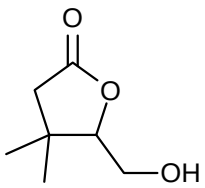
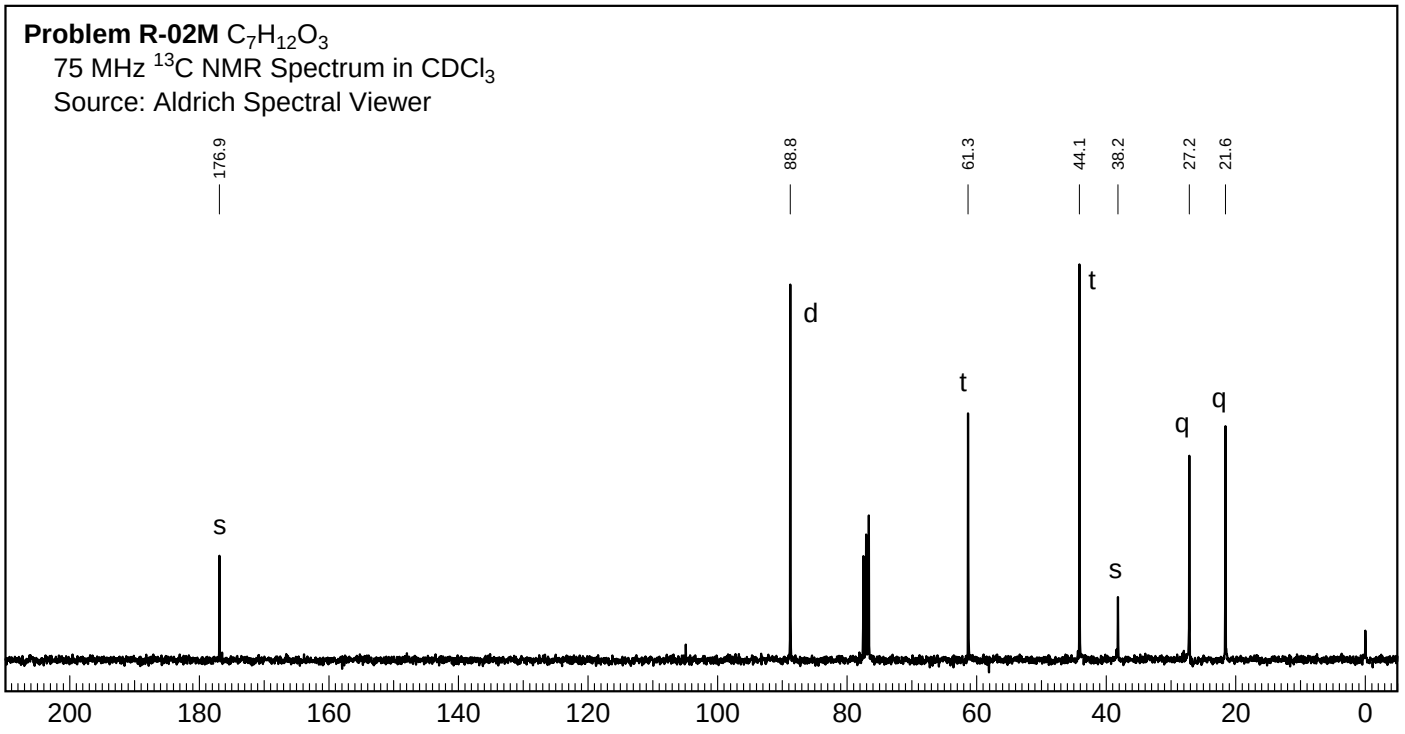
Problem R-02M ($C_7H_{12}O_3$)

