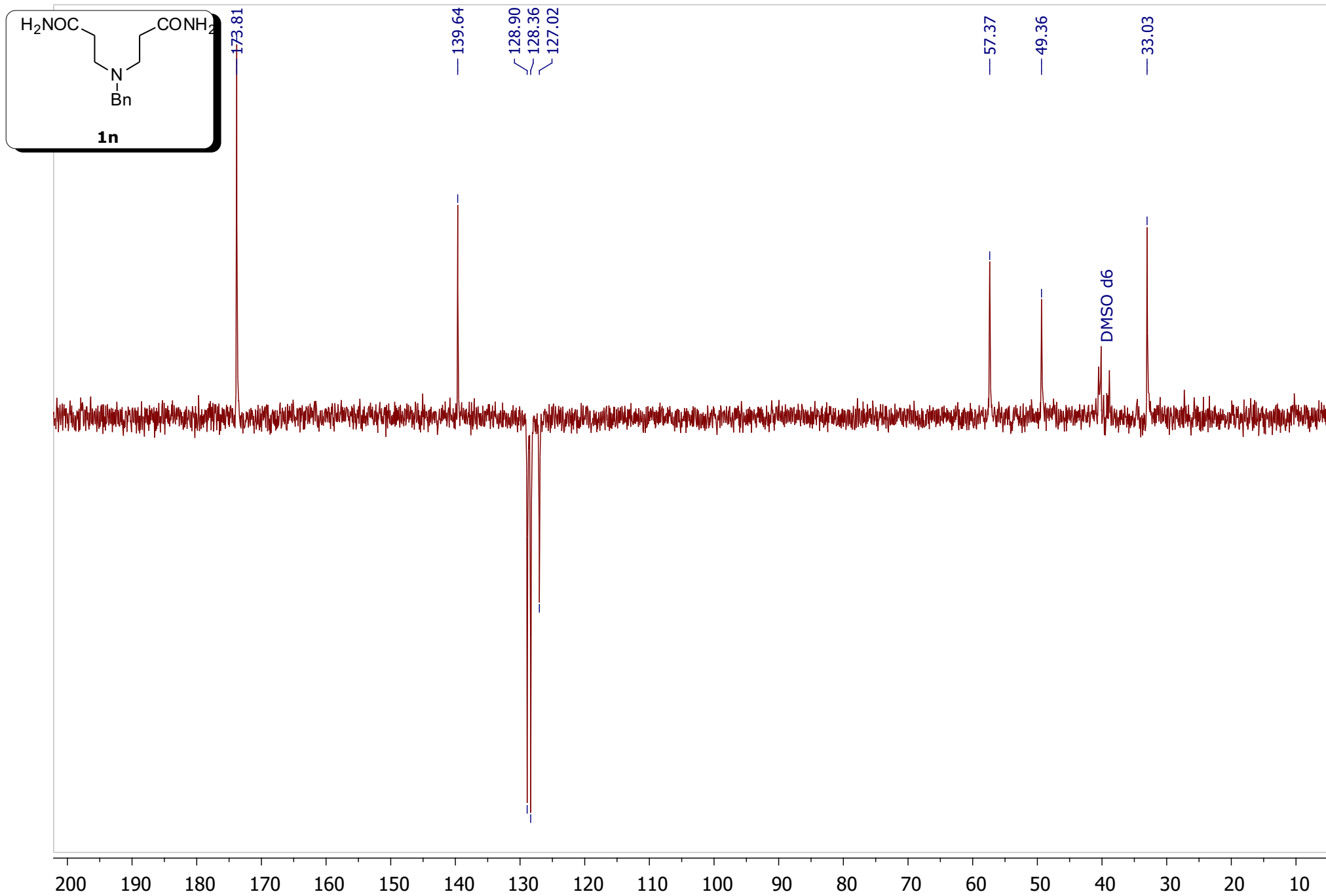


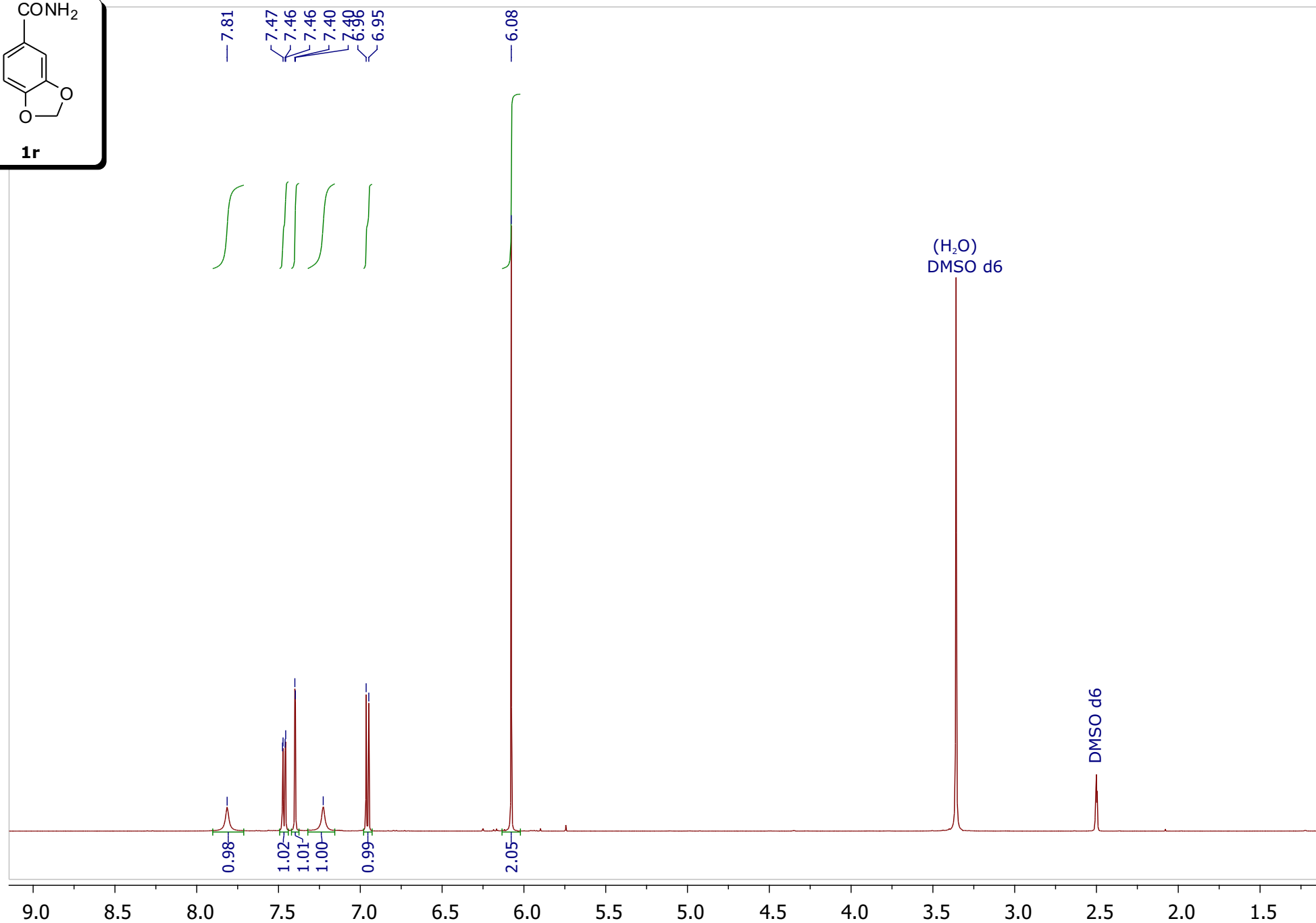
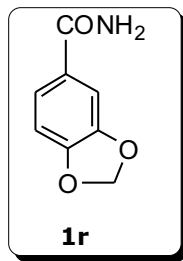


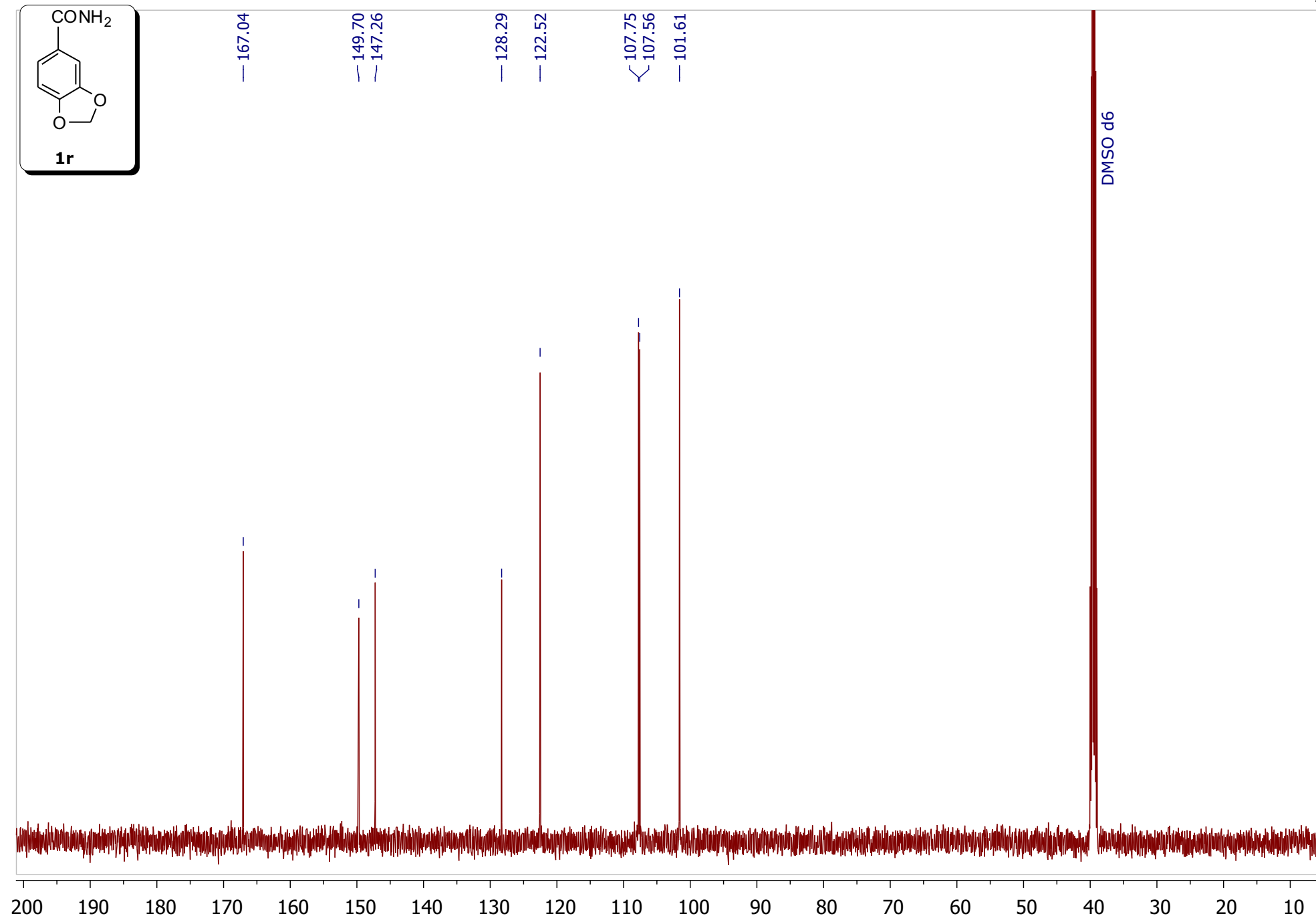
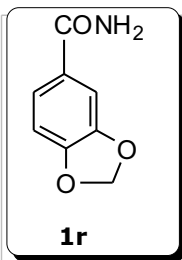


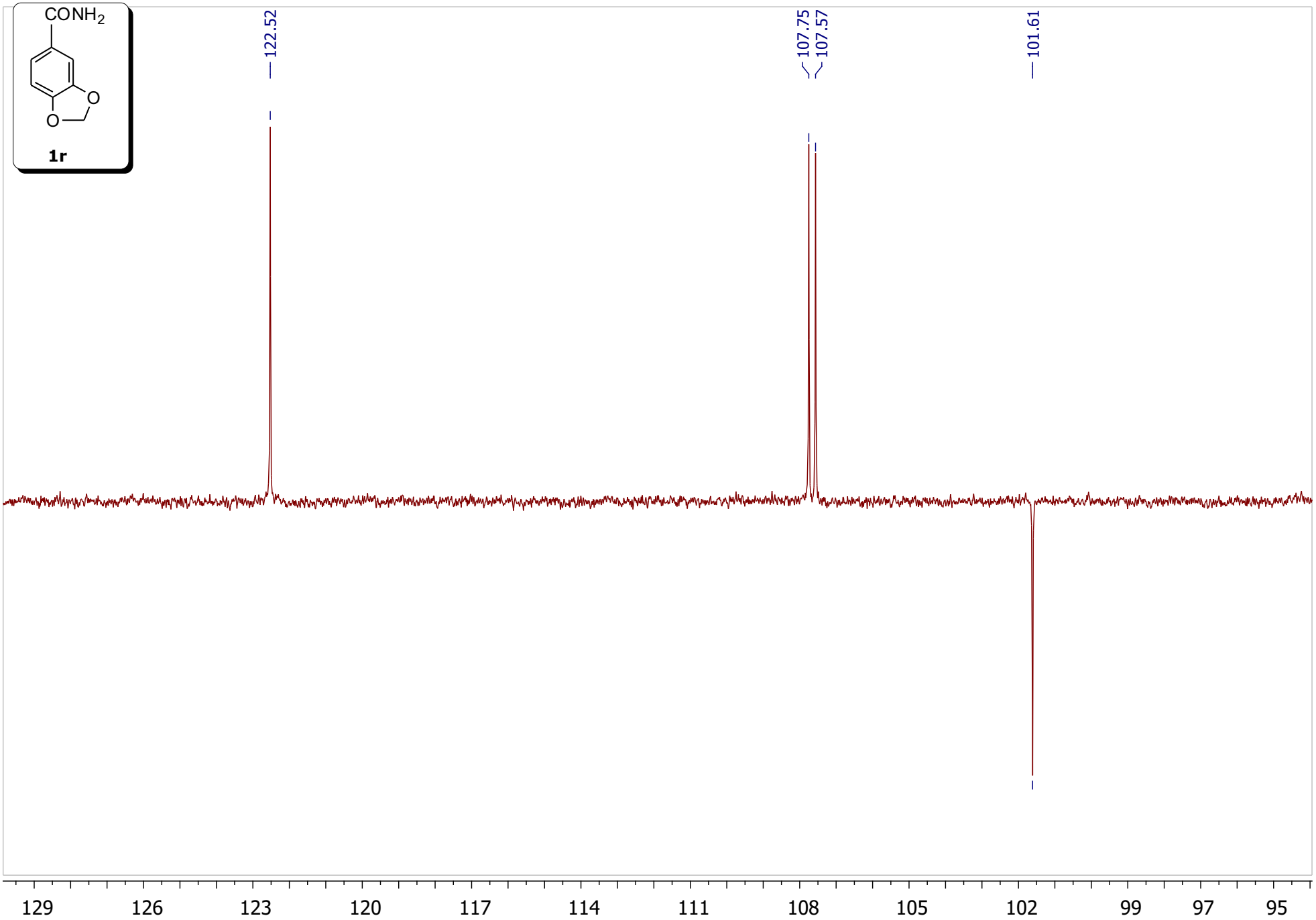


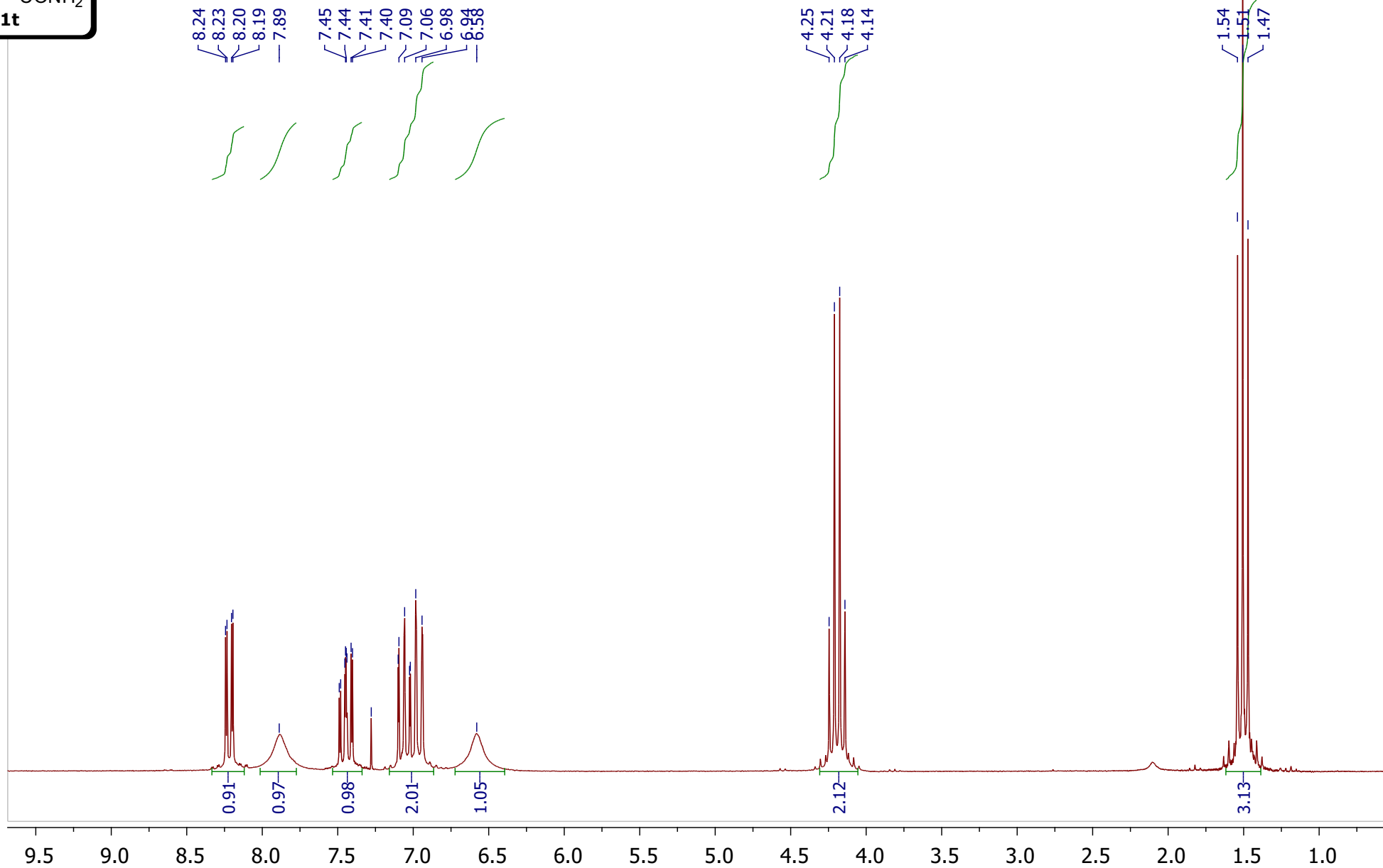
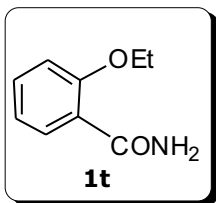


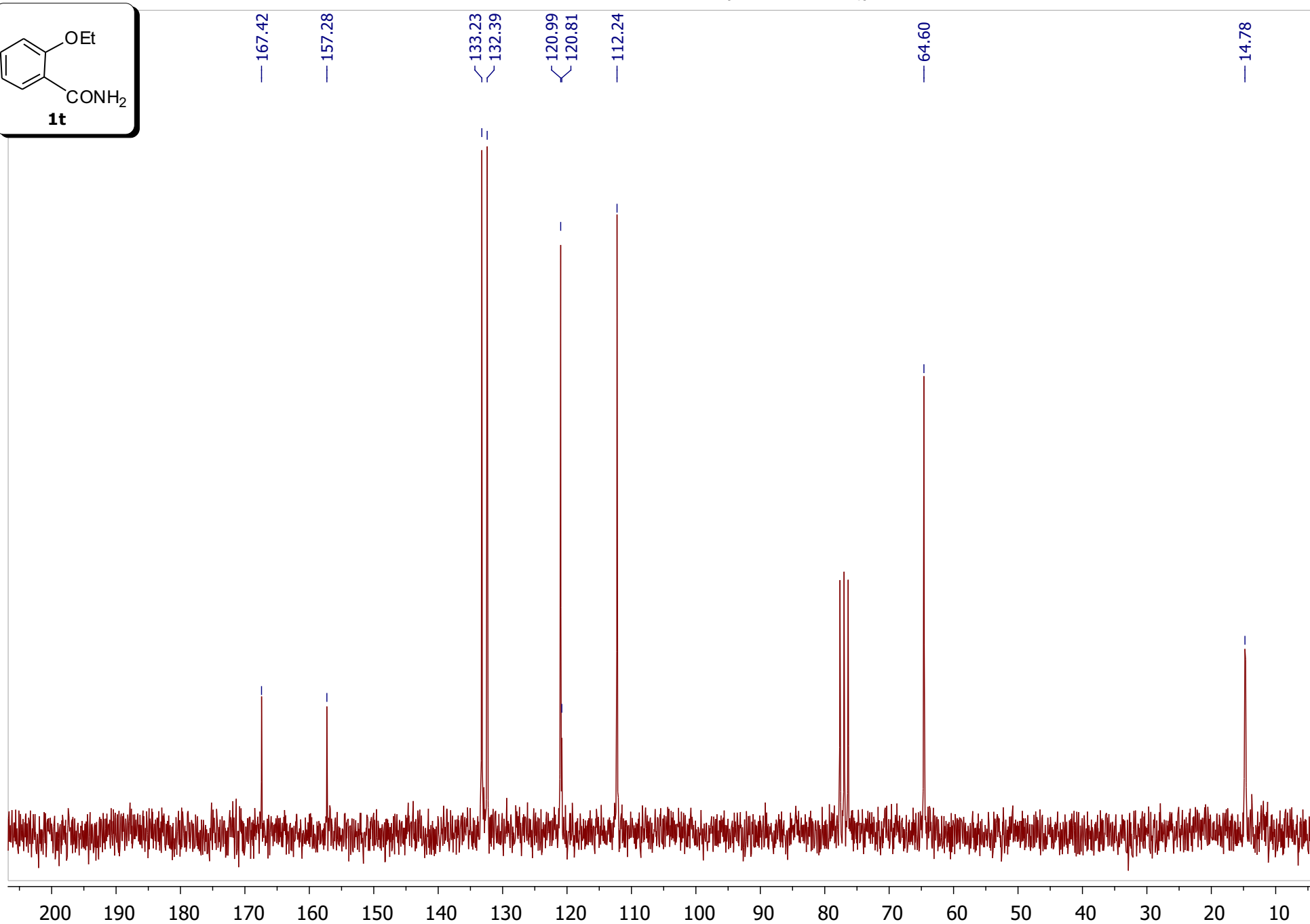
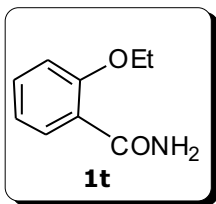


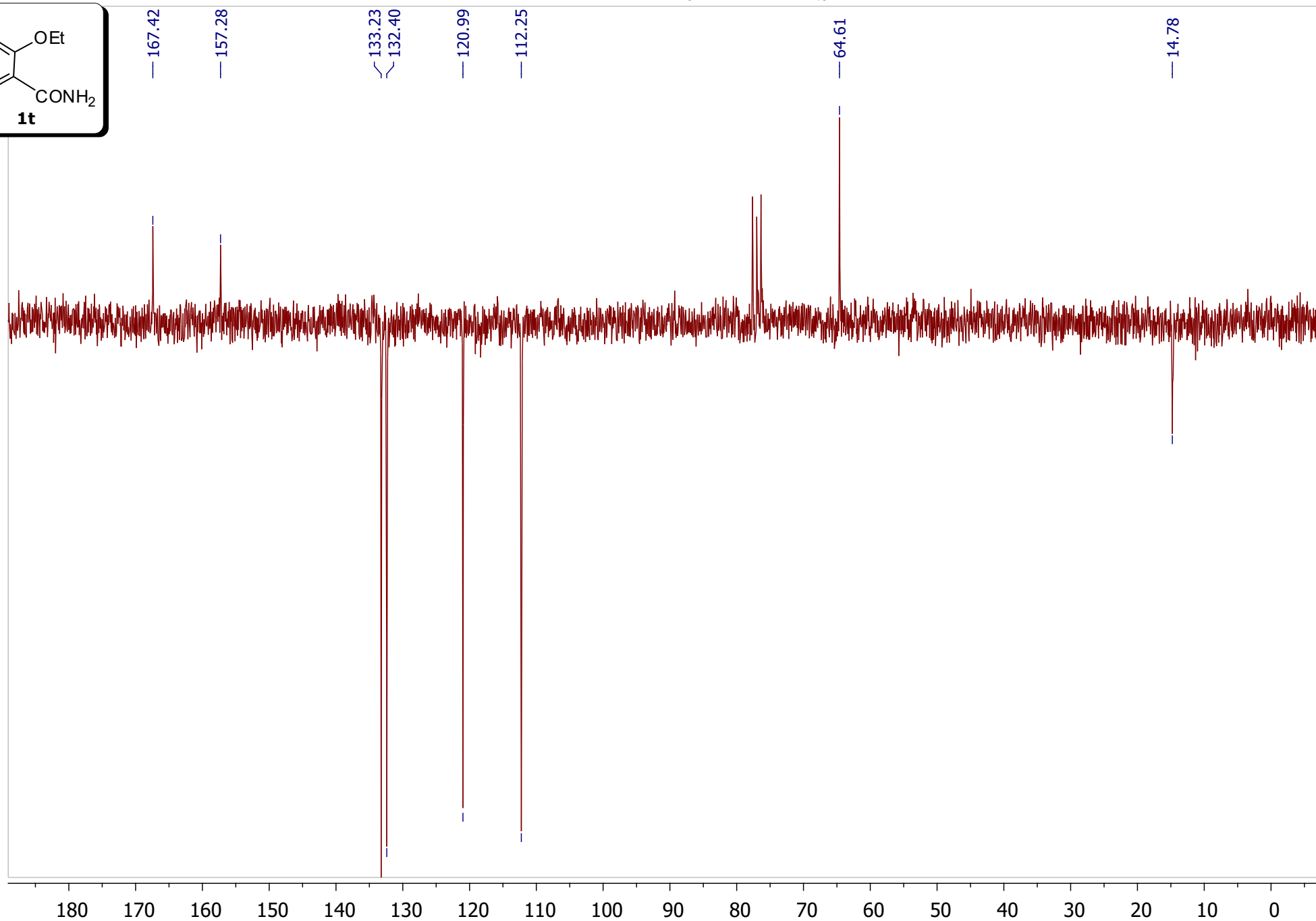
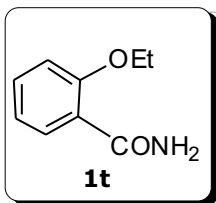


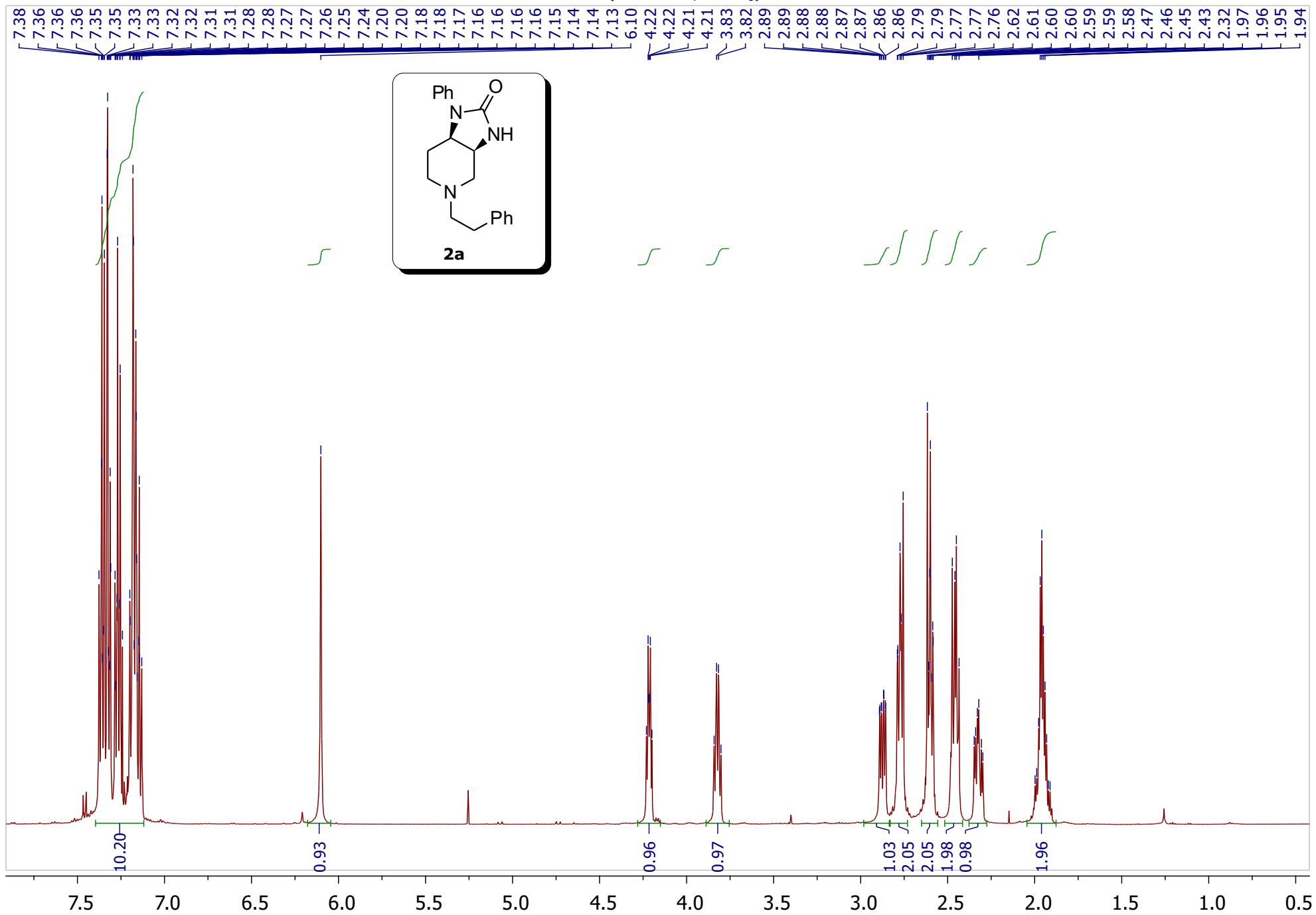


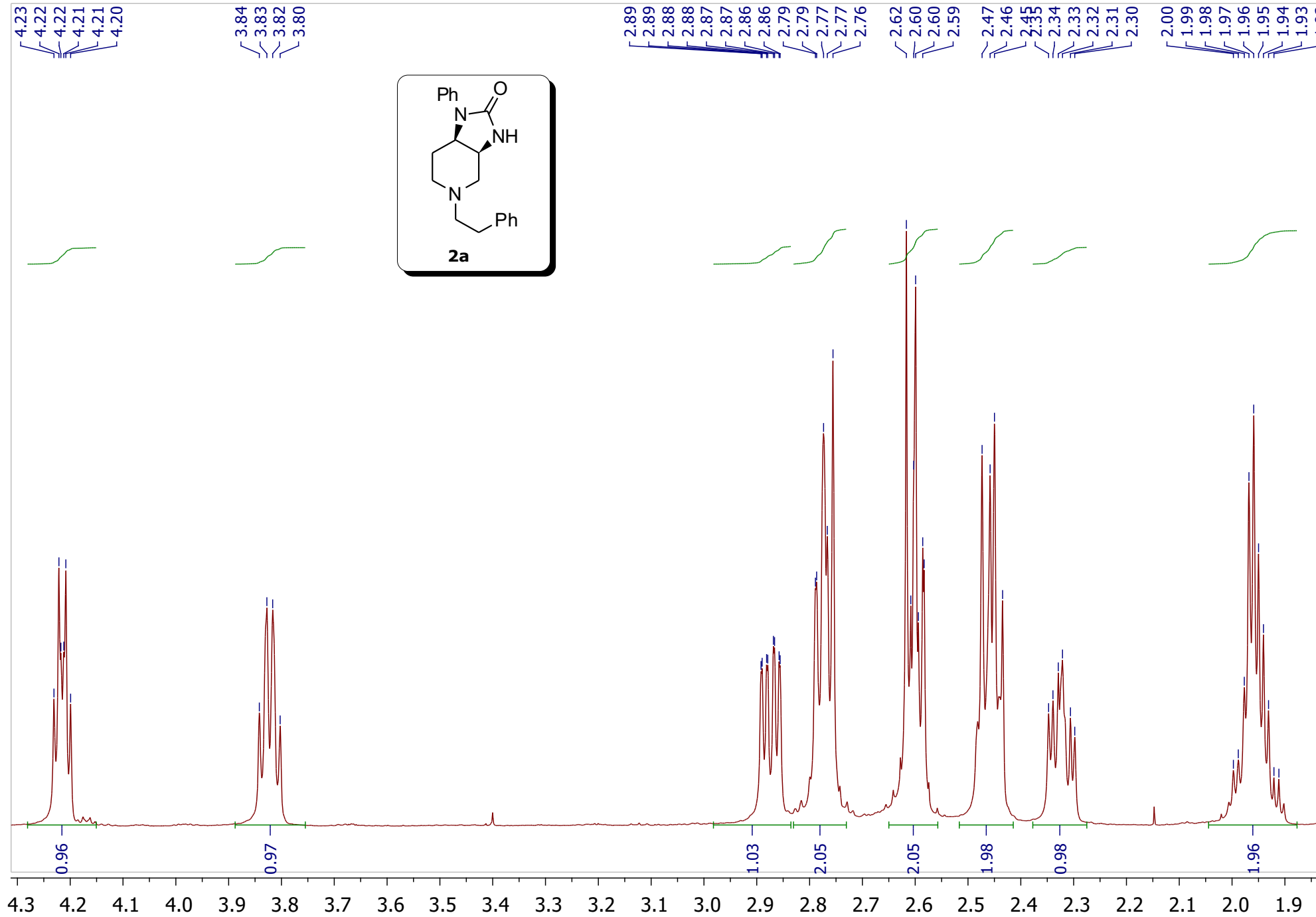
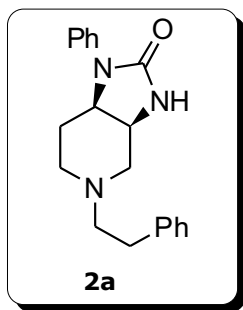


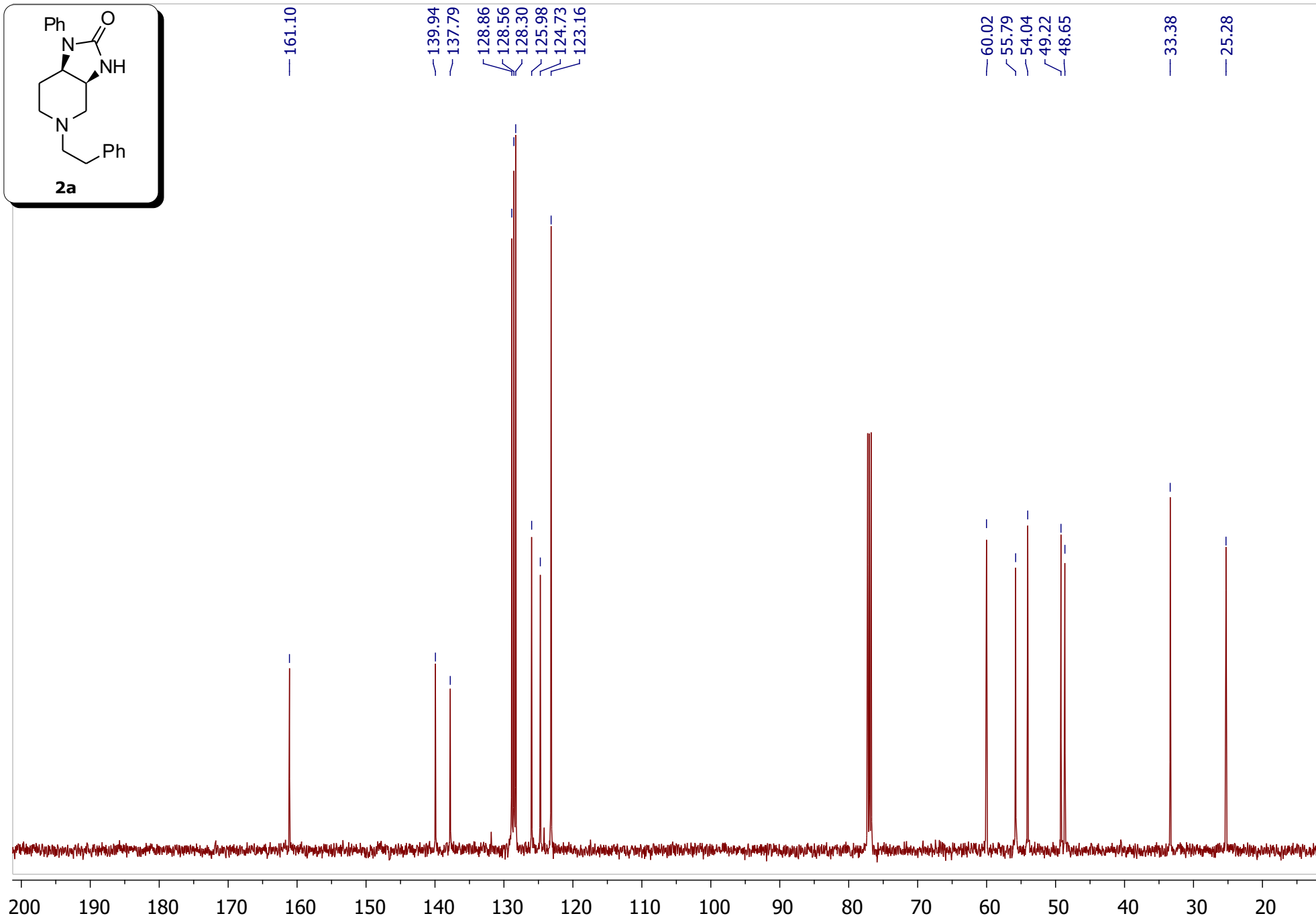
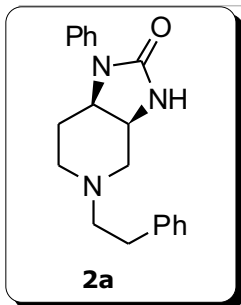






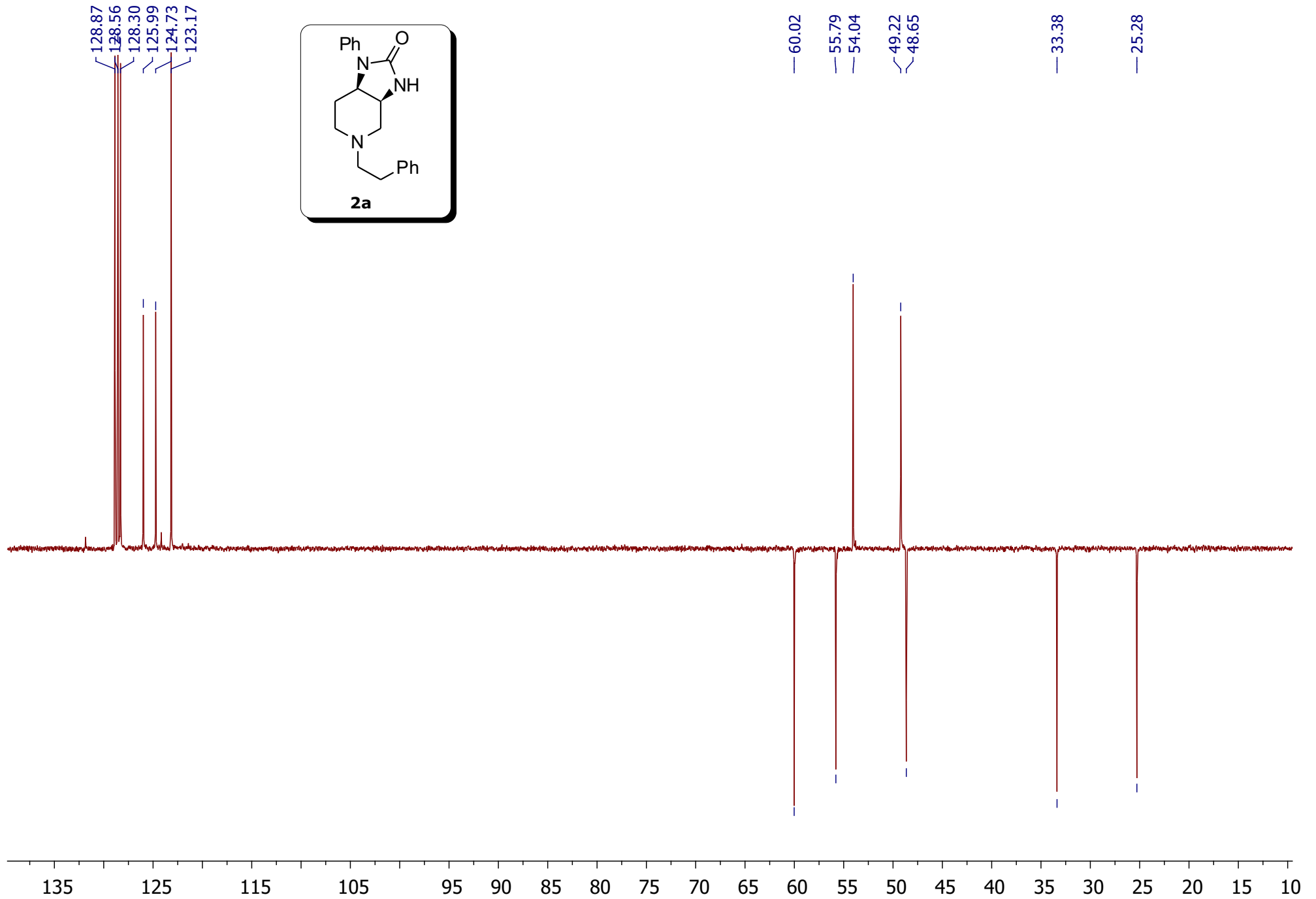
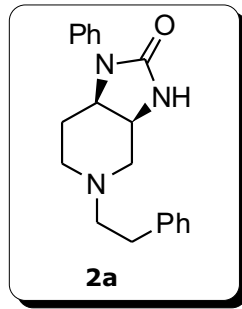


