EXPT. 8 STRUCTURAL DETERMINATION OF SIMPLE ORGANIC COMPOUNDS USING ^{1}H-NMR SPECTROMETRY

Structure

8.1 INTRODUCTION

In the previous experiment you have learnt about the application of IR spectroscopy in the determination of functional groups in an organic molecule. In this experiment you would learn about the application of NMR spectrometry in structure elucidation of simple organic molecules. You have learnt about the principle and instrumentation of NMR spectrometry in Unit 12 of the MCH-003 course.

You would have appreciated from the MCH-003 course that no spectroscopic method can give all the information about the analyte being studied. The same is true of NMR spectrometry also; however it provides significant leads into the structure determination. In this experiment we would recapitulate the salient features of the NMR spectrometric method and use a number of examples of NMR spectra to demonstrate the potential of the technique in determining the structural features of simple organic compounds. You would be required to determine the structure of a few organic compounds on the basis of the provided NMR spectra. Once equipped with the necessary interpretative skills, you can sharpen your skills by interpreting as many spectra as possible to attain a kind of mastery. In the next experiment you would learn about the structure determination of organic compounds on the basis of IR, NMR and Mass spectra of the molecule.

Objectives

After studying the contents of this experiment and interpreting the sample NMR spectra, you should be able to:

- outline the salient features of the NMR spectrometric method,
- identify the presence of different functional groups and other structural features in an organic compound,
- predict the characteristic signals in the NMR spectrum of a given organic compound on the basis of the structure of the compound.

8.2 PRINCIPLE

You would recall from Unit 12 of MCH-003 course that in nuclear magnetic resonance (NMR) spectroscopy, the magnetic properties of certain nuclei are exploited to seek structural information of the molecule. The NMR spectrometry is most widely and routinely used for the identification and structure elucidation of organic, organometallic and biological molecules. However, very few attempts have been made for quantitative determination of analyte species by NMR. In this experiment we are using NMR spectra for structure elucidation. In order to facilitate this process let us recall the

following spectral features of the ^{1}H-NMR and the structural information available from them. Spectral data tells us about the following important aspects of a molecule.

i) The number of different signals in the ^{1}H-NMR spectrum indicates about the different types of protons present in the molecule. For example, the NMR spectrum of dipropyl ether $(CH_3CH_2CH_2)_2O$ contains three distinct sets of signals; for each type (methyl, methylene-1 and methylene-2) of the proton.

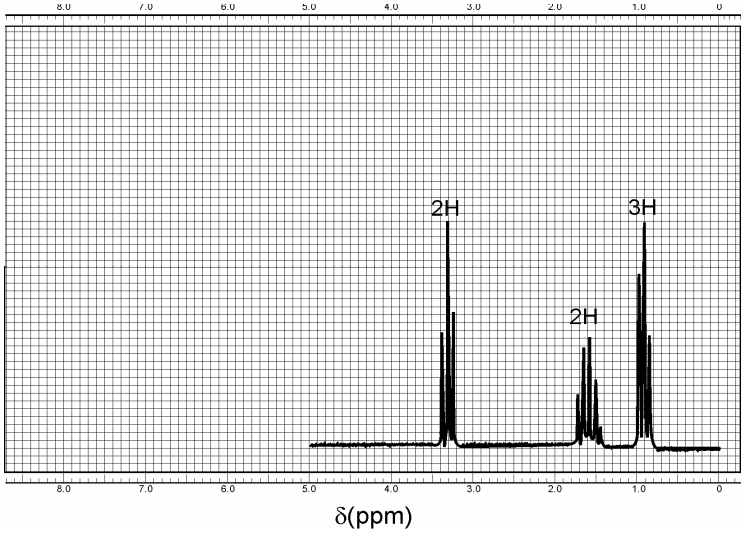


Fig.8.1: Schematic NMR spectrum of dipropyl ether

Structure	*chemical shift (ppm)*
RC**H**$_3$	0.8 - 1.2
R$_2$C**H**$_2$	1.1 - 1.5
R$_3$C**H**	~1.5
ArC**H**$_3$	2.2 - 2.5
R$_2$NC**H**$_3$	2.2 - 2.6
R$_2$C**H**OR	3.2 - 4.3
R$_2$C**H**Cl	3.5 - 3.7
RC(=O)C**H**R$_2$	2.0 - 2.7
RC**H**CR=CR$_2$	~1.7
RC=C**H**	4.9 - 5.9
Ar**H**	6.0 - 8.0
RC(=O)**H**	9.4 - 10.4
RCC**H**	2.3 - 2.9
R$_2$N**H**	2 - 4
RO**H**	1 - 6
ArO**H**	6 - 8
RCO$_2$**H**	10 - 12

