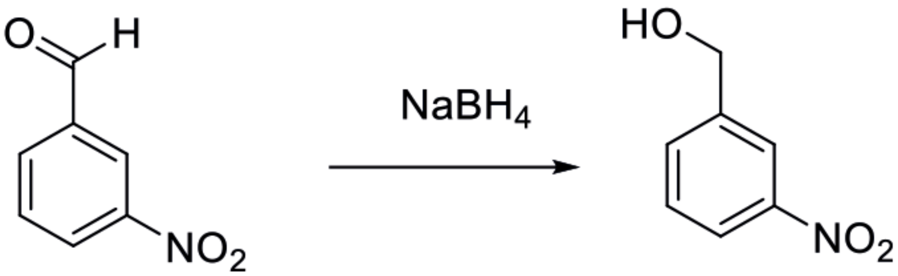
Analysis of the reduction product of 3-nitrobenzaldehyde using **Pulsar**

Dr Vittorio Caprio, Dr Oliver Sutcliffe and Dr Ryan Mewis, Manchester Metropolitan University

Introduction

Conversion of chemical functional groups from one to another is a mainstay of organic chemistry. It enables molecules to be produced that are more reactive for future reactions, for example, or to provide suitable functional groups so that molecules may be coupled together. An example of a functional group conversion is shown in Scheme 1. The reduction of the aldehyde group using sodium borohydride results in the production of an alcohol-containing product. The nitro functional group is unchanged during this chemical process.



Scheme 1 : Conversion of 3-nitrobenzaldehyde to 3-nitrobenzyl alcohol using sodium borohydride.

NMR spectroscopy is one of the main techniques used to confirm the conversion of the functional group. The collection of NMR spectra can also aid in the assessment of the purity of the isolated material by highlighting the presence of starting material and / or other products as a result of the reaction. For aromatic systems, Shoolery's rules can be used to predict the relative chemical shifts of ^{1}H and ^{13}C nuclei of the ring, provided that substituent groups are not located *ortho* to one another. These values are tabulated and readily available for aromatic systems as well as others. Thus, the spectroscopist can begin to construct an idea of how the resulting spectrum will present itself prior to collecting it.

This application note is concerned with analysing the reactant and product as shown in Scheme 1 using ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Shoolery's rules are employed to predict the appearance of the resulting ^{1}H and ^{13}C NMR spectra. The reaction represents a typical undergraduate experiment and as such, exemplifies that students can collect their own ^{1}H and ^{13}C{^{1}H} NMR data of their starting material and product and subsequently analyse and interpret it to gain insight in to the reaction conducted.

Results

^{1}H NMR

The Shoolery predicted aromatic ^{1}H NMR chemical shifts are shown in Table 1. The conversion of the aldehyde group, an electron-withdrawing group, to a methyl alcohol, an electron-donating group, will result in distinct changes in the ^{1}H NMR spectrum. Consequently, the chemical shifts of the aromatic protons are up-field shifted relative to the reactant. The shifts are such that they will be readily observable in the ^{1}H NMR spectrum.

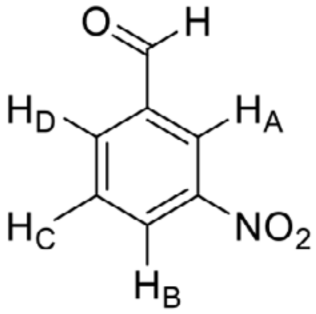
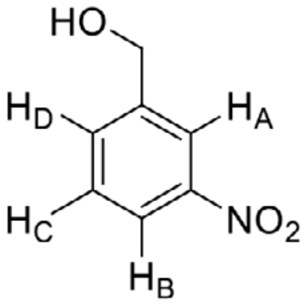
	Reactant 			Product 		
	Substituent constant for $-NO_2$	**Substituent constant for –CHO**	**Predicted δ (ppm)**	**Substituent constant for $-NO_2$**	**Substituent constant for $-CH_2OH$**	**δ**
H_A	0.95	0.58	8.80	0.95	–0.07	8.15
H_B	0.95	0.27	8.49	0.95	–0.07	8.15
H_C	0.17	0.21	7.65	0.17	–0.07	7.37
H_D	0.33	0.58	8.18	0.33	–0.07	7.53