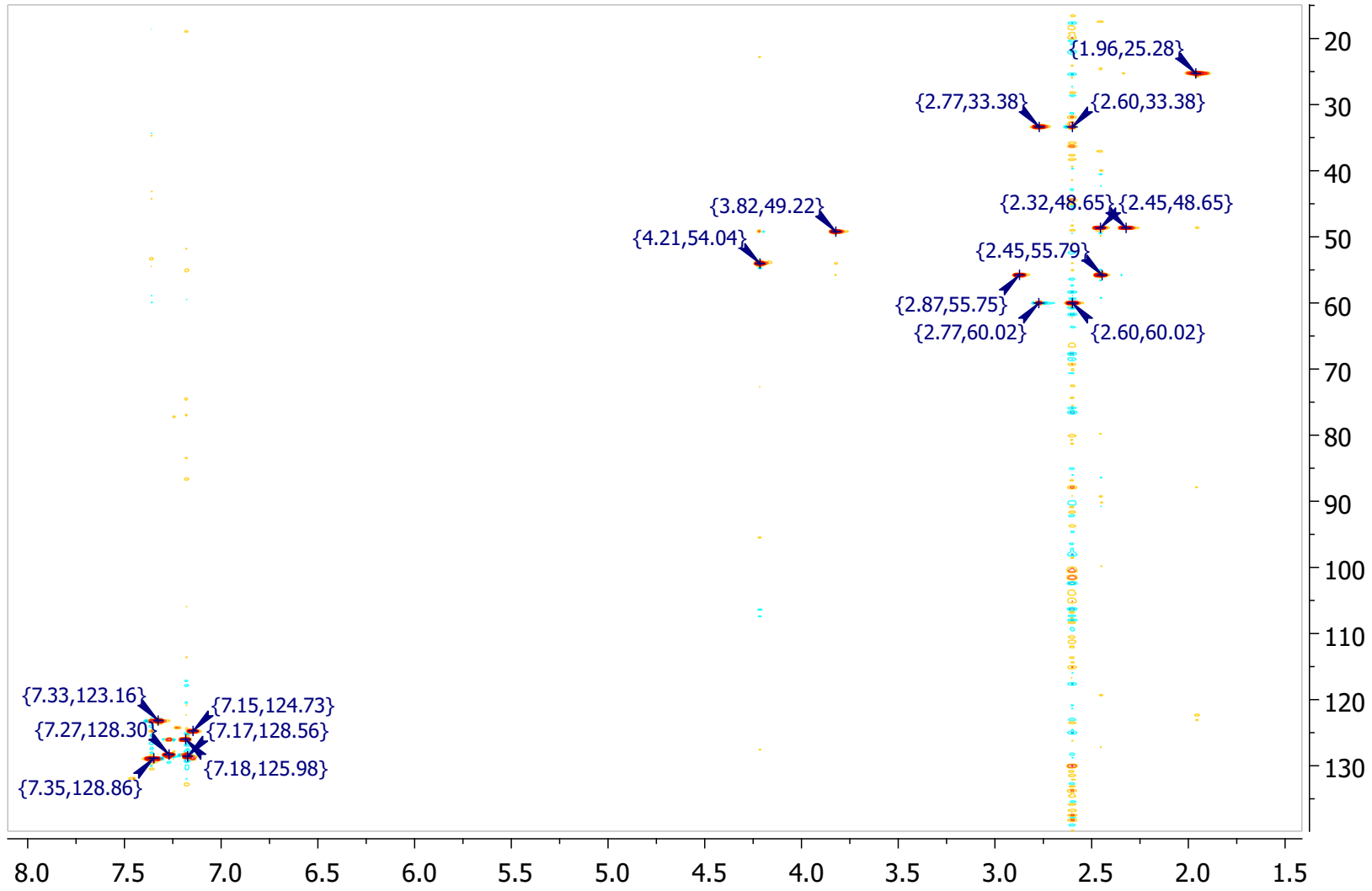
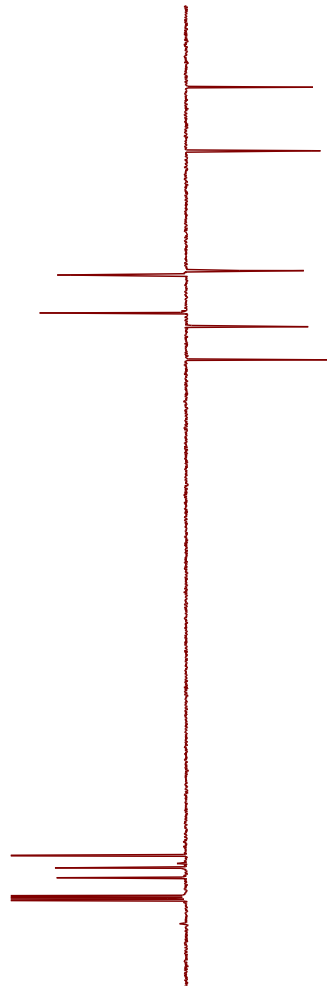
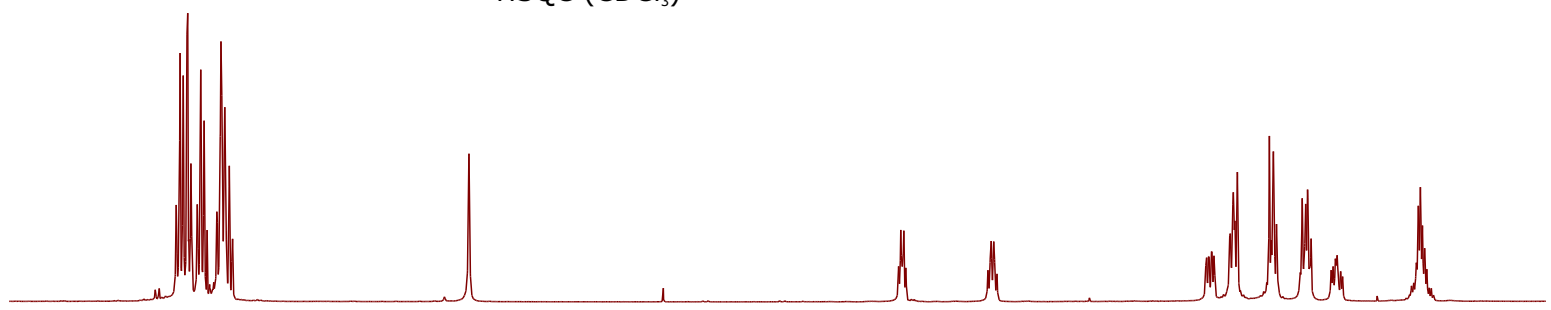
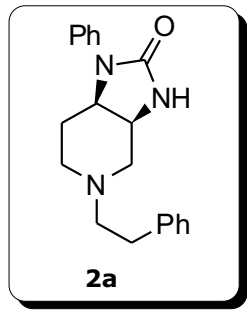


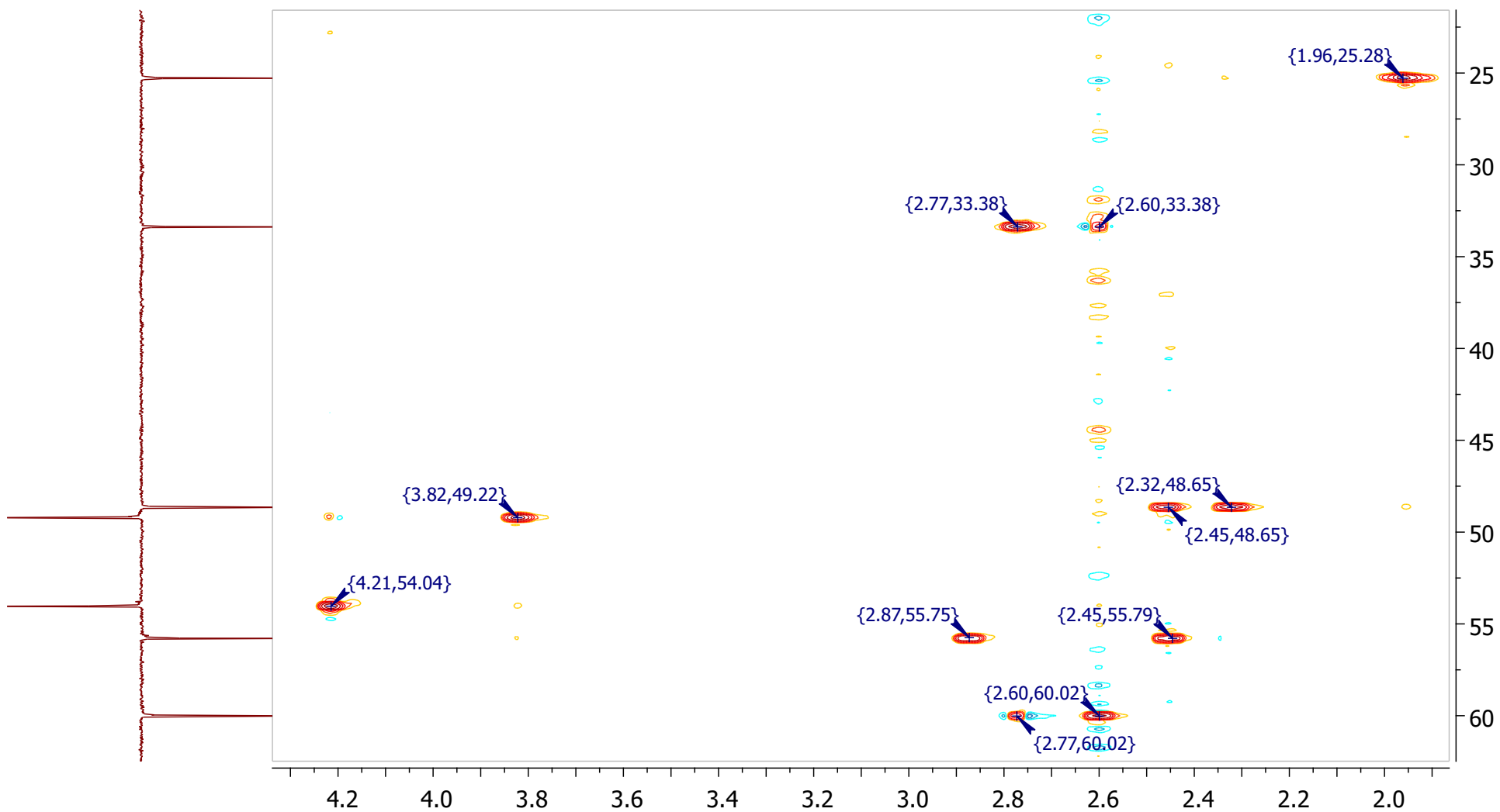
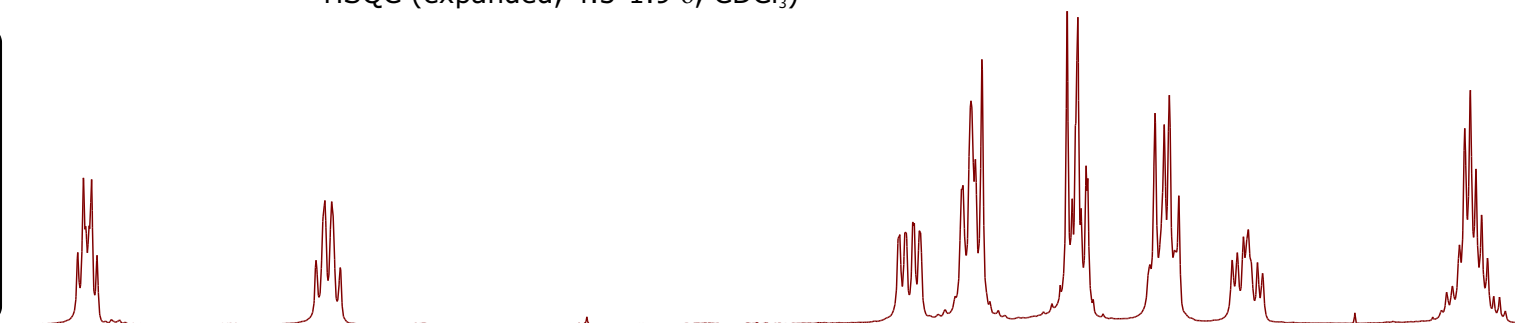
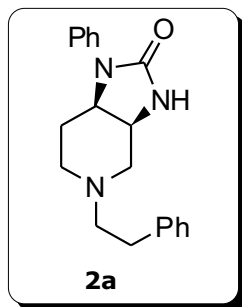


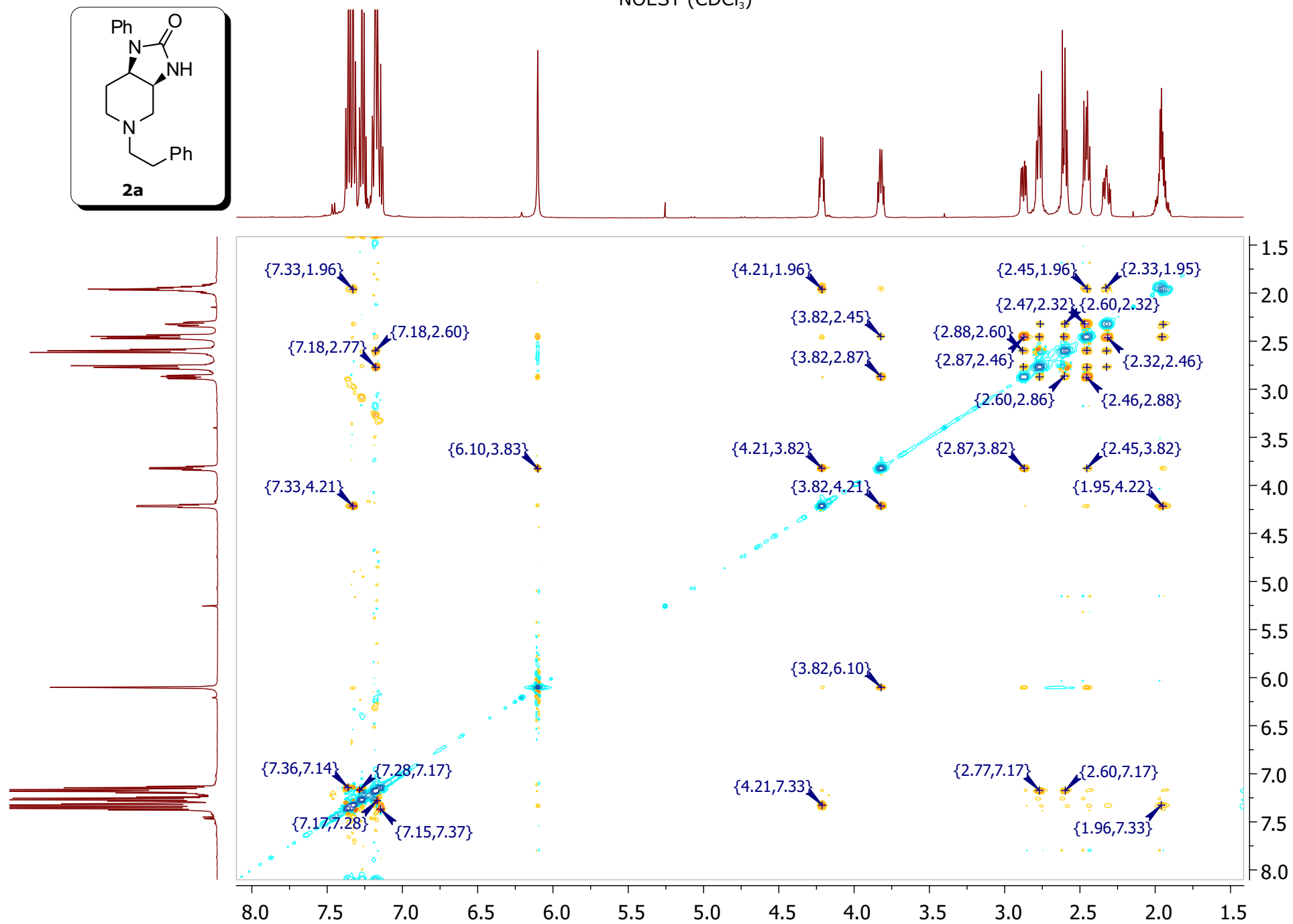
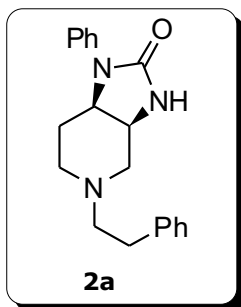
DEPT (126 MHz, CDCl₃)

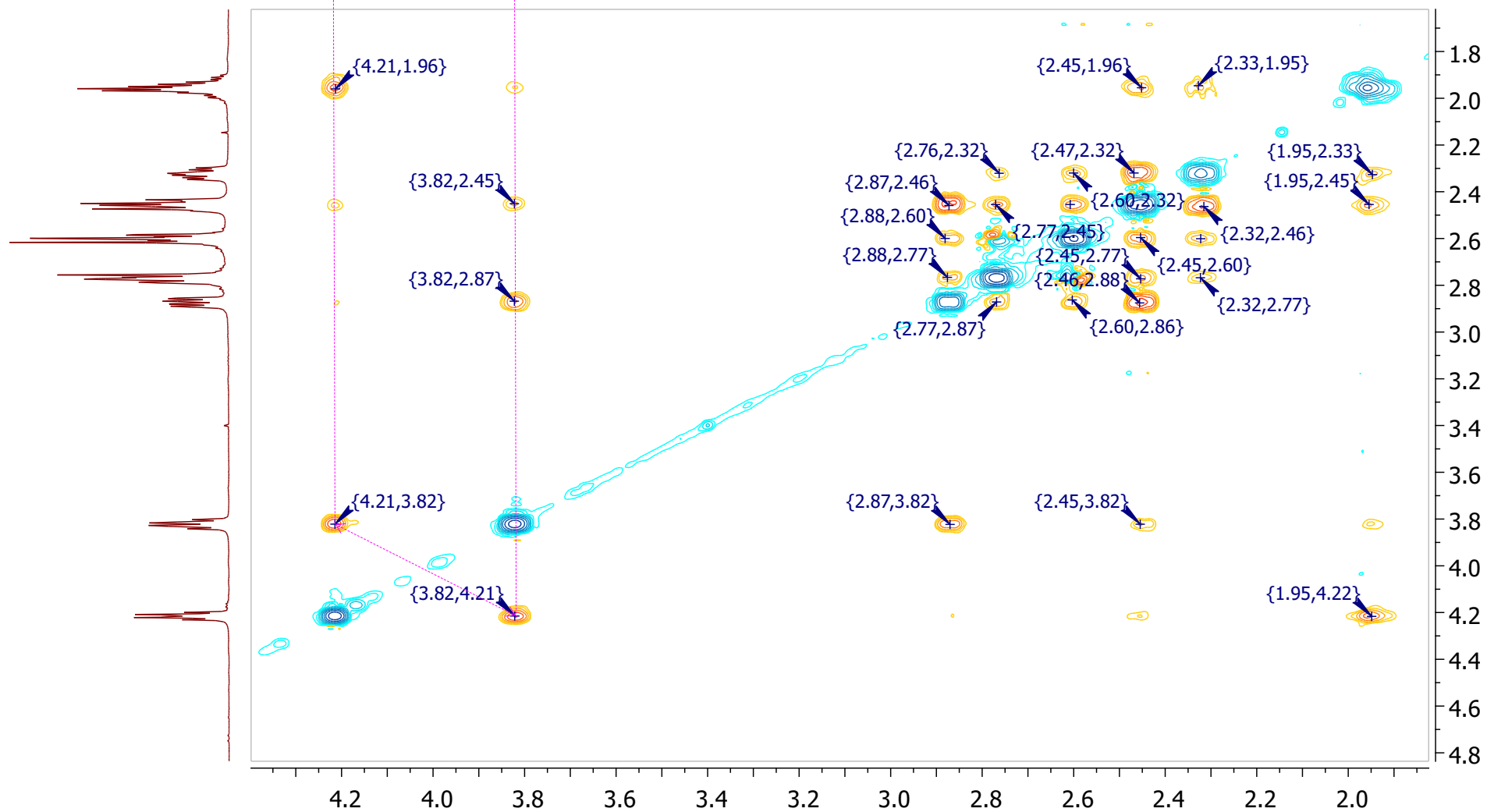
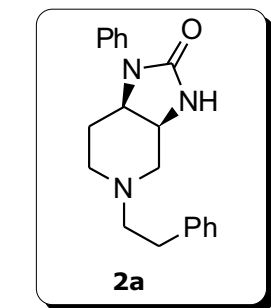
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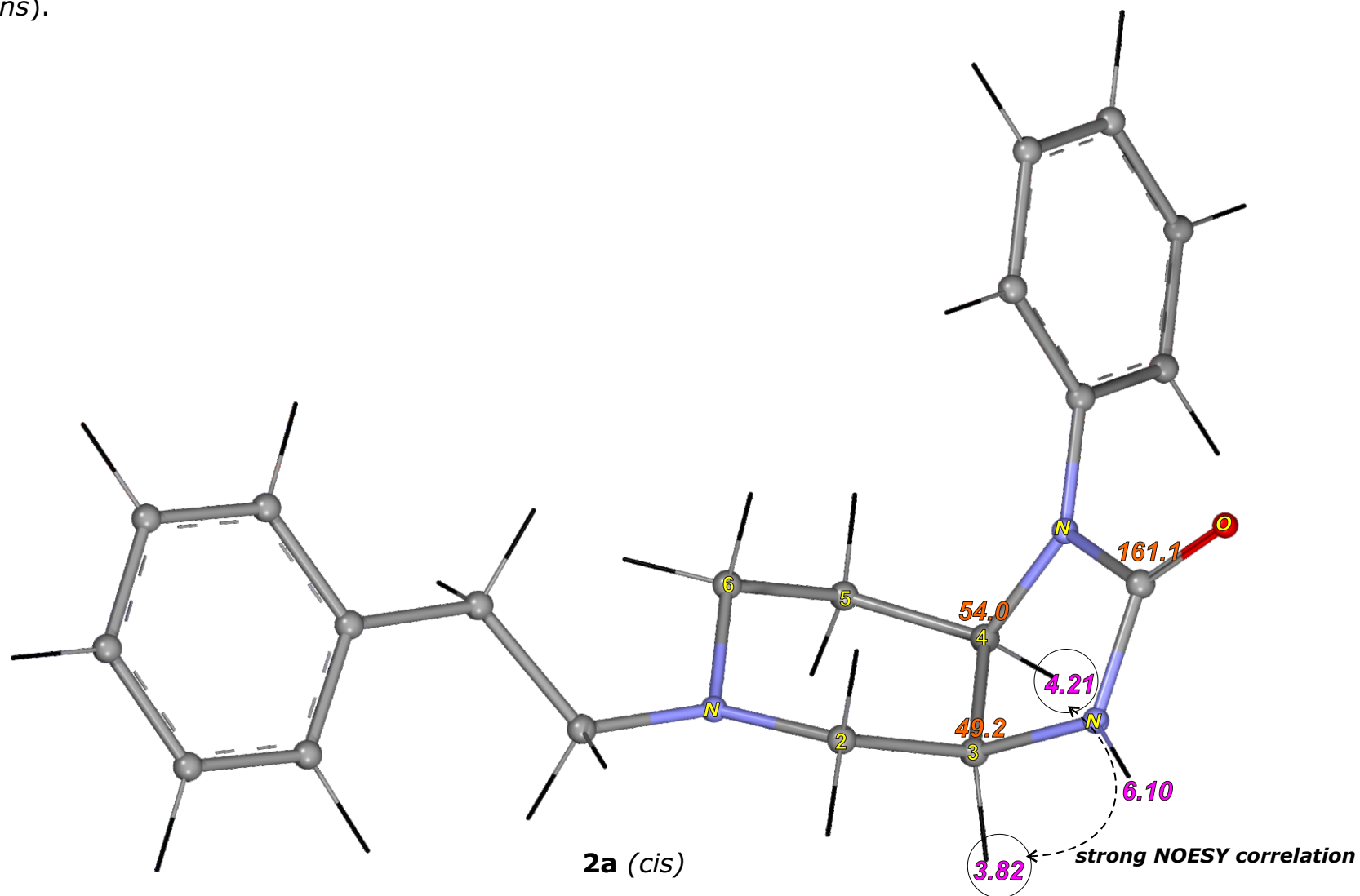


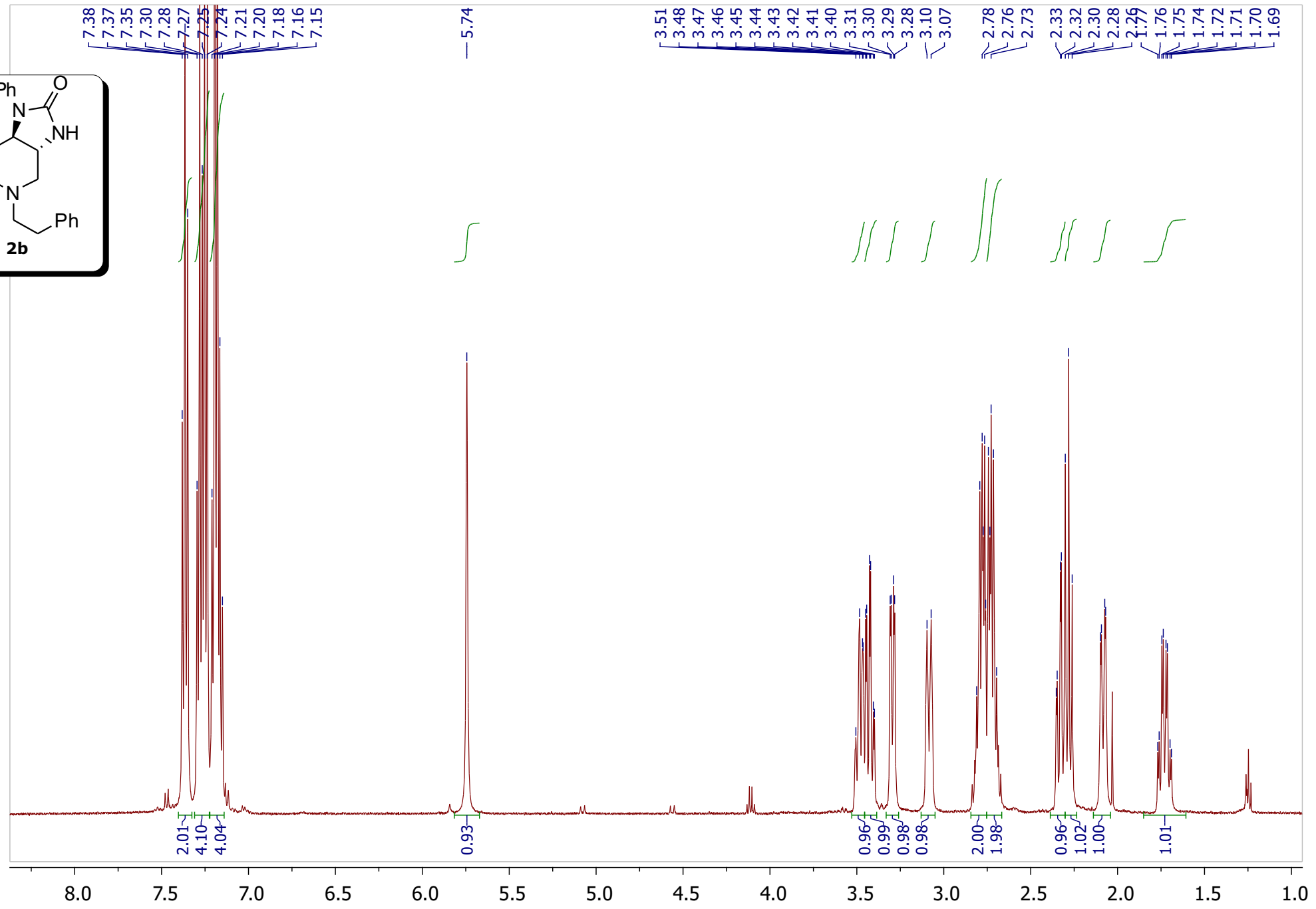
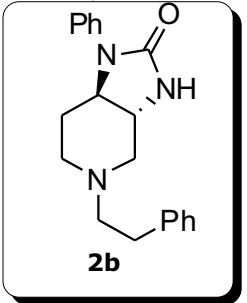


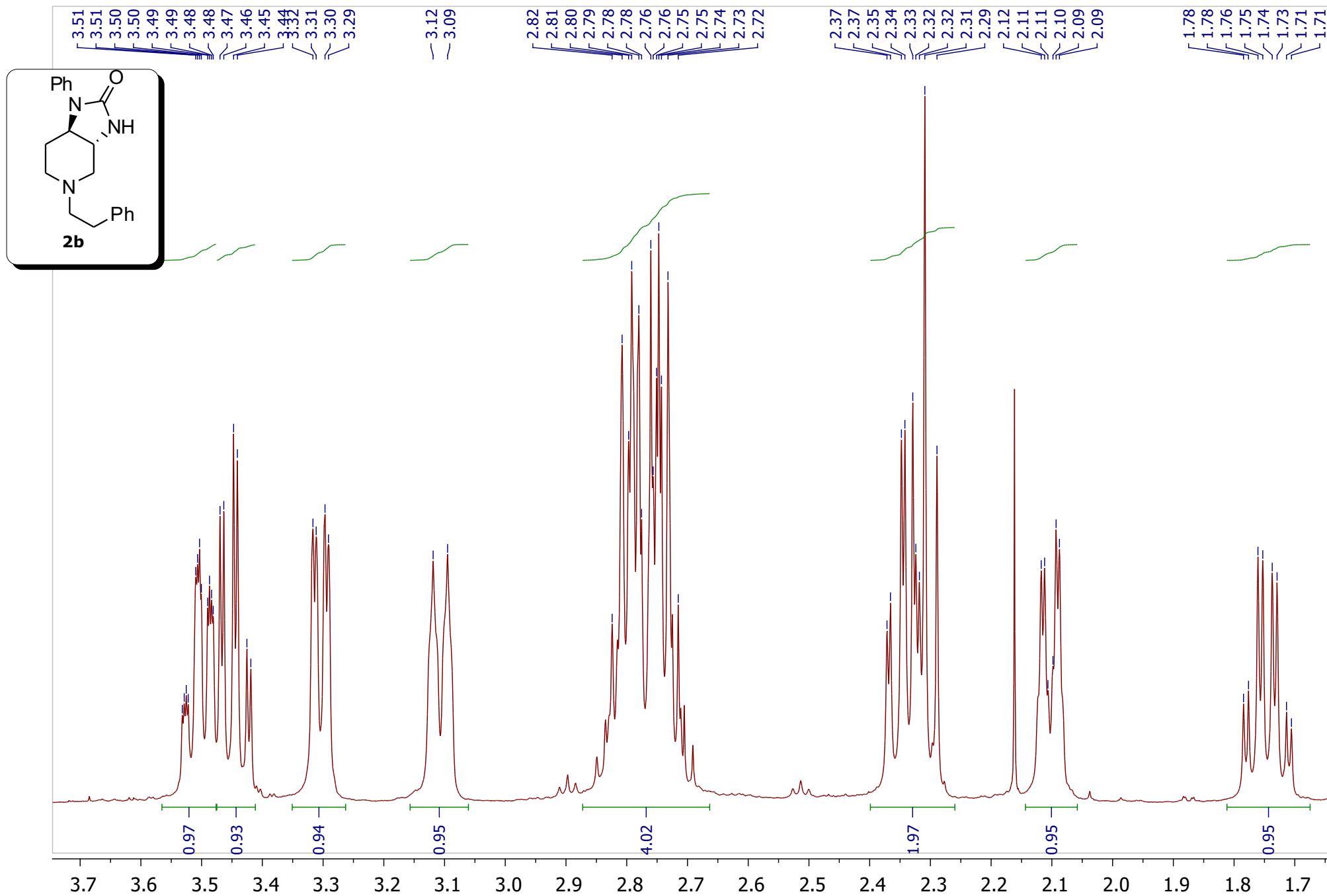
NOESY (CDCl₃)

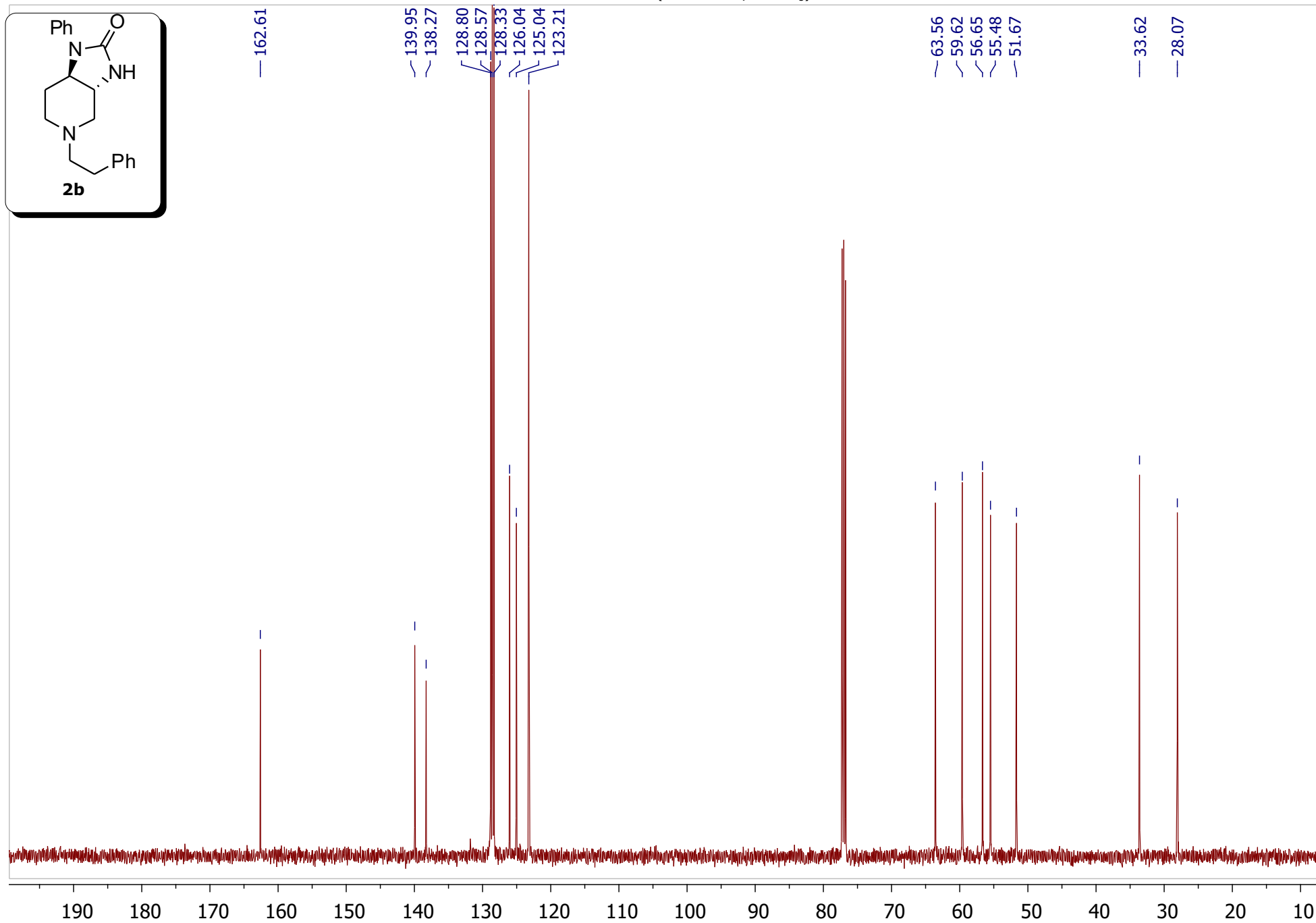


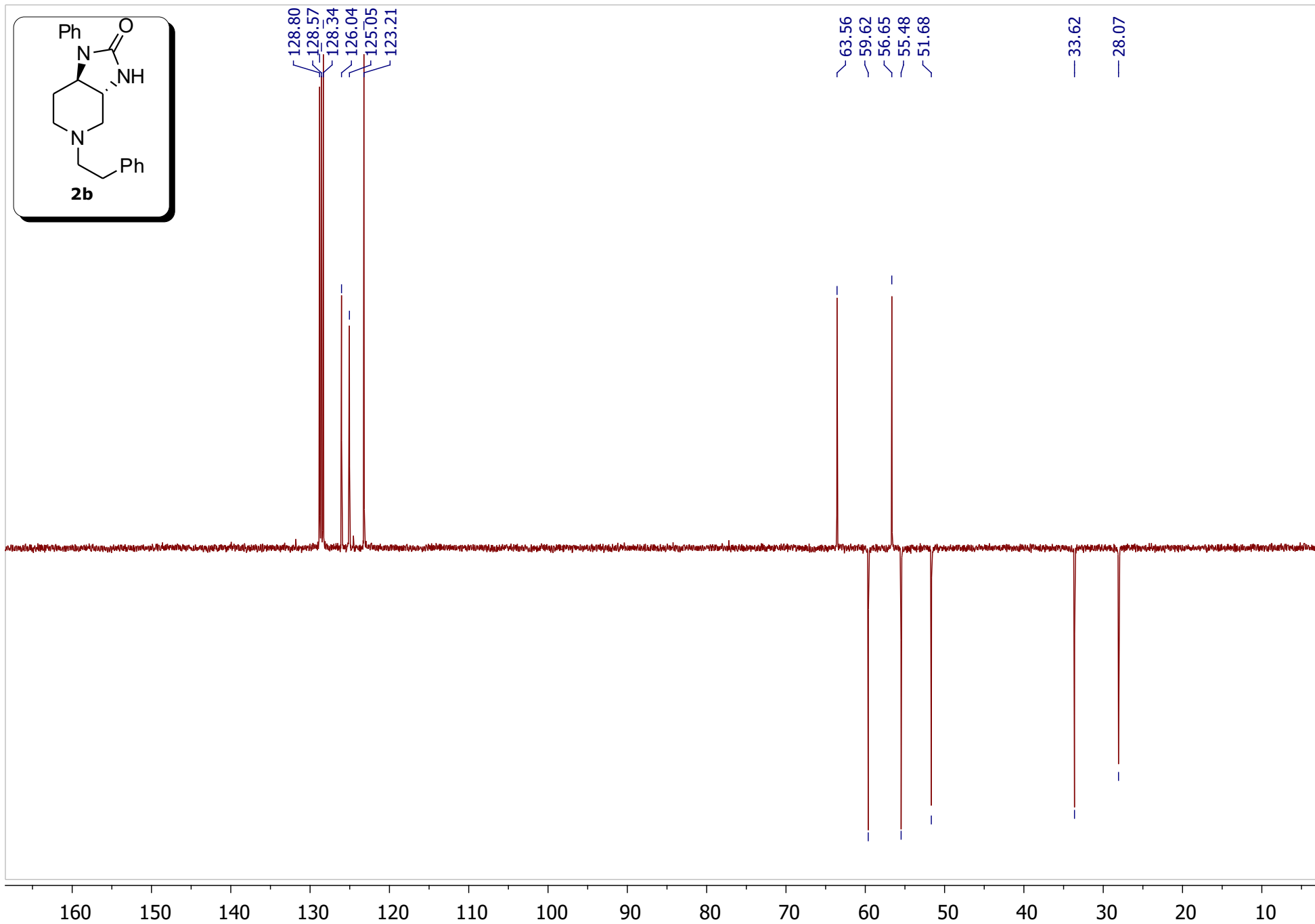
Approximate 3D model of urea **2a**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*cis*) is corroborated by spectral data of amide **1a**, amide **1b** (*trans*), urea **2a** (*cis*) and urea **2b** (*trans*).