ii) The position of the signals i.e. their chemical shift values, tells about the electronic environment of a particular proton. In the spectrum of dipropylether you can clearly note that difference in the chemical shift positions of two methylene groups. The methylene group attached to the oxygen atom is observed at 3.4 *ppm* while the other methylene group appears at 1.6 *ppm*. The chemical shifts of different types of protons are given in Fig. 8.1.

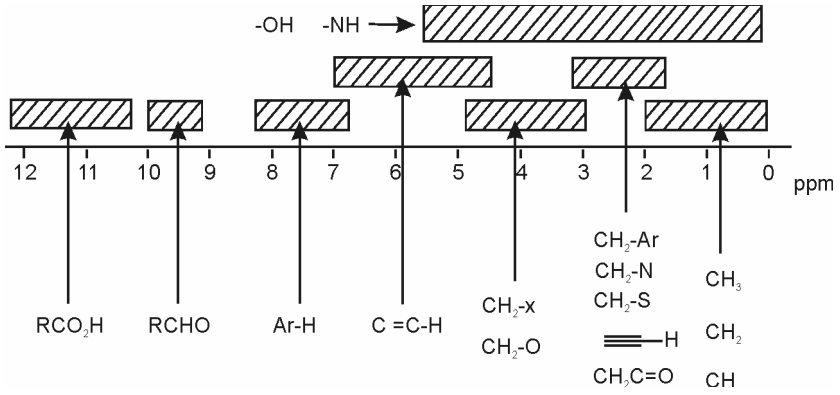


Fig. 8.1: Range of Chemical shift values for different types of protons

iii) The area under the peaks obtained from the integrals for the signals of various types of protons provides information about the ratio of the numbers of different types of protons present in a molecule. The areas under the signals in the spectrum given in Fig. 8.1 is in the ratio of 2:2:3 as indicated by the corresponding integrals.

iv) The spin-spin splitting pattern of a particular signal gives information about the number of neighbouring protons present around the given type of protons. In the spectrum of dipropyl ether you can clearly note that the splitting pattern is in

accordance with the n+1 rule. The methylene-2 protons signal splits into a multiplet due to the coupling with the neighbouring methyl and methylene group protons. In fact it is a triplet of quartrets that can be accounted for in terms of the sequential splitting of the methylene proton signal by the neighbours. On the other hand the methyl protons and the methylene-1 protons appear as triplets due to two neighbours.

Having learnt about the information available from the NMR we can now take up how to use it to arrive at the structure of a given compound. As mentioned in the previous experiment there is no unique way of interpreting a NMR spectrum, yet let us starts with some strategy outlined in the section 8.4.

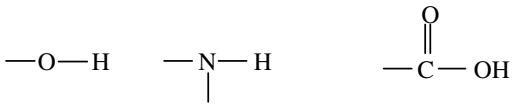
8.3 REQUIREMENTS

As mentioned in the introduction, the main objective of this experiment is to highlight the structure-spectrum relationships of organic molecules and formulate a strategy to interpret the NMR spectrum of some simple organic molecules. We intend to inculcate elementary skills in you so that you can take up the interpretation of the NMR spectrum of some simple molecules to determine their structure. Accordingly, we need some typical NMR spectra to be used as examples and some to be used as study problems.

8.4 GUIDELINES FOR INTERPRETATION OF NMR SPECTRA

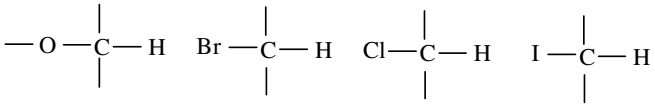
When you first look at an NMR spectrum, look for the important features before getting down to the minor details. Some of the important features that you should look for are:

1. First, if the molecular formula of the compound is known, determine the index of hydrogen deficiency (IHD) or the elements of unsaturation. This suggests about the presence of rings, or double or triple bonds.
2. Using the integrated peak areas and the number of protons in the molecular formula you can compute the numbers of protons represented by the individual peaks.
3. The broadened singles in the spectrum indicate towards the presence of –OH or –NH protons.