Table 1 : Predicted values for the ring ^1H NMR chemical shift environments of the reactant and product using Shoolery's rules. Shoolery's rules states that for aromatic protons $\delta = 7.27 + \Sigma S_i$ where S_i are the substituent constants

The ^1H NMR spectrum of the reactant, 3-nitrobenzaldehyde, is shown in Figure 1. The aldehyde proton is present at δ 10.14. Despite the aromatic region being crowded, it is possible to integrate the region to give a 3 : 1 ratio (regions 8.57 – 8.20 ppm and 7.91 – 7.65 ppm respectively). In comparison to the predicted chemical shifts as listed in Table 1, this integral ratio corresponds accordingly. The peak that presents as a triplet at δ 7.78 has a coupling constant of 7.8 Hz. It also shows strong second order effects. A further two doublets, which both show second order coupling, are observed at δ 8.50 and 8.27; they possess J-coupling of 8.4 and 7.8 Hz respectively. This is of the same magnitude as the peak at δ 7.78 and therefore, these peaks are coupled with one another. Thus, these peaks are assigned as being H_B (δ 8.50) and H_D (δ 8.27). This leaves a singlet at δ 8.70. The absence of coupling and that it is the most down-shifted aromatic peak leads to the conclusion that this peak is H_A in the starting material. By reference to Table 1, the chemical shift values deduced from Figure 1 correspond strongly with those calculated using Shoolerys' rules.