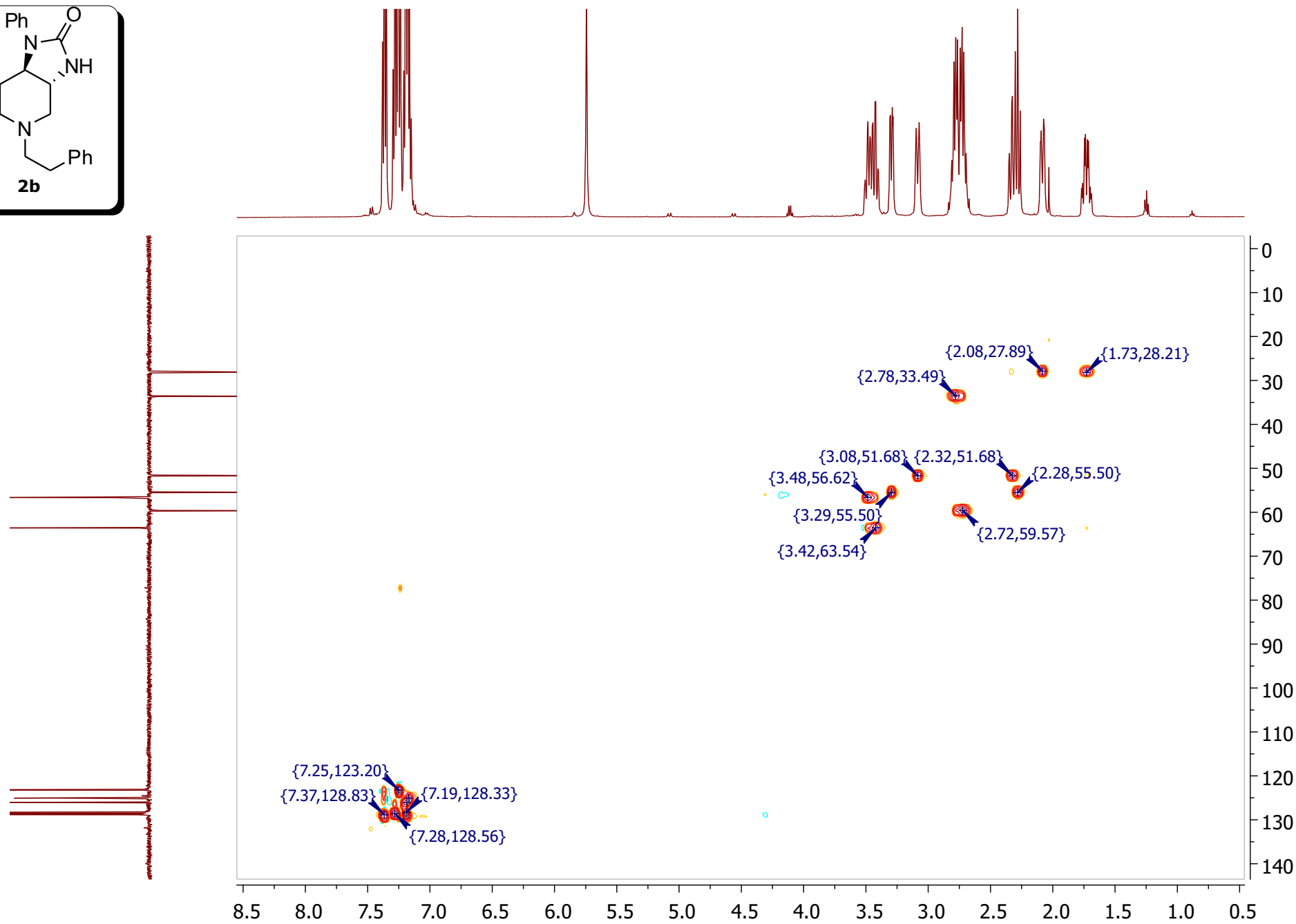
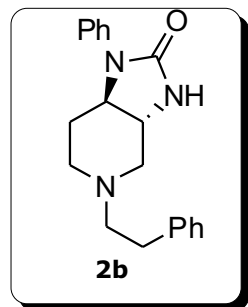


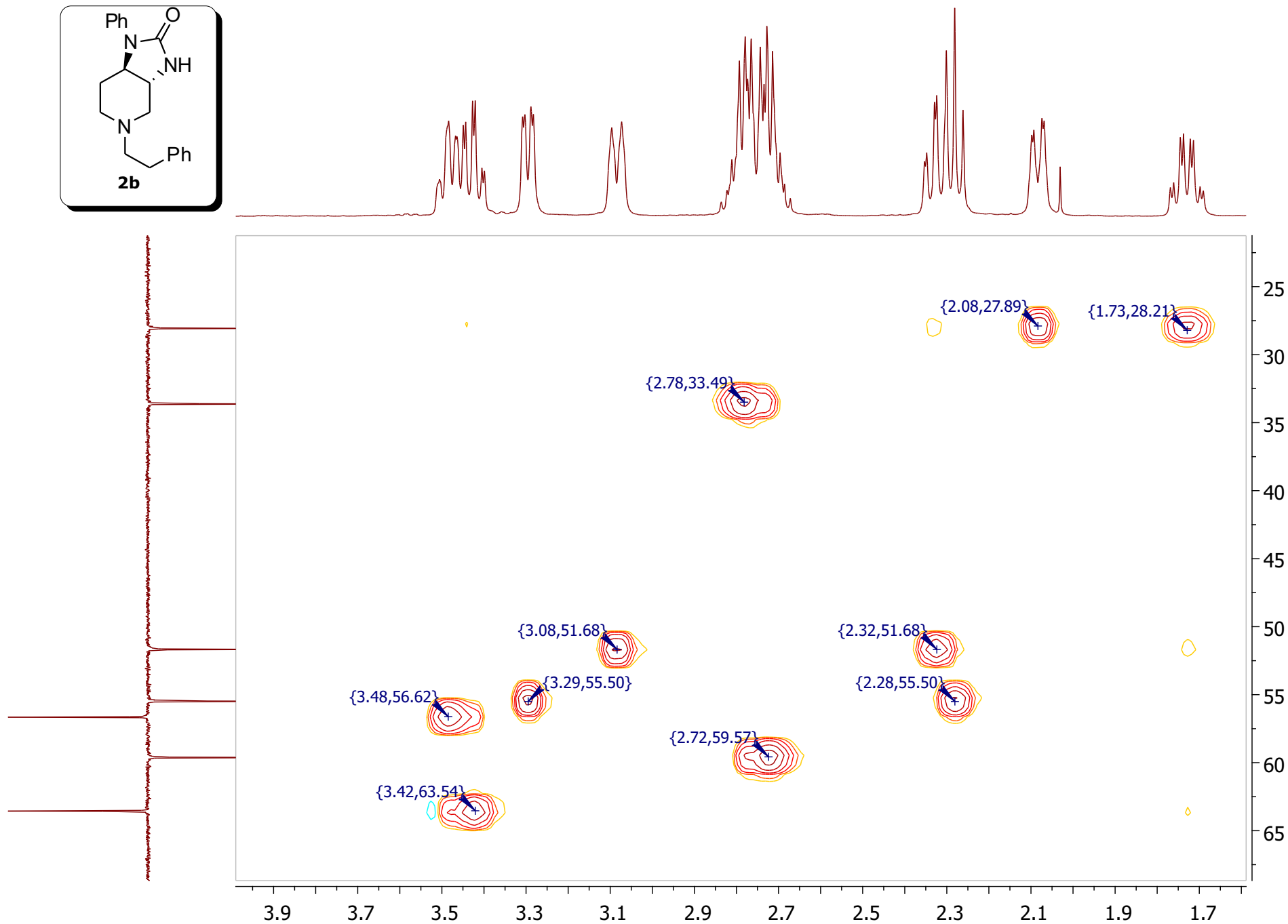
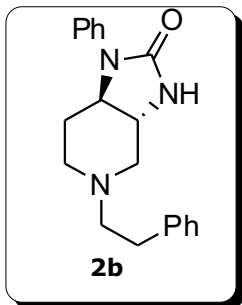


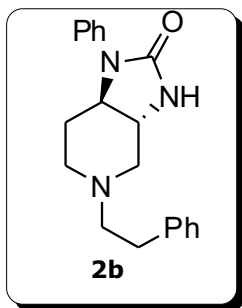
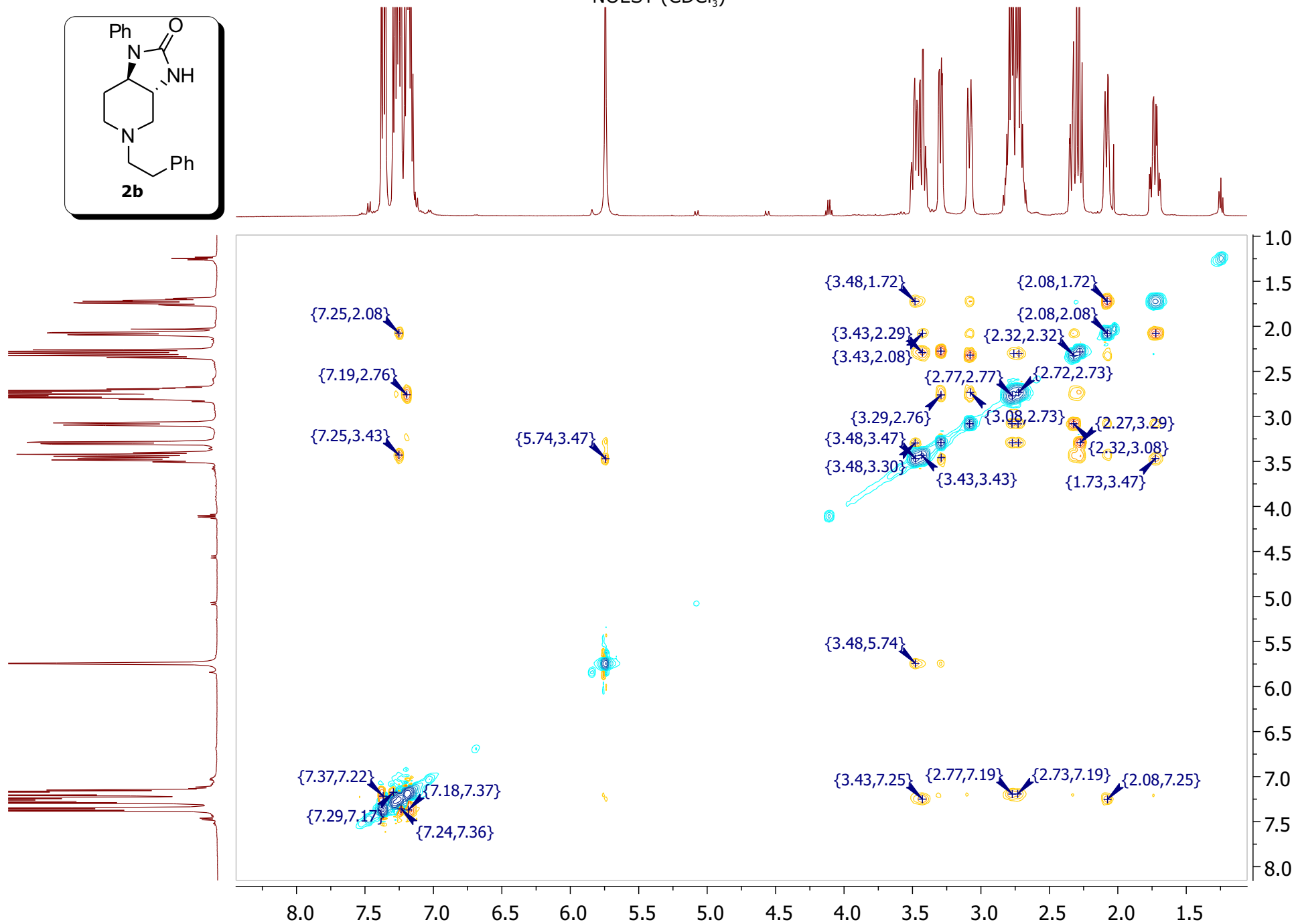


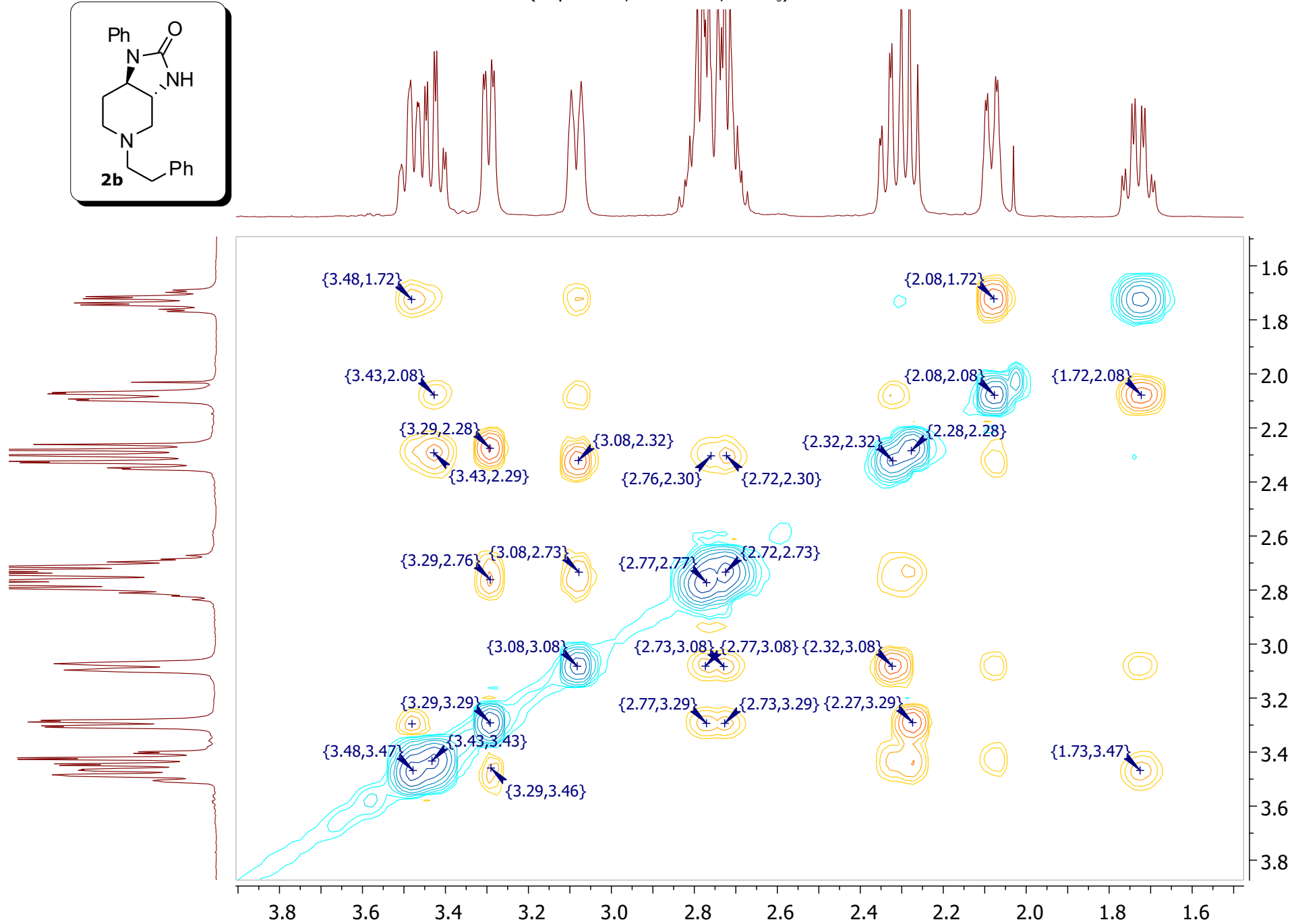
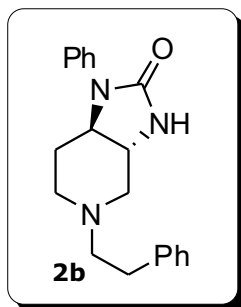




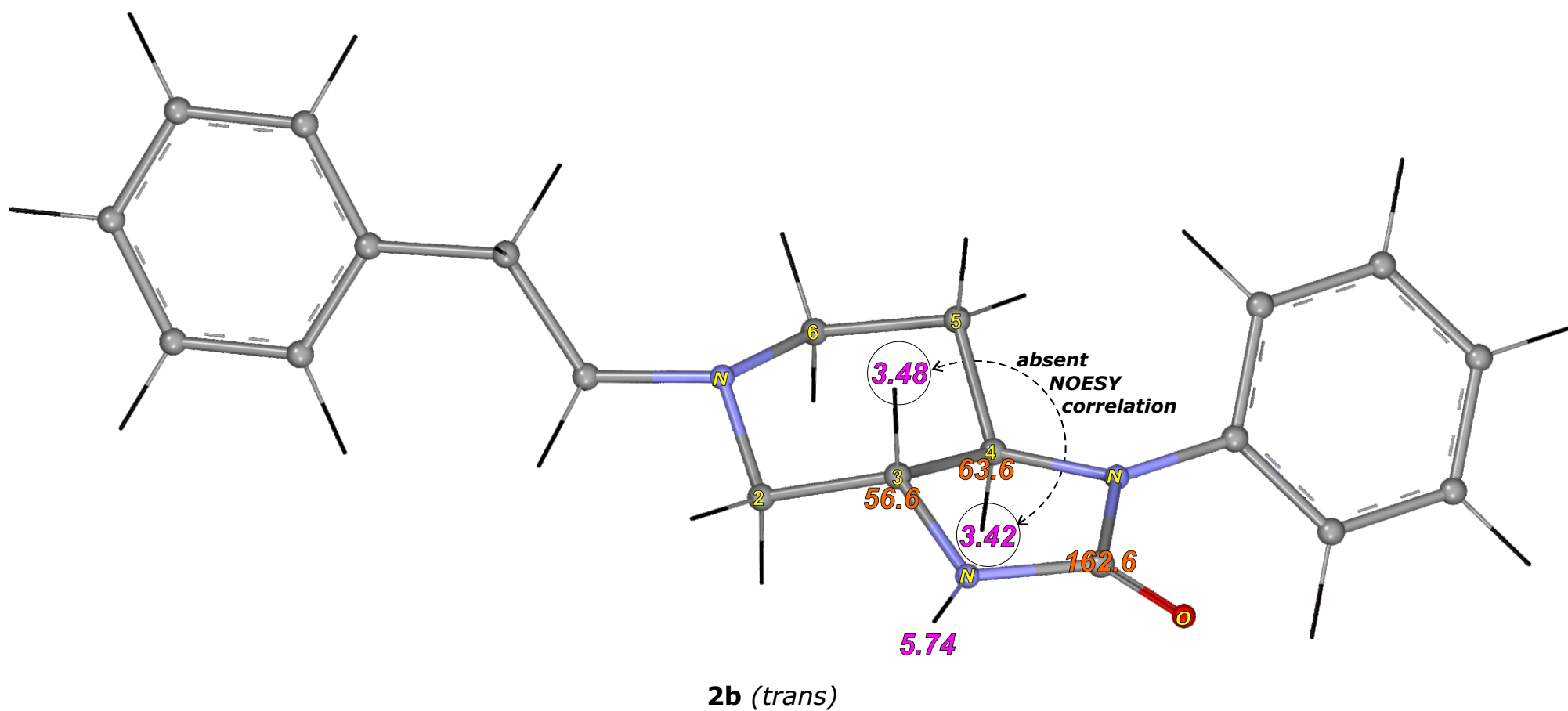


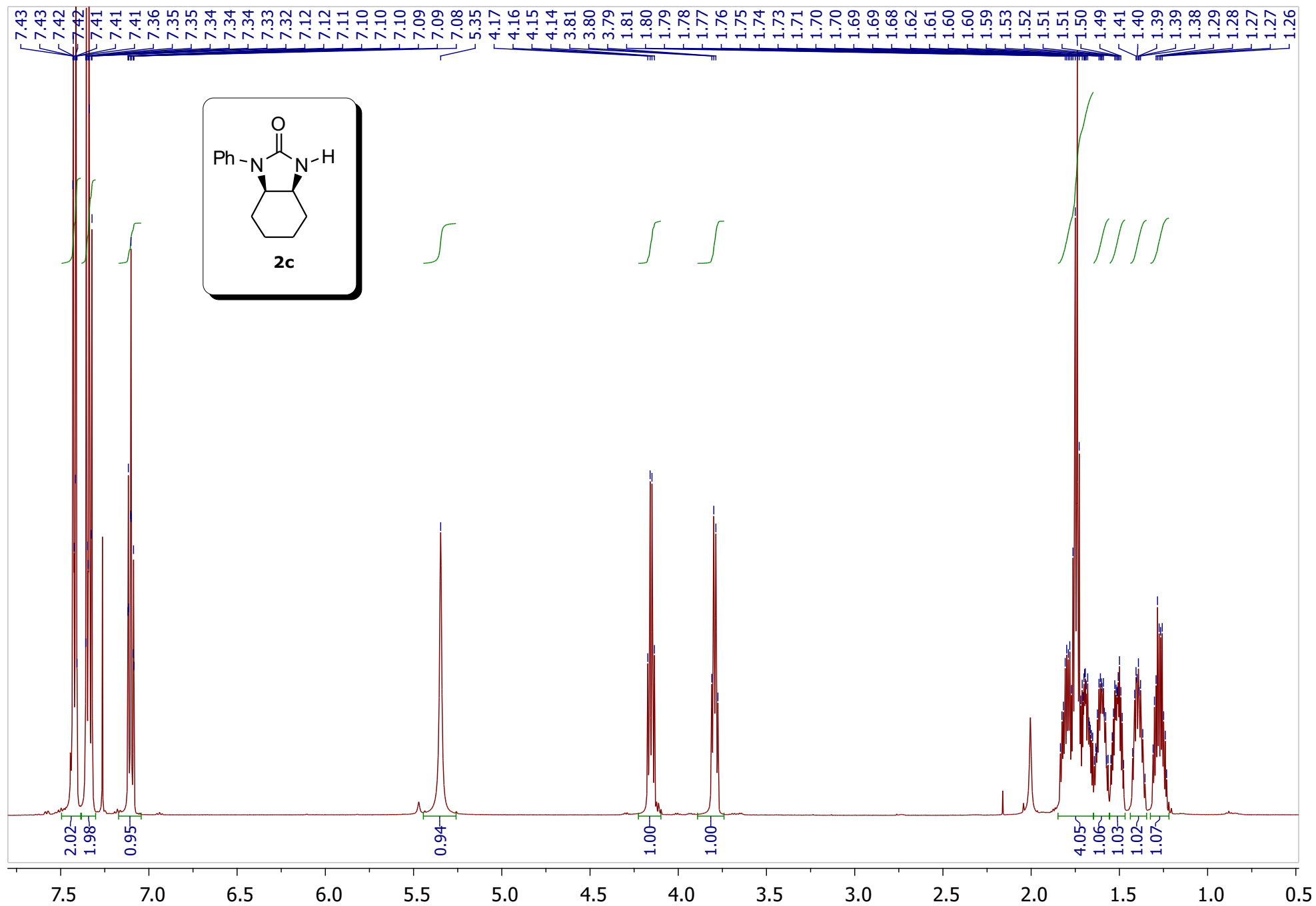


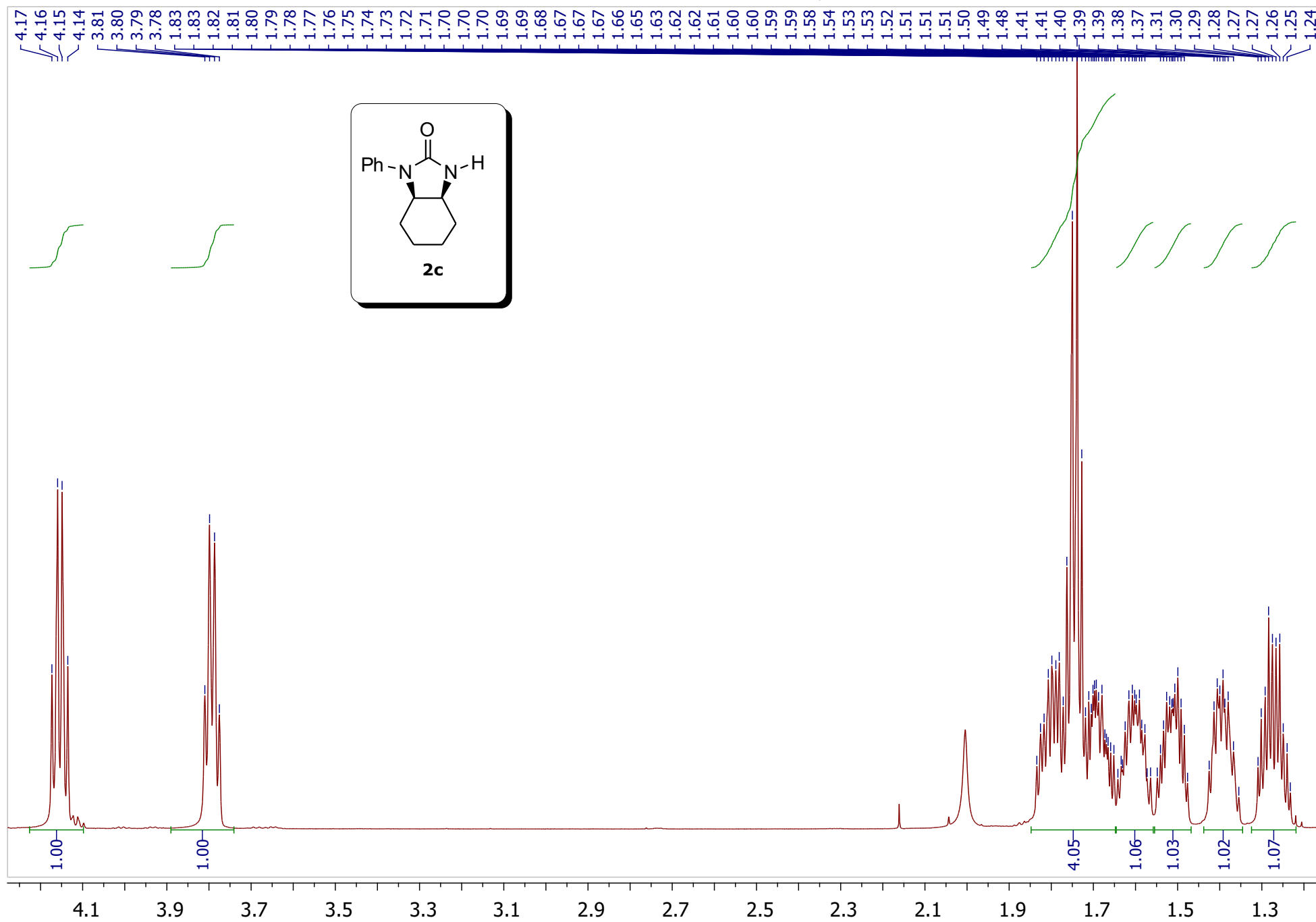
NOESY (CDCl₃)

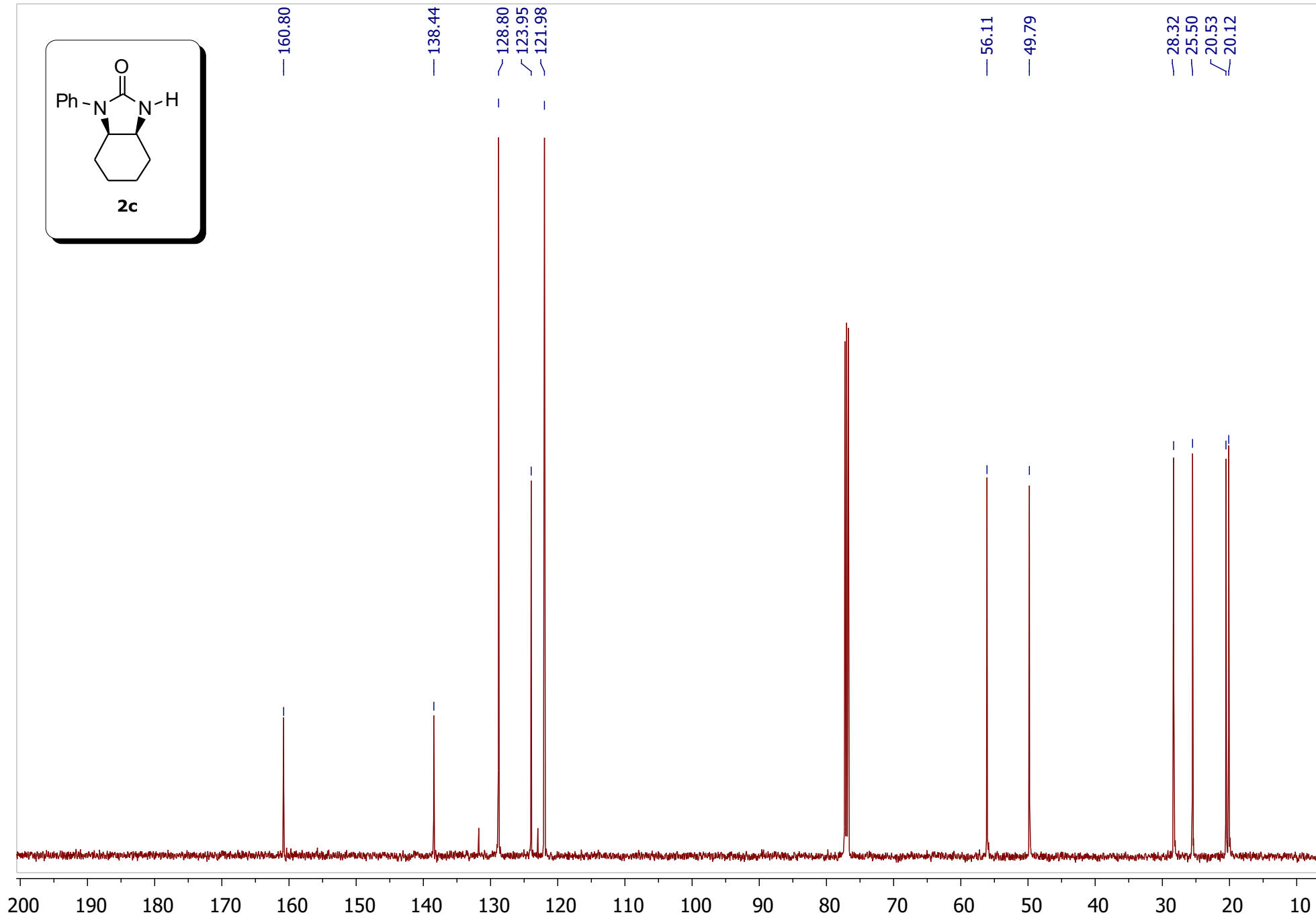
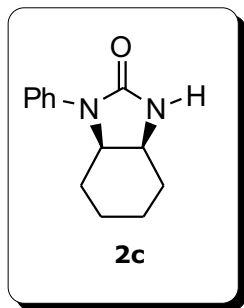


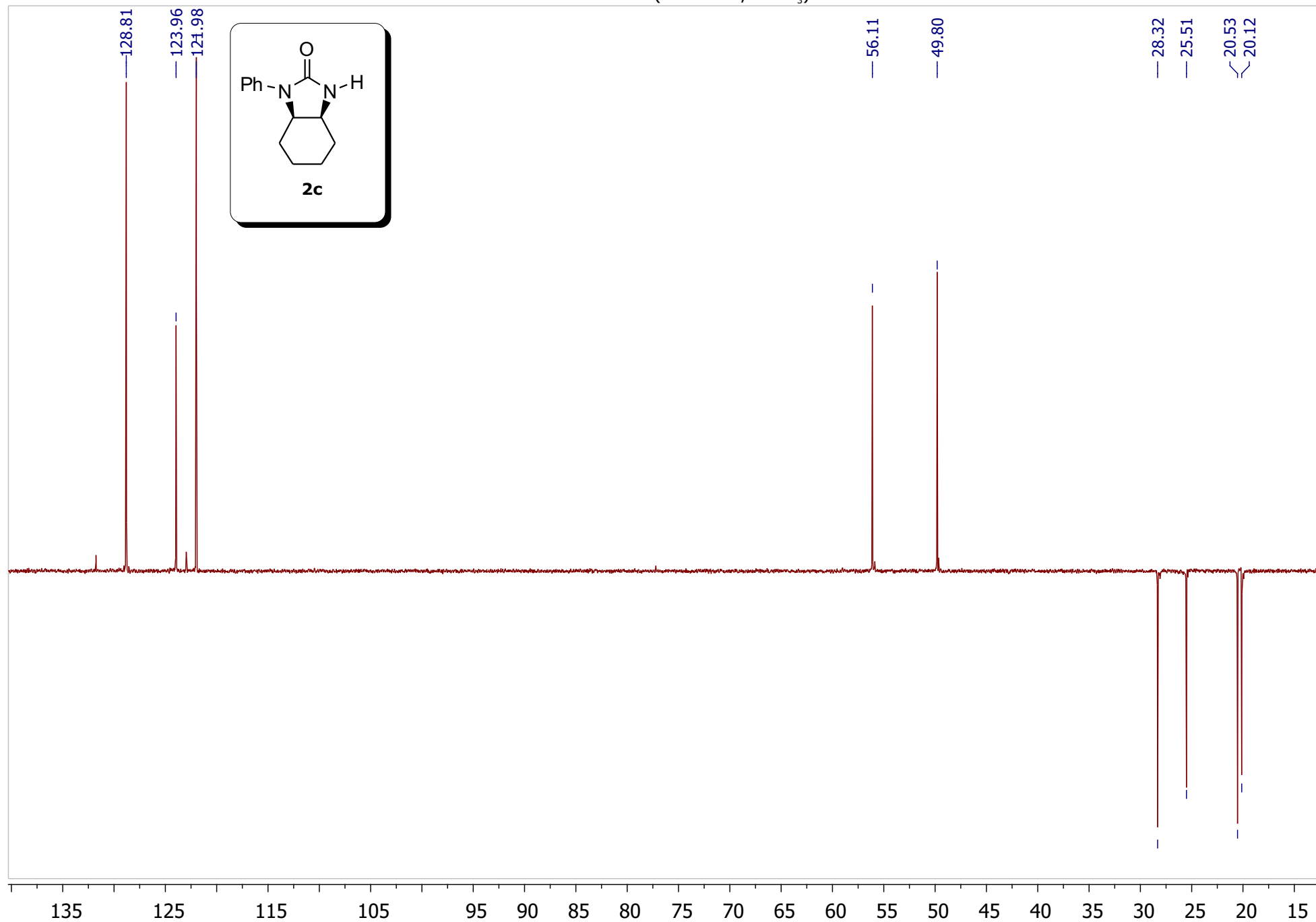
Approximate 3D model of urea **2b**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (*trans*) is corroborated by spectral data of amide **1a** (*cis*), amide **1b** (*trans*), urea **2a** (*cis*) and urea **2b** (*trans*).

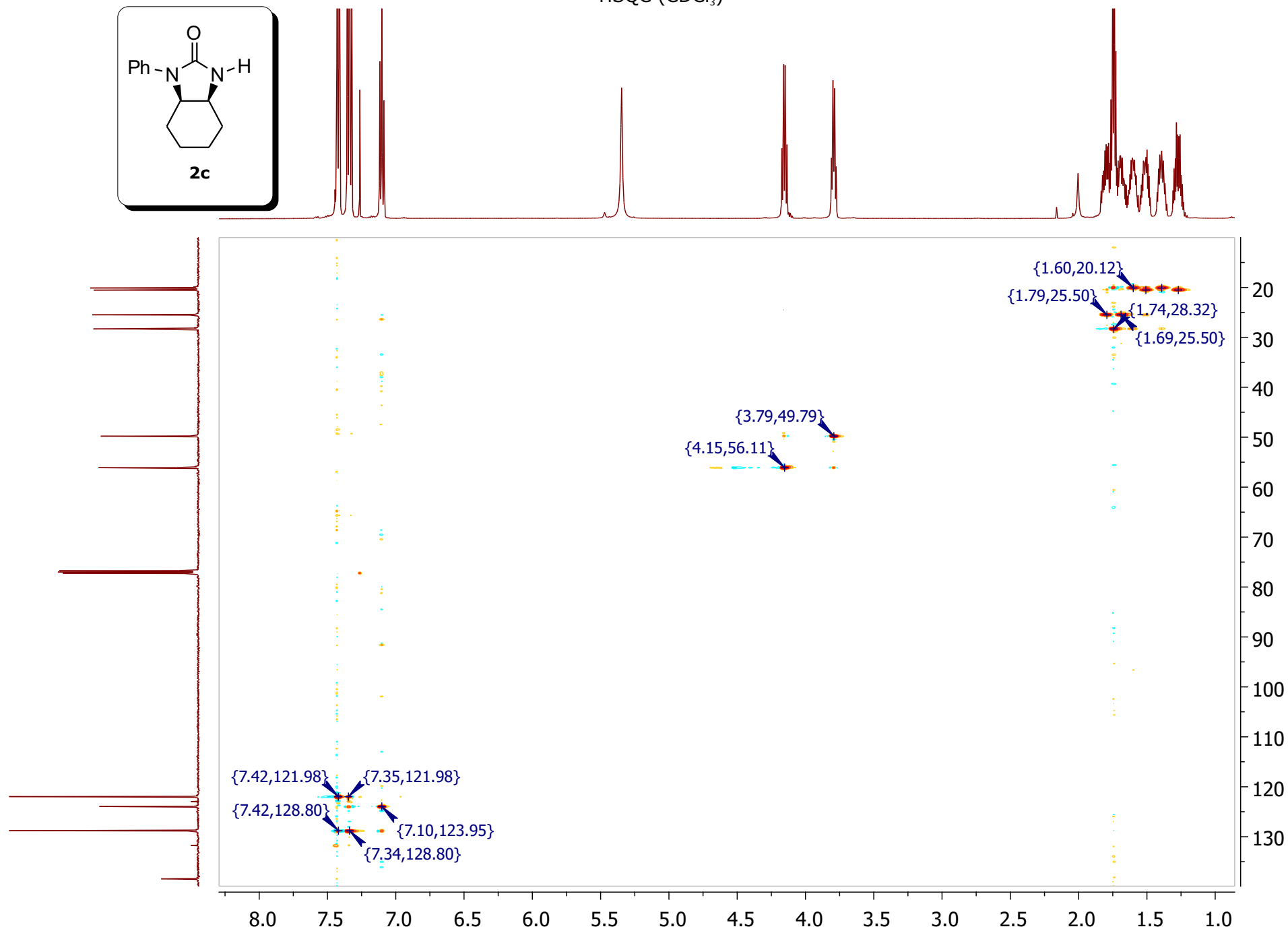
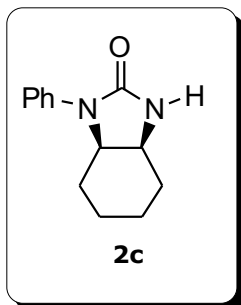


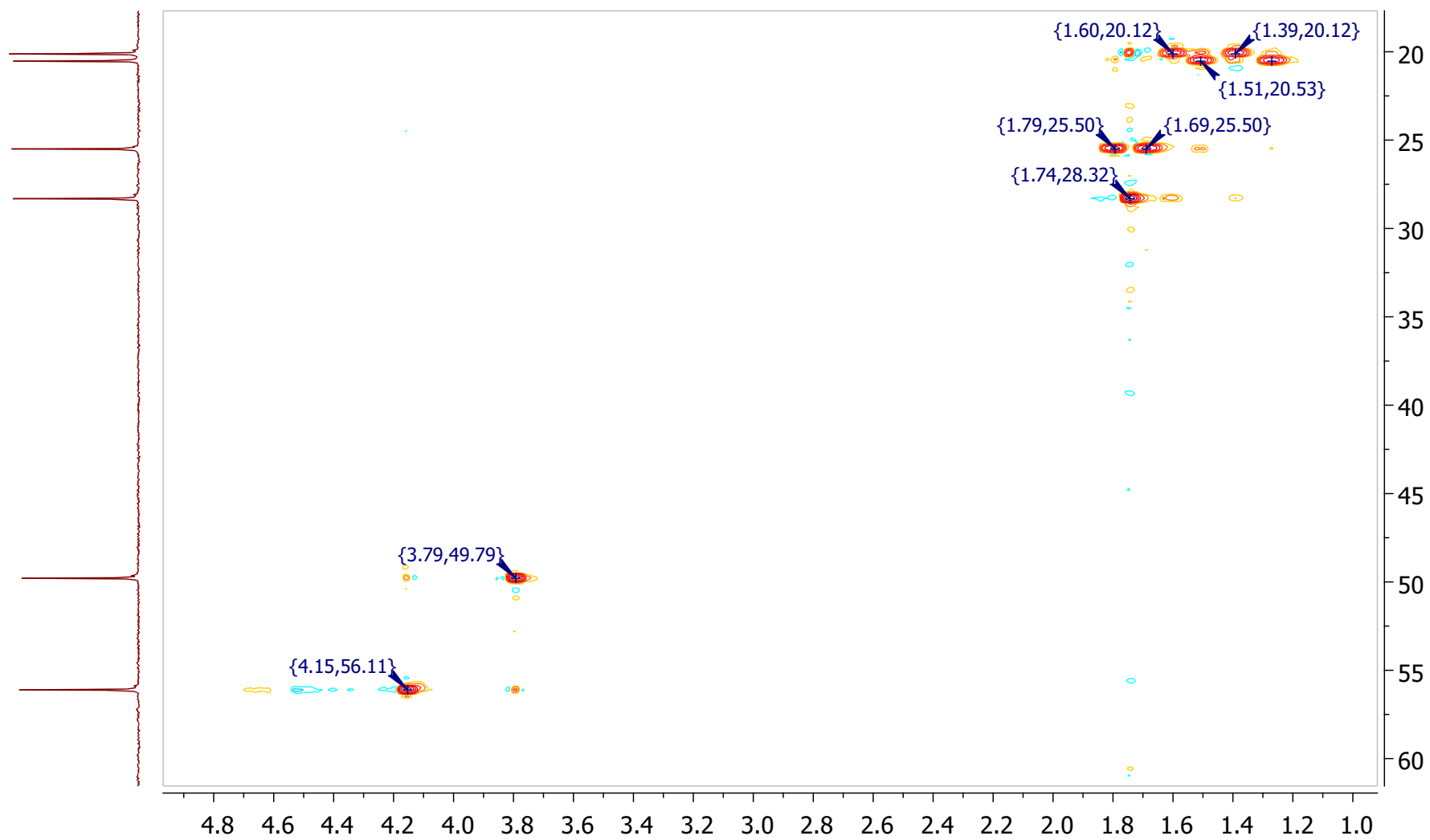
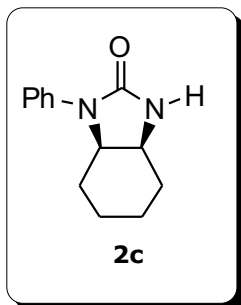
^1H NMR (500 MHz, CDCl_3)

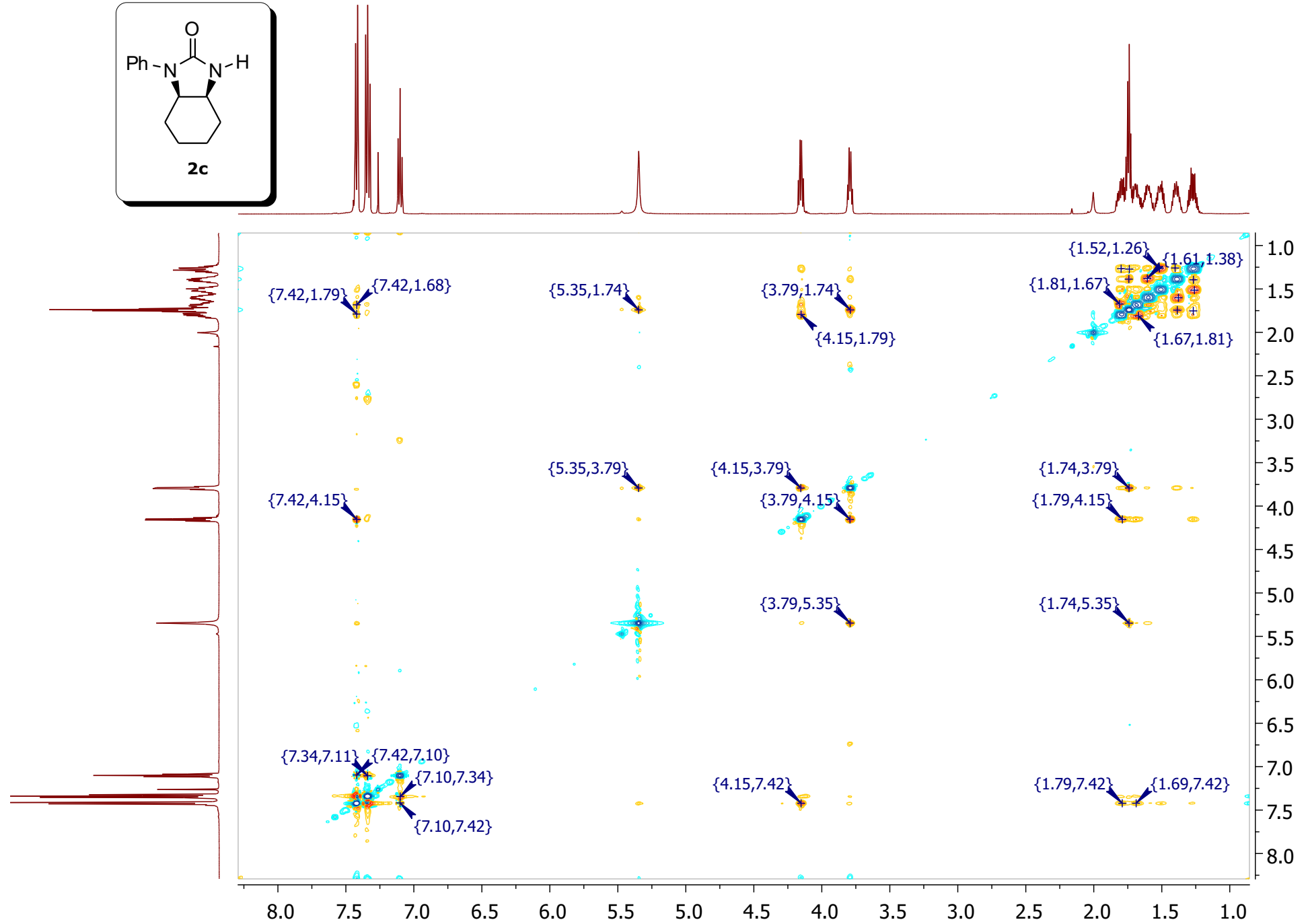
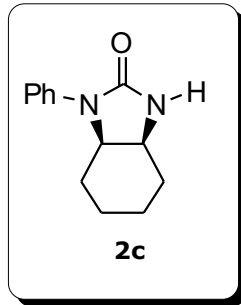
¹H NMR (expanded, 4.2-1.2 δ , 500 MHz, CDCl₃)