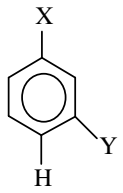


frequently broad singlets broad (or sharp) singlet, $\delta > 10$

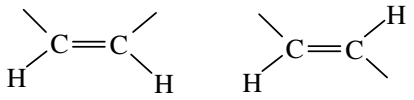
4. If the broad singlet is deshielded past 10 ppm, an acid –OH group is likely.
5. Absorptions around $\delta = 3$ to $\delta = 4$ are due to the protons on a carbon bearing an electronegative element like oxygen or a halogen. The relative position is determined by the distance form the elecltronegative atom; larger the distance lesser the deshielding.



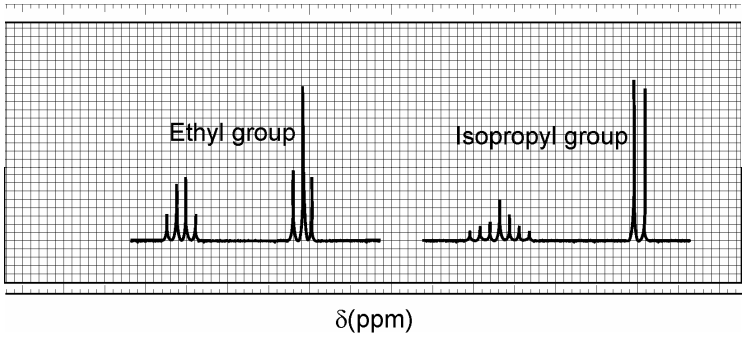
6. Benzene absorbs at 7.27 ppm. The absorptions in the range of $7-8\,ppm$ suggest the presence of an aromatic ring. If some of the aromatic absorptions are farther downfield than $\delta = 7.27$, this may be due to electron-withdrawing substituents.



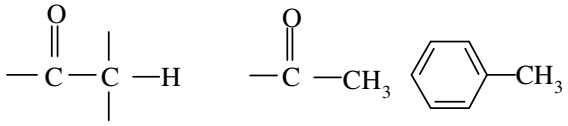
7. The signals around $\delta = 5$ to $\delta = 6$ suggest the presence of vinyl protons. The magnitude of coupling constants can be used to differentiate cis and trans protons



8. VThe ethyl and isopropyl groups (and structures that resemble these groups) have characteristic splitting patterns as shown below.



9. The absorptions in the region of $\delta = 2.1$ to $\delta = 2.5$ are indicative of the protons adjacent to a carbonyl group or an aromatic ring. A singlet at $\delta = 2.1$ often results from a methyl group bonded to a carbonyl group.



10. Absorptions in the range $\delta = 9$ to $\delta = 10$ ppm are characteristic of an aldehyde

11. A sharp singlet around $\delta = 2.5$ suggests the presence of a terminal alkyne.

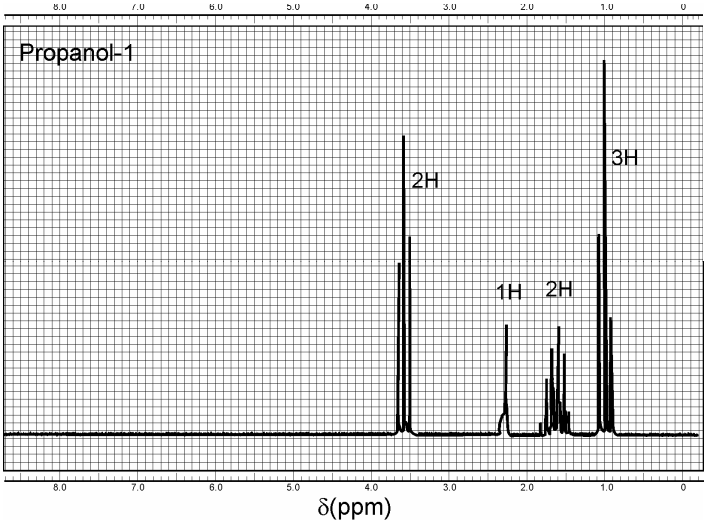
The guidelines outlined above are suggestive and are neither exact nor complete. These can be used for the preliminary approach to the interpretation of the NMR spectrum and helps in making educated guesses about the major features of a compound. The guesses can be used to draw partial structures of the molecule which can be suitably combined to get the overall structure of the molecule.