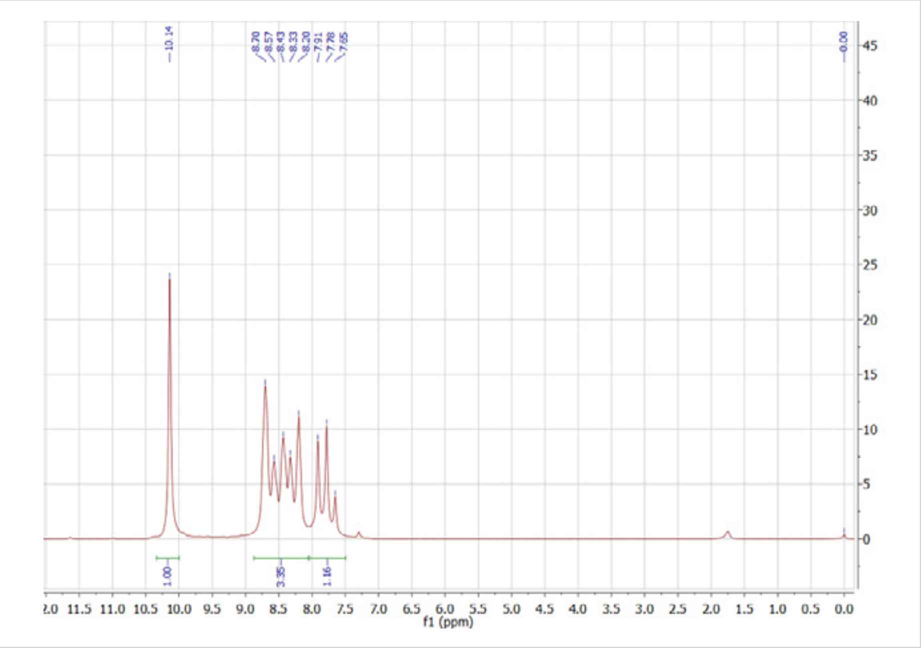
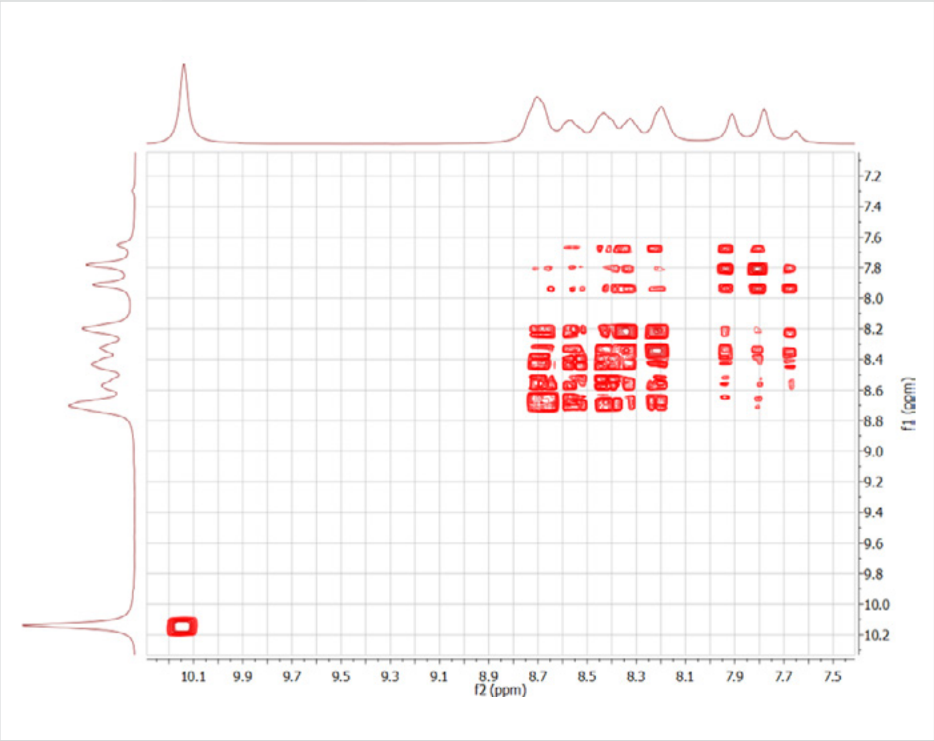


Figure 1 : ^1H NMR spectrum of 3-nitrobenzaldehyde in $CDCl_3$ collected at 60 MHz.

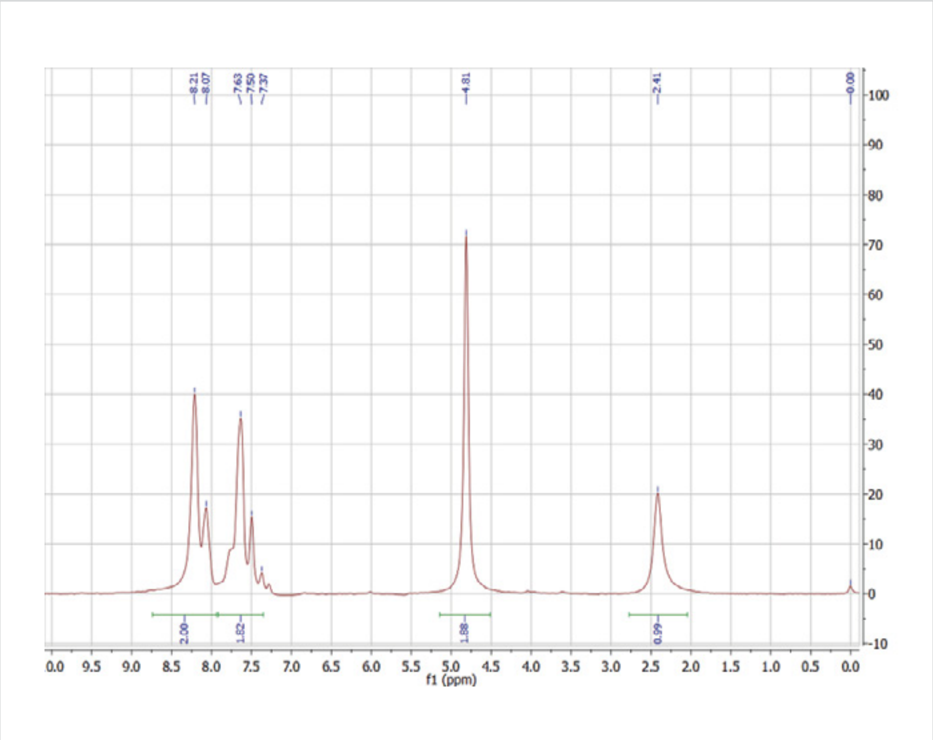
The COSY spectrum of 3-nitrobenzaladehyde is shown in Figure 2. This shows the complex coupling that is present between the four aromatic ^1H nuclei. However, upon closer inspection it is noticeable that the peak at δ 8.70 shows minimal interaction with the other peaks whereas the other peaks all display strong coupling to one another. This confirms that one of the aromatic proton nuclei, H_A, is isolated from the remainder protons in the aromatic ring.