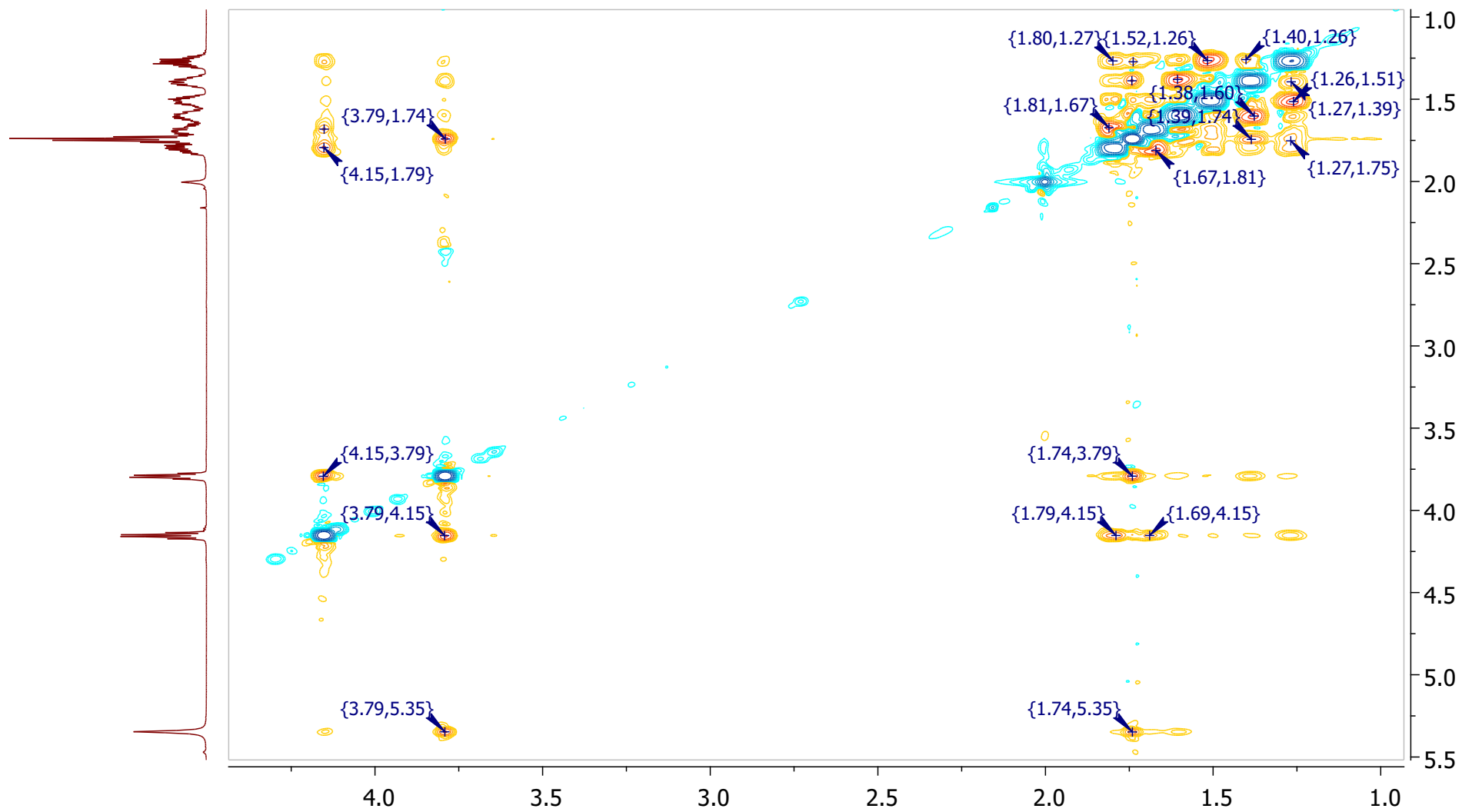
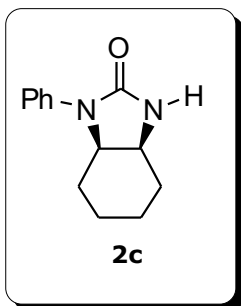


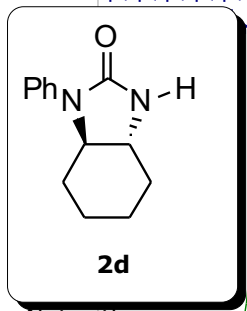


HSQC (CDCl₃)

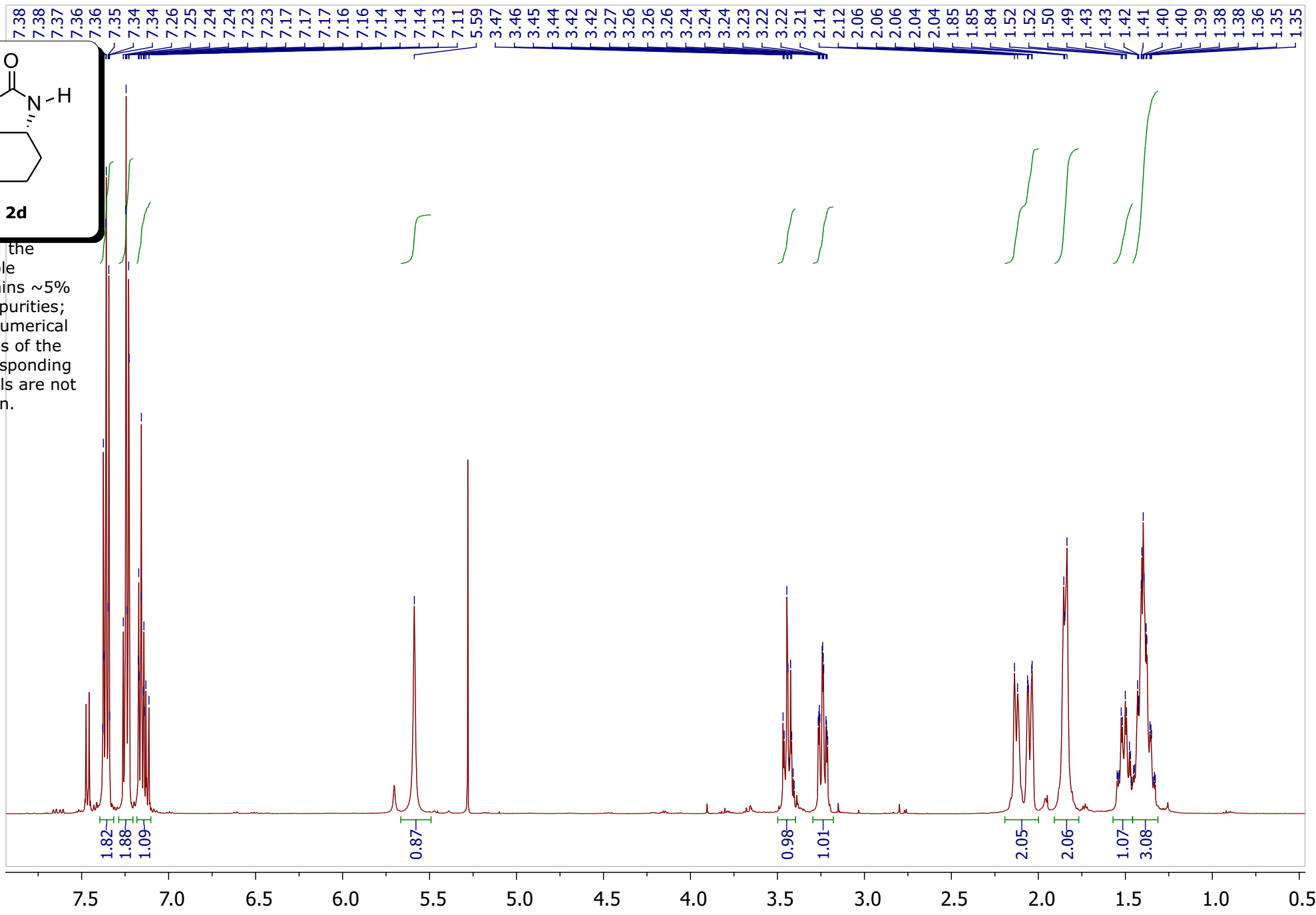
HSQC (expanded, 4.9-1.0 δ , CDCl₃)

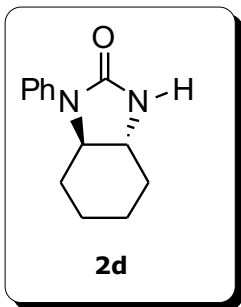




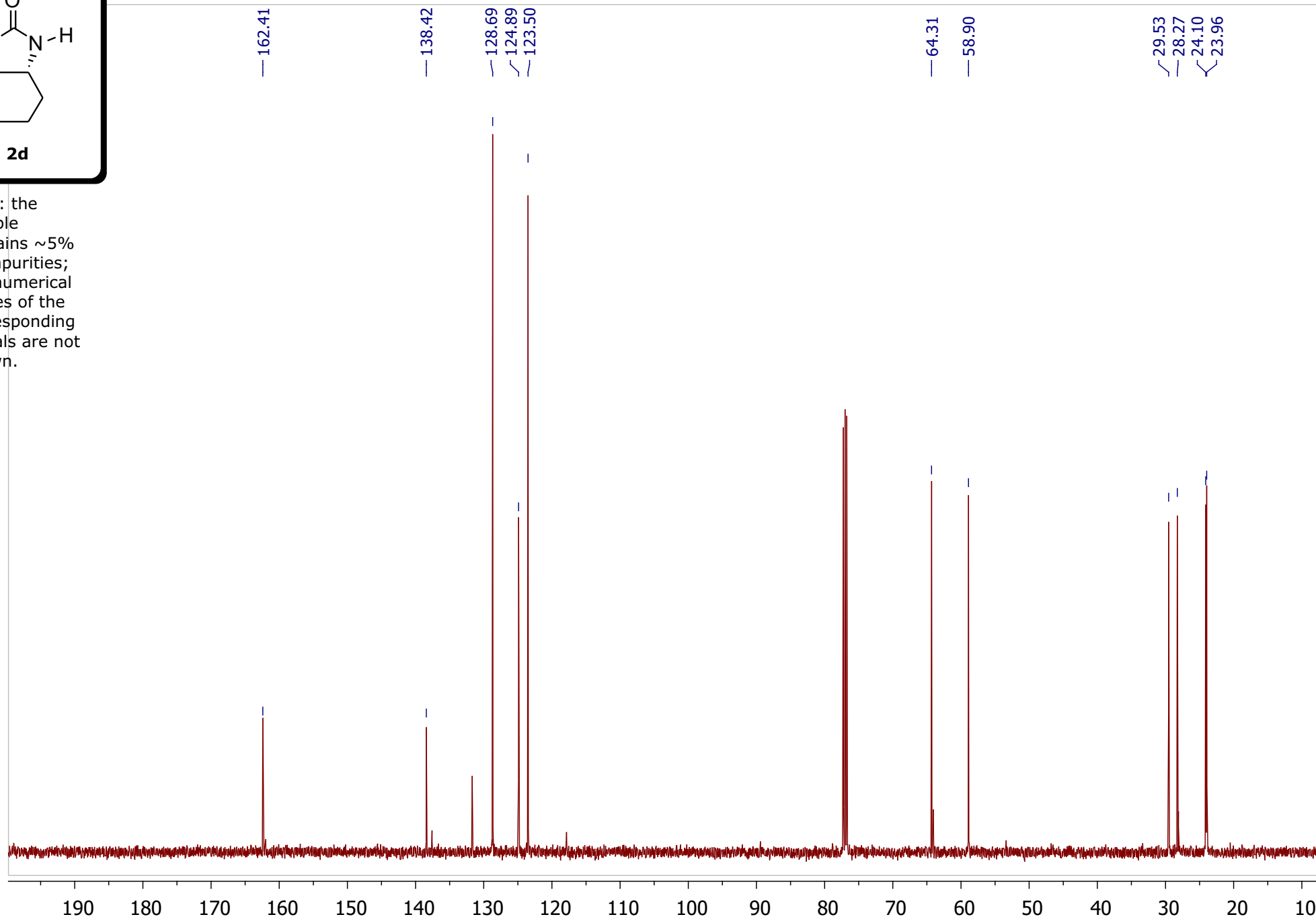


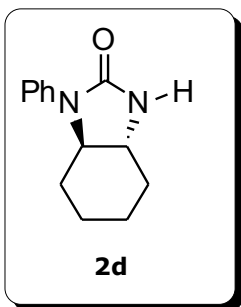
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



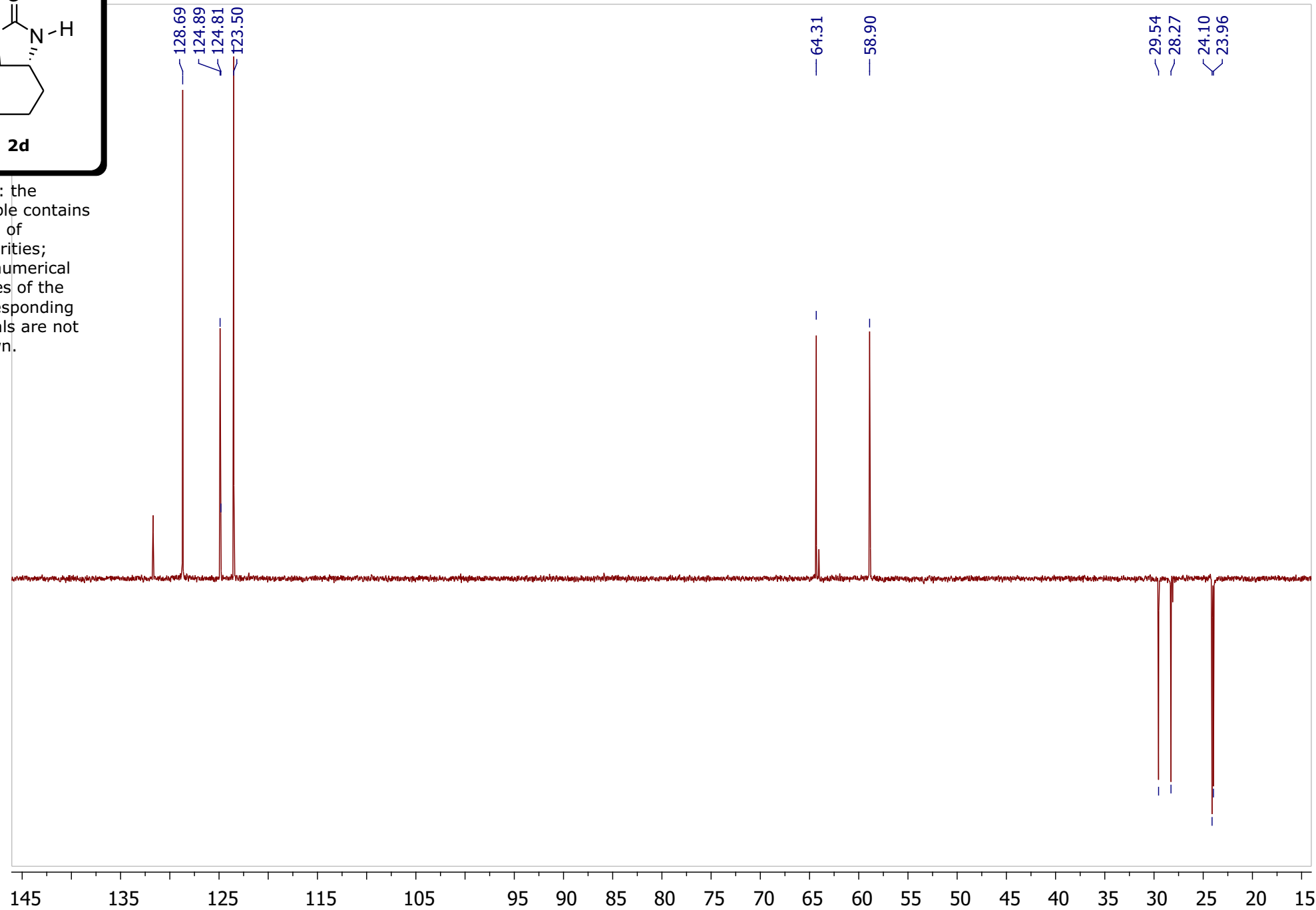


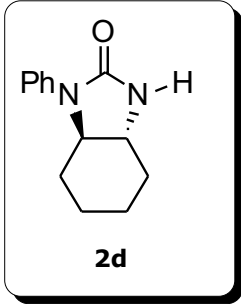
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



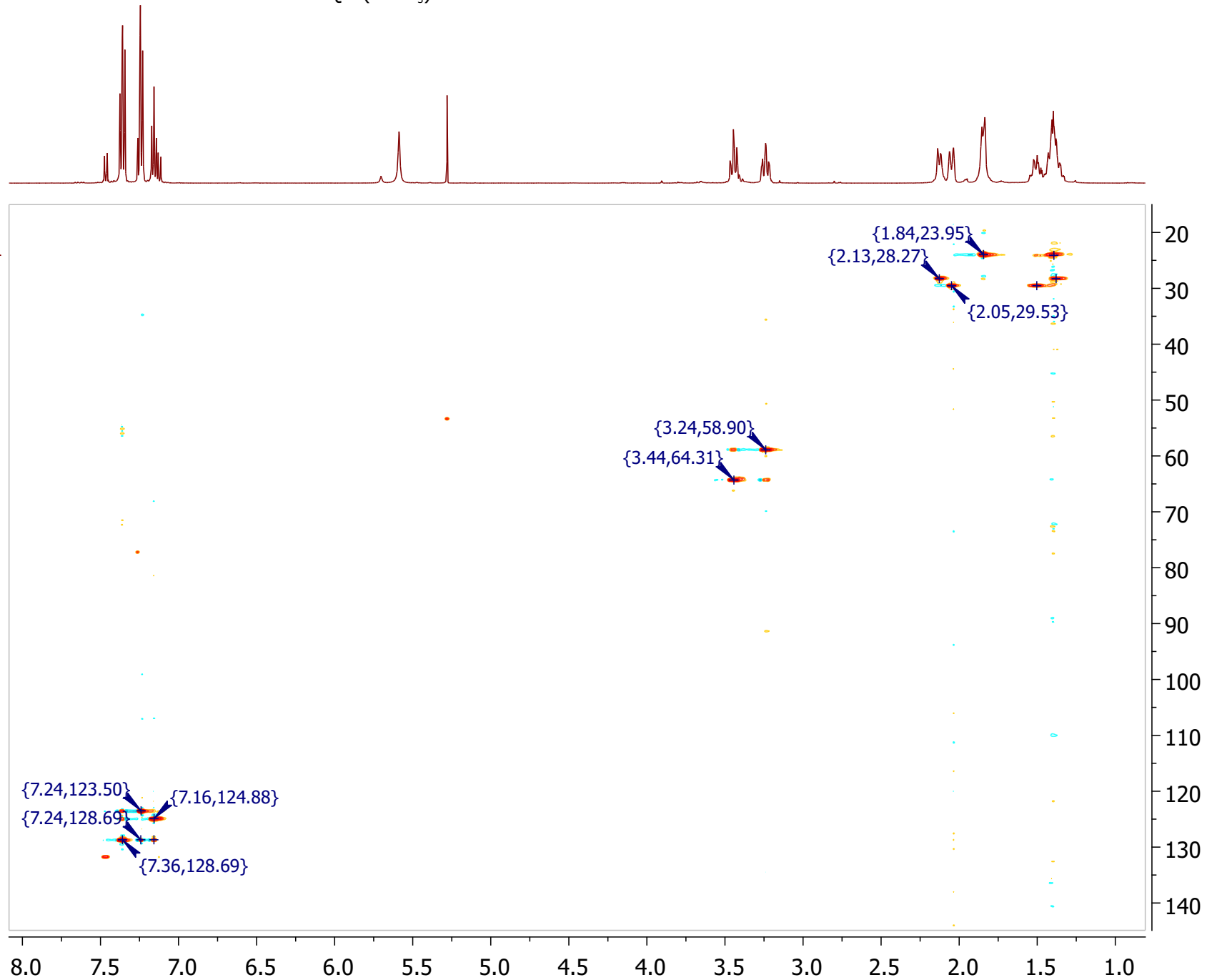


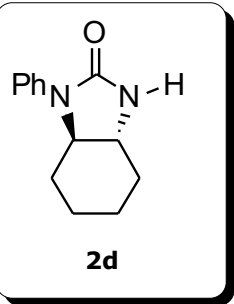
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



HSQC (CDCl₃)

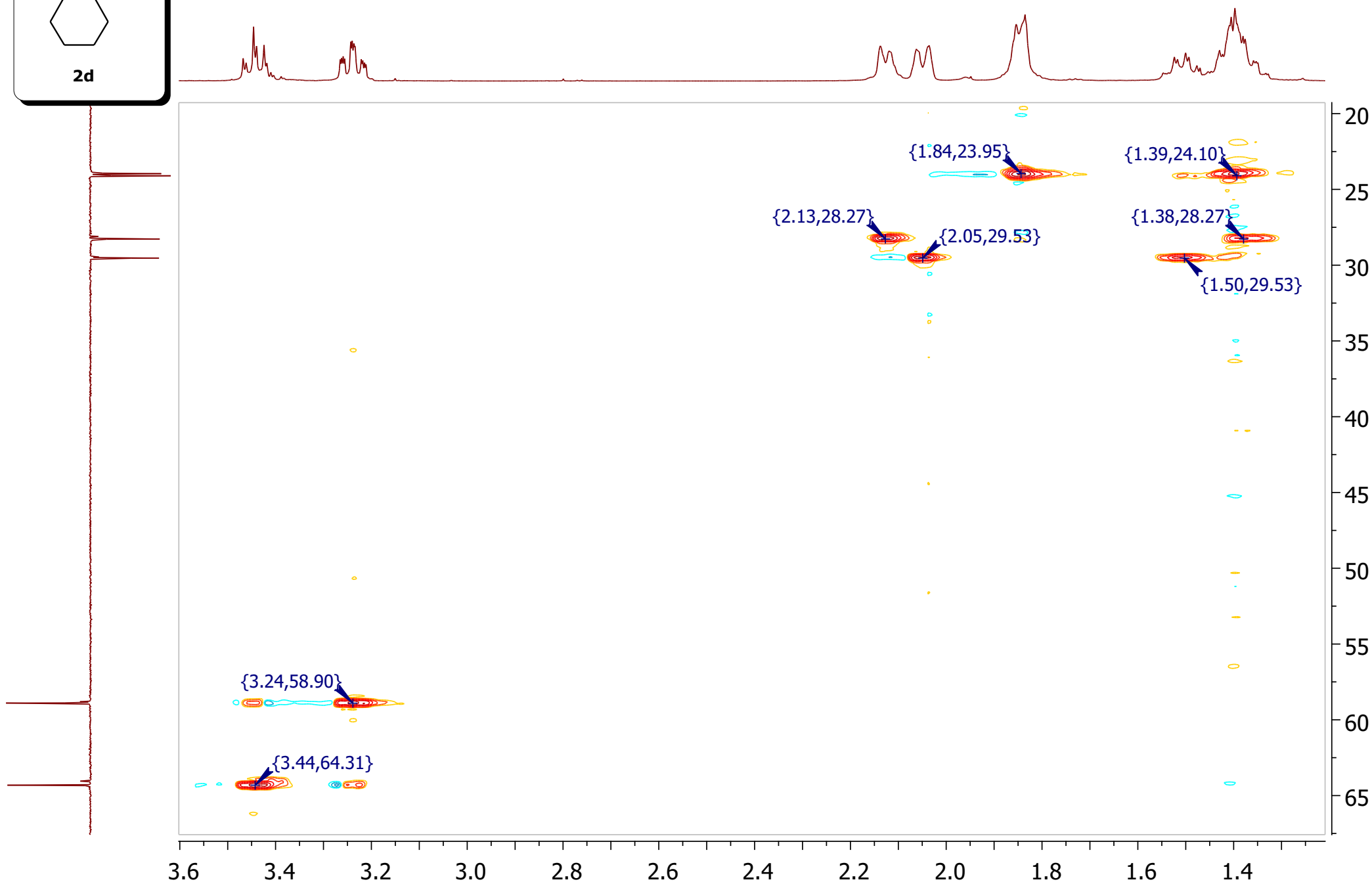
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.

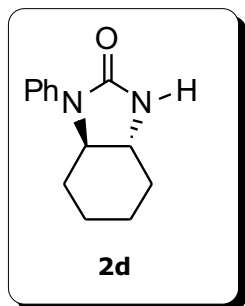




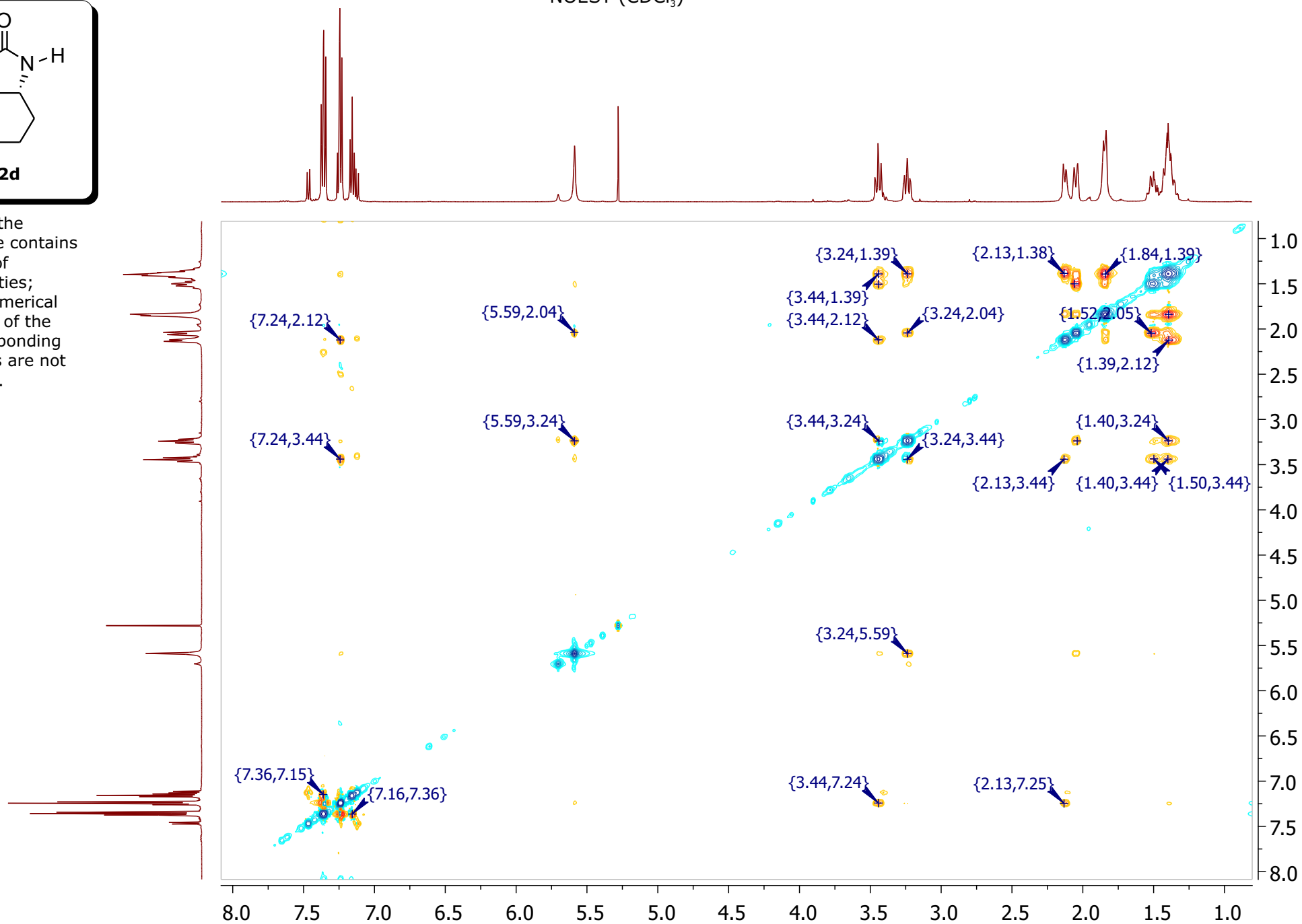
HSQC (expanded, 3.6-1.3 δ , CDCl₃)

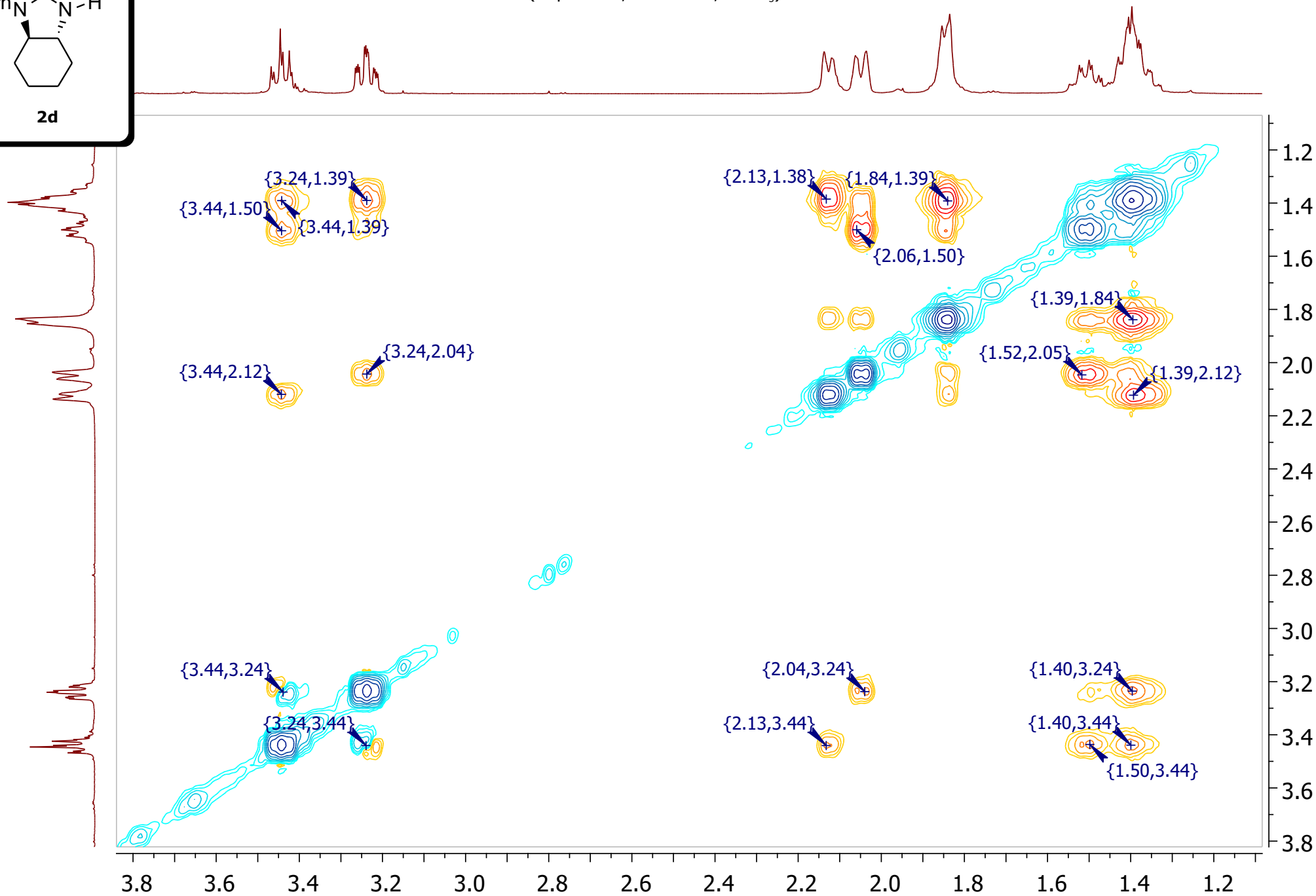
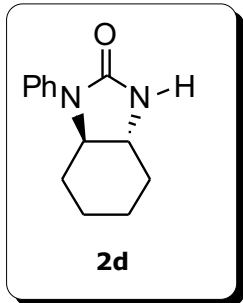
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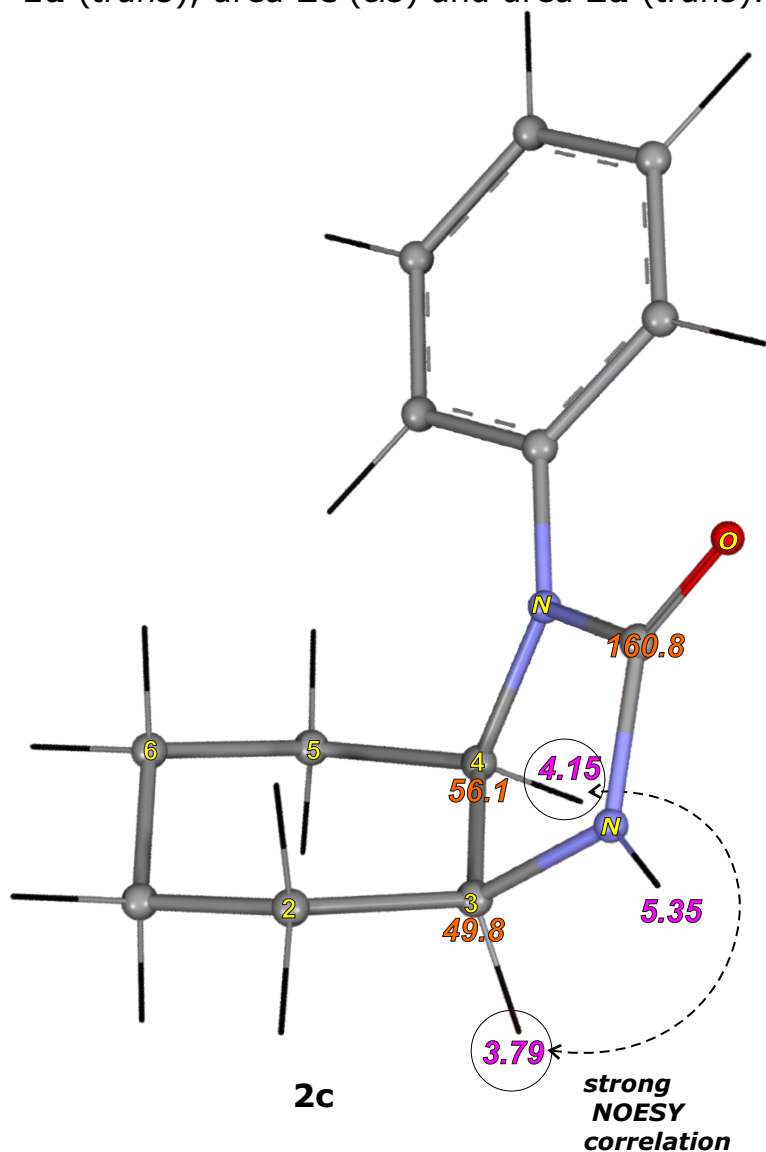


Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.

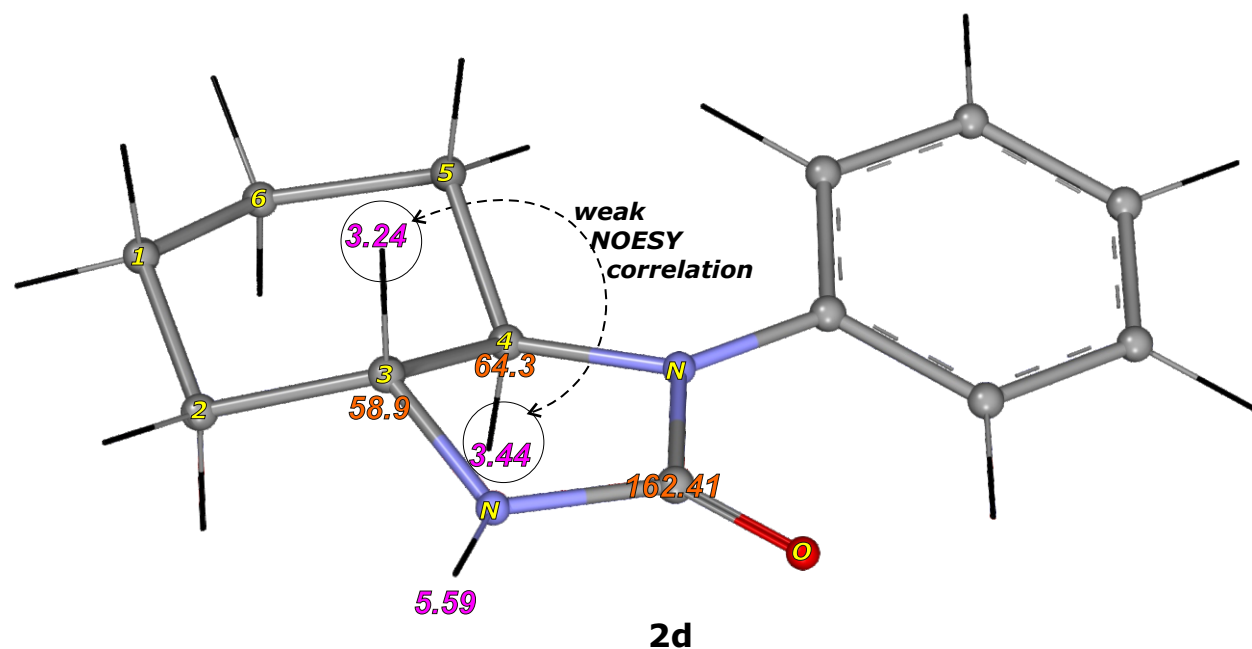
NOESY (CDCl₃)

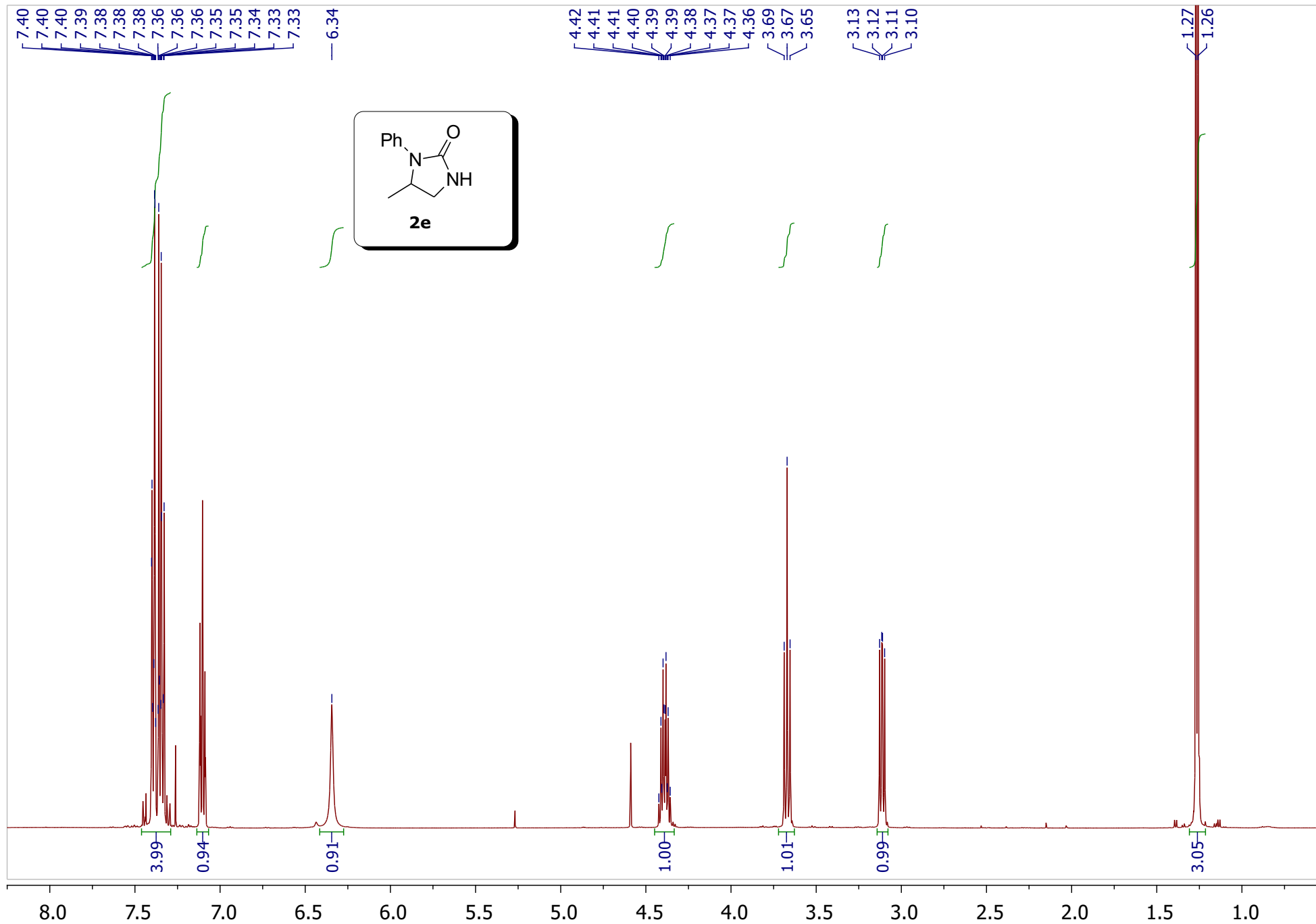


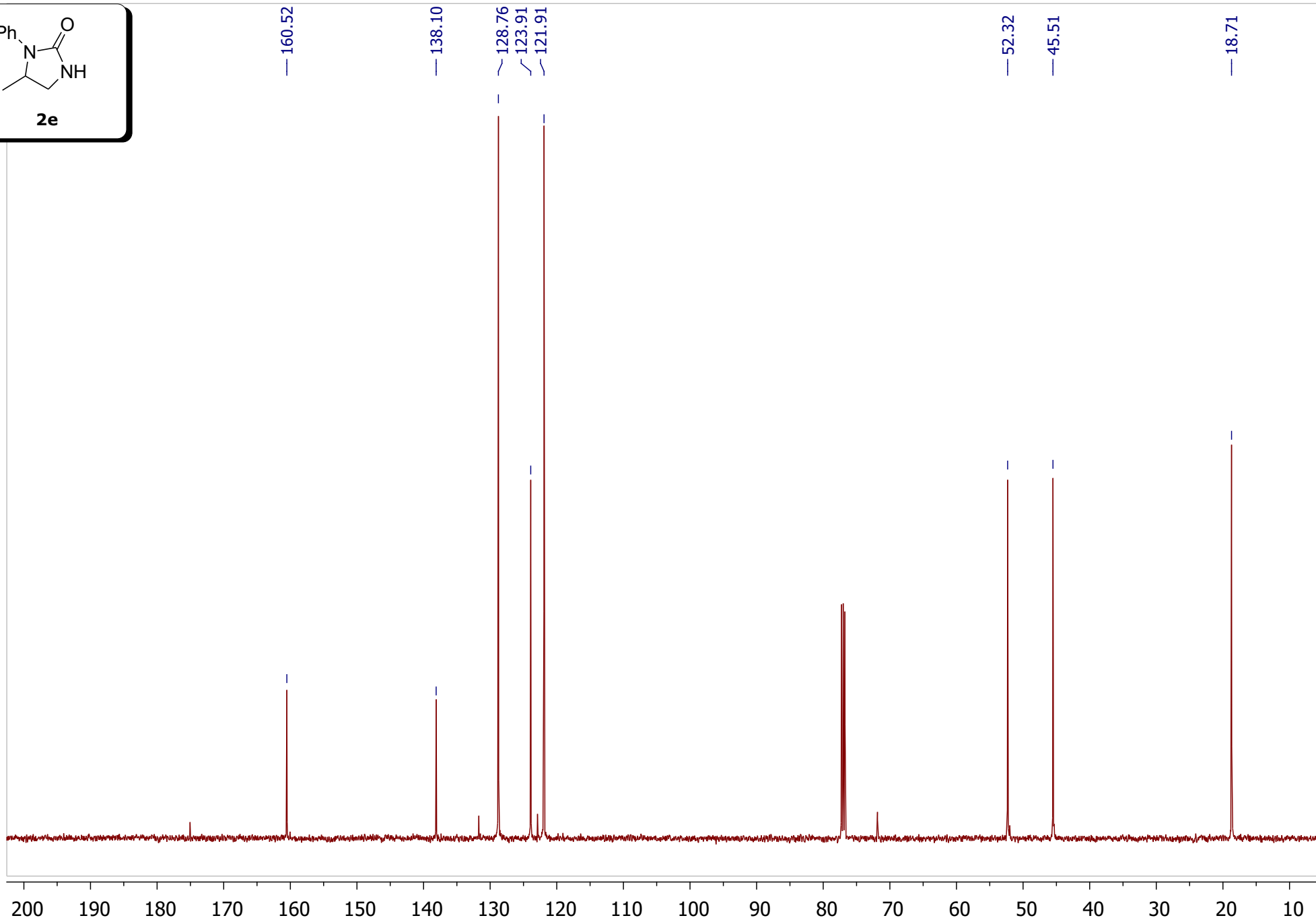
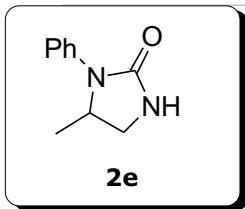
Approximate 3D models of ureas **2c** and **2d**. Assignments of the selected H and C signals are based on NMR spectral data and the predicted values. The relative stereochemistry (**2c** *cis* and **2d** *trans*) is corroborated by spectral data of amide **1c** (*cis*), amide **1d** (*trans*), urea **2c** (*cis*) and urea **2d** (*trans*).

