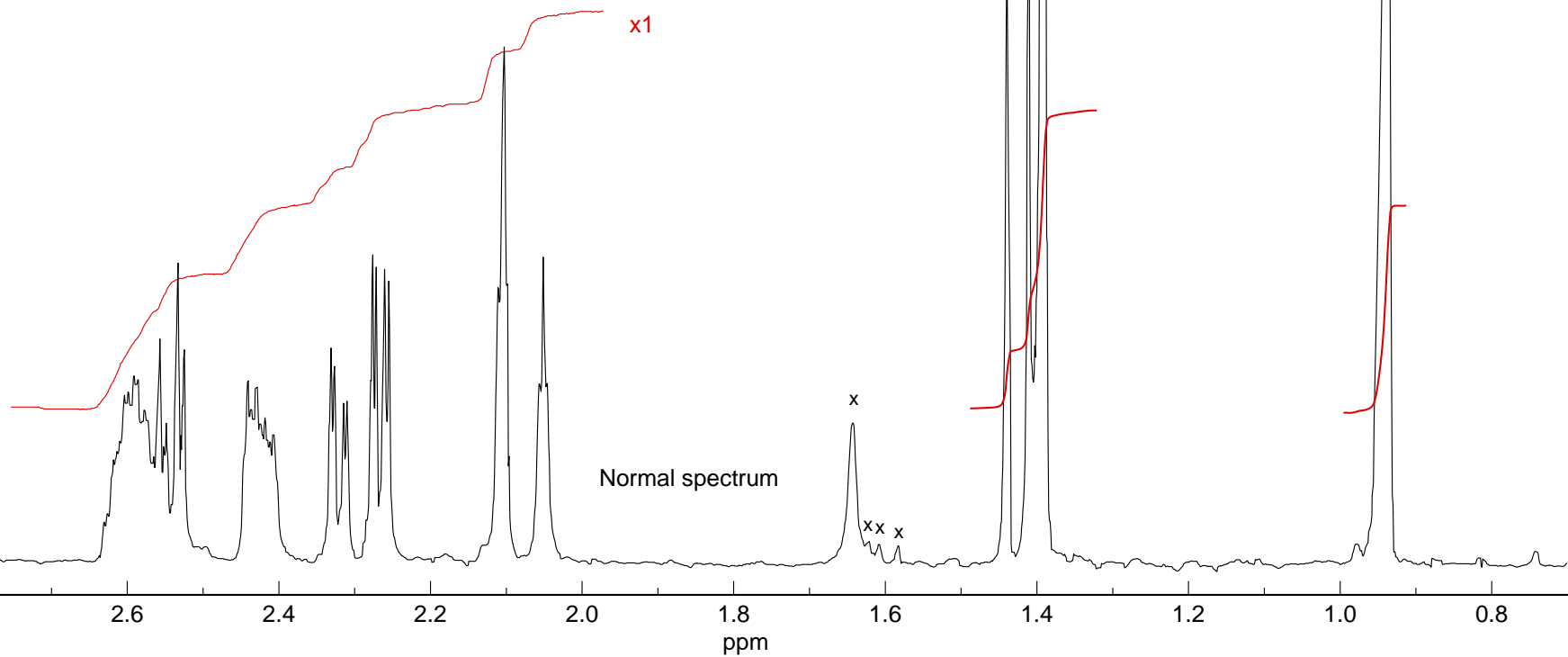
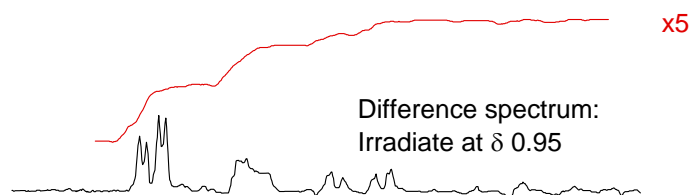
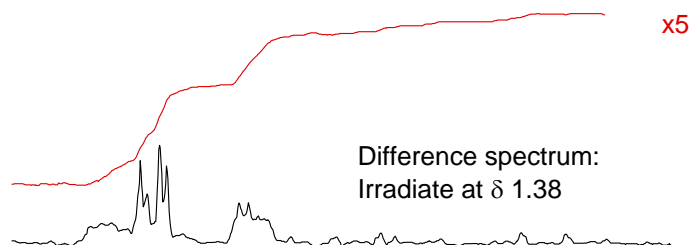
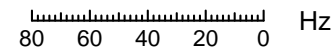
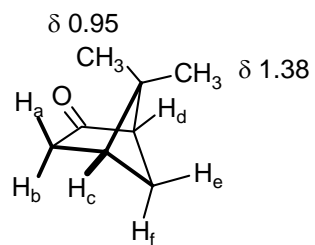