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

Source: Aldrich Spectra Collection/Reich g



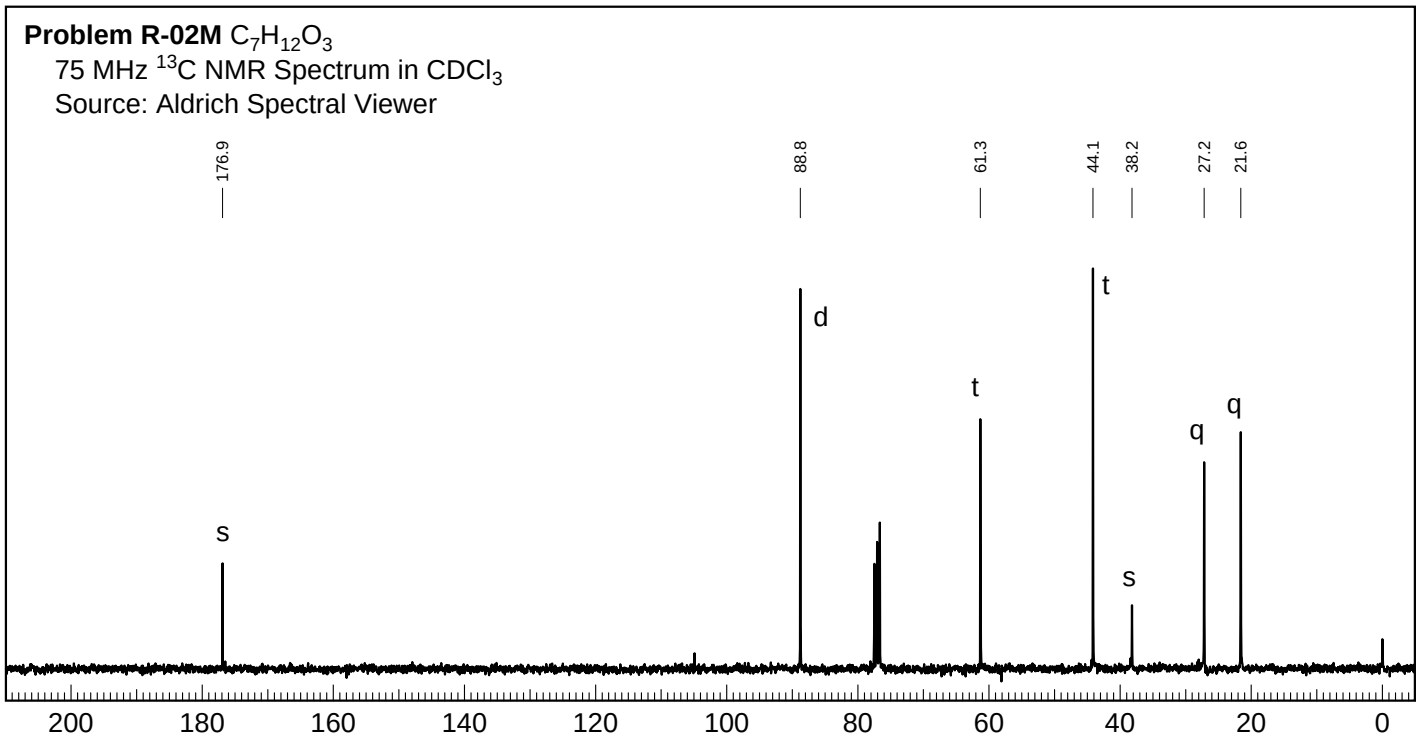
PLT ex-2-2002-gq.plt



PLT ex-2-2002-gq.plt

Problem **R-02M** ($C_7H_{12}O_3$). This problem requires you to analyze the ^{13}C and ^{1}H NMR spectra of **R-02M**, and determine the structure.

(a) DBE _____



(b) Interpret the ^{13}C NMR spectrum. For each of the signals, suggest possible structural types.

