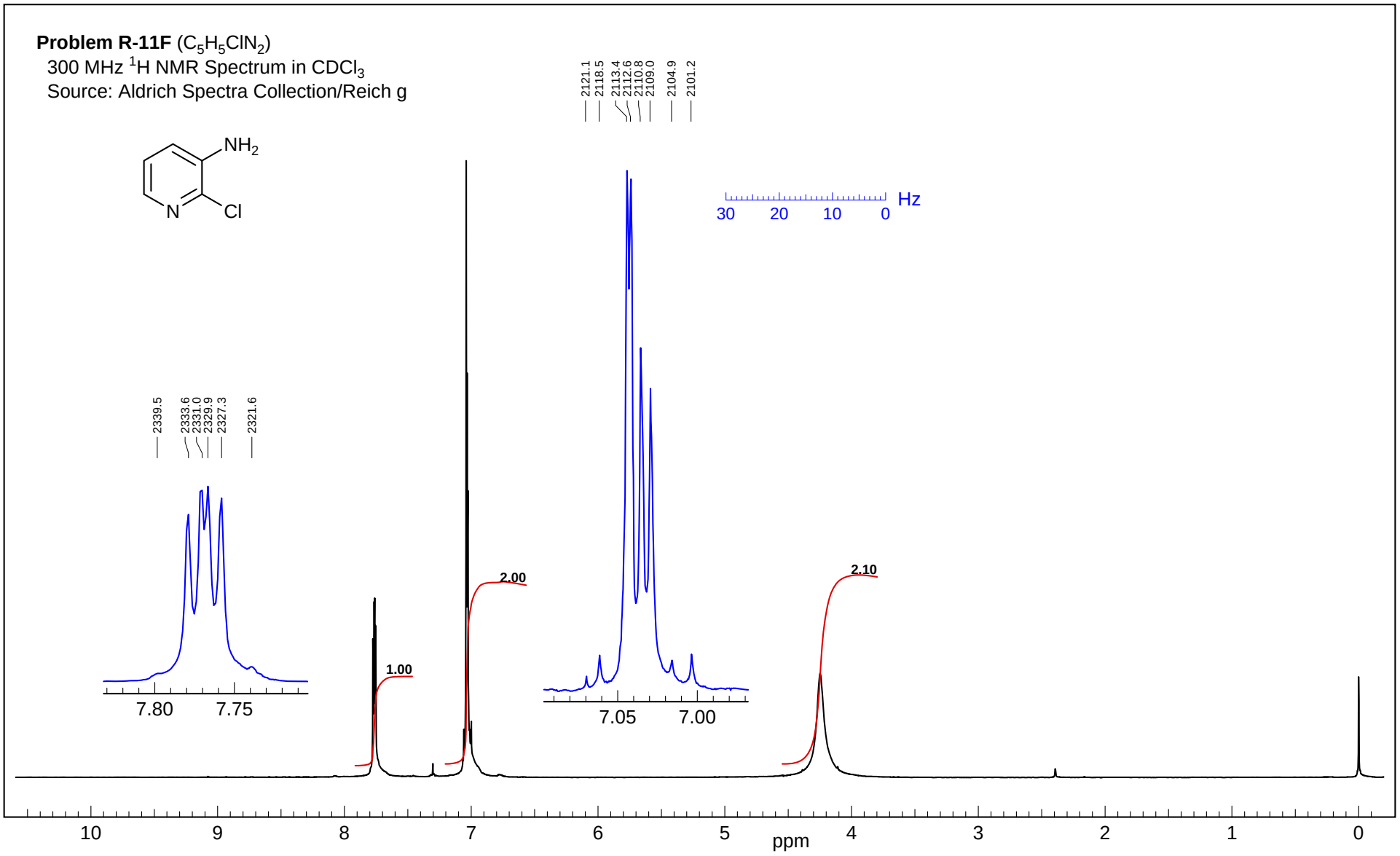
Problem R-11F ($C_5H_5ClN_2$)