Problem R-12P (C₈H₁₂O)

300 MHz ¹H NMR Spectrum

Source: The XL Series NMR Spectra Collection Vol 1

Varian Associates (digitized hard copy) g



Problem R-12P. This question requires you to assign the protons of compound **R-12P** using the 300 MHz proton NMR spectra given. The spectrum shows the normal ^1H NMR, and two inserts which are difference spectra resulting from subtraction of the normal spectrum from one in which the large signal at δ 0.95 or at δ 1.4 was irradiated for a second or so, and then the decoupler was turned off during acquisition of the FID. The assignment of these signals is shown on the structures. The integration of the insets has been expanded five times (5x) compared to the normal spectrum

(a) What kind of experiment is being performed here? What information does this experiment provide?

(b) For the NMR signals below assign each to one of the protons labeled H_a to H_f . Briefly summarize the evidence you used in making each assignment. Each of the signals corresponds to a single proton. The signals marked with an x are impurities.

δ 1.43 _____

δ 2.08 _____

δ 2.28 _____

δ 2.43 _____

δ 2.55 _____

δ 2.60 _____

Are there any ambiguities in the assignments you have made?

(c) Comment on the chemical shift difference between the two methyl signals, as well as the protons H_e and H_f .

Problem R-12P ($C_8H_{12}O$). This question requires you to assign the protons of compound **R-12P** using the 300 MHz proton NMR spectra given. The spectrum shows the normal 1H NMR, and two inserts which are difference spectra resulting from subtraction of the normal spectrum from one in which the large signal at δ 0.95 or at δ 1.4 was preirradiated for a second or so, and then the decoupler was turned off during acquisition of the FID. The assignment of these signals is shown on the structures. The integration of the insets has been expanded five times (5x) compared to the normal spectrum

(a) What kind of experiment is being performed here? What information does this experiment provide?

4 Homonuclear NOE difference experiment. One proton signal is irradiated until it is saturated, increase in area of other protons tells us which ones are close in space to the one being irradiated, provided that the irradiated proton is causing DD relaxation of the observed proton.

(b) For the NMR signals below assign each to one of the protons labeled H_a to H_f . Briefly summarize the evidence you used in making each assignment. Each of the signals corresponds to a single proton. The signals marked with an x are impurities.

13	δ 1.43 <u> </u> H_f	Assigned by difference - just a doublet, coupled only to H_e . There must be a 90° dihedral angle with H_c and H_d
These should be together	δ 2.08 <u> </u> H_b	2.08 and 2.28 should be the α -keto protons H_a and H_b . They are coupled to each other, and show a characteristic large geminal coupling of 17 Hz.
These should be together	δ 2.28 <u> </u> H_a	This signal shows an NOE effect when the endo Me group is irradiated (δ 0.95), so it must be H_a , other is H_b
These should be together	δ 2.43 <u> </u> H_c	2.43 and 2.55 both show NOE effect when either Me group is irradiated, so they must be the H_c and H_d protons. 2.55 is just a dd, so must be H_d ; H_c is complex, since it could be coupled to H_a , H_b , H_d , H_e , and H_f
These should be together	δ 2.55 <u> </u> H_d	
These should be together	δ 2.60 <u> </u> H_e	This signal shows an NOE effect when the exo Me group is irradiated (δ 1.38), so it must be H_e , other is H_f (δ 1.43)

Are there any ambiguities in the assignments you have made?

None

(c) Comment on the chemical shift difference between the two methyl signals, as well as the protons H_e and H_f .

3 The endo methyl group (δ 0.95) and H_f may both be over the shielding cone above and below the $C=O$ group, hence the unusual upfield shift.

Problem R-12P (C₈H₁₂O)

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