176.6

88.8

61.3

44.1

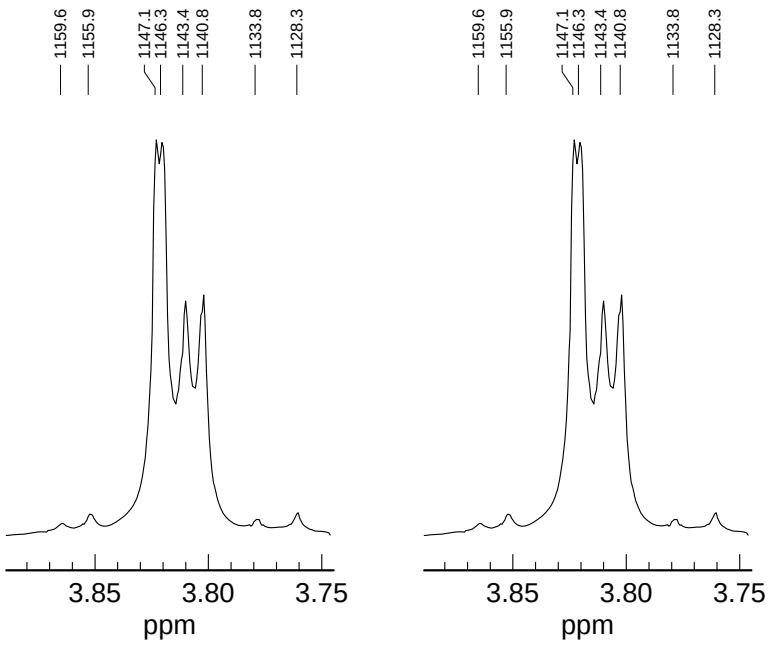
38.2

27.2

21.6

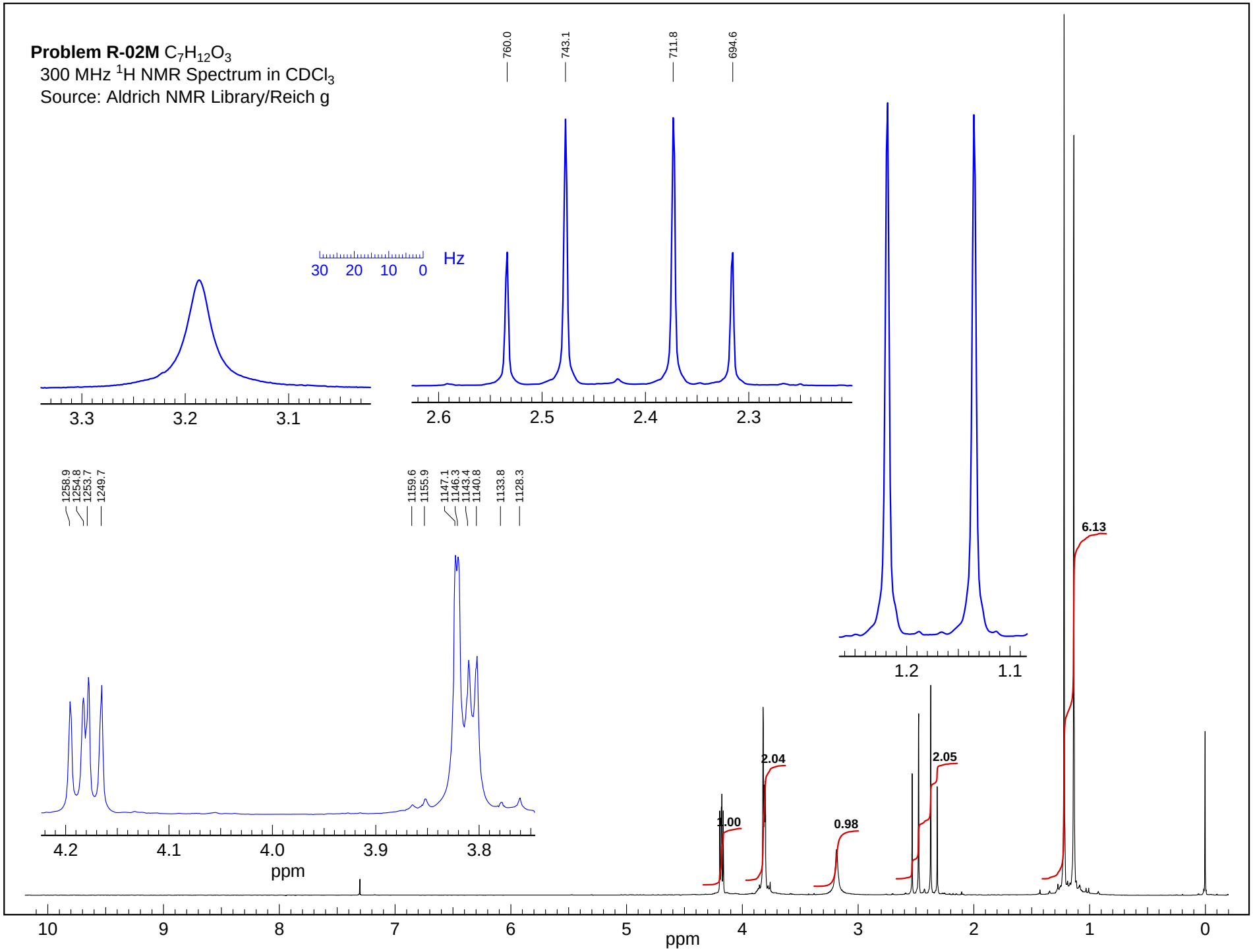
(c) Do an accurate analysis of the signals at δ 2.4. What part structure is suggested by these signals?