8.5 PRACTICE PROBLEMS

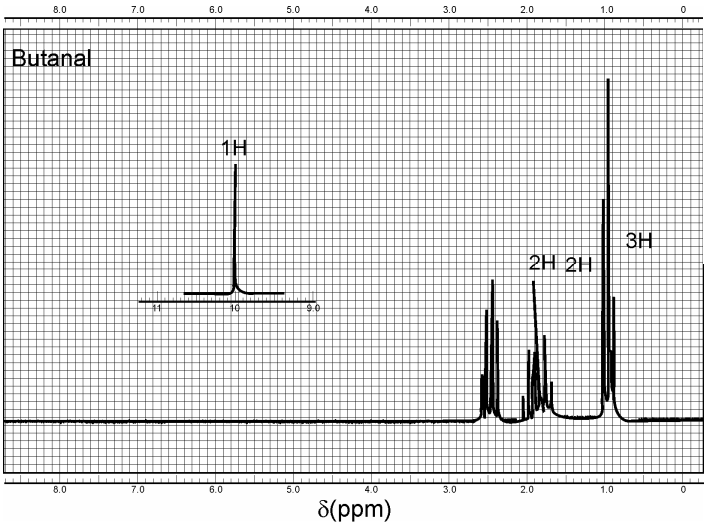
The NMR spectra of a few common organic molecules are given below. The number of protons responsible for the respective signals is suitably indicated. You may familiarise yourself with the nature of spectra and try to interpret the origin of different signals in the light of the suggestive guidelines given above.

The assignment of the characteristic peaks in these spectra is given at the end of the experiment. You may compare your interpretation with the one given there. Please do solve the problem before venturing into looking into the answers. You may proceed to the next section only after solving the practice problems and when you feel confident about taking up newer problems.