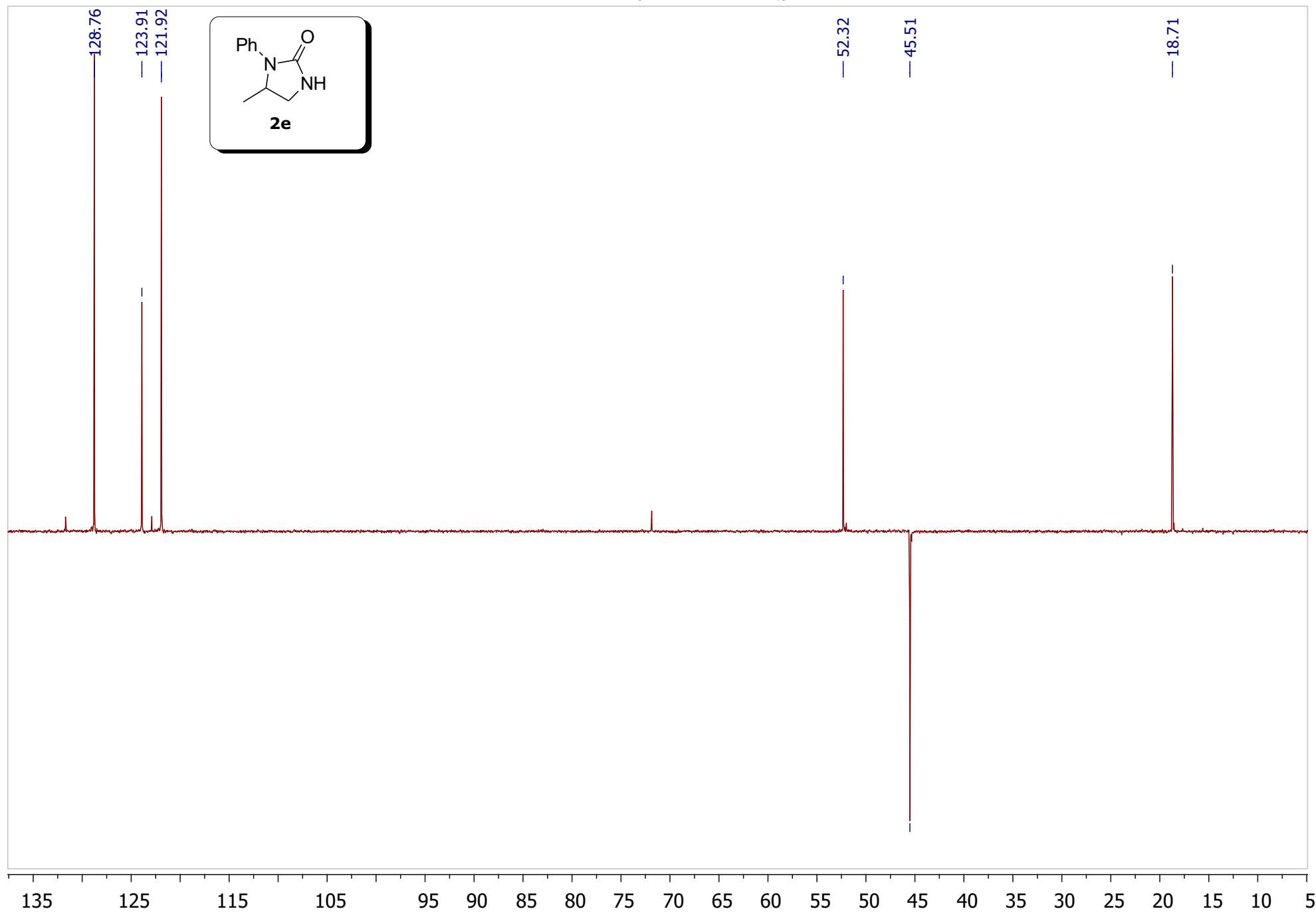


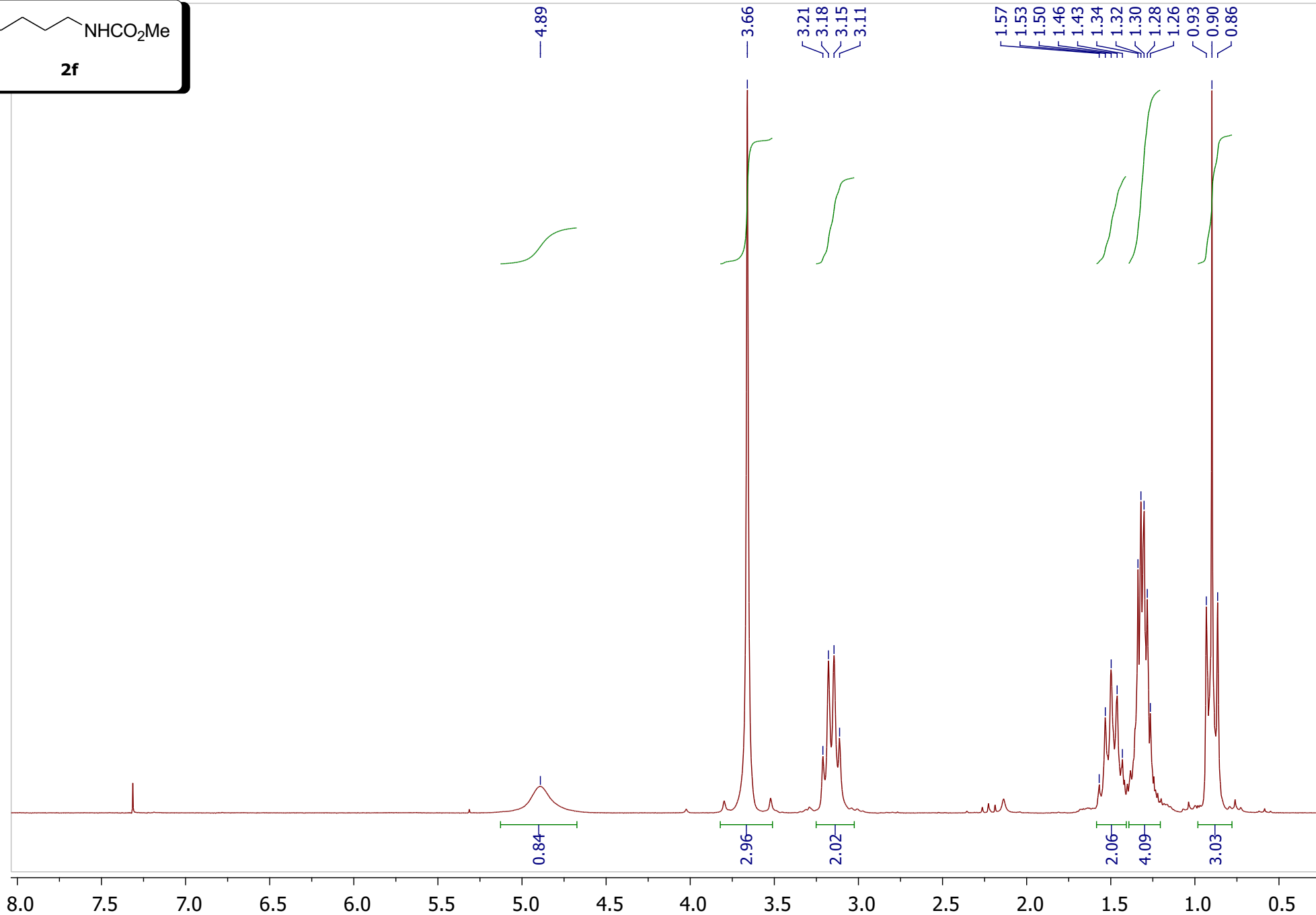
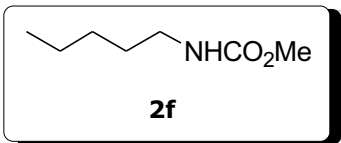
It is significant that **2c** was obtained stereospecifically from **1c**, while **2d** originated stereospecifically from **1d**. Both **1c** and **2c** have strong NOESY correlation, while **1d** and **2d** both have weak NOESY correlation. Ureas **2c** and **2d** are diastereomers as well as the amides **1c** and **1d** (as confirmed by NMR and HRMS data). Thus, the represented relative configurations can be ascribed with good confidence.

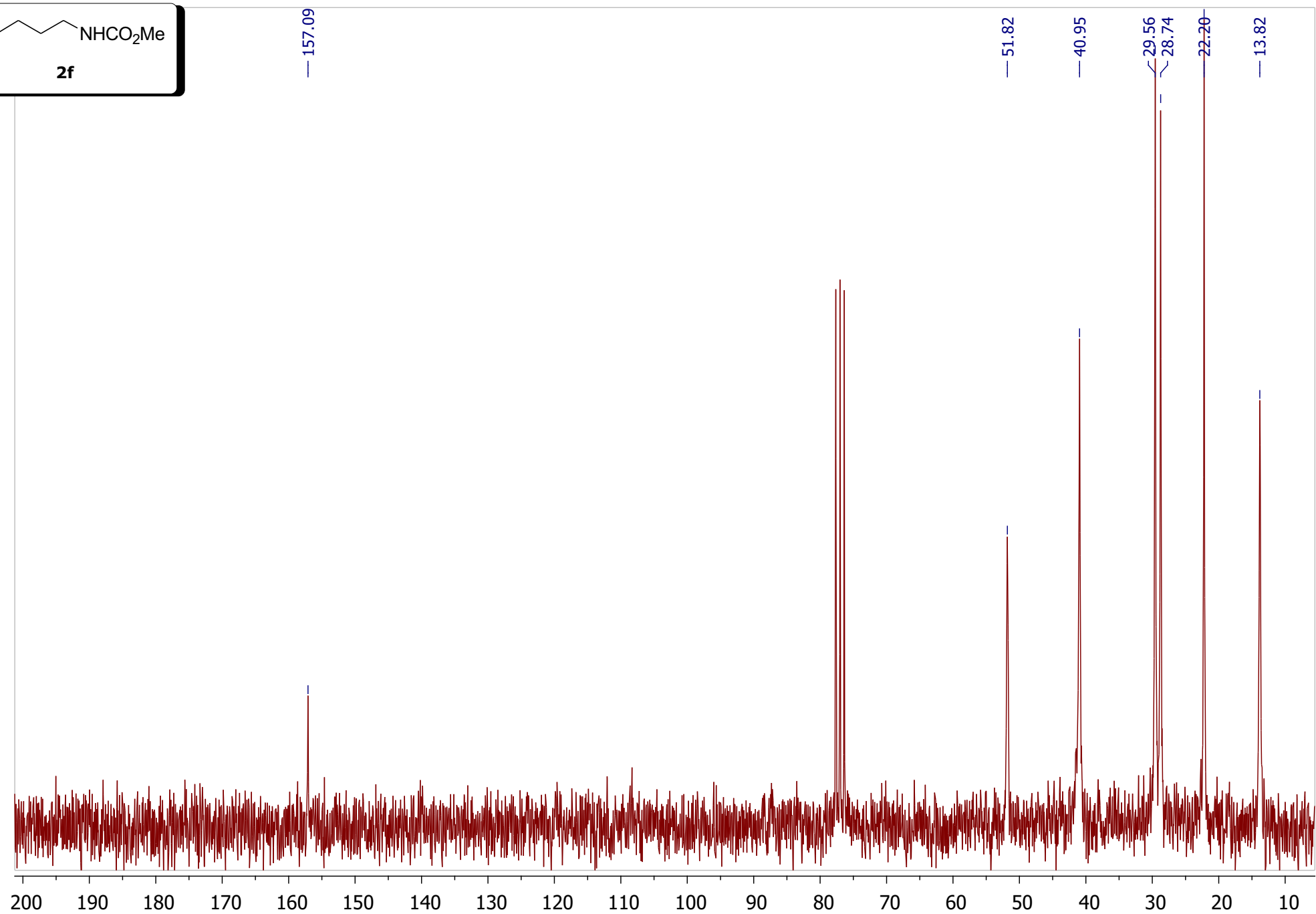
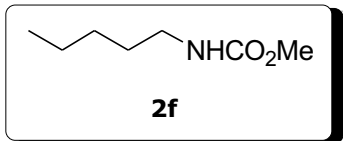


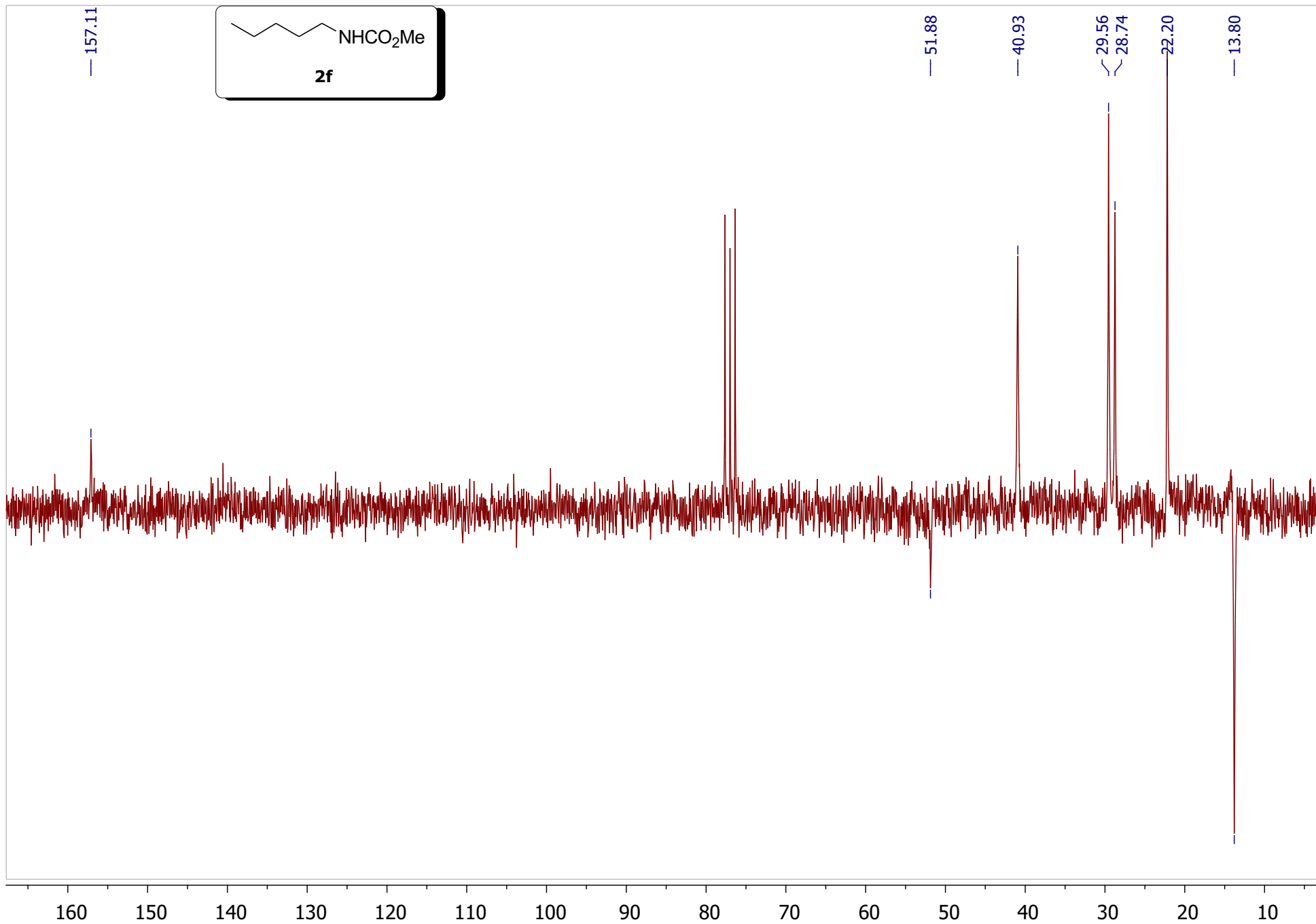


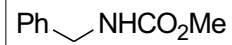




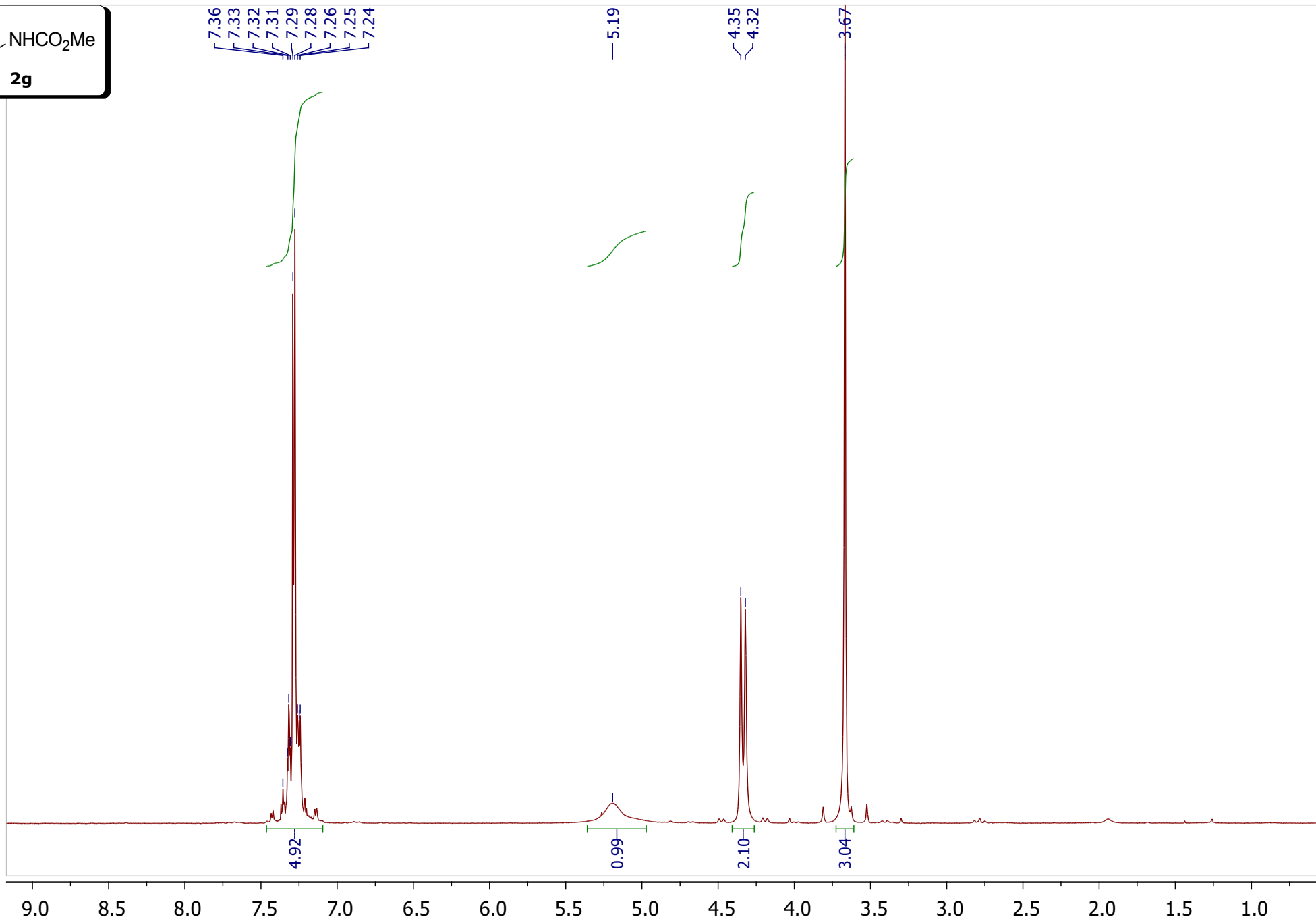


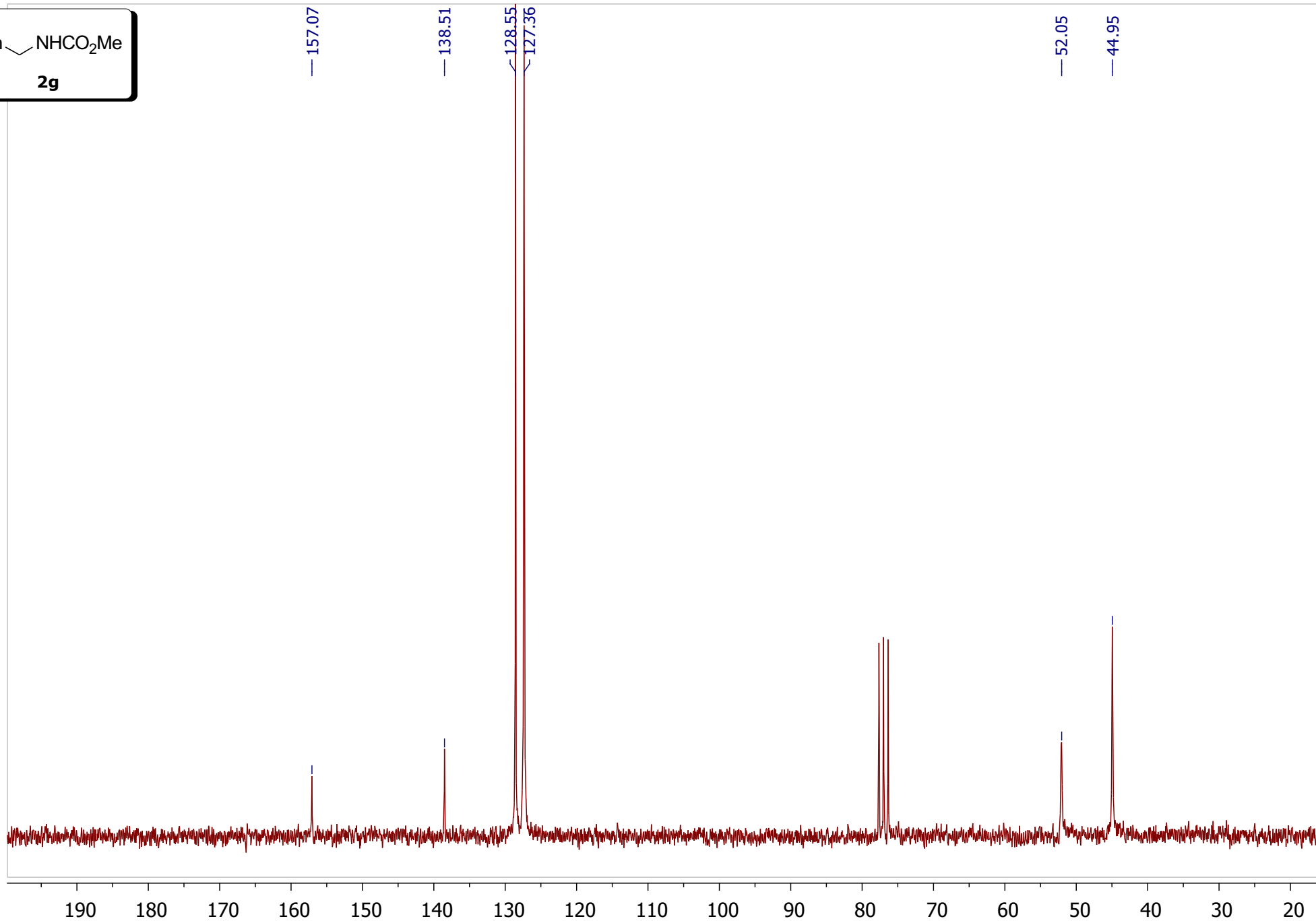
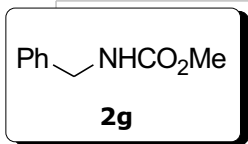