(d) Do an accurate (quantitative) analysis of the signals at δ 3.8. Use the frequencies shown. If more than one solution is possible, show them both, and draw the proper coupling tree on the spectra below. Use appropriate criteria to distinguish the two. Show your work, and tabulate your data in an easily readable form.



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

(f) Draw the structure of **R-02M** below. If more than one structure is possible, identify your first choice by circling it. **Label the structure with ^{13}C chemical shifts from part (b)**.



PLT ex-2-2002-gq.plt

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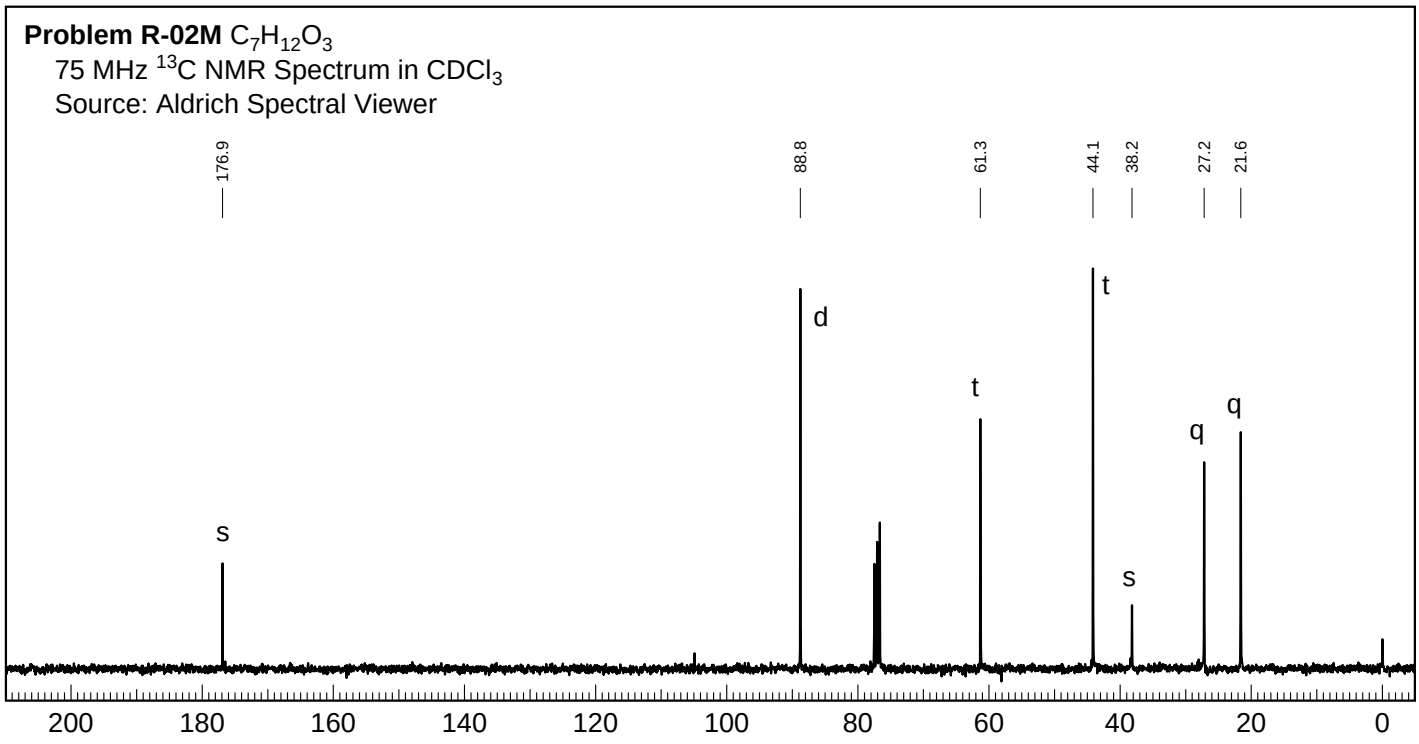
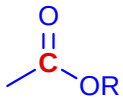
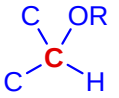
(a) DBE _____