300 MHz ^{1}H NMR Spectrum in $CDCl_3$

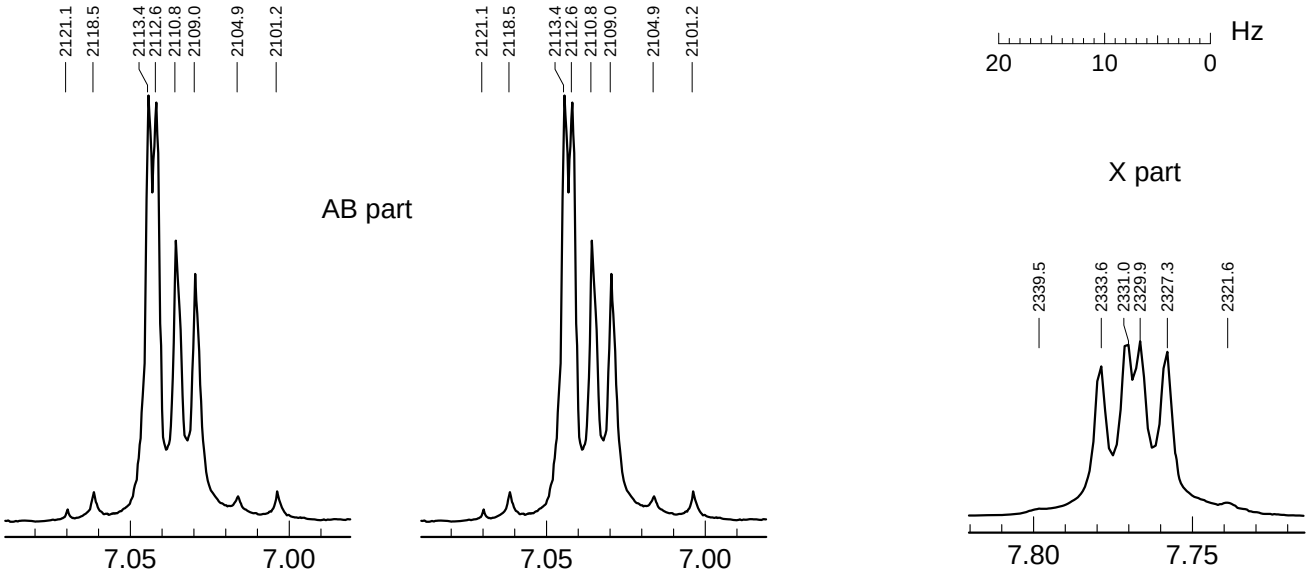
Source: Aldrich Spectra Collection/Reich g



PLT ex-1-2011-12-gq.plt

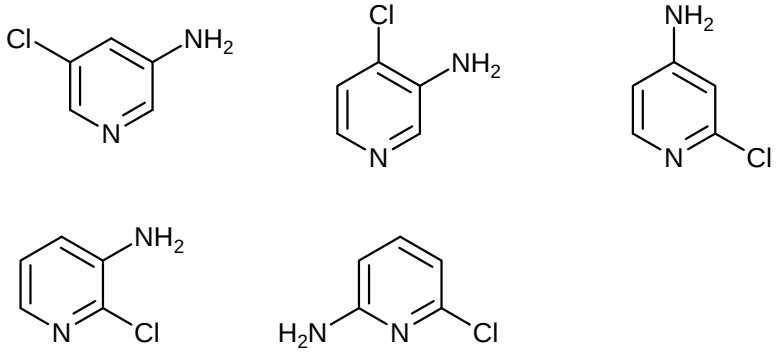
Problem R-11F ($C_5H_5ClN_2$). The 300 MHz NMR spectrum of of a disubstituted pyridine is shown below (the complete spectrum on the next page. This means there are three aromatic protons, which form an ABX pattern.

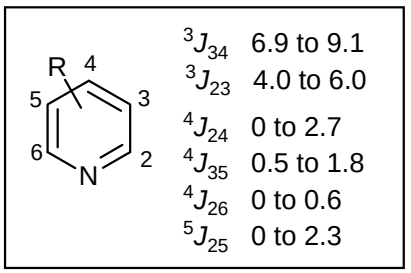
(a) Do an accurate calculation and determine couplings and chemical shifts, and **tabulate your results in an easily readable format**. If there are two solutions, report them both, and draw coupling trees on the spectra. For your convenience two copies of the AB part of the spectrum are shown.



