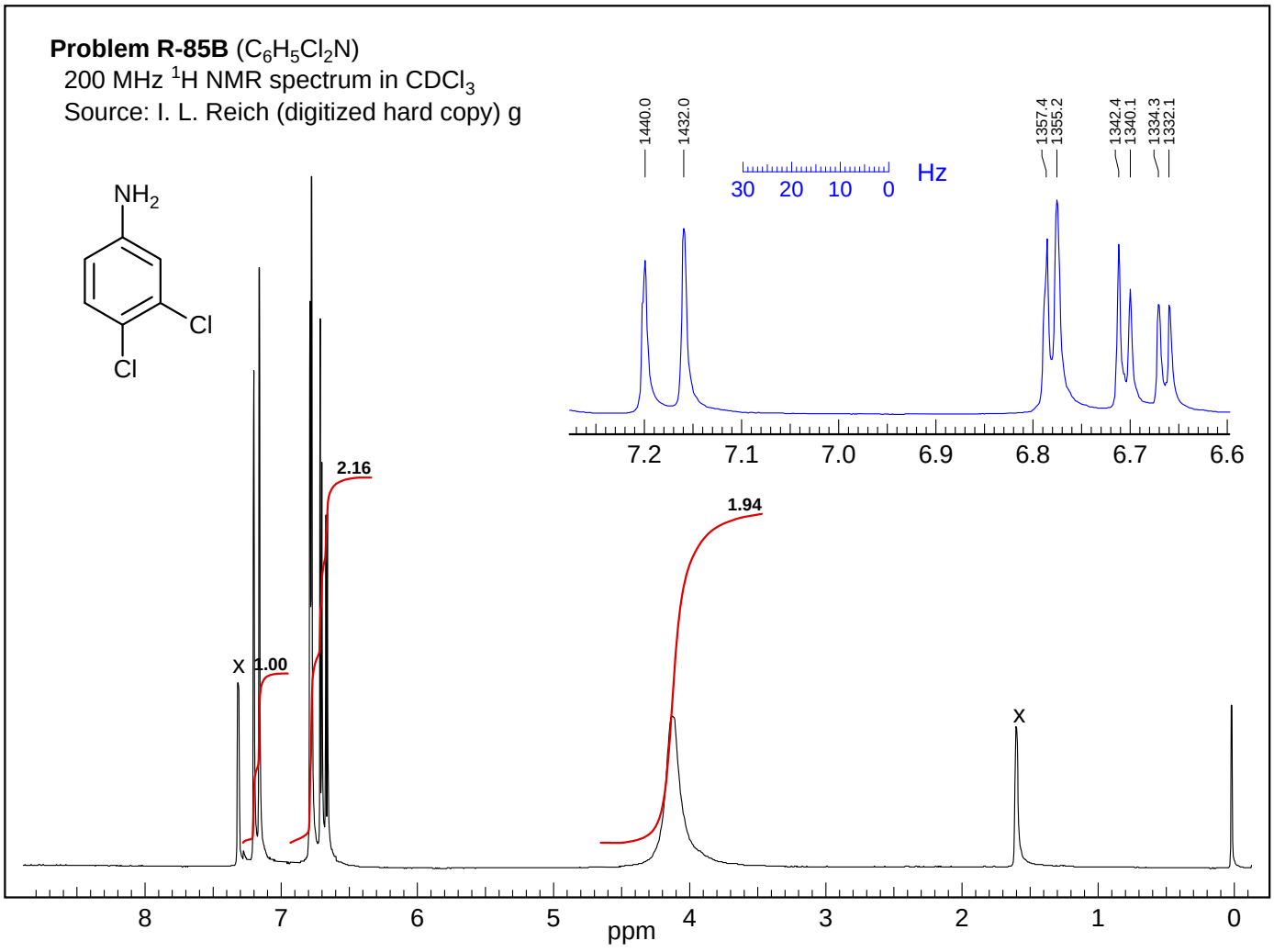


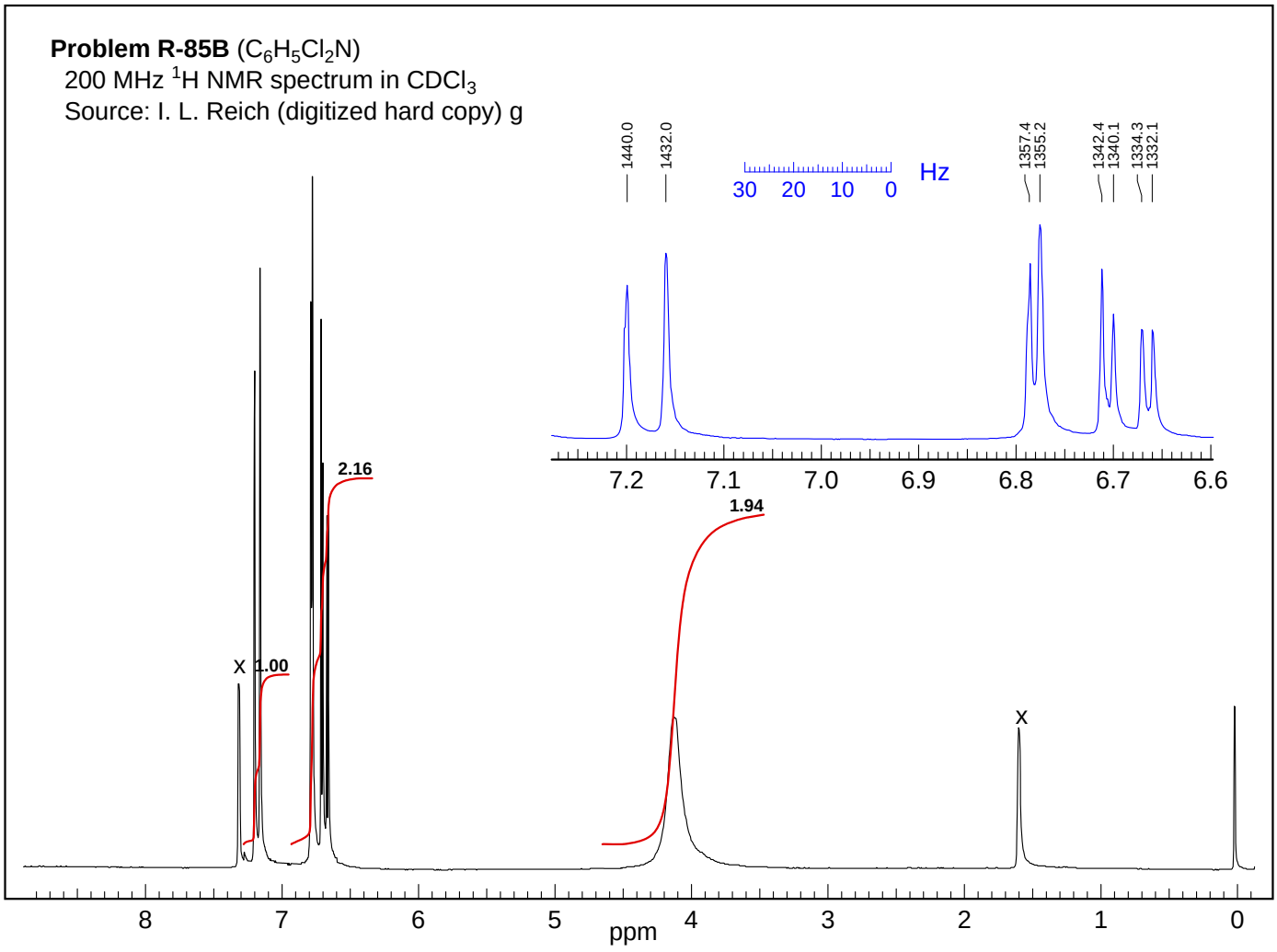
PLT pr-080-to-86.plt

Problem R-85B ($C_6H_5Cl_2N$). Determine the structure of the compound whose 200 MHz ^1H NMR spectrum is given. Ignore the signals marked "x."

(a) DBE?_____

(b) Analyze he pattern between δ 6.5 and 7.5. Estimate chemical shifts and coupling constants.

(c) Draw possible structures for compound **R-85B**. Place the appropriate δ values next to each proton of every proposed structure.