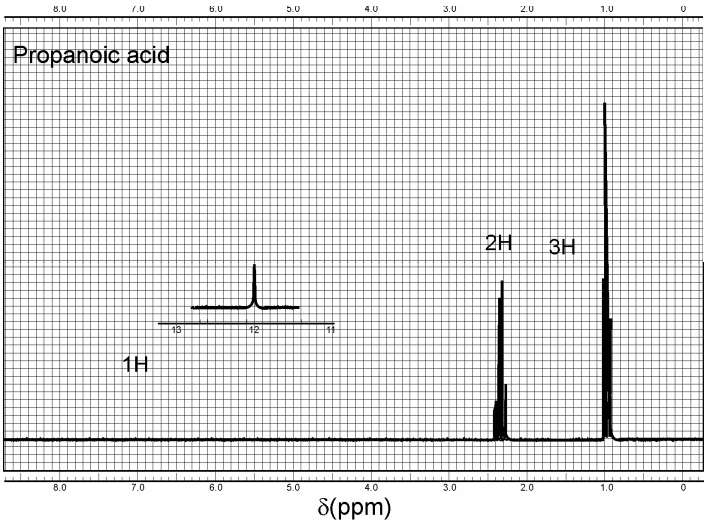
Practice spectrum 1



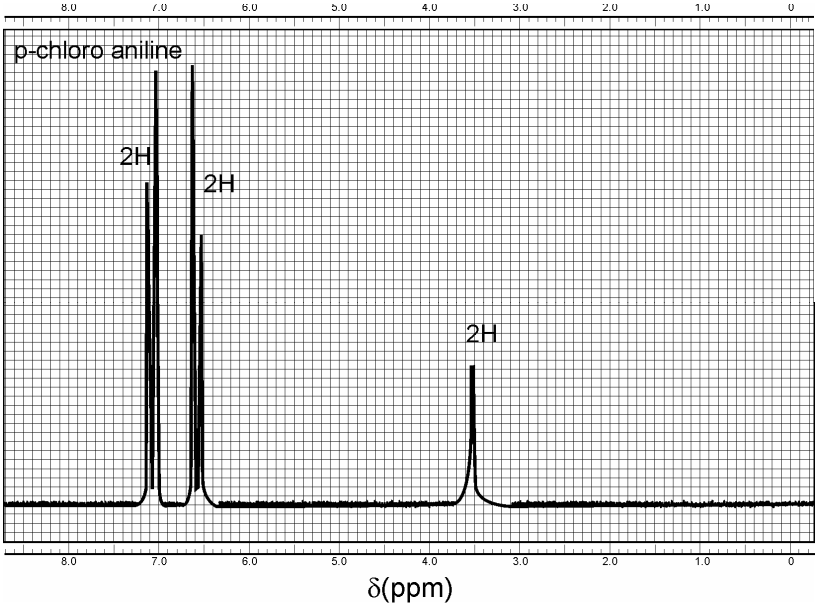
Practice spectrum 2



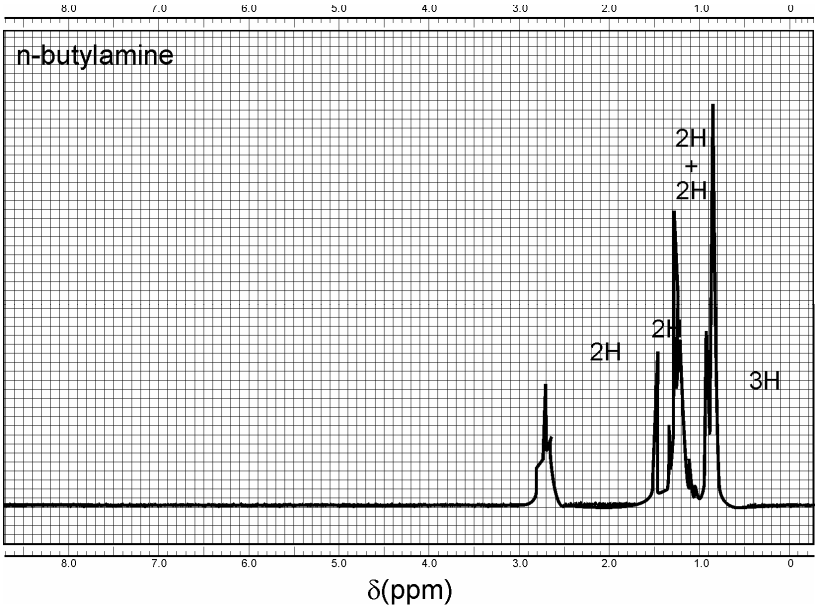
Practice spectrum 3



Practice spectrum 4



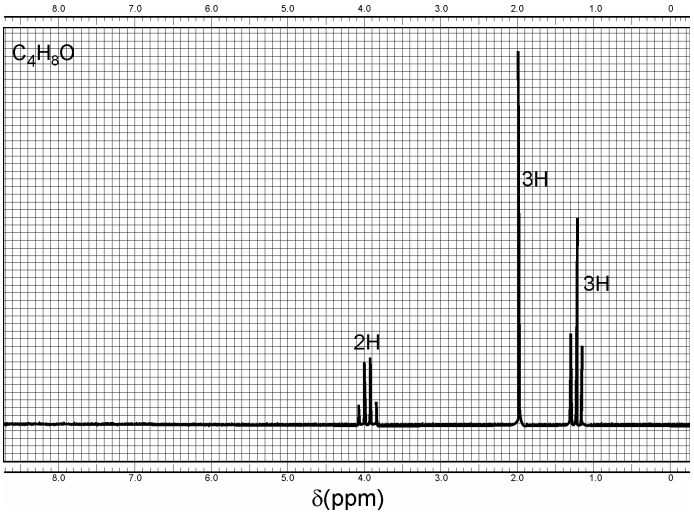
Practice spectrum 5



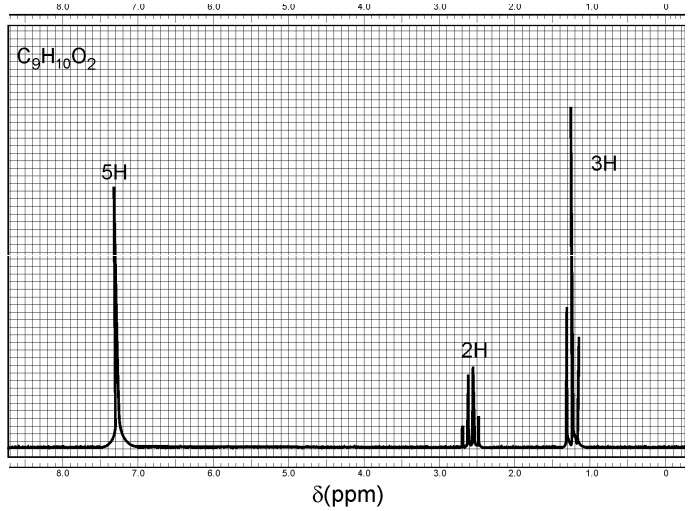
8.6 PROBLEMS FOR THE SESSION

Having solved the problems raised in the previous section we hope you are some what equipped to interpret the given NMR spectra of some simple organic molecule and determine the structure of the compound. You are provided with five spectra for interpretation. You may take the spectra in any sequence and try to interpret on the basis of the knowledge gained and the Table and other hints provided in the section 