The ^1H NMR spectrum of the product, 3-nitrobenzyl alcohol possesses four protons in the aromatic region (integrated to give a 2 : 2 ratio), a CH_2 peak at 4.81 ppm and an OH peak at 2.41 ppm. The latter two peaks result due to the reduction of the aldehyde; the peak for the aldehyde proton is no longer visible in the ^1H NMR spectrum.

Figure 2 : ^1H-^1H COSY NMR spectrum of 3-nitrobenzaldehyde in $CDCl_3$ collected at 60 MHz. The spectrum has been truncated to focus on only the aromatic and aldehyde regions

The ^1H-^1H COSY spectrum of 3-nitrobenzyl alcohol provides good insight in to the coupling between proton nuclei. In particular, there are COSY interactions between the peak centred at 8.21 and 7.63 ppm, and also between peaks at 7.63 and 7.50 ppm. Because of the connectivity that the peak at 7.63 ppm shows, this must be the H_C-resonance. The peaks at 8.21 and 7.63 are H_B and H_D respectively. The peak at 8.07 ppm shows no COSY interaction and is, therefore, the peak responsible for H_A. Thus, the values obtained for the ^1H NMR chemical shifts for the aromatic protons are δ 8.07, 8.21, 7.63 and 7.50 for H_A-H_D respectively.



These again compare well against the predicted Shoolery values given in Table 1 and integrate accordingly in the ^1H NMR spectrum (Figure 3). This deduction would not have been possible using the ^1H NMR spectrum shown in Figure 3 due to the convoluted nature of the aromatic region.

Figure 3 : ^1H NMR spectrum of 3-nitrobenzyl alcohol in $CDCl_3$ collected at 60 MHz.