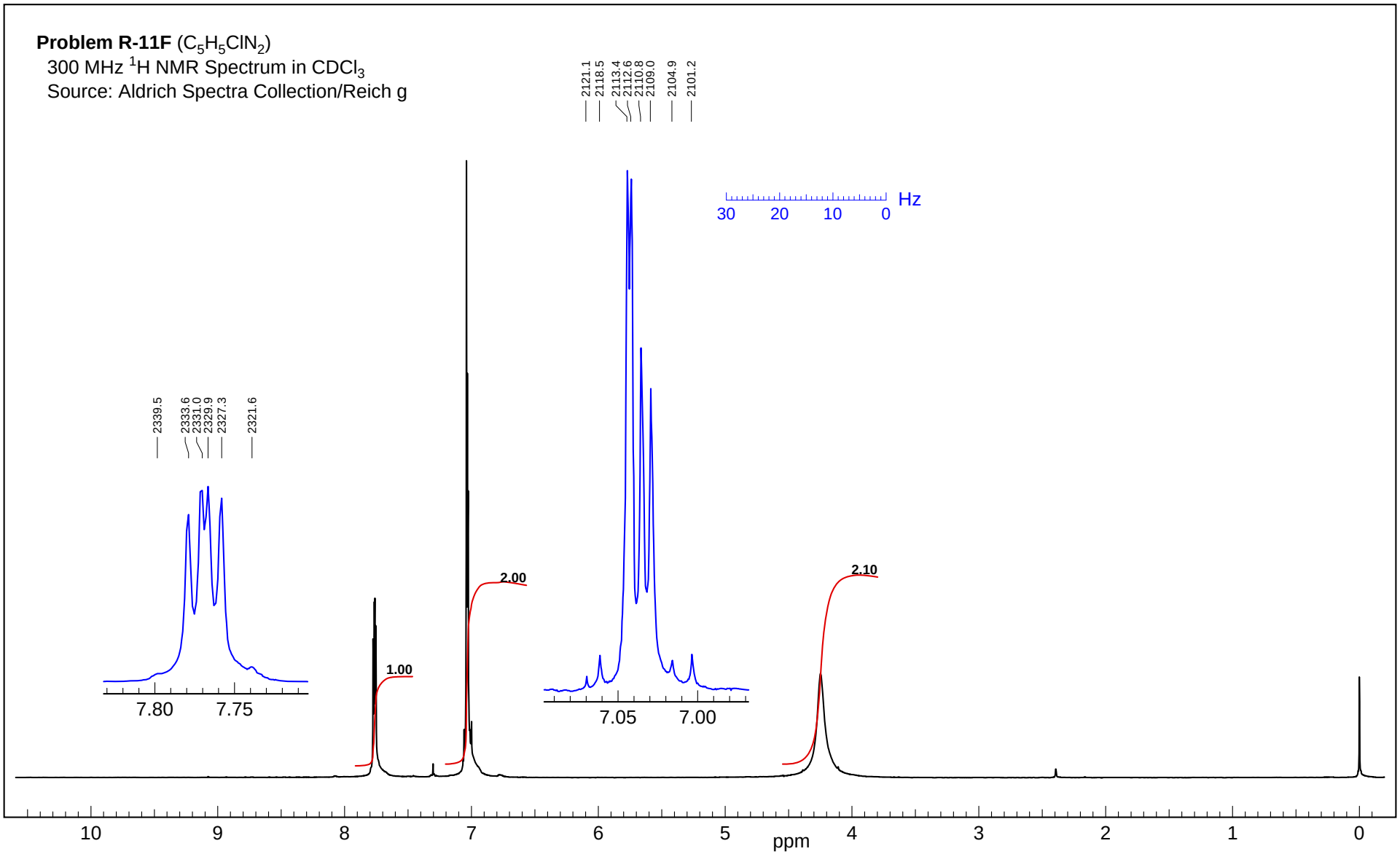
(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

(c) Which of the following structures best fits the NMR *J* and δ values?. Label your preferred structure with H_A, H_B and H_X. For your convenience, the typical coupling constants in pyridines are reproduced below.