8.3. (Your counselor may provide you other NMR spectra of simple organic molecules to assess your understanding). You must pin up the spectra in the record book and submit your observations and results to your counsellor for evaluation.

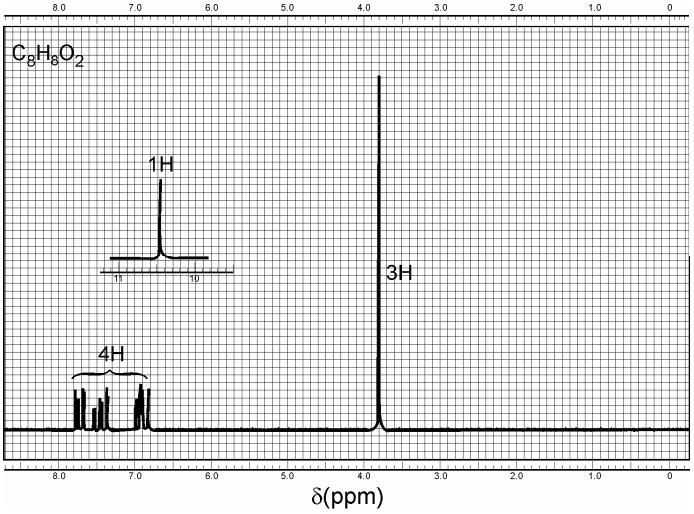
Session problem 1



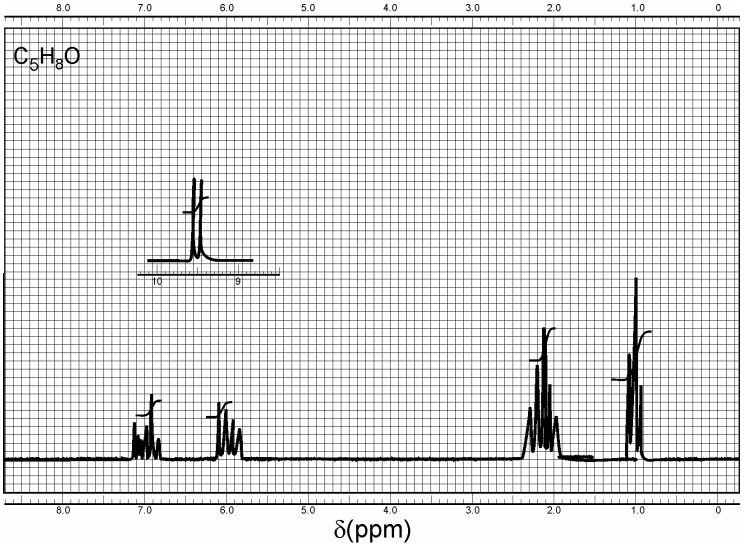
Session problem 2



Session problem 3



Session problem 4



8.7 SOLUTION TO PRACTICE PROBLEMS

Practice spectrum 1

δ = 0.94 1.57 3.58 2.26

CH_3—CH_2—CH_2—OH

Practice spectrum 2

δ = 0.97 1.64 2.37 9.67

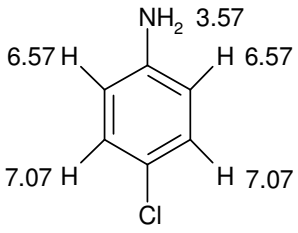
CH_3—CH_2—CH_2—CHO

Practice spectrum 3

δ = 1.16 2.38 11.73

CH_3—CH_2—COOH

Practice spectrum 4



Practice spectrum 5

δ = 0.92 1.33 1.43 2.68 1.77

CH_3—CH_2—CH_2—CH_2—NH_2