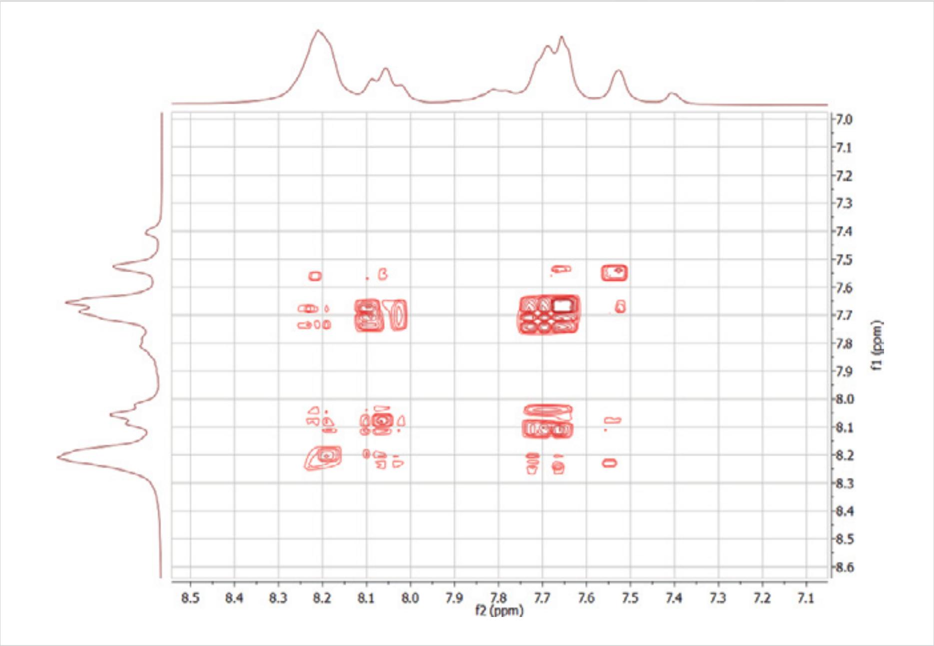


Figure 4 : ^1H-^1H COSY NMR spectrum of 3-nitrobenzyl alcohol in $CDCl_3$ collected at 60 MHz. The spectrum has been truncated to focus on only the aromatic region

Figure 5 shows the overlaid ^1H NMR data obtained for the reactant and product. In this figure, the up-field shift of the aromatic protons is visible for the product relative to the reactant. This change is brought about through the conversion of an electron-withdrawing group (aldehyde) to one that is electron donating (CH_2OH). The reduction, therefore, not only changes the chemical identity of the molecule but also the electronic effects within the ring system. The signals created and lost as a result of the reduction of the aldehyde to the methyl alcohol are readily apparent, due largely to the significant difference in terms of chemical shift and because the remainder of the ^1H nuclei are all aromatic protons.

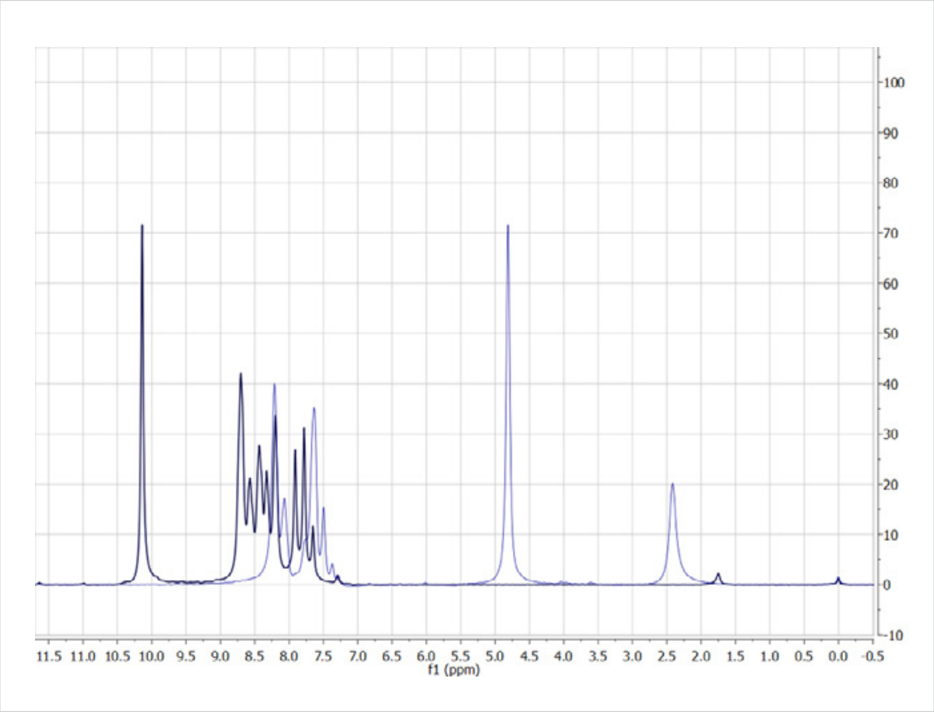


Figure 5 : Overlaid ^1H NMR spectra of 3-nitrobenzaldehyde (dark blue) and 3-nitrobenzyl alcohol (light blue) in $CDCl_3$ collected at 60 MHz.