All coupling constants are positive



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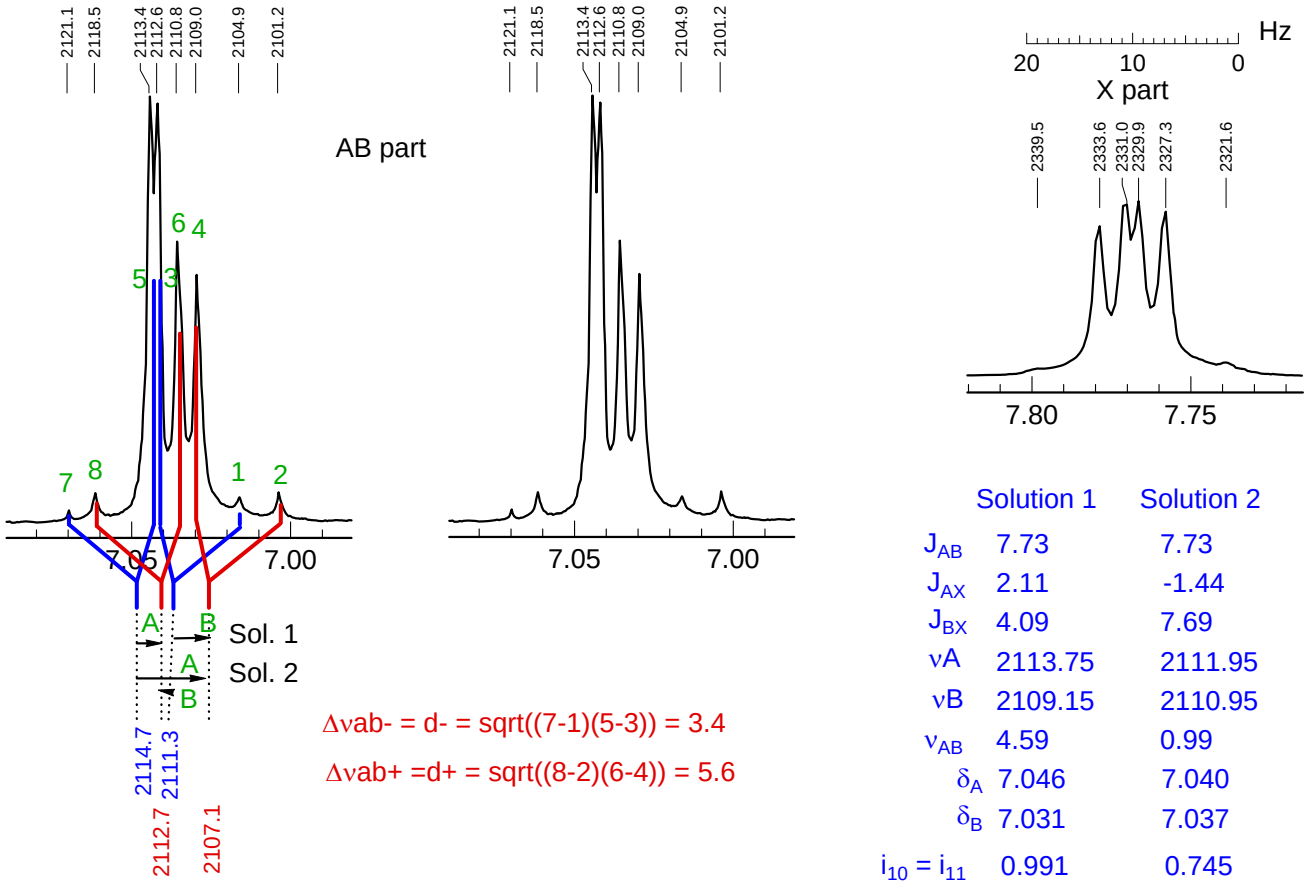

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	Solution 1	Solution 2
J_{AB}	7.73	7.73
J_{AX}	2.11	-1.44
J_{BX}	4.09	7.69
νA	2113.75	2111.95
νB	2109.15	2110.95
ν_{AB}	4.59	0.99
δ_A	7.046	7.040
δ_B	7.031	7.037
$i_{10} = i_{11}$	0.991	0.745

$\Delta\nu ab- = d- = \sqrt{(7-1)(5-3)} = 3.4$

$\Delta\nu ab+ = d+ = \sqrt{(8-2)(6-4)} = 5.6$

(b) If you are proposing two solutions, suggest at least one criterion which allows you to identify the correct one.

This must be solution 1:

1. The outer peaks would have to be 25% of the tallest peaks, they are barely visible
2. One of the couplings would have to be negative, in pyridines all couplings are positive
3. Size of the ortho-couplings fits better - J2,3 is small, Sol 2 requires both be large - 7.73 and 7.66

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(c) Which of the following structures best fits the NMR *J* and δ values?. Label your preferred structure with H_A, H_B and H_X. For your convenience, the typical coupling constants in pyridines are reproduced below.