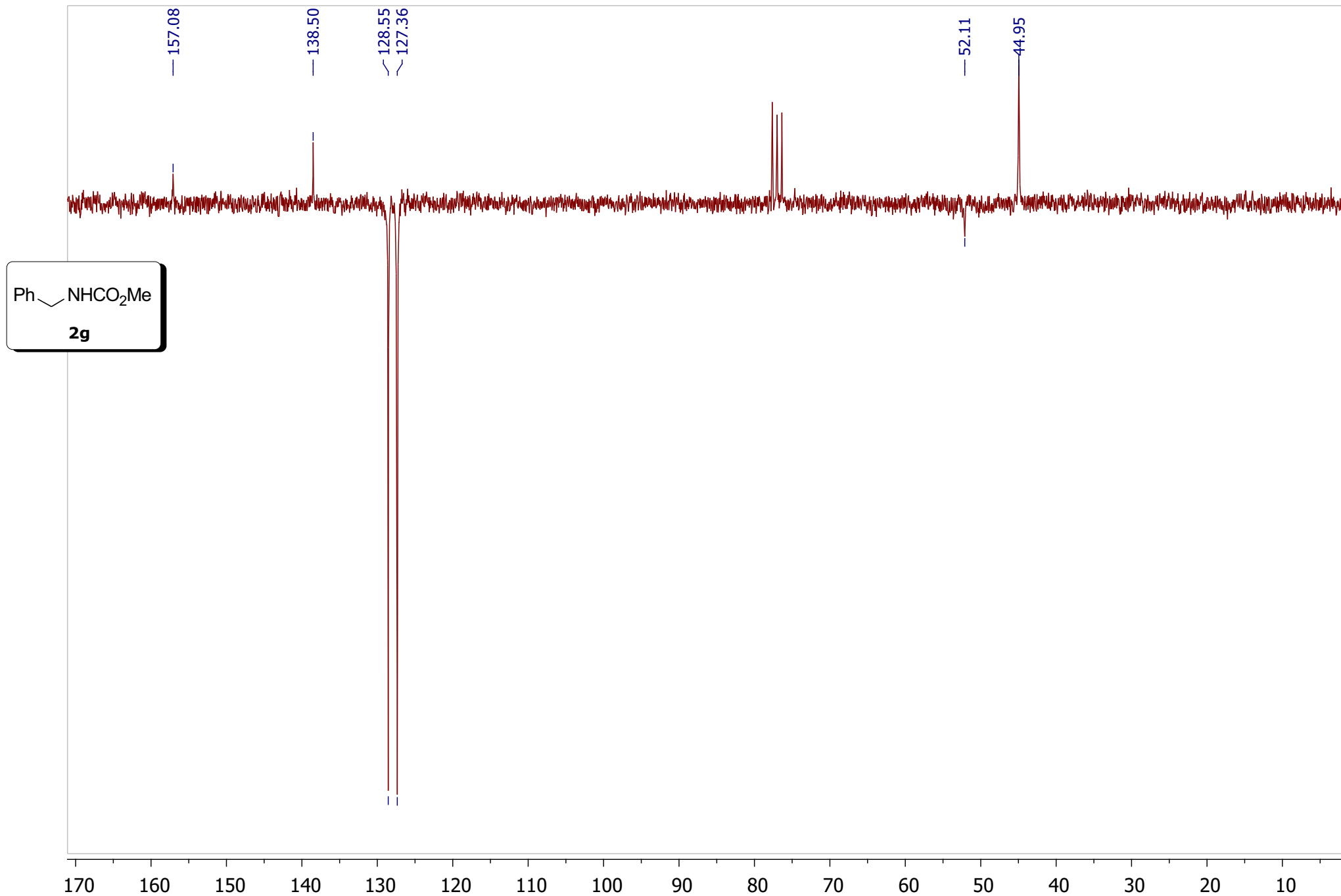


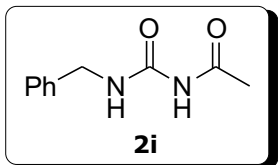


2g

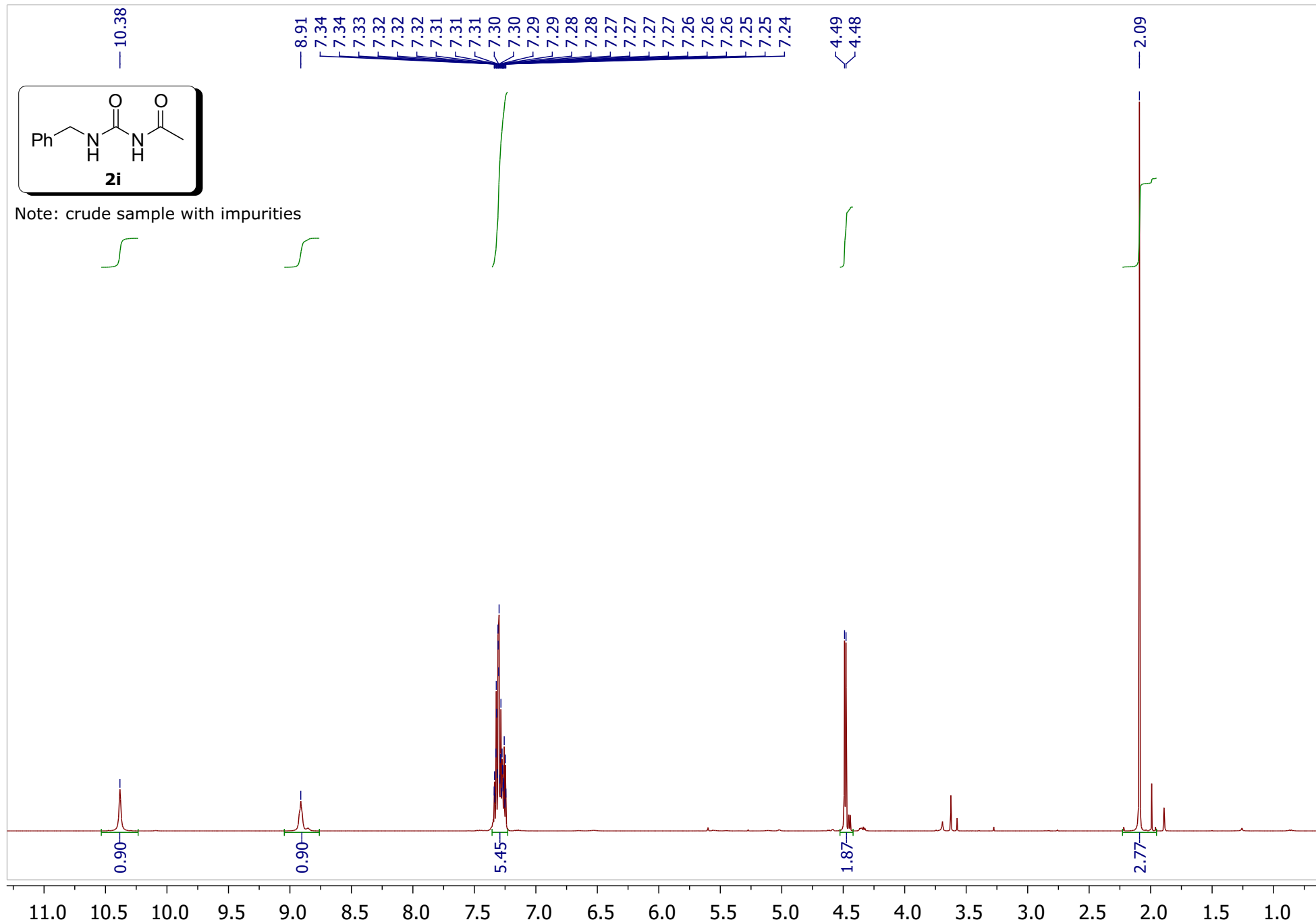


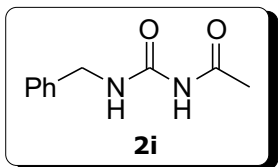




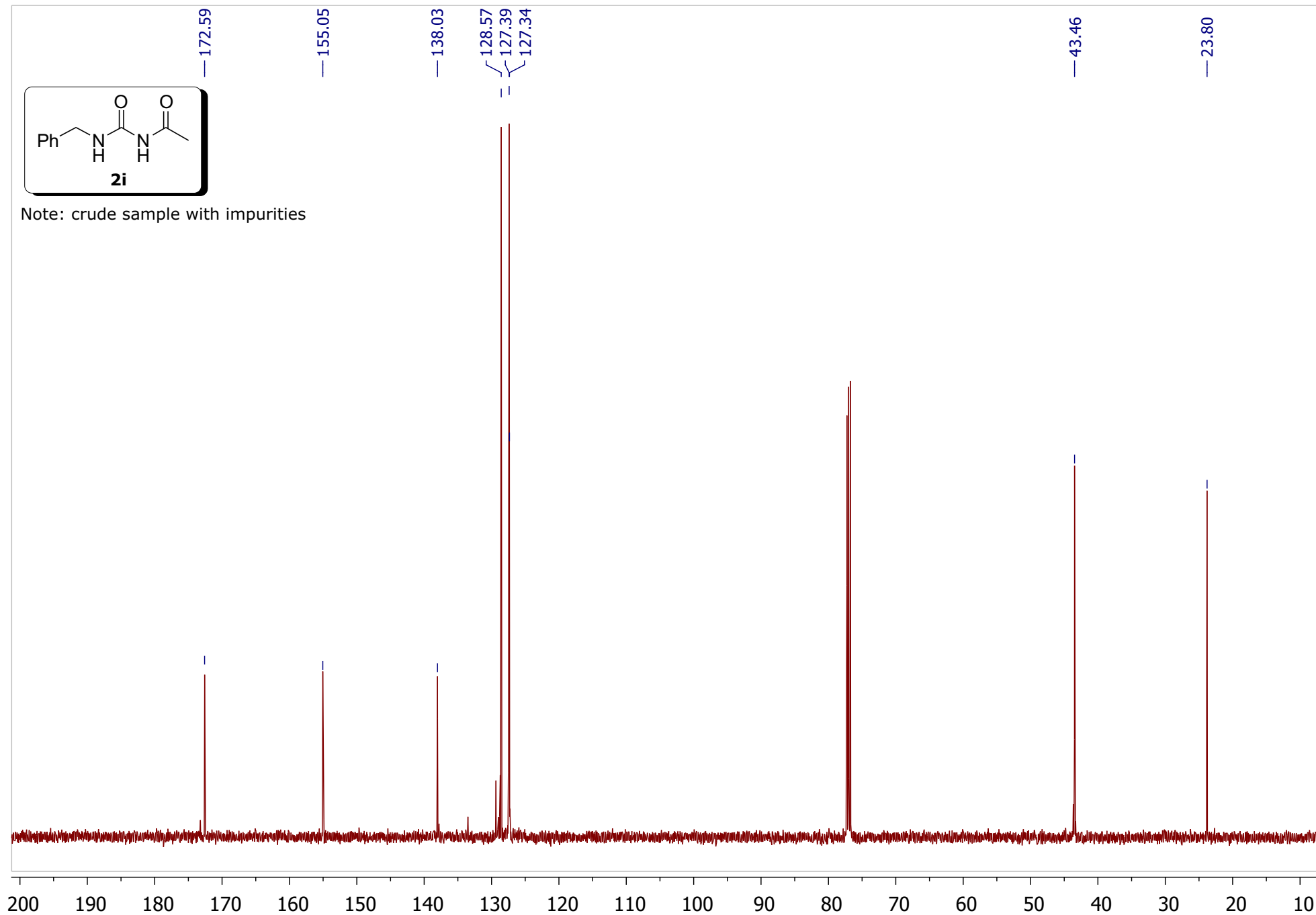


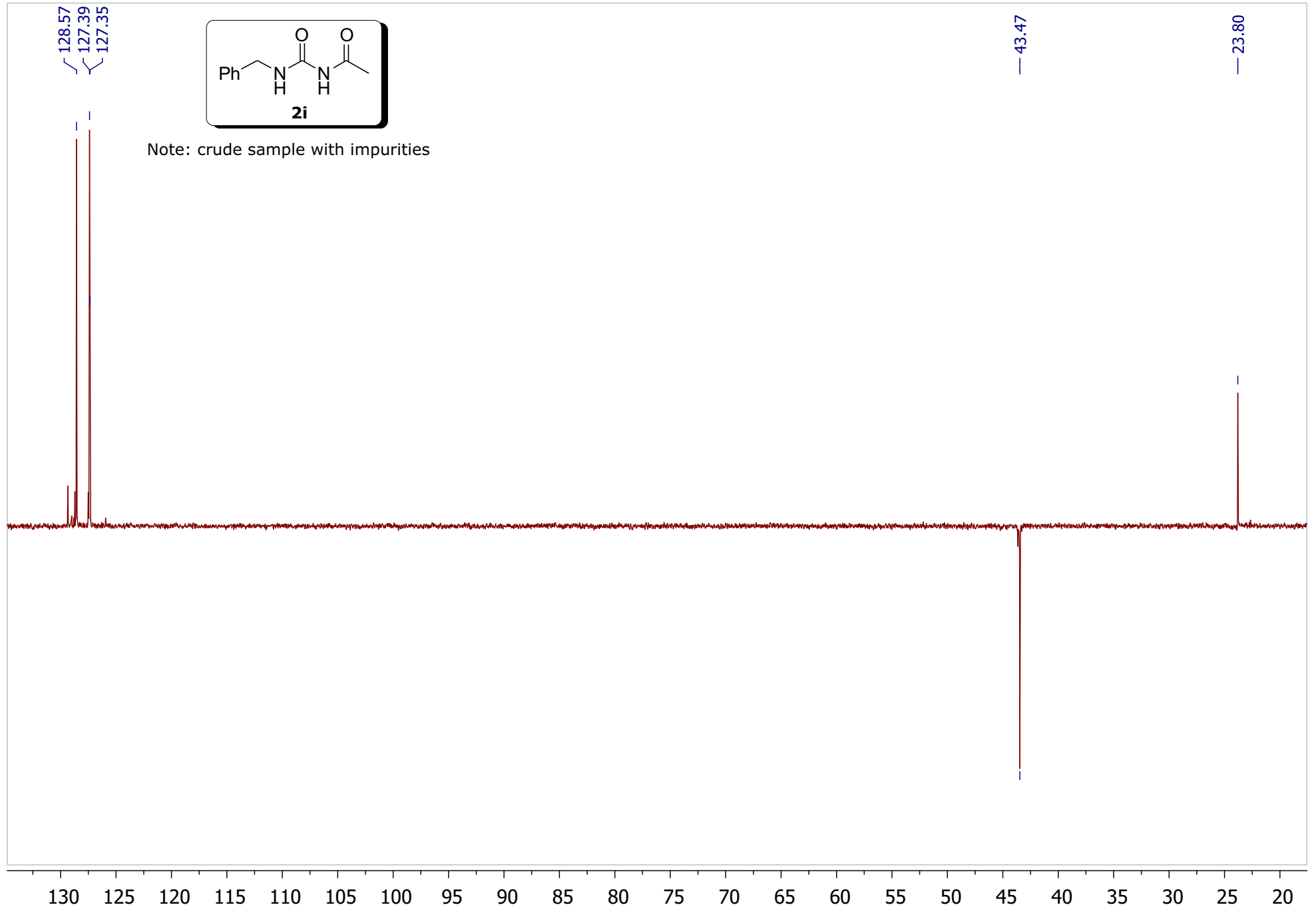
Note: crude sample with impurities

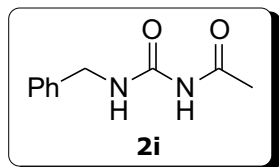




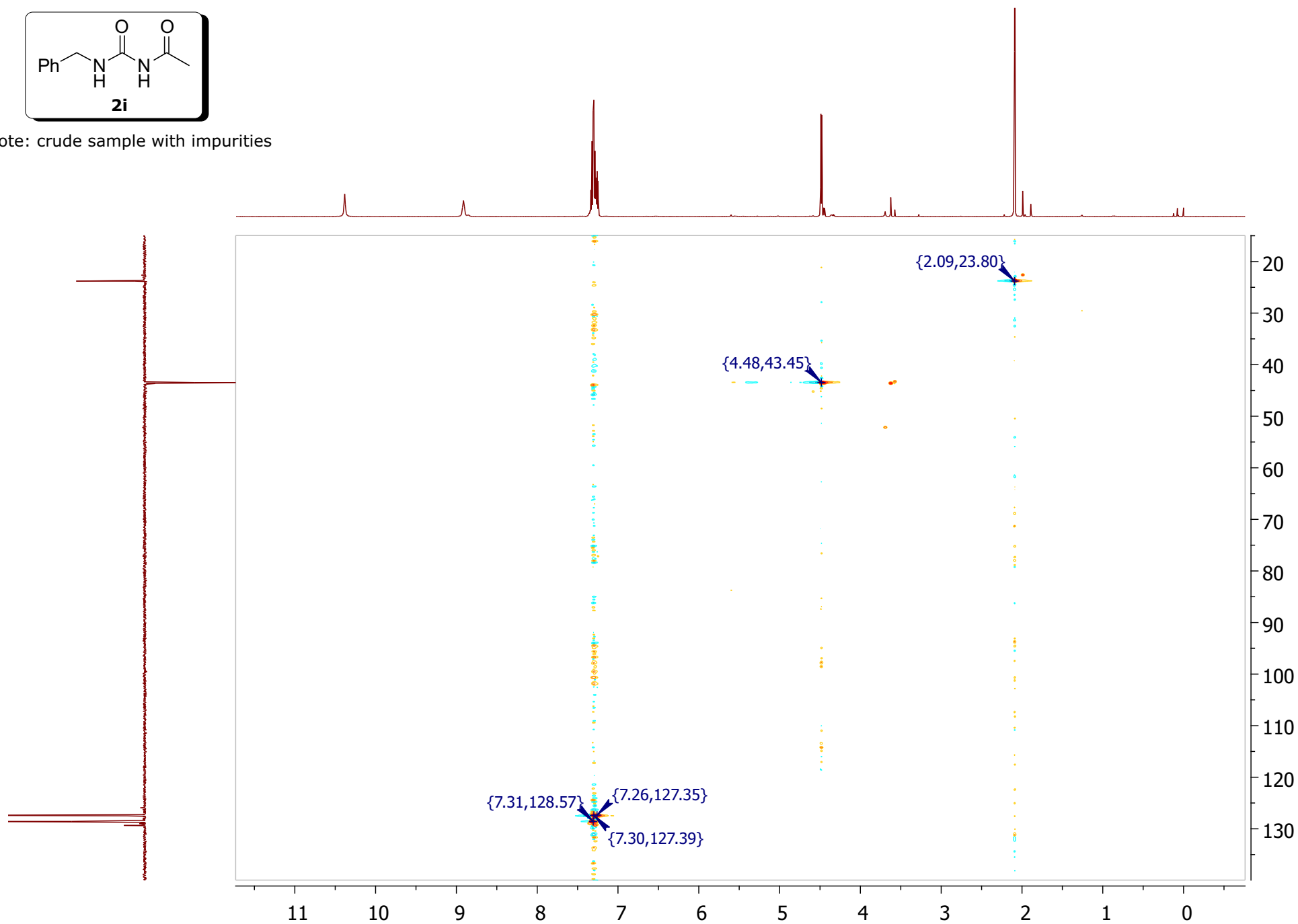
Note: crude sample with impurities

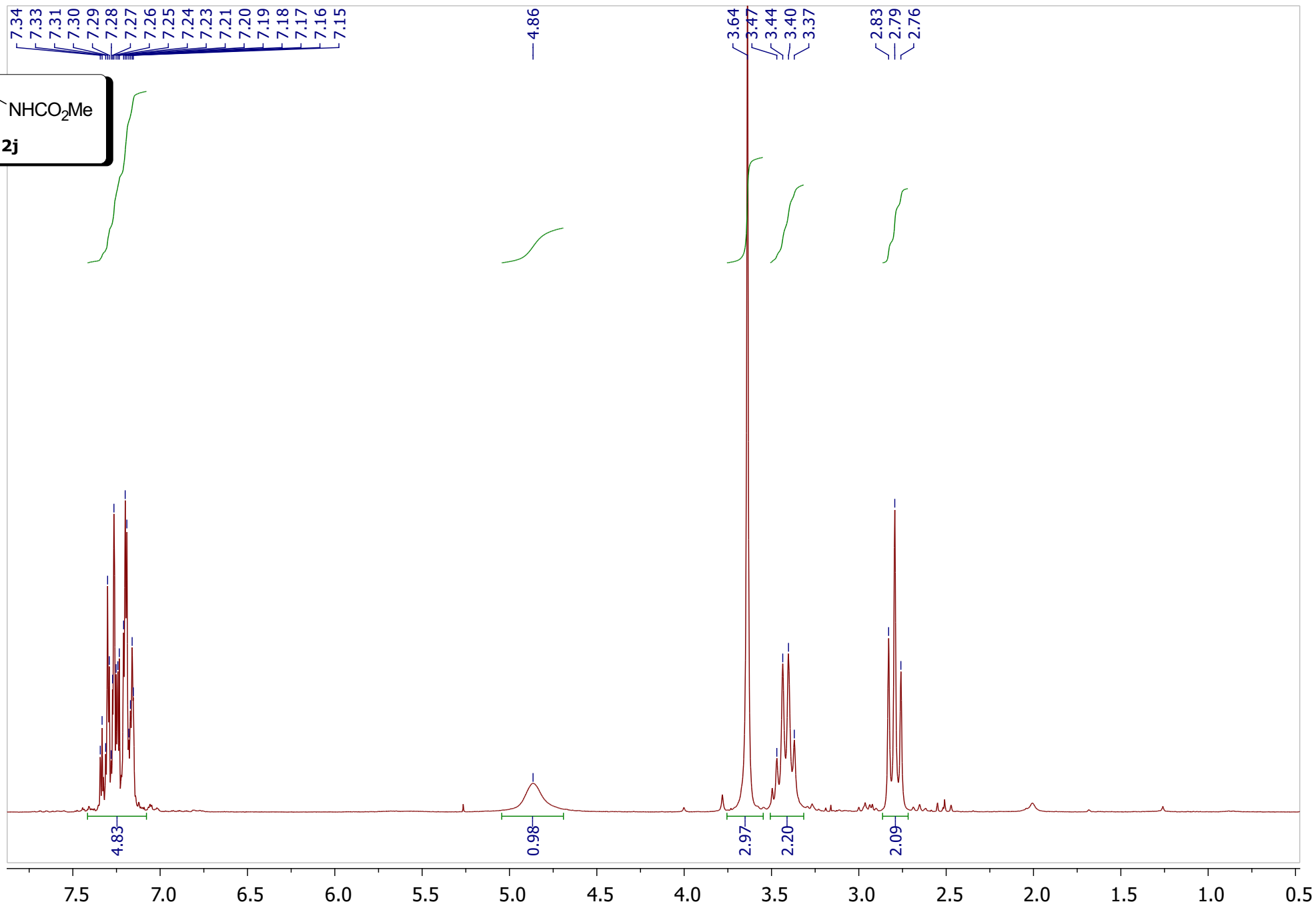
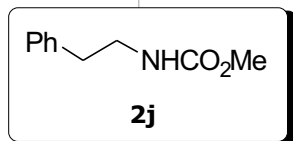


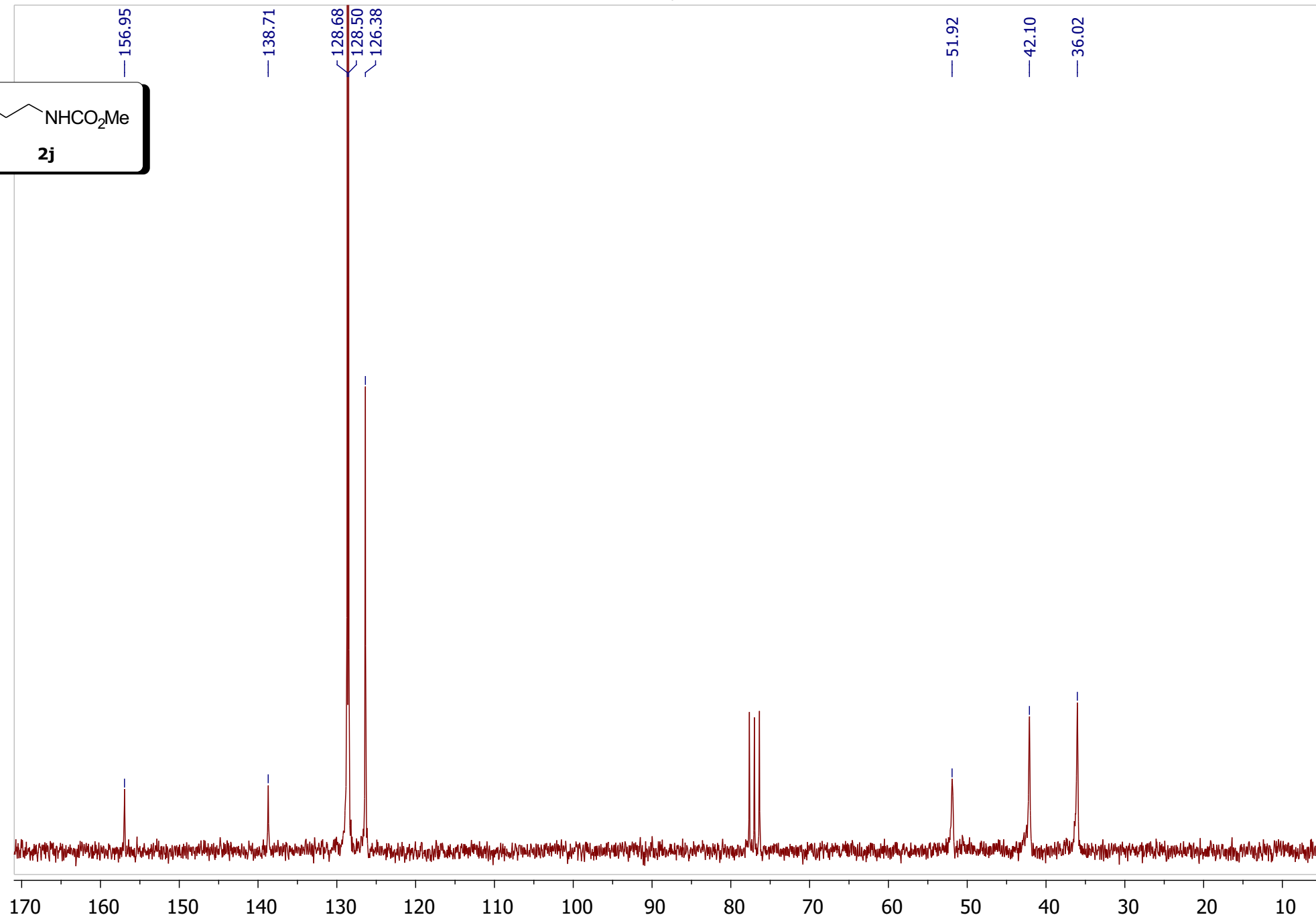
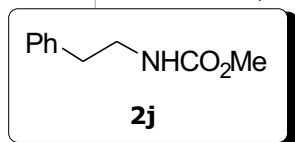


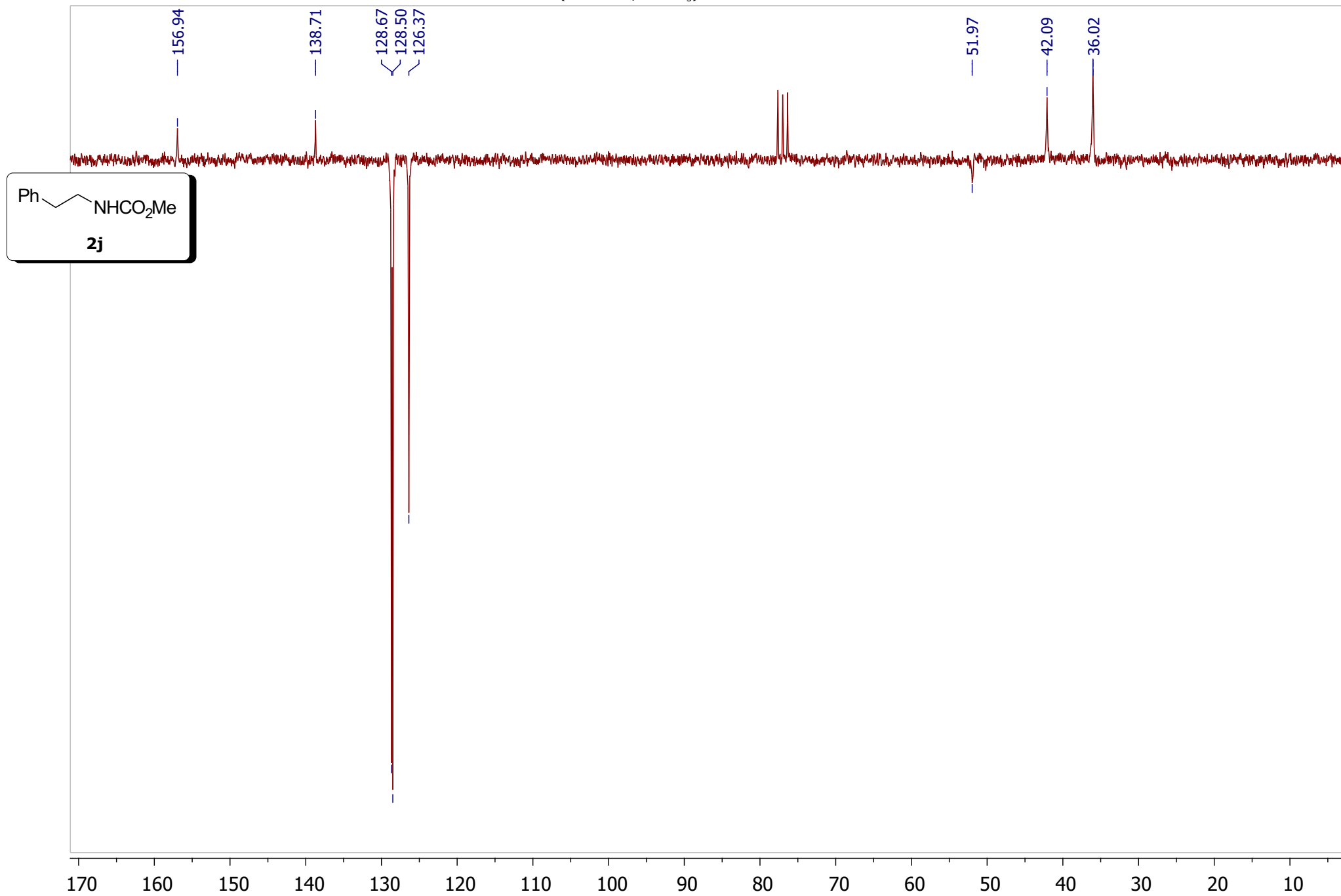


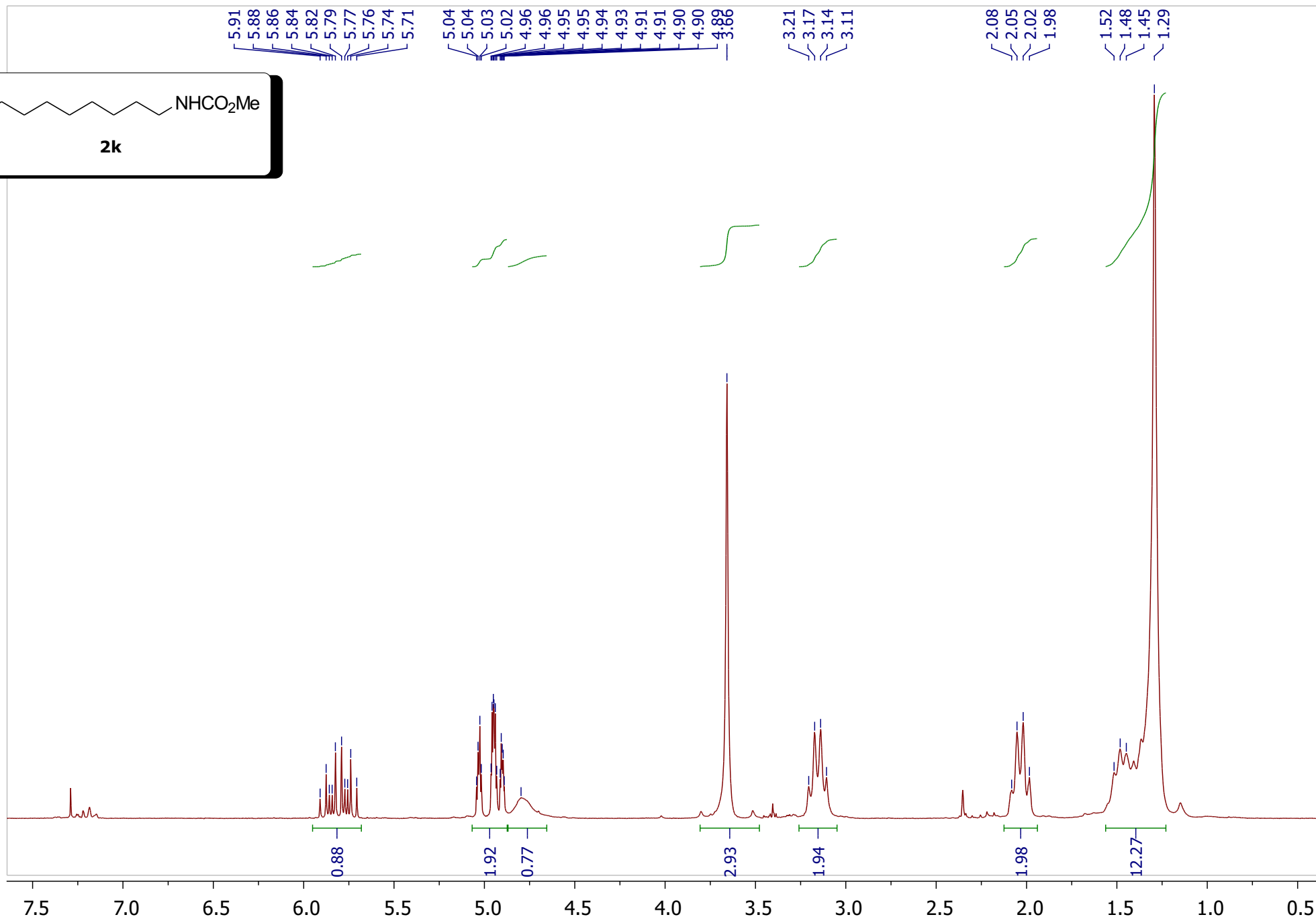
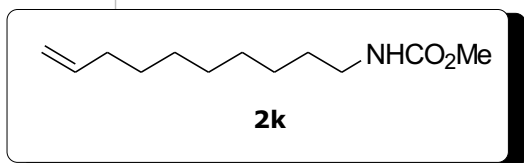
Note: crude sample with impurities

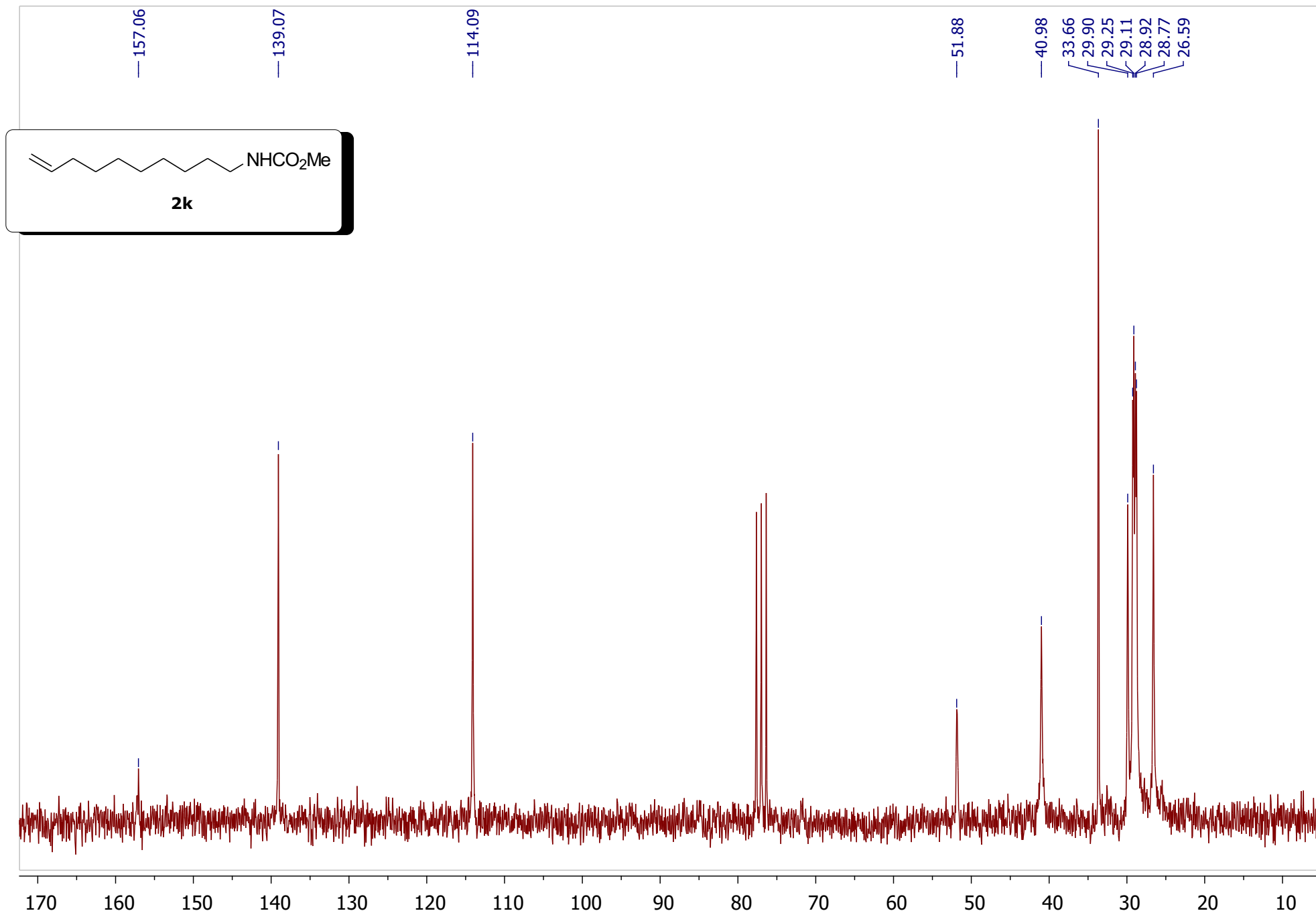


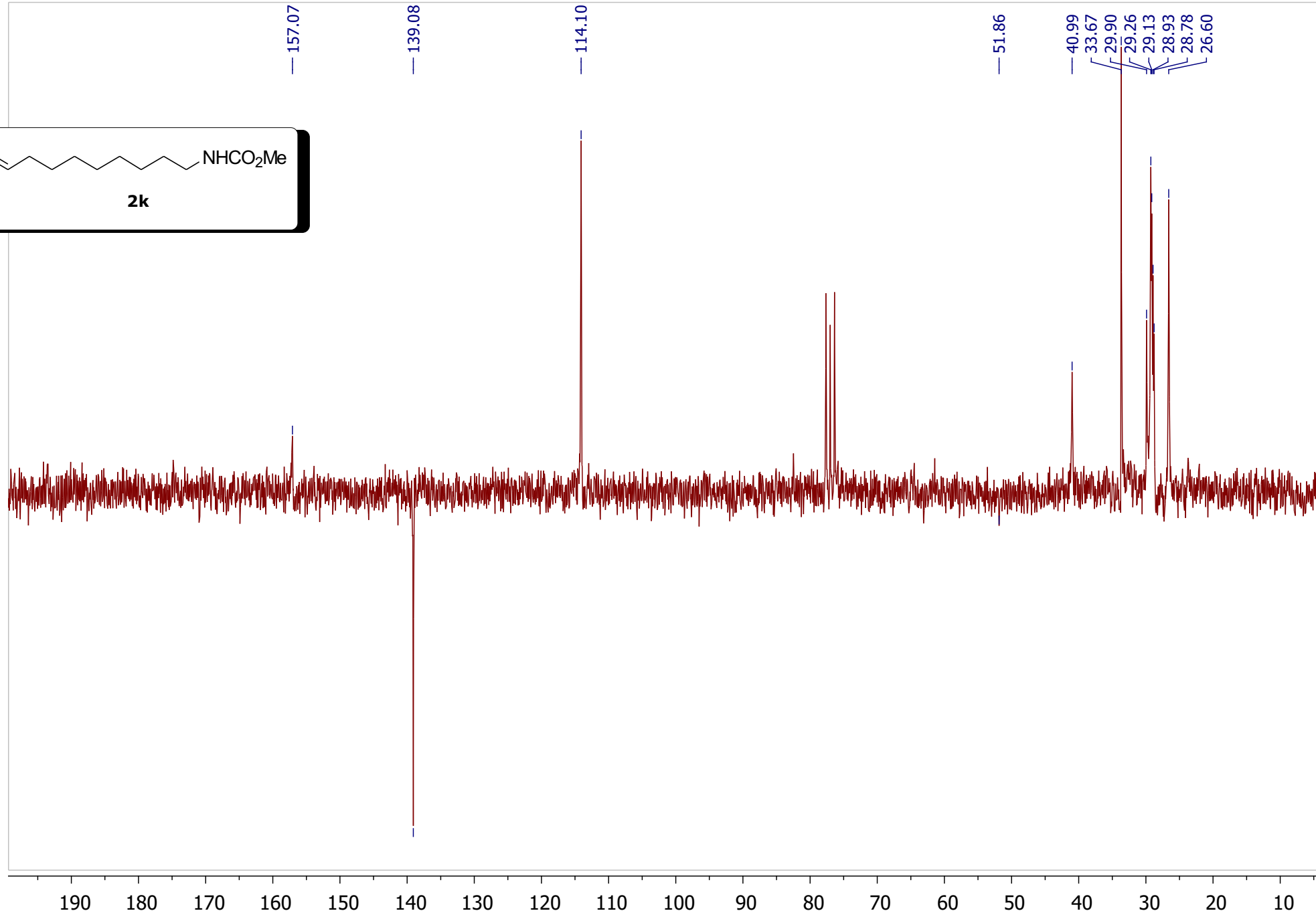
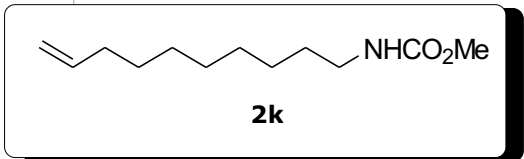


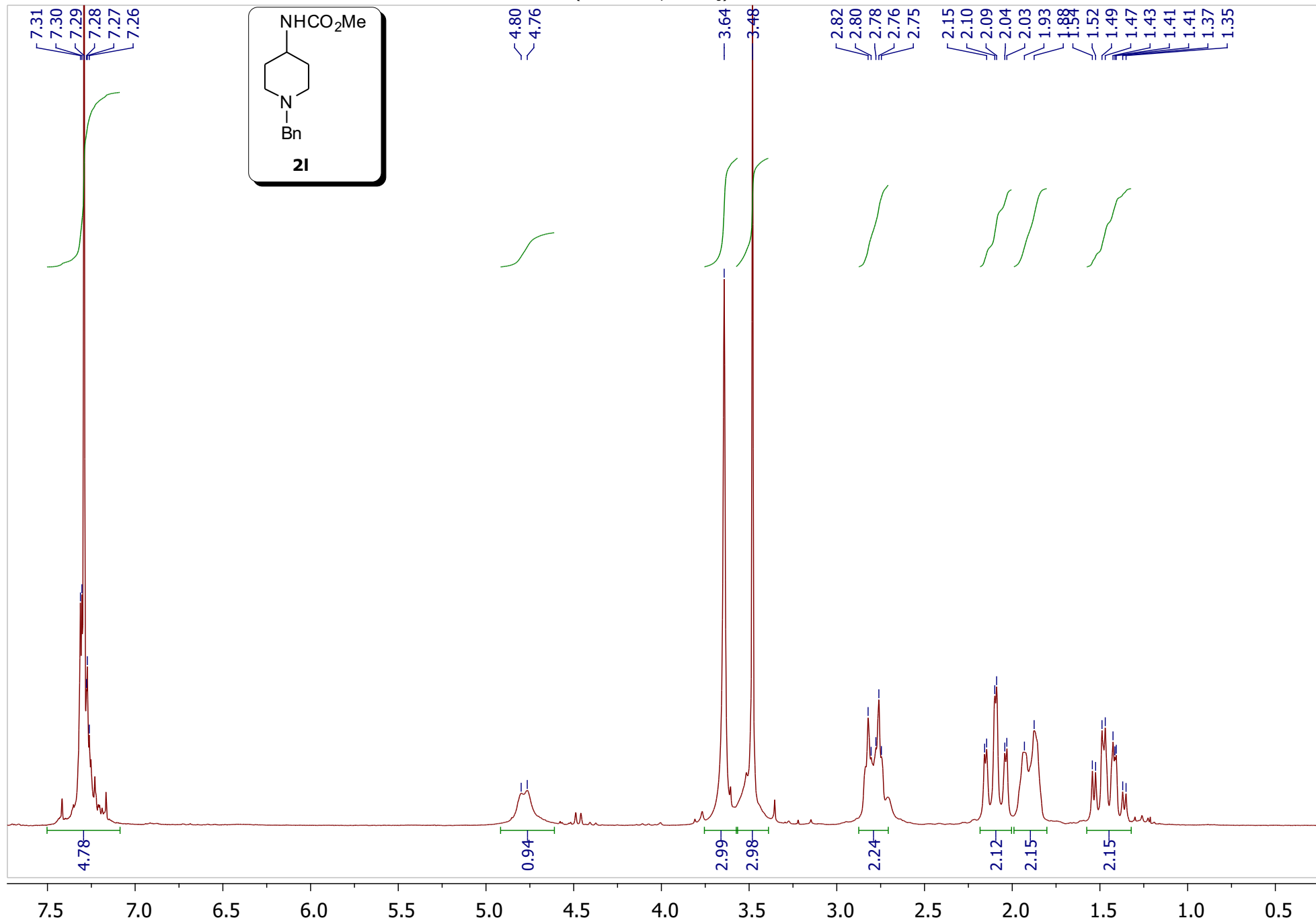


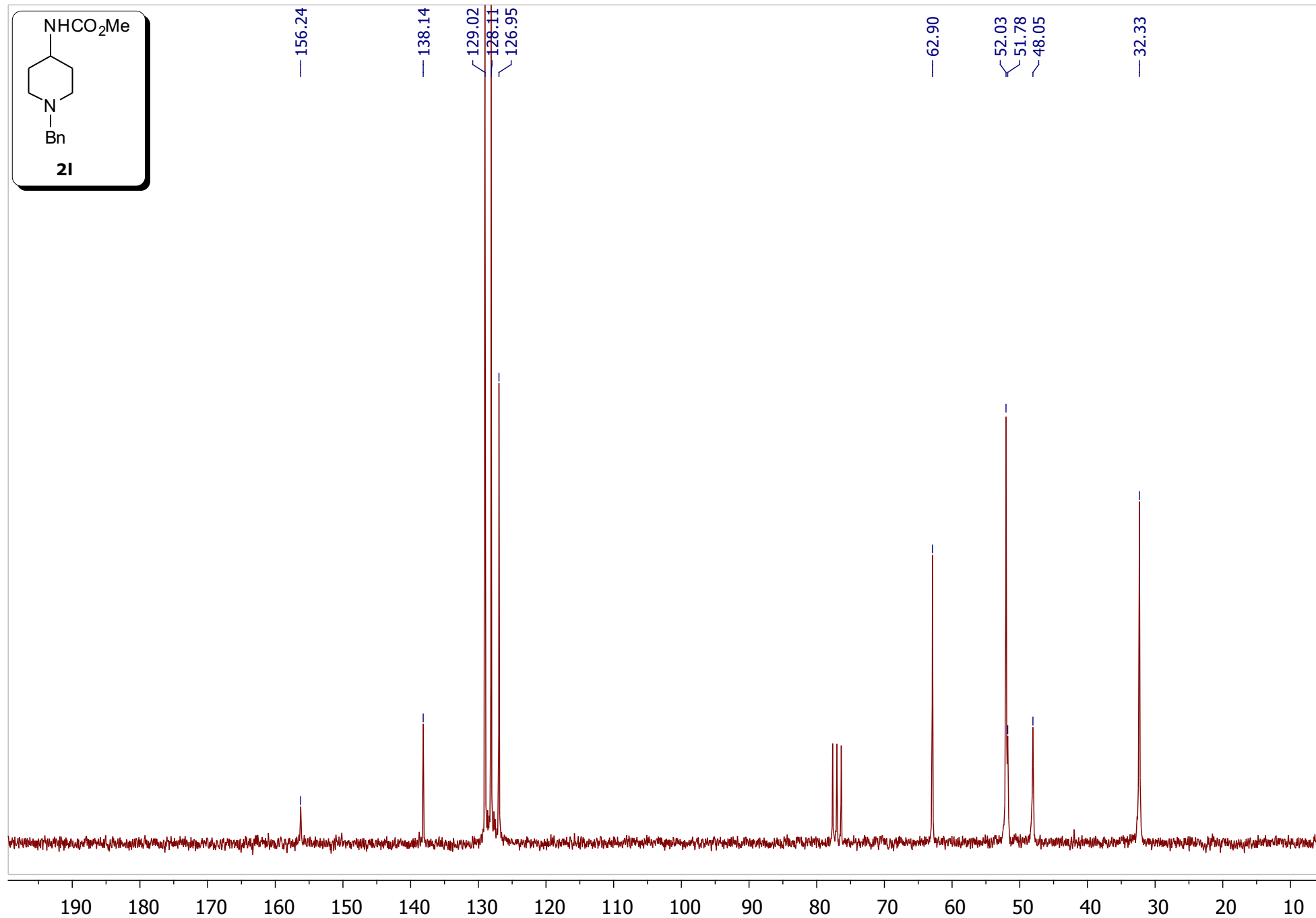
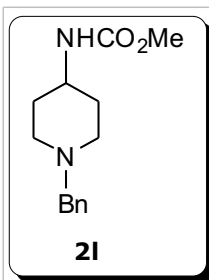


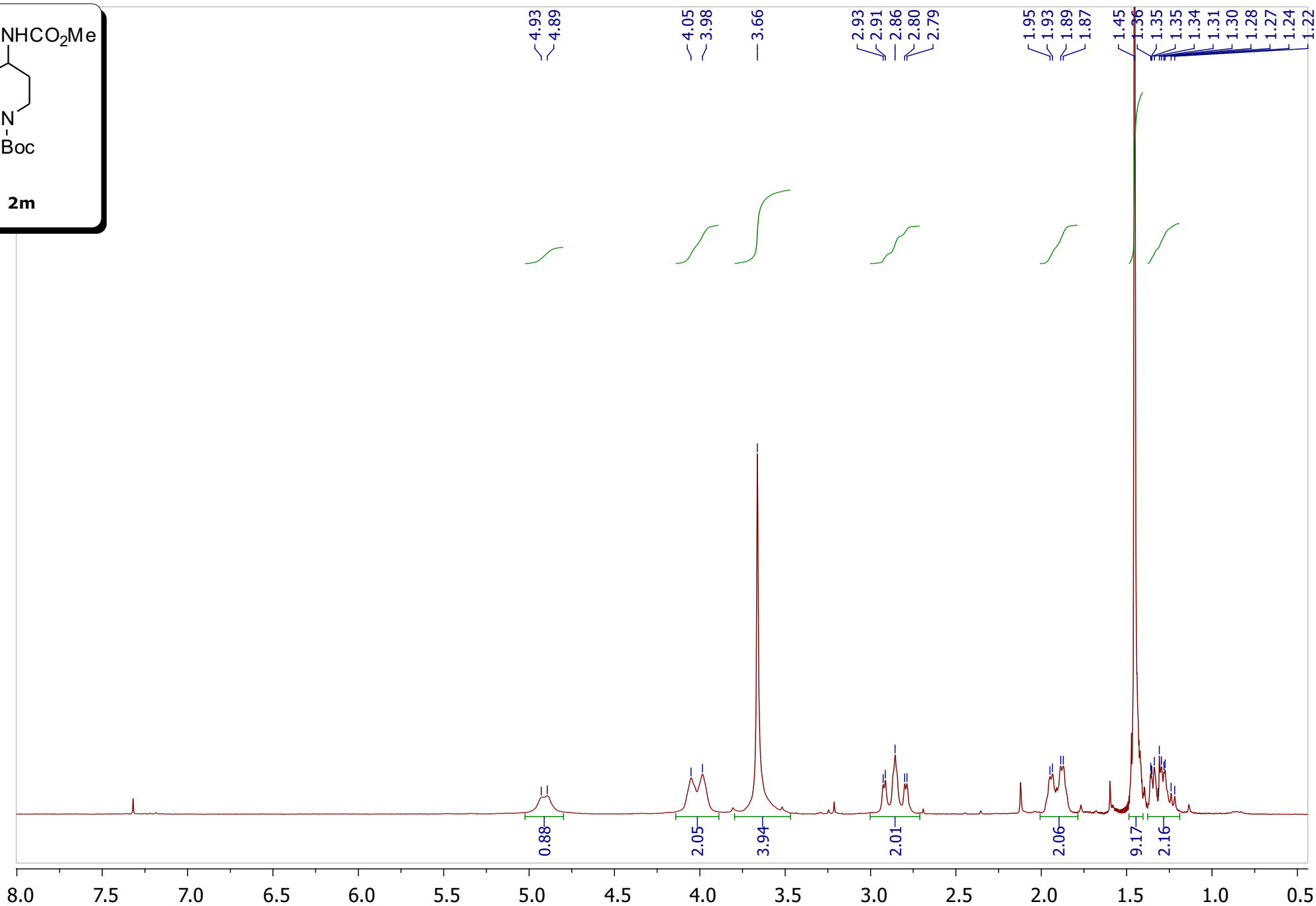
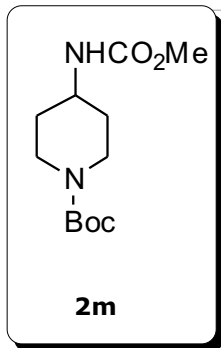