^{13}C NMR

The chemical shifts of the aromatic ^{13}C nuclei can be predicted similarly using Shoolery's rules. Table 2 lists the predicted and experimentally determined ^{13}C NMR peaks for the aromatic ^{13}C nuclei of the reactant and product

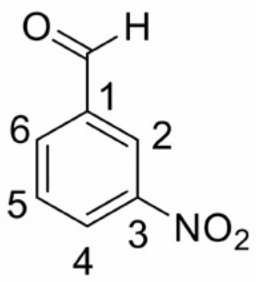
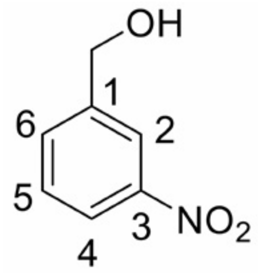
	Reactant 		**Product** 	
^{13}C nucleus	**Predicted δ / ppm**	**Experimental δ / ppm**	**Predicted δ / ppm**	**Experimental δ / ppm**
1	138.2	137.6	142.5	143.2
2	124.3	124.3	122.3	121.3
3	149.2	145.0	147.4	148.2
4	129.1	128.6	122.7	122.3
5	130.4	130.6	128.6	129.5
6	135.6	134.9	133.6	132.8

Table 2 : Predicted and experimentally determined chemical shift values for the aromatic ^{13}C nuclei of the reactant and product using Shoolery's rules. Shoolery's rules states that for aromatic protons δ = 128.4 + ΣS_i where S_i are the substituent constants

In general, there is good agreement between the theoretical and experimental chemical shift data for both compounds. As was seen for the ^{1}H nuclei , there is a shift up-field for all the ^{13}C chemical shifts of the product relative to the reactant, with the exception of carbon 1, which displays a down-field shift. In addition to the data contained within Table 2, the reactant possesses a peak at δ 189.9 for the aldehyde carbon and the product has a peak at δ 63.4 for the CH_2 carbon.

For both substances, the quaternary carbons display as peaks with a low intensity; this is due to the elongated T_1 values that they possess relative to the other ^{13}C environments coupled with the relatively short relaxation delay that is used in the experiment (1 s). The ^{13}C{^{1}H} NMR spectra of the reactant and product are shown in Figures 6 and 7 respectively.