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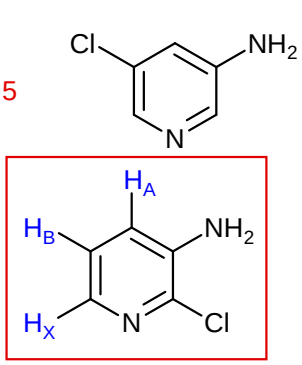

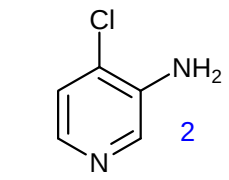

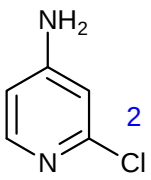

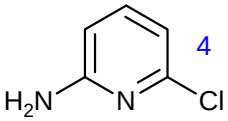

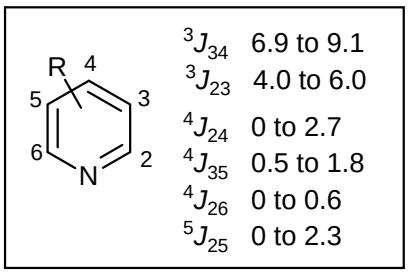

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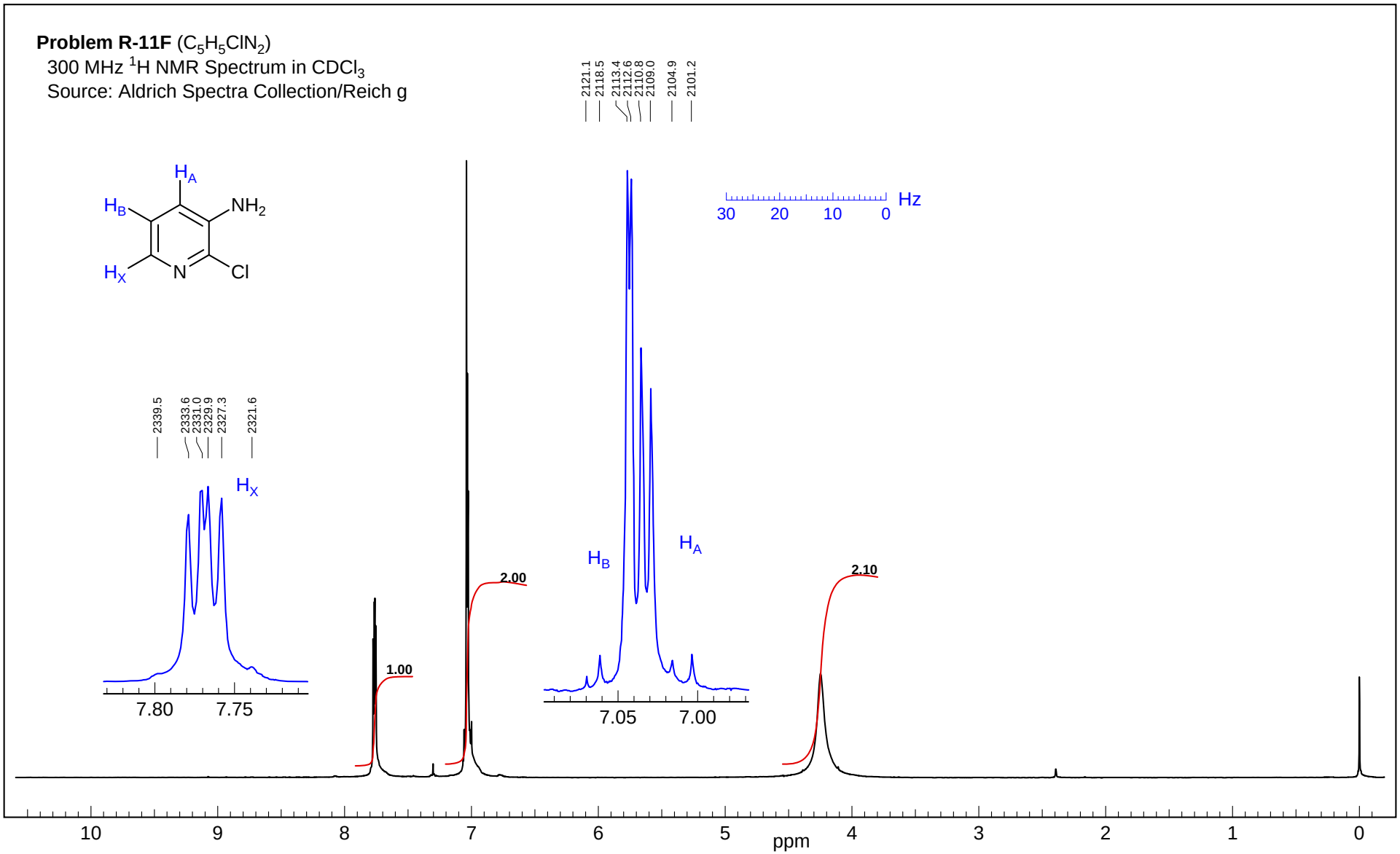

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