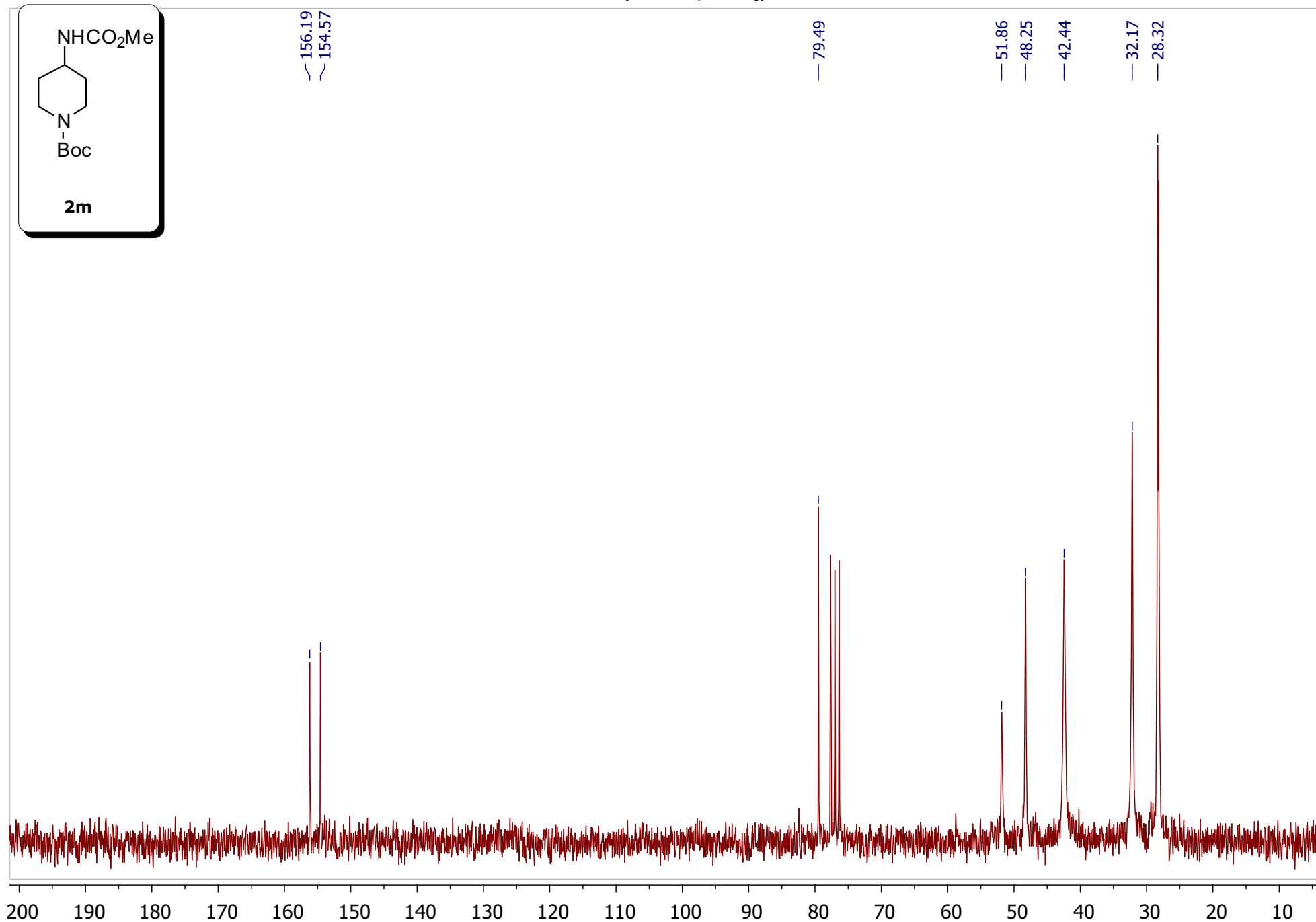


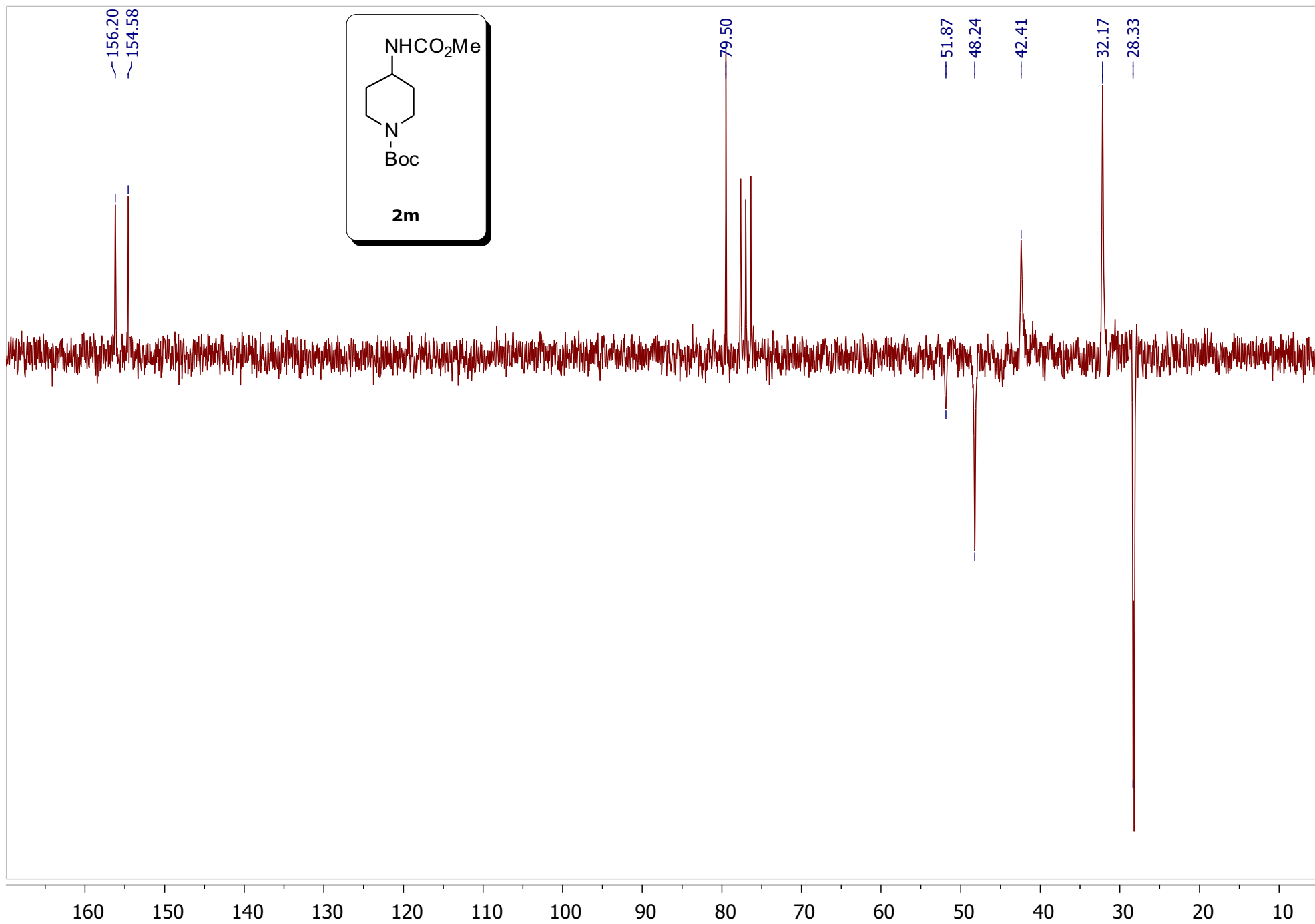


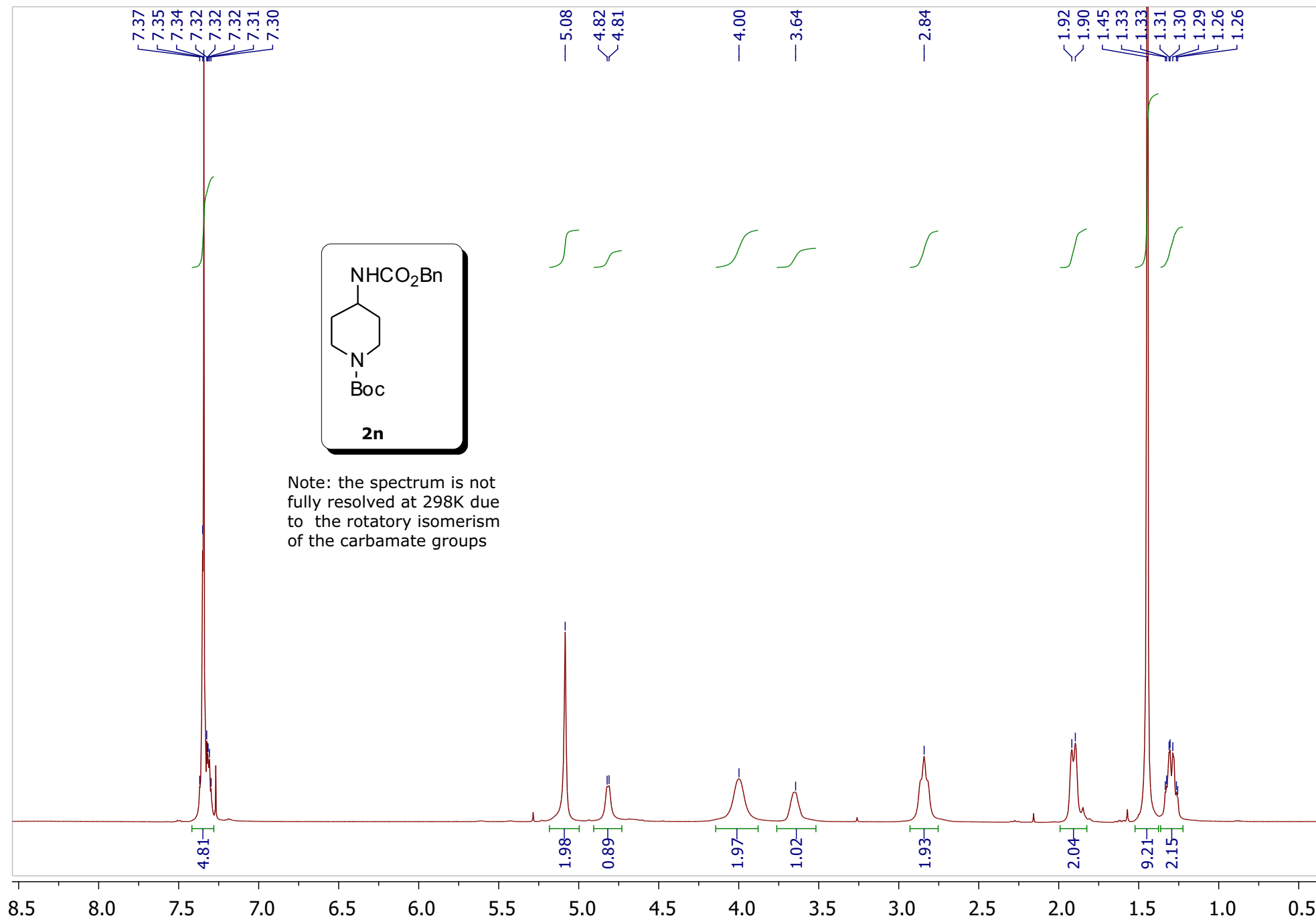
^1H NMR (200 MHz, CDCl_3)

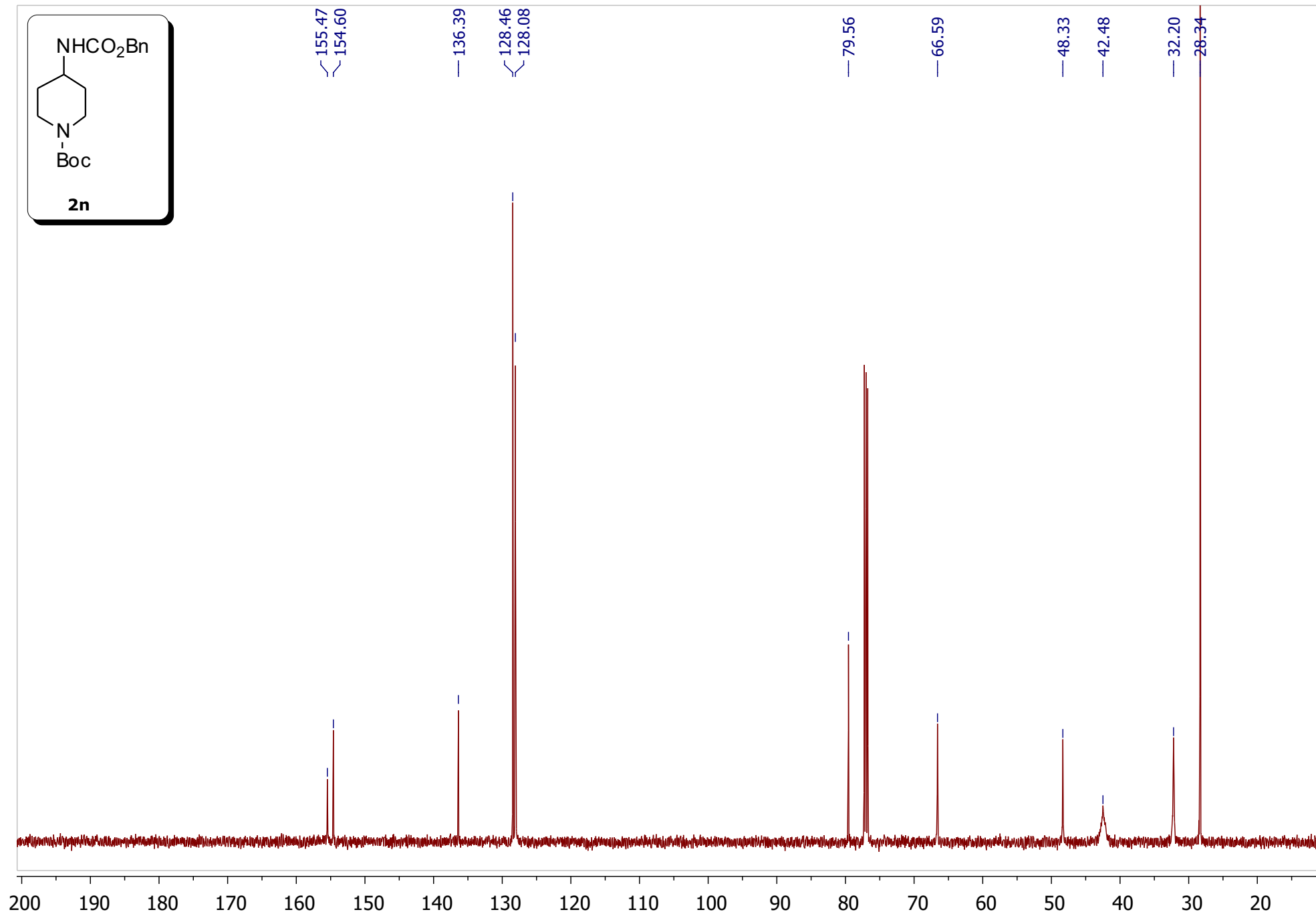
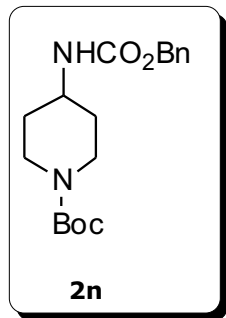


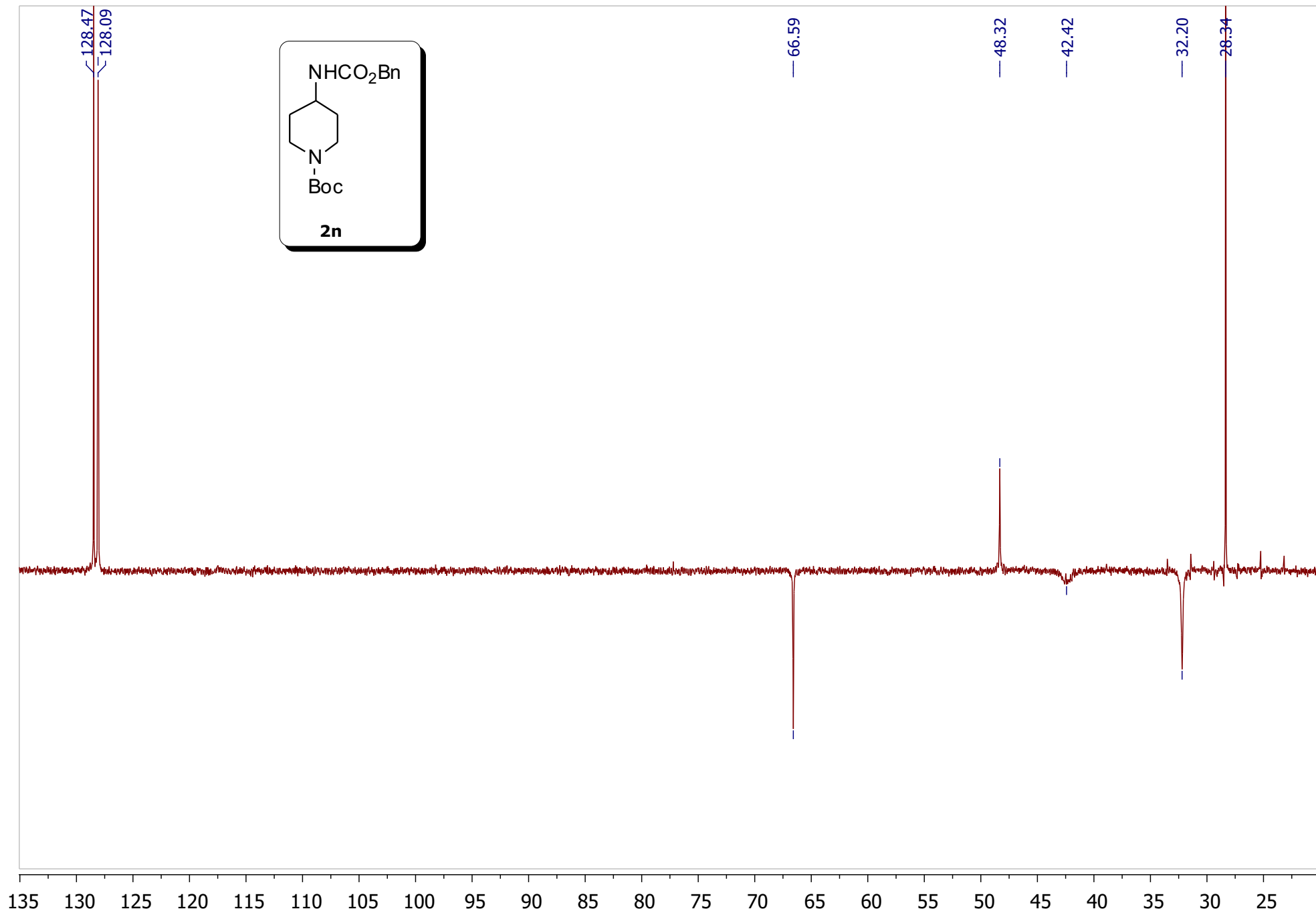


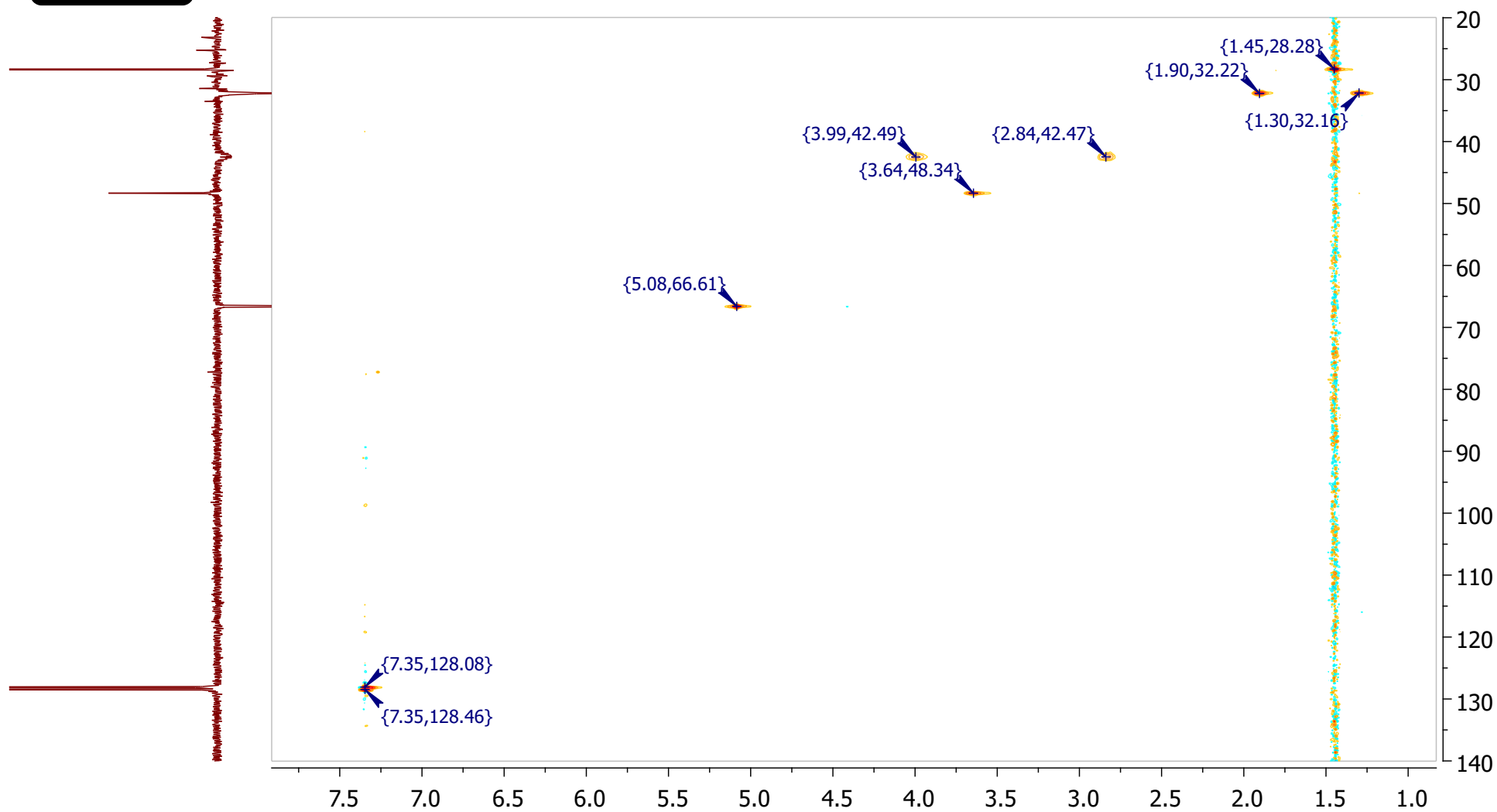
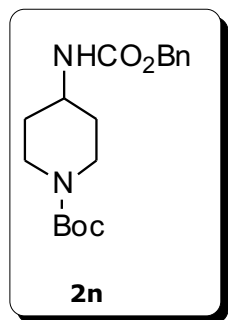


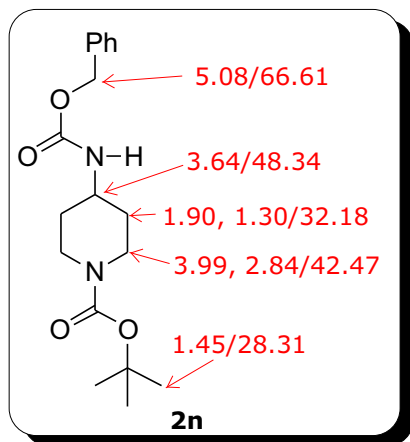
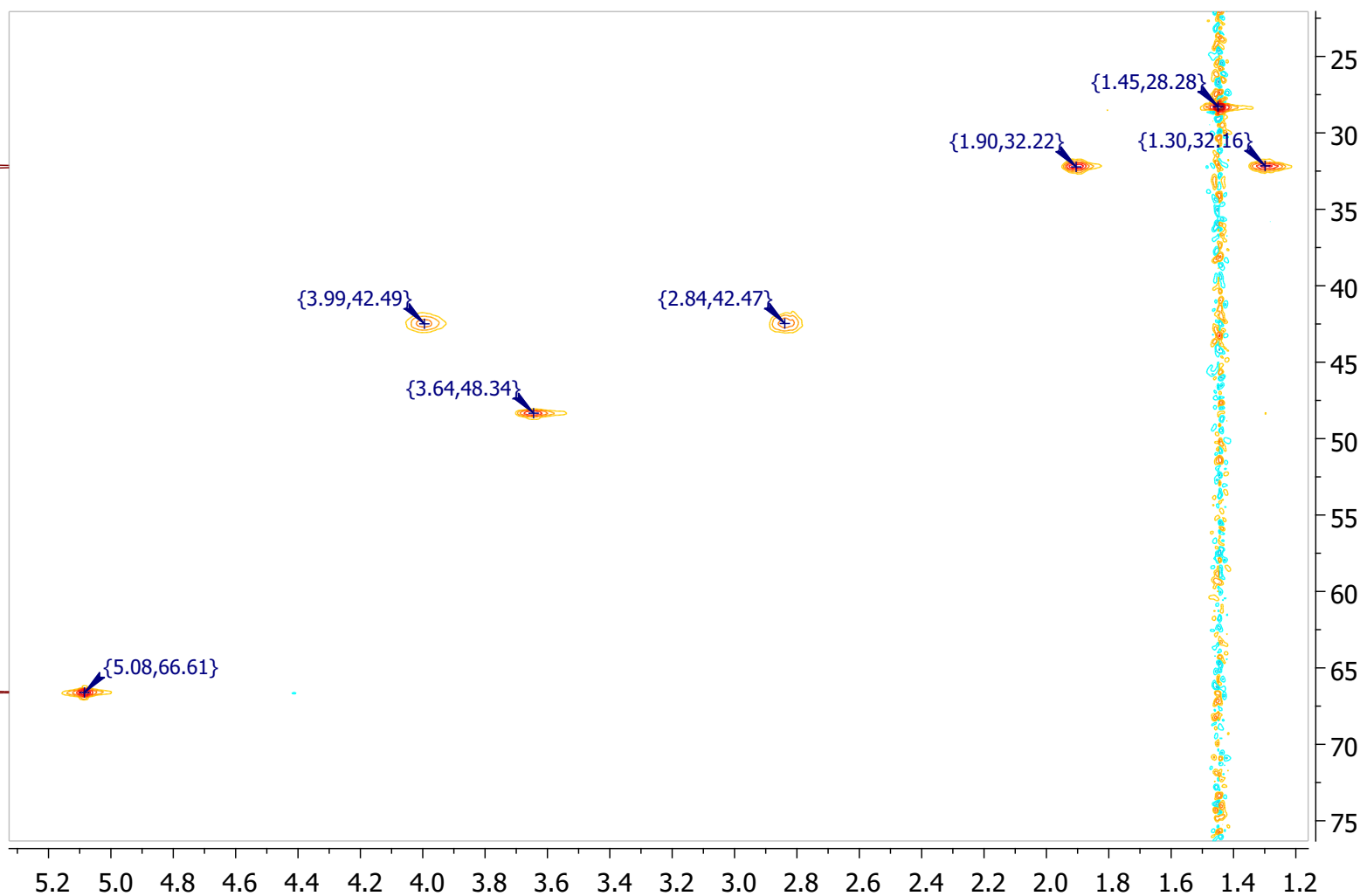
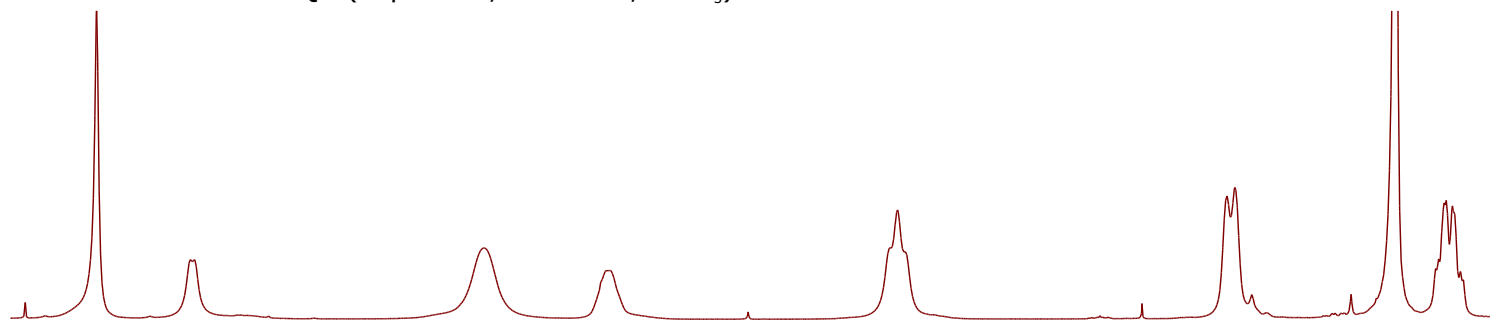




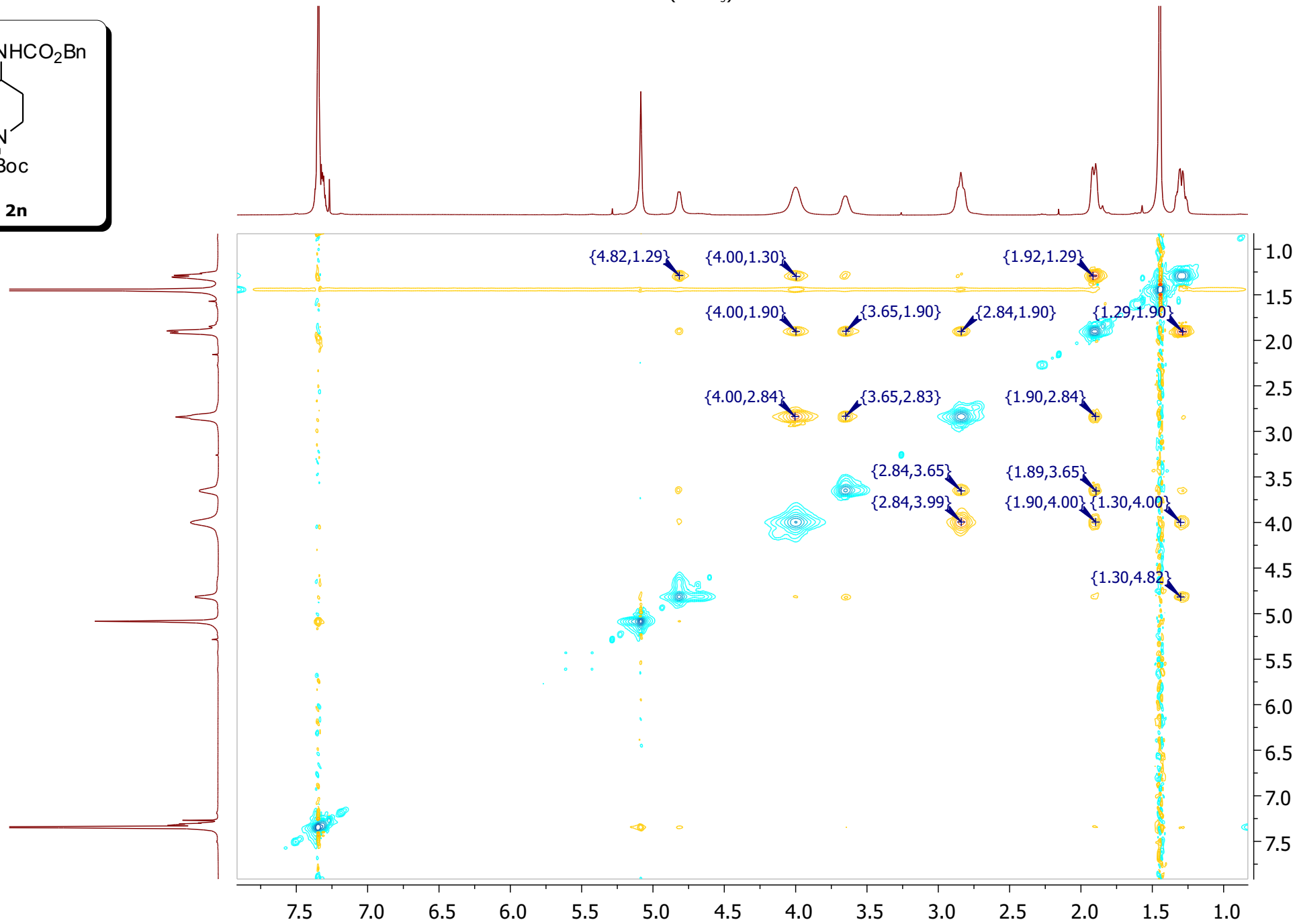
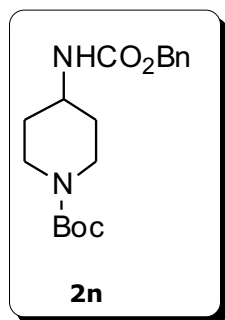


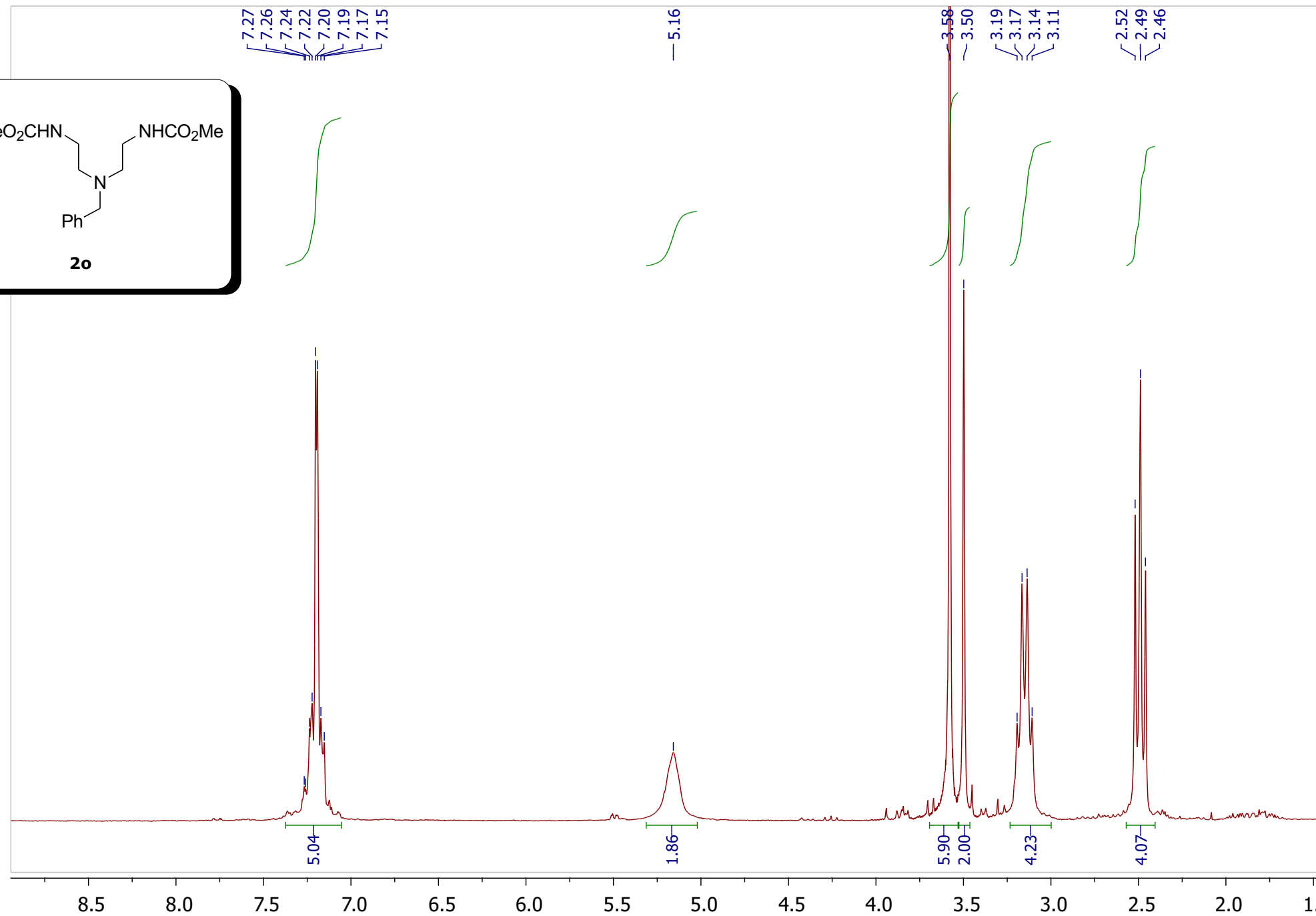
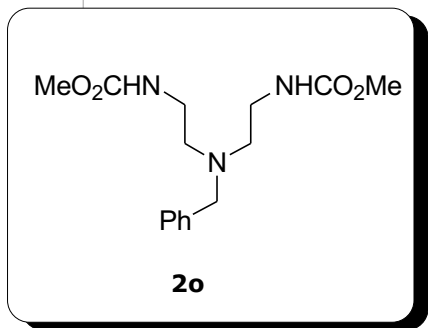


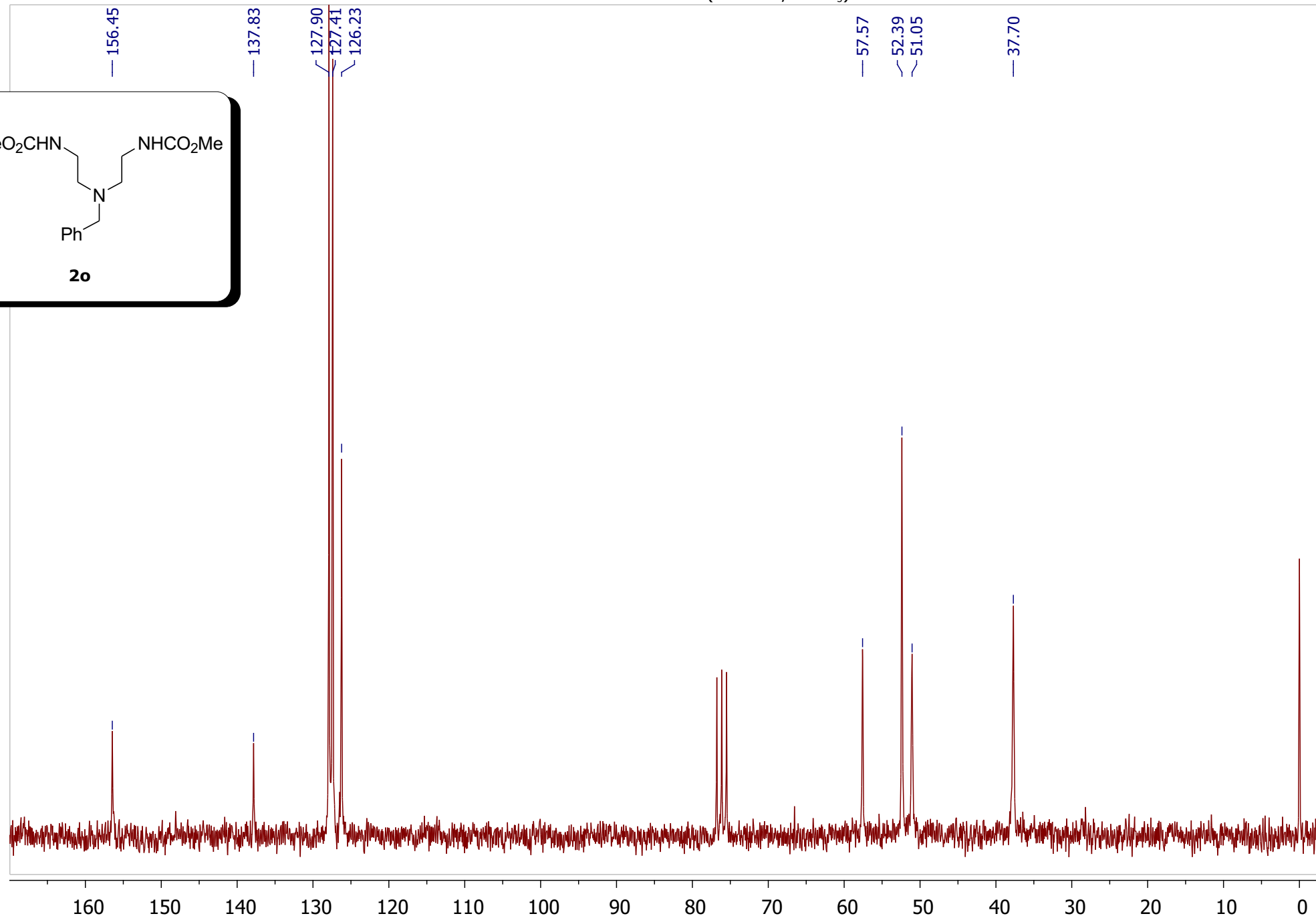
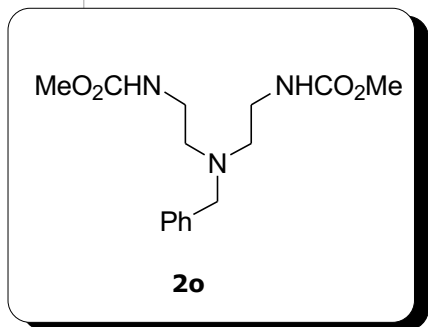
HSQC (CDCl₃)