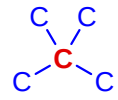
(b) Interpret the ^{13}C NMR spectrum. For each of the signals, suggest possible structural types.

176.6 

88.8 

61.3 -C-**C**H_2-OR

44.1 C-**C**H_2-C

38.2 

27.2 C-**C**H_3

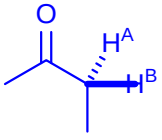
21.6 C-**C**H_3

(c) Do an accurate analysis of the signals at δ 2.4. What part structure is suggested by these signals?

This is an AB quartet, probably a diastereotopic isolated CH_2

J_{AB} = 16.2, 16.9 Hz

The large gem J_{AB} means the CH_2 is probably α to a carbonyl group



$\nu_{AB} = \sqrt{(758.3-694.7)(742.1-711.6)}$

$= 44.0$ Hz

$\nu_c = 726.9$ Hz

$\nu_A = 726.9 + 22.0 = 748.9, \ \delta\ 2.496$

$\nu_B = 726.9 - 22.0 = 704.9, \ \delta\ 2.350$

(d) Do an accurate (quantitative) analysis of the signals at δ 3.8. Use the frequencies shown. If more than one solution is possible, show them both, and draw the proper coupling tree on the spectra below. Use appropriate criteria to distinguish the two. Show your work, and tabulate your data in an easily readable form.

c_+=(6+4)/2 = 1146.7

$\Delta\nu_{ab}+ = \delta_+$ = sqrt((8-2)(6-4)) = 8.47

$c_+ \pm \Delta\delta_+/2$ = 1144.4 1137.9

c_-=(5+3)/2 = 1142.1

$\Delta\nu_{ab}- = \delta_-$ = sqrt((7-1)(5-3)) = 4.54

$c_- \pm \Delta\delta_-/2$ = 1149.0 1146.3

	Solution 1	Solution 2
J_{AB}	12.5	12.5
J_{AX}	+4.2	+11.1
J_{BX}	+7.0	-1.9
ν_A	1147.7	1143.5
ν_B	1141.2	1145.4
$\Delta\nu_{AB}$	8.5	4.5
δ_A	3.83	3.81
δ_B	3.80	3.82