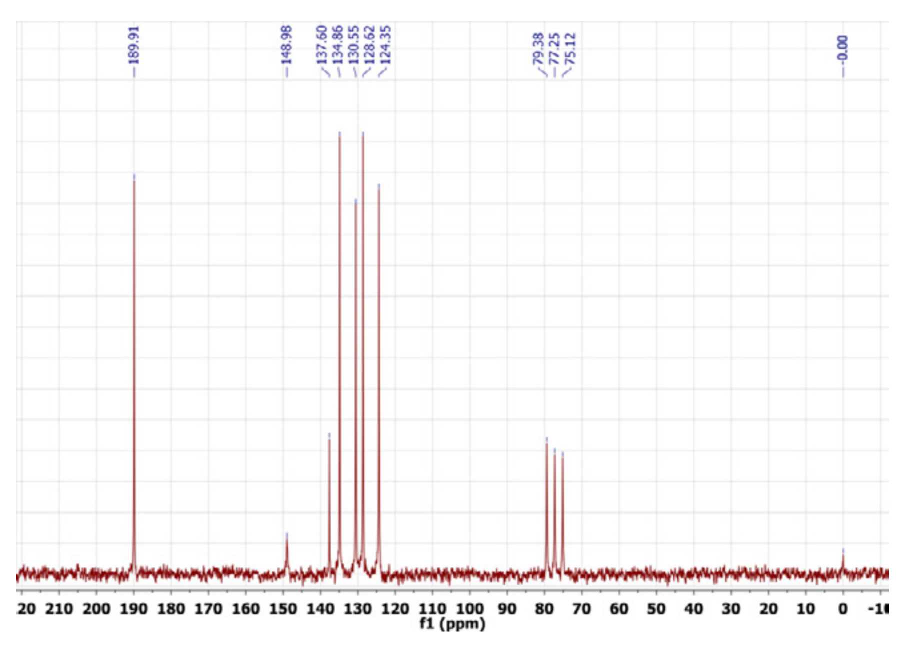


Figure 6: ^{13}C{^{1}H} NMR spectrum of 3-nitrobenzaldehyde collected in $CDCl_3$.

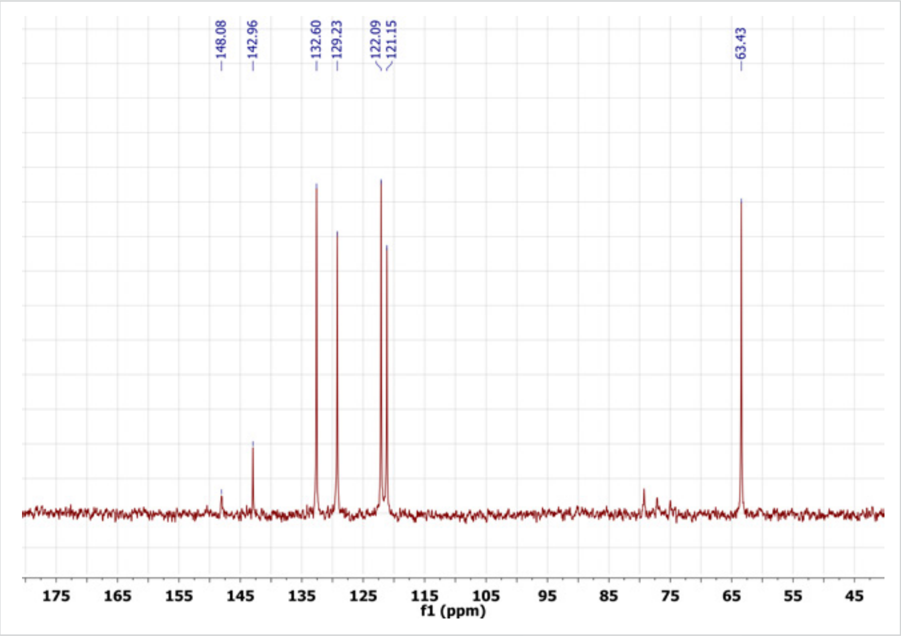


Figure 7: $^{13}C\{^1H\}$ *NMR spectrum of 3-nitrobenzyl alcohol collected in* $CDCl_3$

Conclusion

The **Pulsar** system is capable of being used to track an organic reaction, for example, as detailed herein, a hydride mediated reduction. The spectra that are obtained contain sufficient information to be used by undergraduate students to elucidate the chemical structure of their reaction product by reference to the starting material. Laboratory instructors can probe students understanding, through reference to the ^1H and $^{13}C\{^1H\}$ NMR spectra collected, of the electron-withdrawing / electron-donating effects upon the shielding experienced by the aromatic proton nuclei. The utilisation of Shoolerys' rules enable students to predict the appearance of the resulting ^1H and $^{13}C\{^1H\}$ NMR spectra, from which they can validate the identity of the product produced.

For more information visit: **www.oxinst.com/pulsar** or email: **magres@oxinst.com**

OXFORD INSTRUMENTS

The Business of Science®