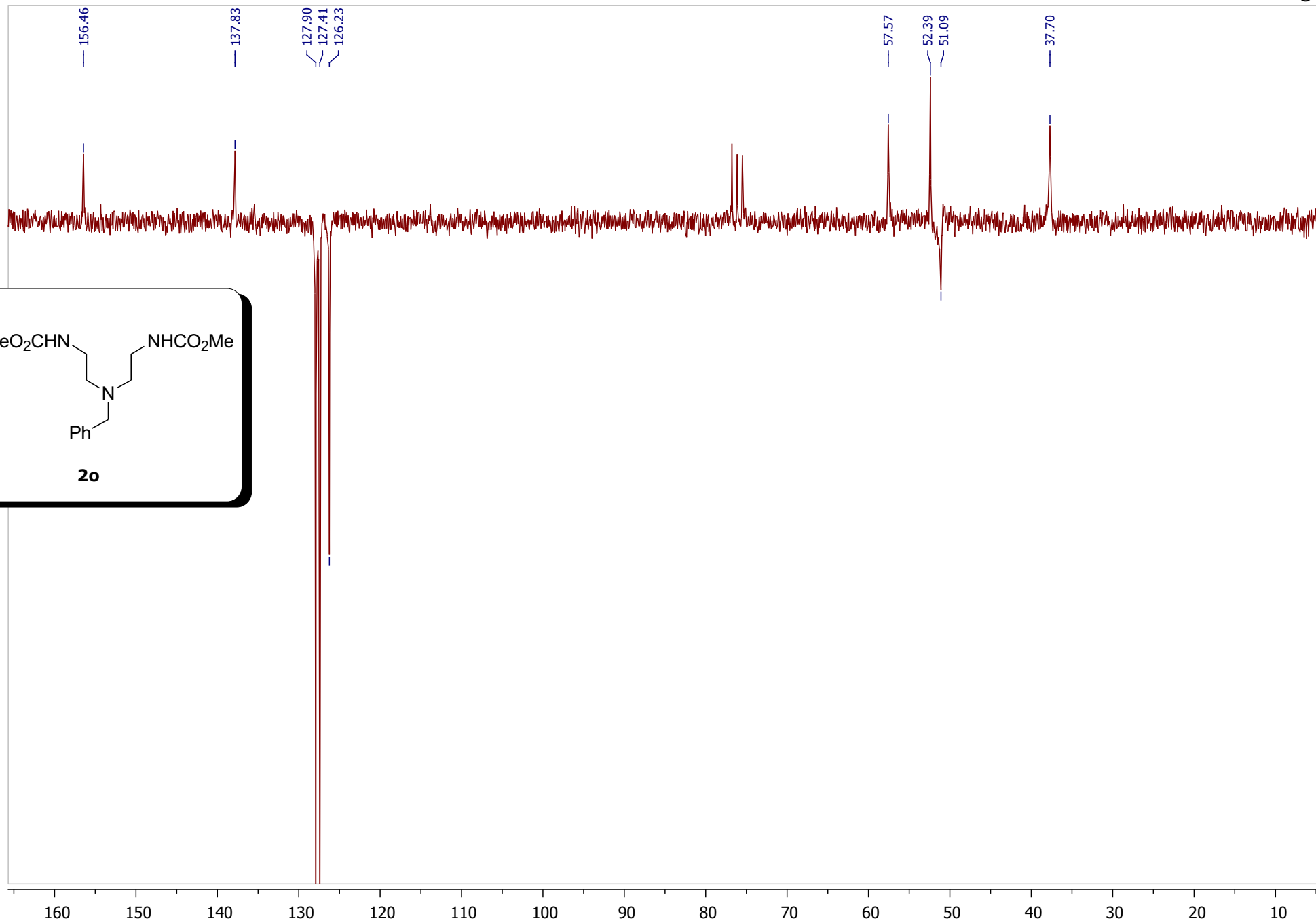


tentative assignments
of the relevant signals







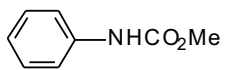


MeO₂CHN

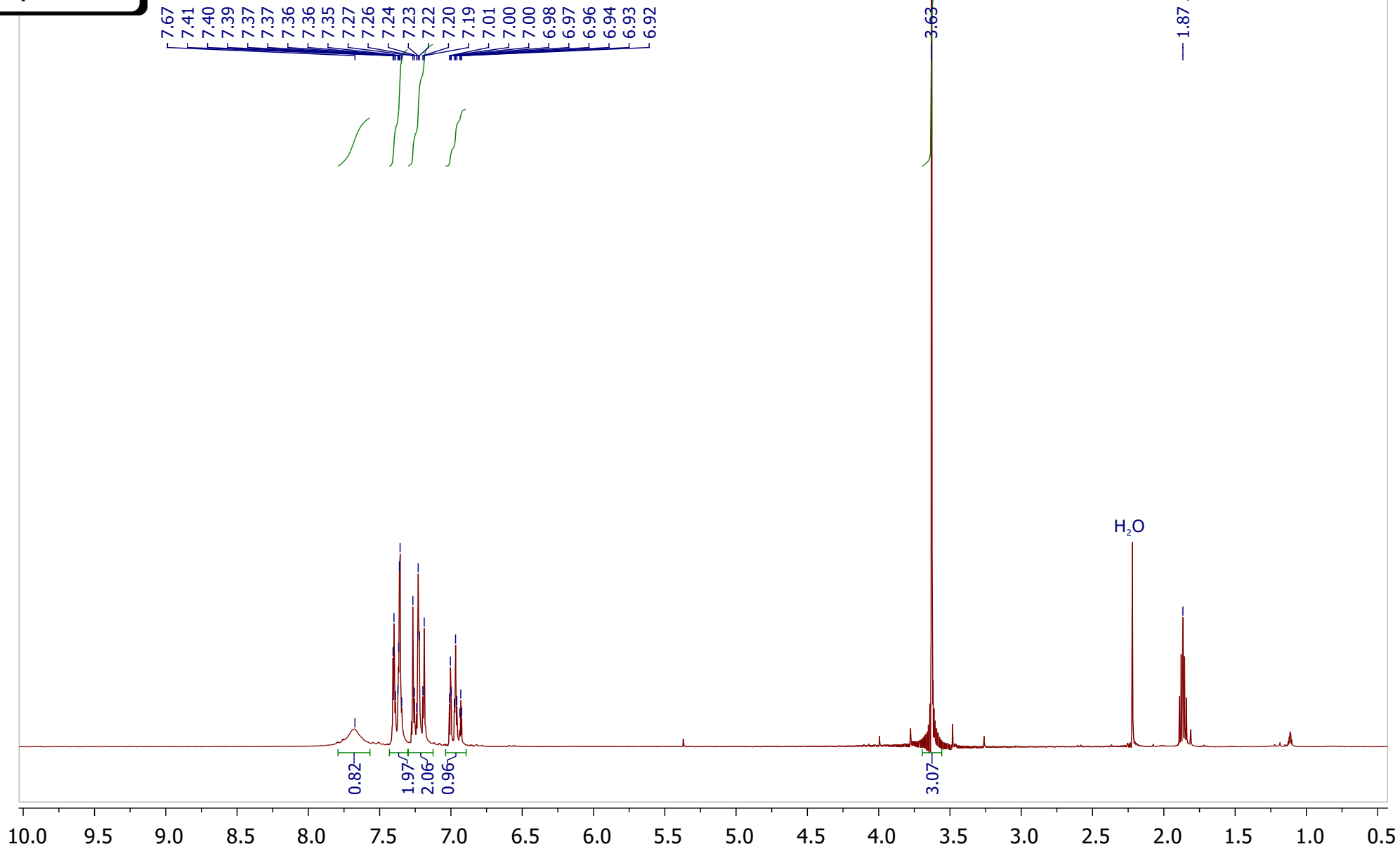
NHCO₂Me

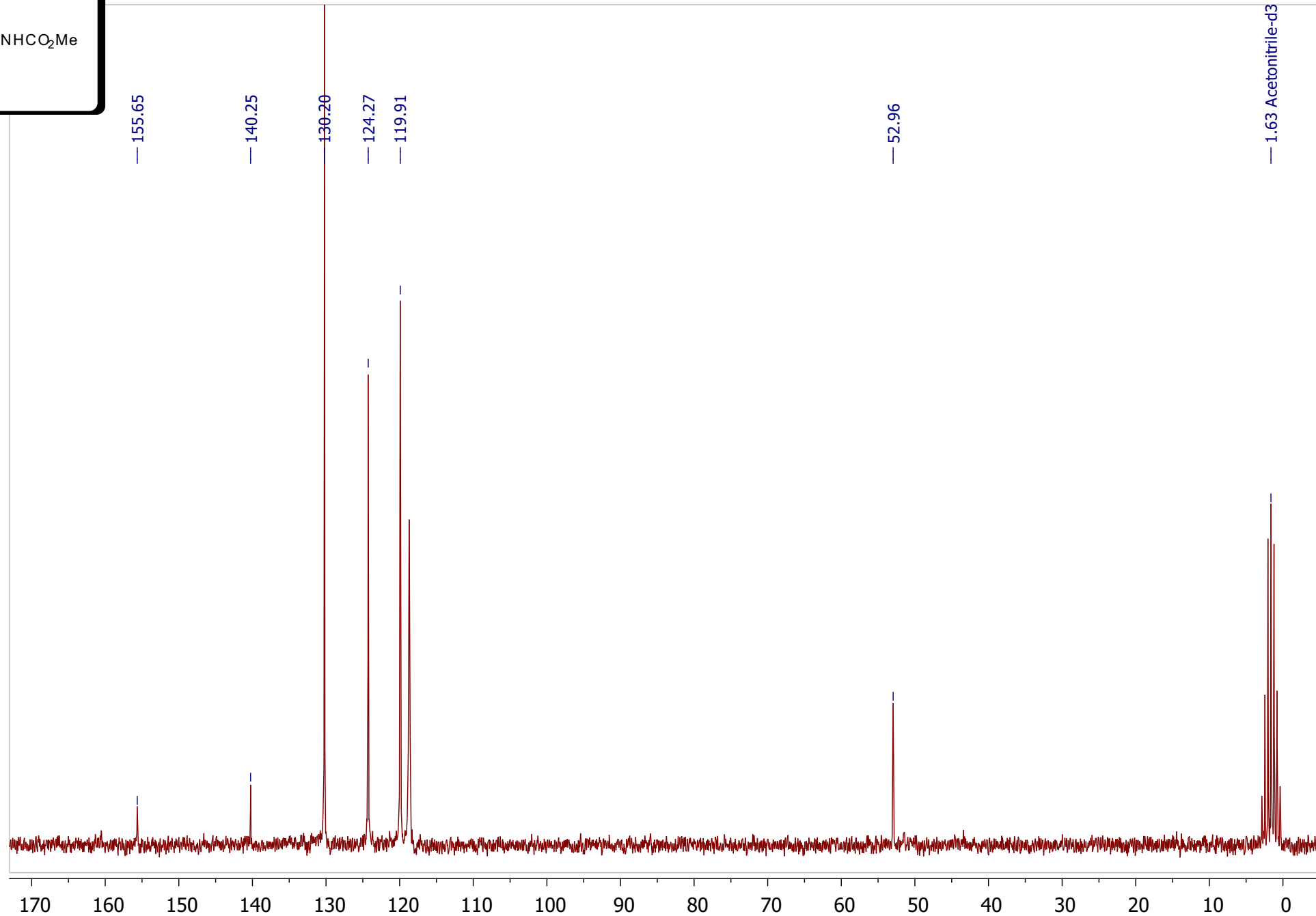
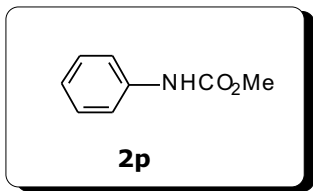
Ph

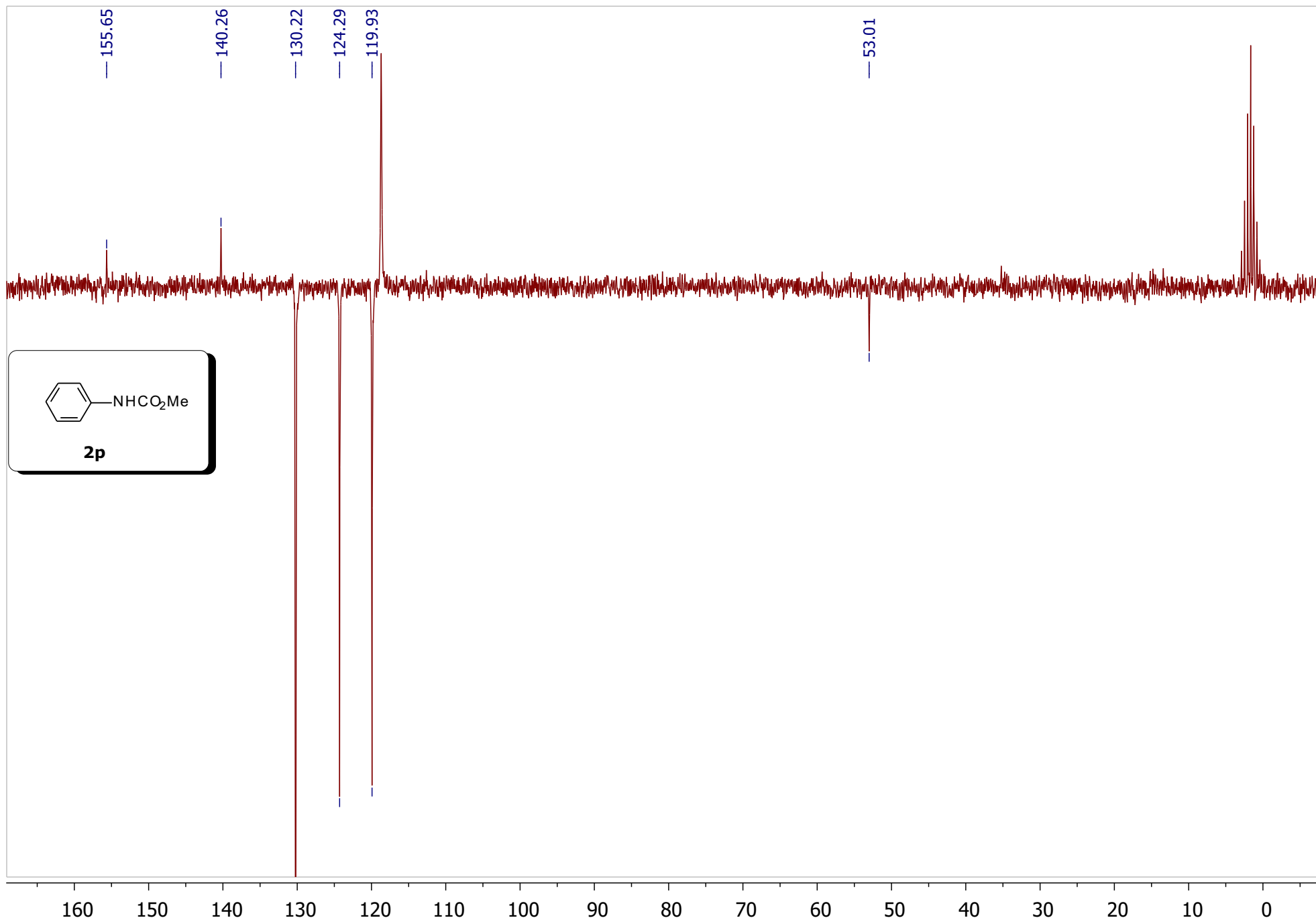
2o

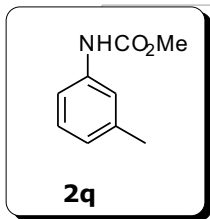


2p

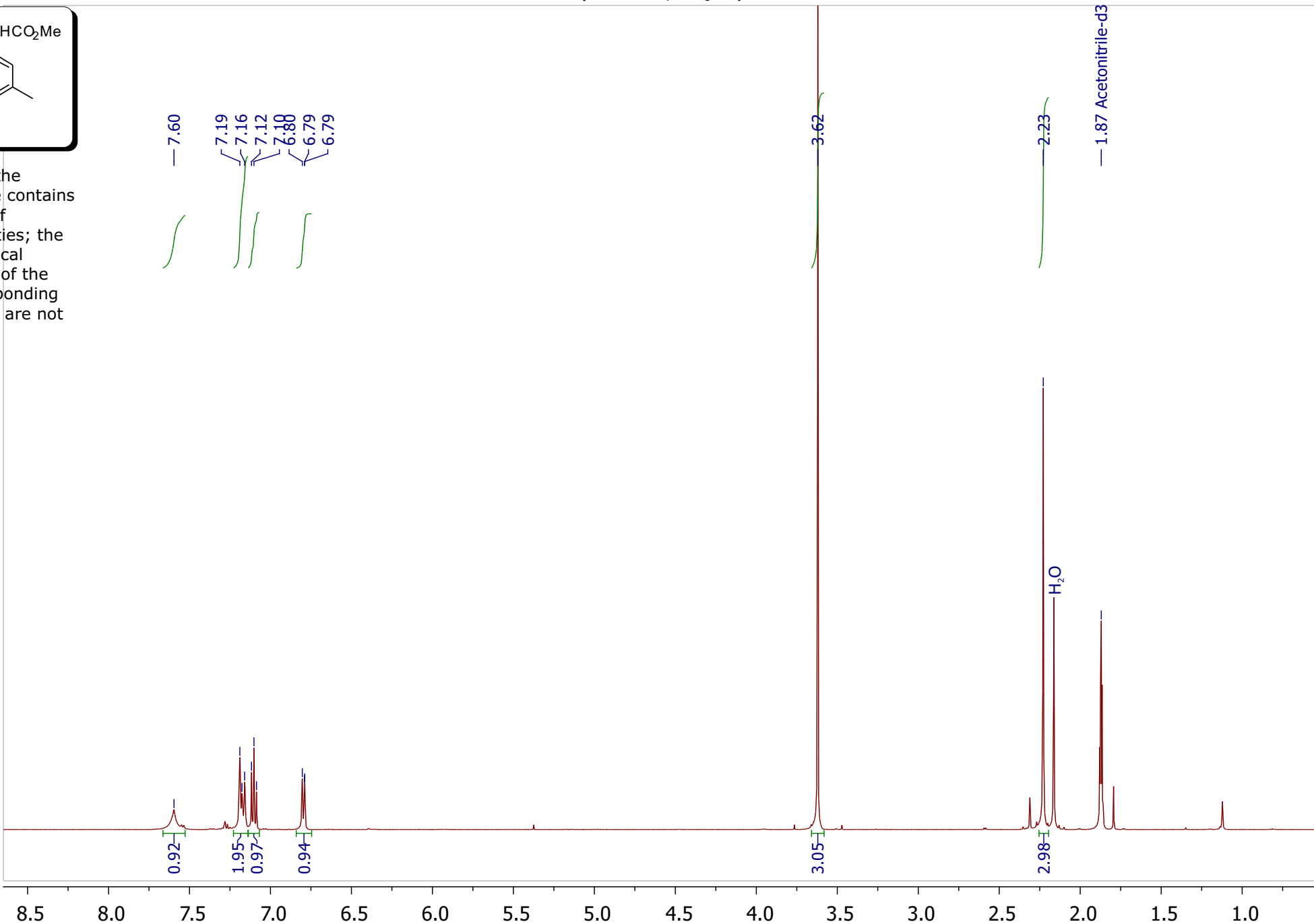


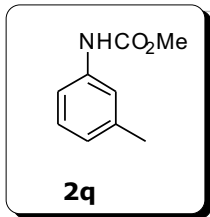




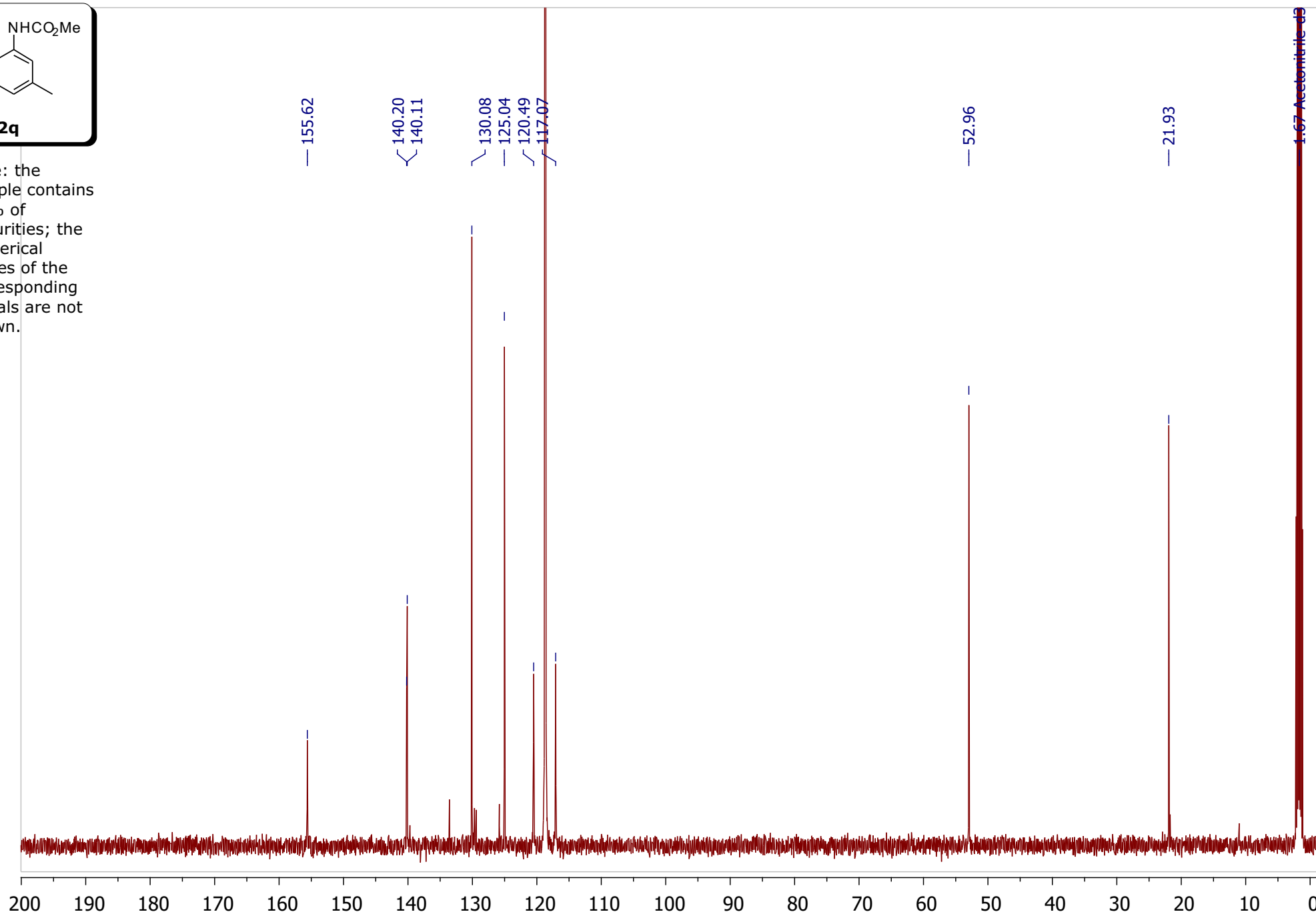


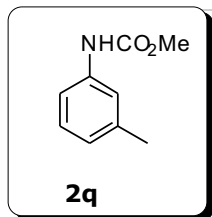
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



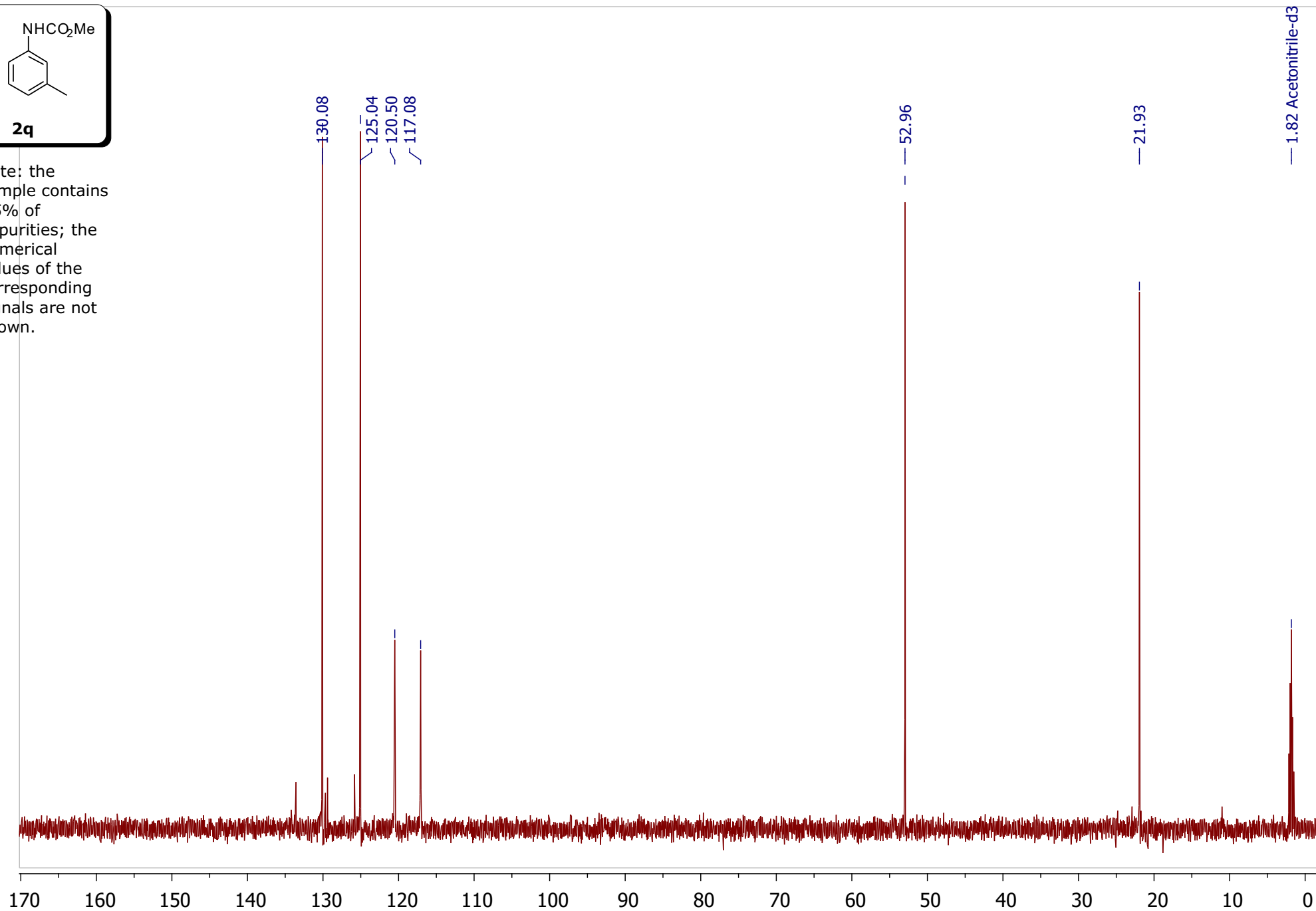


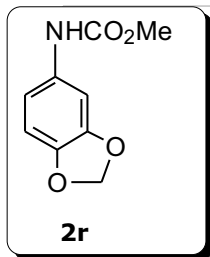
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



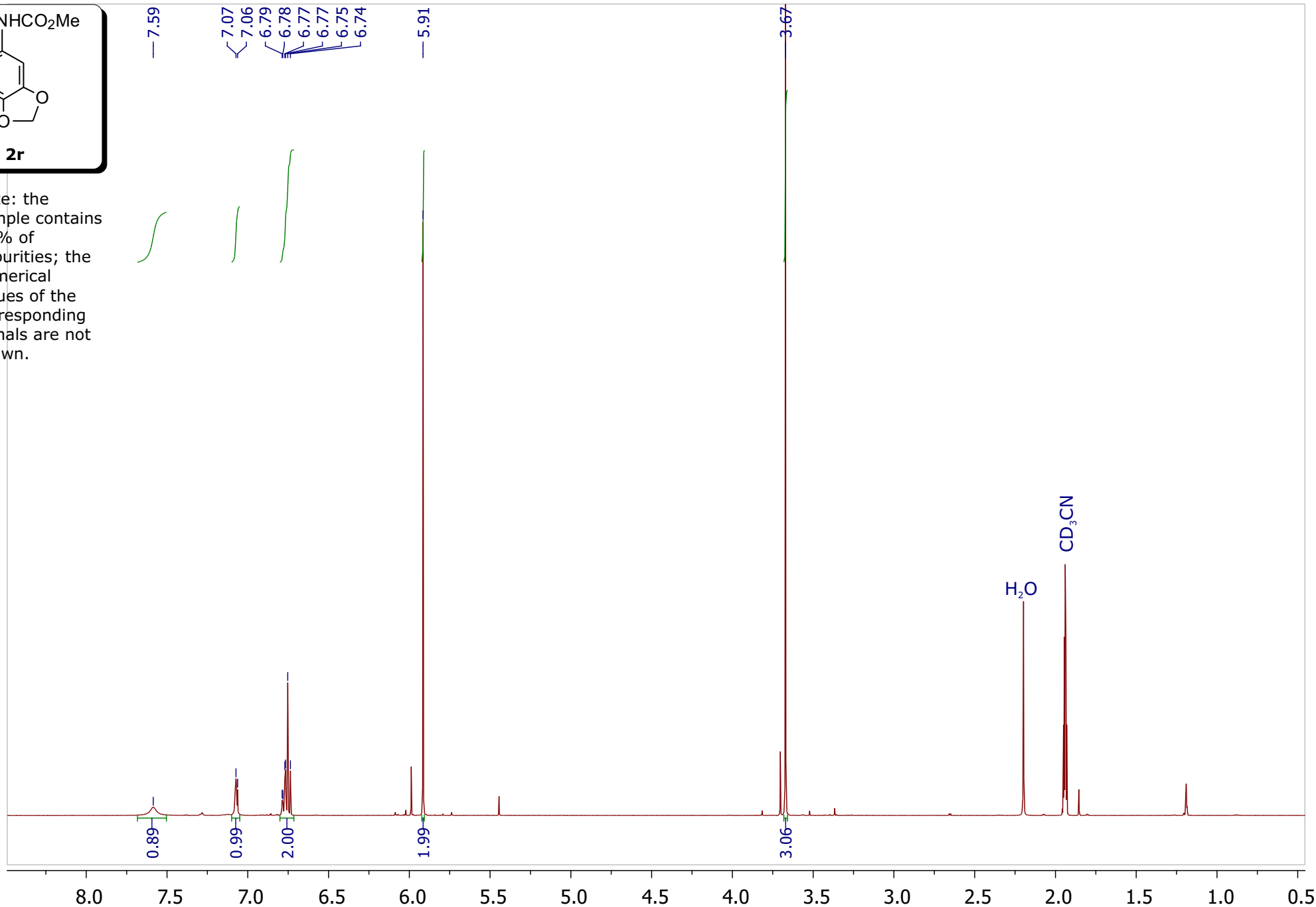


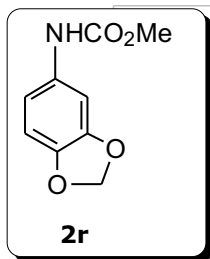
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



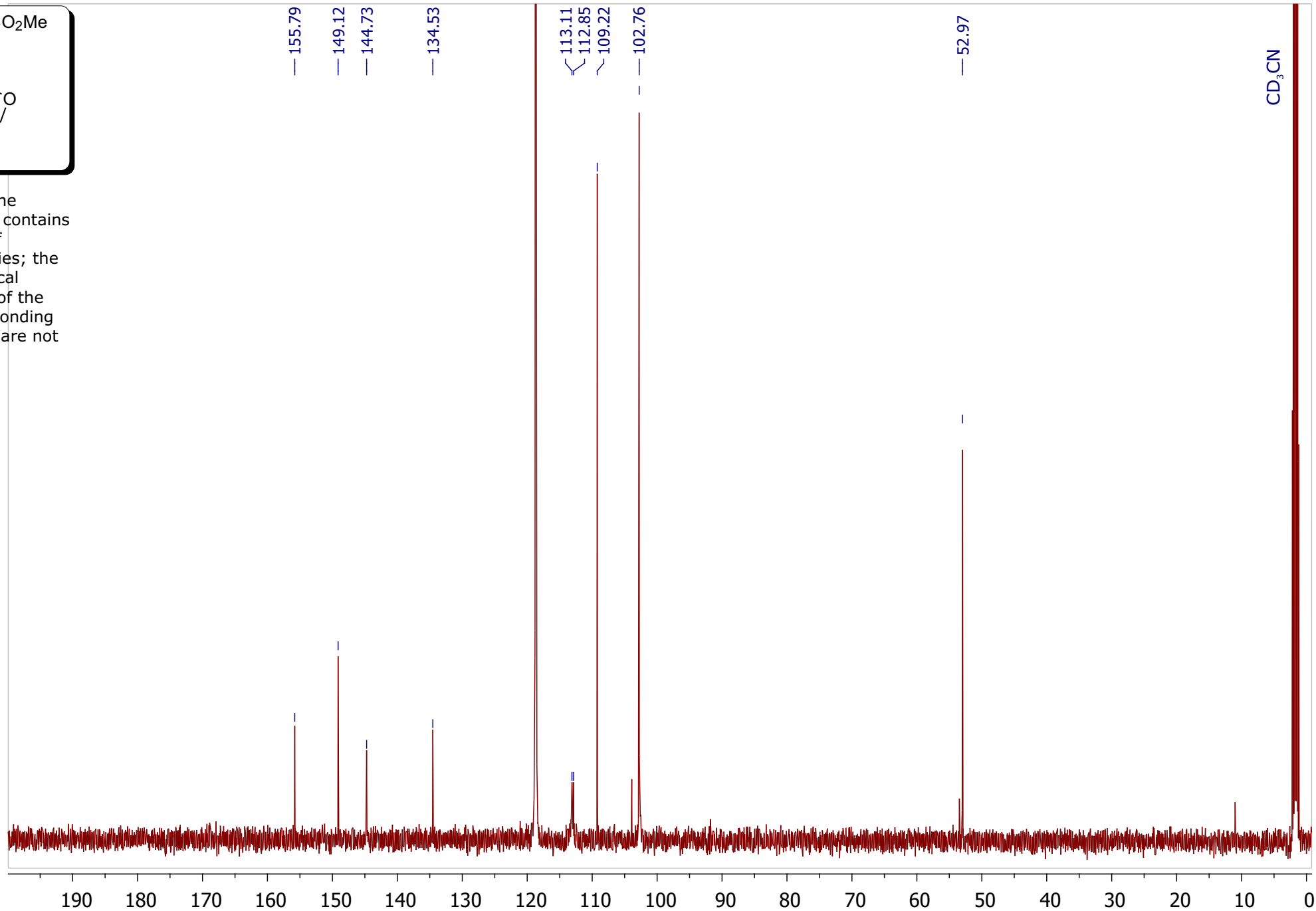


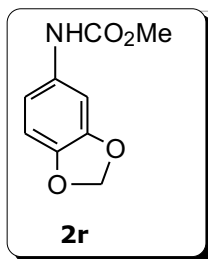
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



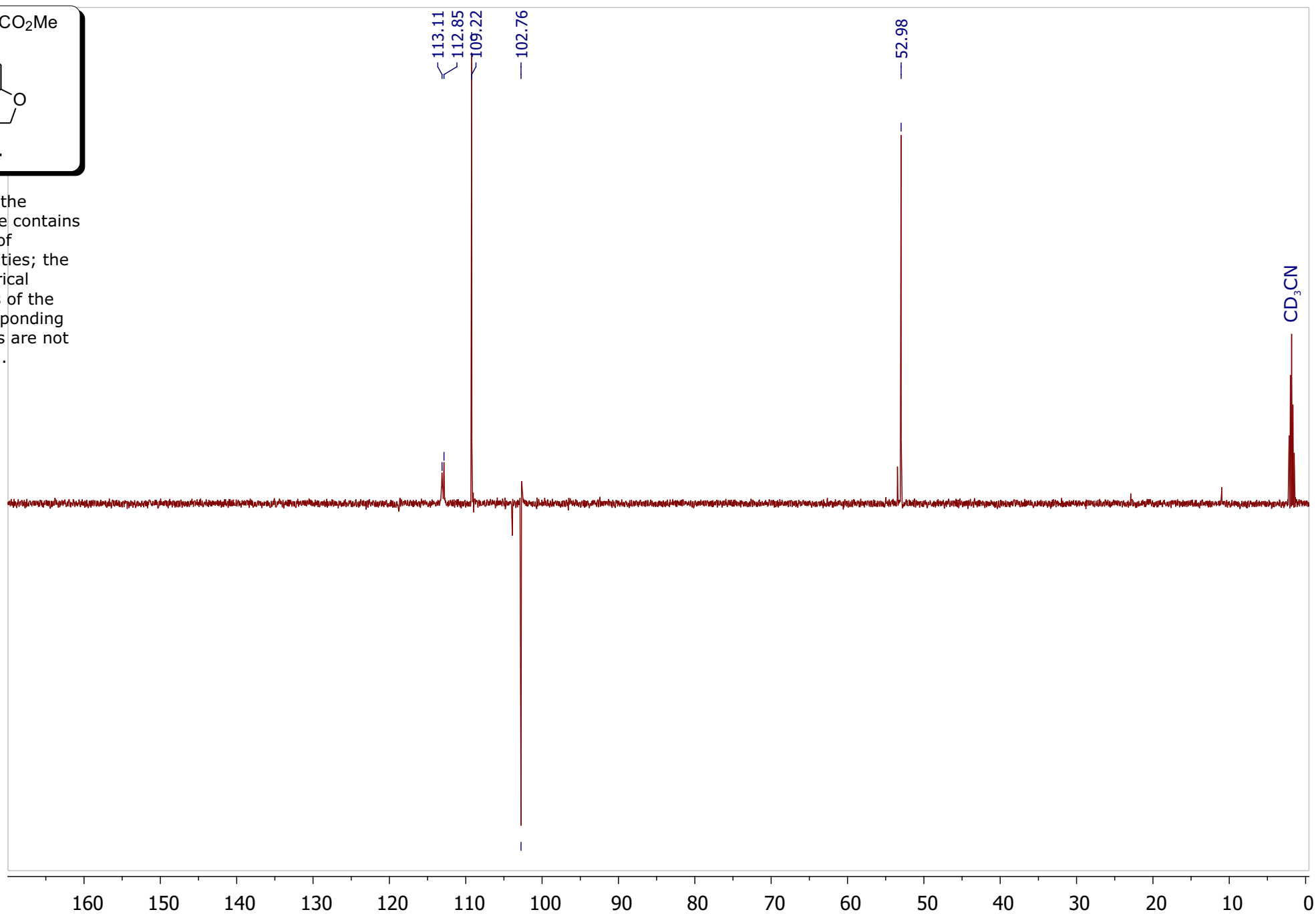


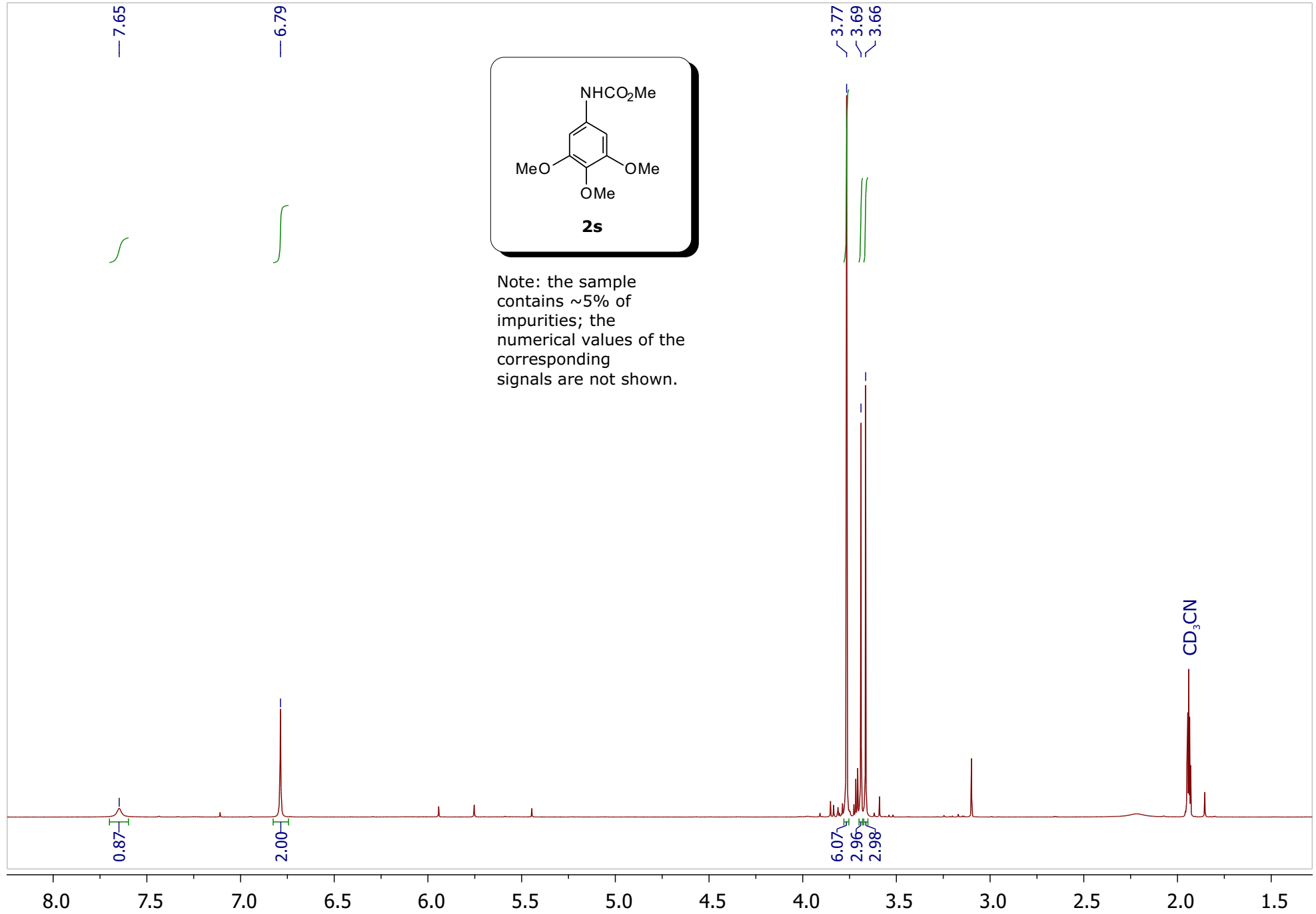
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.

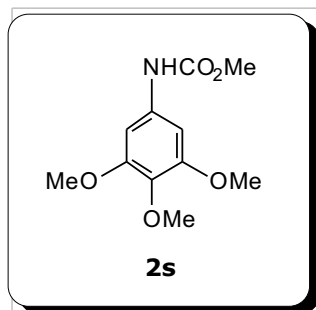




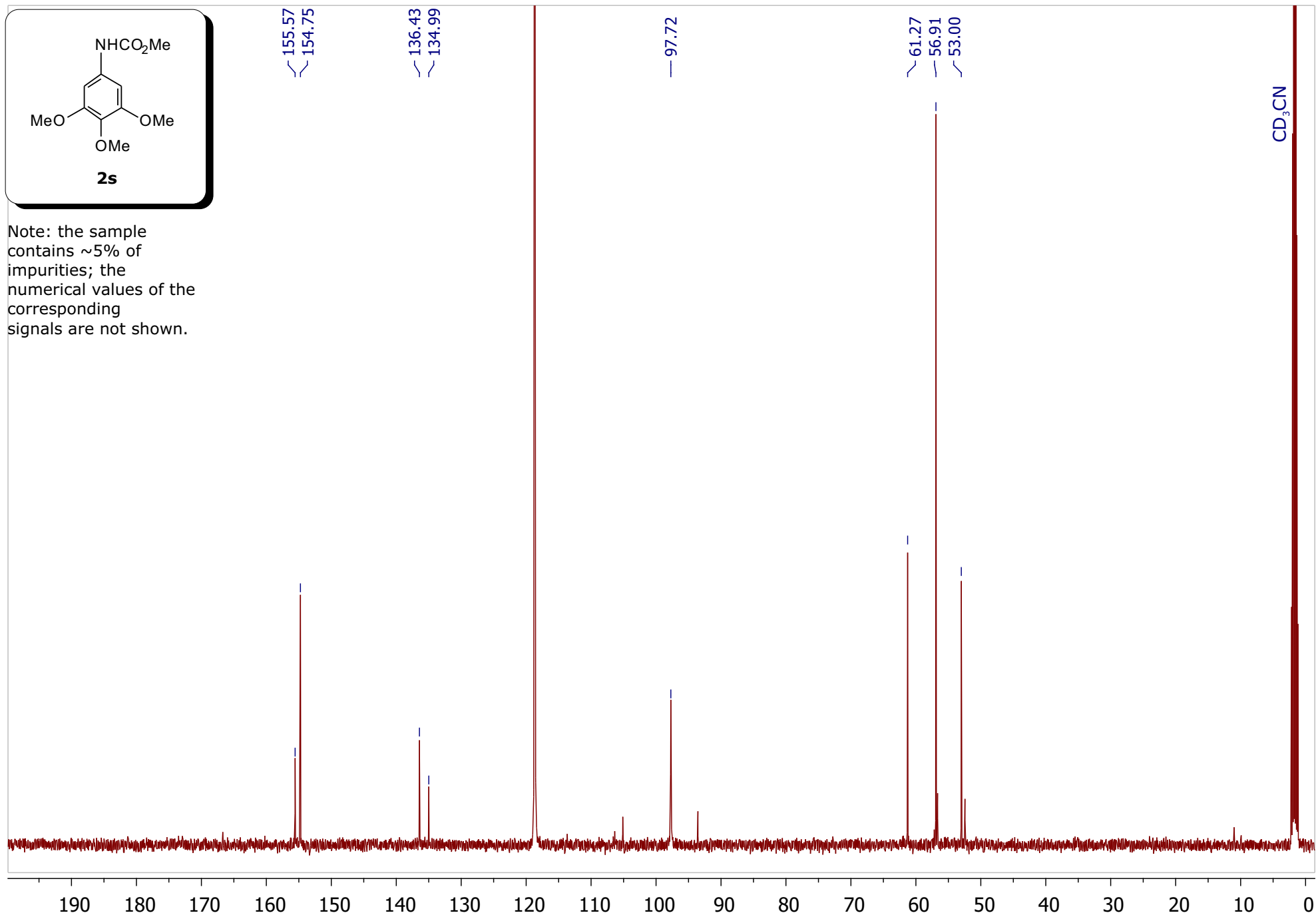
Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.

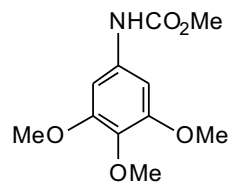






Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.



**2s**

Note: the sample contains ~5% of impurities; the numerical values of the corresponding signals are not shown.