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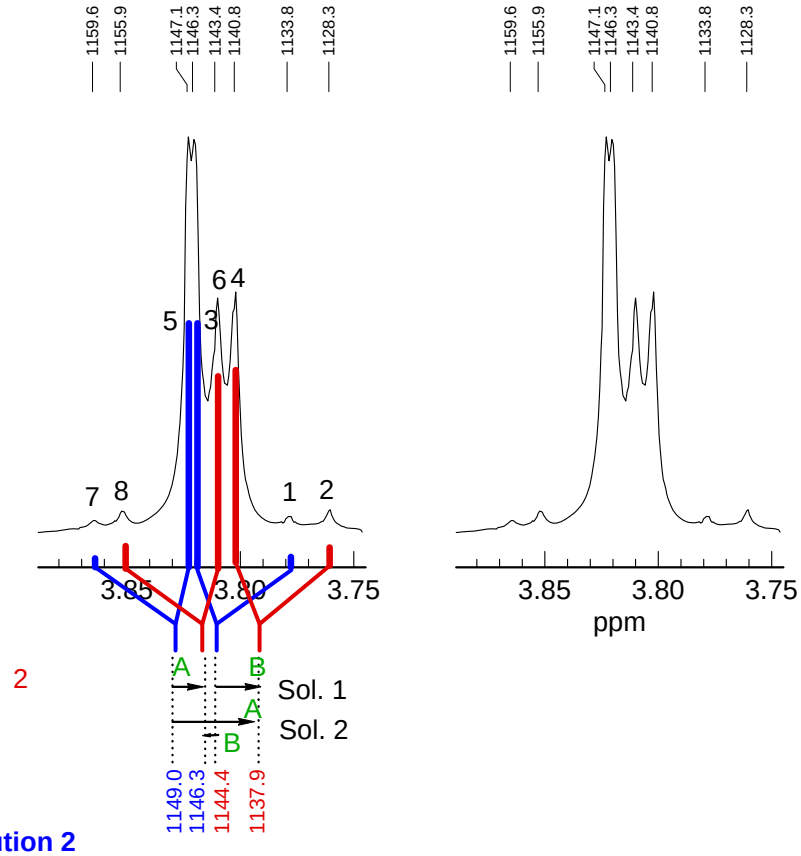

2

Intensity Calculation

Solution 1

Φ1+ = 0.5 arcsin(J_{AB}/2D+) = 35.01

Φ1- = 0.5 arcsin(J_{AB}/2D-) = 27.94

$i_{10} = i_{11}$ = 0.985

$i_{14} = i_{15}$ = 0.015

Solution 2

$\Phi_2+ = \Phi 1$ = 35.01

$\Phi_2- = 90 - \Phi 1-$ = 62.06

$i_{10} = i_{11}$ = 0.792

$i_{14} = i_{15}$ = 0.208

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

The size of the coupling constants is OK for both solutions, so this is not a useful criterion.

The two coupling constants are opposite signs in Sol. 2. If both are ^3J. then this cannot be correct

2

In the spectrum of the X part (δ 4.18) the lines 14 and 15 are too small to detect, as predicted for solution 1. For solution two the extra lines should be 20% of the largest lines, thsy should be easily visible

Thus Solution 1 is correct

(f) Draw the structure of **R-02M** below. If more than one structure is possible, identify your first choice by circling it. **Label the structure with ^{13}C chemical shifts from part (b)**.

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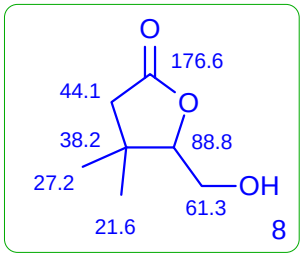
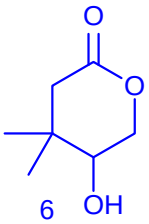
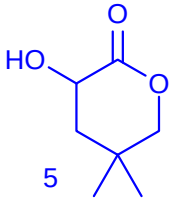
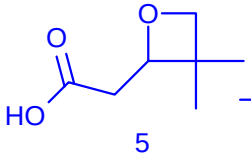
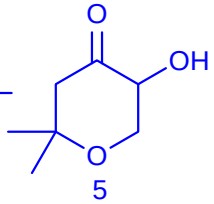


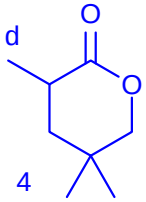


3J not right









plus 3 more structures