Problem R-85B (C6H5Cl2N)
200 MHz 1H NMR spectrum in CDCl3
Source: I. L. Reich (digitized hard copy) g
1440.0
1432.0
30 20 10 0
Hz
1357.4
1355.2
1342.4
1340.1
1334.3
1332.1
7.2 7.1 7.0 6.9 6.8 6.7 6.6
2.16
1.94
x 1.00
x
8 7 6 5 4 3 2 1 0
ppm

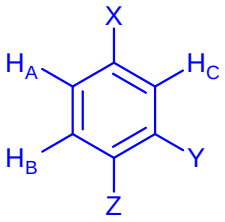
Problem R-85B ($C_6H_5Cl_2N$). Determine the structure of the compound whose 200 MHz ^1H NMR spectrum is given. Ignore the signals marked "x."

(a) DBE? 4

(b) Analyze the pattern between δ 6.5 and 7.5. Estimate chemical shifts and coupling constants.

	Δδ benzene:
H_A: δ 6.68, dd, J 8.2, 2.2 Hz	-0.68
H_B: δ 7.18, d, J = 8.2 Hz	-0.18
H_C: δ 6.78, J = 2.5 Hz	-0.58

These are clearly aromatic protons, must be a 1,2,4-tribstituted benzene



The groups X, Y and Z are Cl, Cl, NH_2, but in what order?

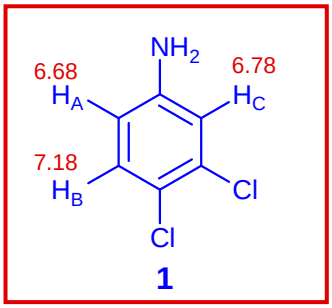
(c) Draw possible structures for compound **R-85B**. Place the appropriate δ values next to each proton of every proposed structure.

There are three possible isomers: we can try and decide which fits the chemical shifts best by comparing calculated to observed values for each isomer:

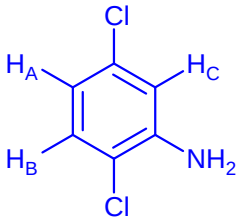
Observed Δδ from benzene (7.36):
H_A: -0.68
H_B: -0.18
H_C: -0.58

o-Cl: -0.02
m-Cl: -0.07
p-Cl: -0.13

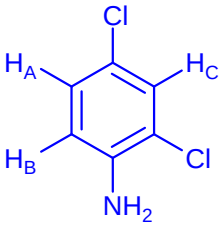
o-NH_2: -0.71
m-NH_2: -0.22
p-NH_2: -0.62



1



2



3

	H_A	H_B	H_C
	o-NH_2: -0.71	m-NH_2: -0.22	o-NH_2: -0.71
	m-Cl: -0.07	o-Cl: -0.02	o-Cl: -0.02
	p-Cl: -0.13	m-Cl: -0.07	m-Cl: -0.07
Calc:	-0.90	-0.29	-0.80
Error:	-0.22	-0.11	-0.22

Σ (errors): 0.55

	H_A	H_B	H_C
	p-NH_2: -0.62	m-NH_2: -0.22	o-NH_2: -0.71
	o-Cl: -0.02	o-Cl: -0.02	o-Cl: -0.02
	p-Cl: -0.13	p-Cl: -0.13	p-Cl: -0.13
Calc:	-0.77	-0.37	-0.86
Error:	-0.09	-0.19	-0.22

Σ (errors): 0.50

	H_A	H_B	H_C
	m-NH_2: -0.22	o-NH_2: -0.71	m-NH_2: -0.22
	o-Cl: -0.02	m-Cl: -0.07	o-Cl: -0.02
	p-Cl: -0.13	m-Cl: -0.07	o-Cl: -0.02
Calc:	-0.37	-0.85	-0.26
Error:	+0.31	-0.67	+0.32

Σ (errors): 1.30

We can definitely rule out **3** (error: 1.30 ppm), but the calculations are too close to call for **1** and **2**. The actual structure is **1**, even though **2** gives a slightly smaller difference between observed and calculated shifts. Isomer **1** does give the correct *sequence* of shifts, whereas **2** does not.