

## Practice problems on the NMR of amino acids

Test your ability to correlate NMR spectra with structure by trying the following problems.

Use the correlation tables, the relative sizes of the signal, electronegativity and the number of signals and logic to connect the structures with the spectra.

NMR units are ppm (parts per million). We discuss where this ppm unit comes from in class.

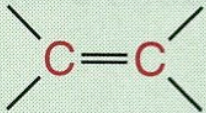
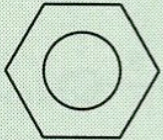
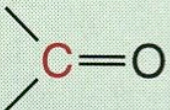
**TABLE 13.1**

Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift ( $\delta$ ), ppm*	Type of proton	Chemical shift ( $\delta$ ), ppm*
$\text{H}-\text{C}-\text{R}$	0.9–1.8	$\text{H}-\text{C}-\text{NR}$	2.2–2.9
$\text{H}-\text{C}-\text{C}=\text{C}$	1.6–2.6	$\text{H}-\text{C}-\text{Cl}$	3.1–4.1
$\text{H}-\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$	2.1–2.5	$\text{H}-\text{C}-\text{Br}$	2.7–4.1
$\text{H}-\text{C}\equiv\text{C}-$	2.5	$\text{H}-\text{C}-\text{O}$	3.3–3.7
$\text{H}-\text{C}-\text{Ar}$	2.3–2.8	$\text{H}-\text{NR}$	1–3†
$\text{H}-\text{C}=\overset{\diagup}{\text{C}}\diagdown$	4.5–6.5	$\text{H}-\text{OR}$	0.5–5†
$\text{H}-\text{Ar}$	6.5–8.5	$\text{H}-\text{OAr}$	6–8†
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-$	9–10	$\text{H}-\overset{\text{O}}{\parallel}{\text{O}}\text{C}-$	10–13†

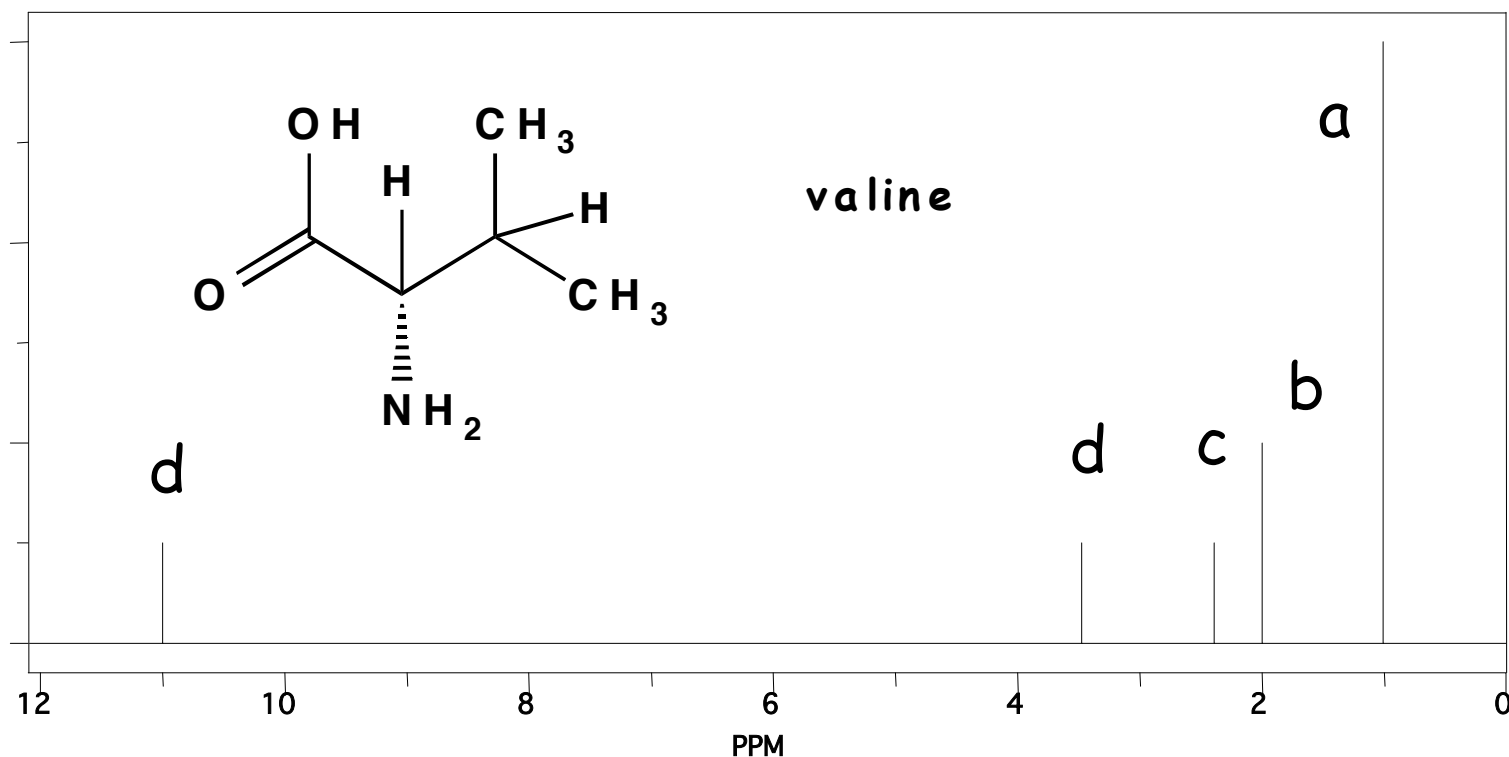
These are the signals of protons ( $^1\text{H}$  NMR). We think of the position (in ppm) of the NMR signals in the same way we viewed the frequency of IR signals. The  $^1\text{H}$  NMR signals are characteristic of certain types of protons in molecules

**TABLE 13.3**  
**Chemical Shifts of Representative Carbons**

Type of carbon	Chemical shift ( $\delta$ ) ppm*	Type of carbon	Chemical shift ( $\delta$ ) ppm*
RCH <sub>3</sub>	0–35		100–150
R <sub>2</sub> CH <sub>2</sub>	15–40		110–175
RCH <sub>2</sub> Br	20–40		190–220
R <sub>3</sub> CH	25–50		
RCH <sub>2</sub> Cl	25–50		
RCH <sub>2</sub> NH <sub>2</sub>	35–50		
RCH <sub>2</sub> OH	50–65		
—C≡C—	65–90		

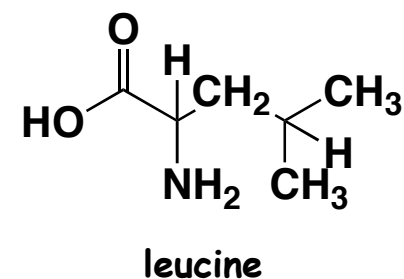
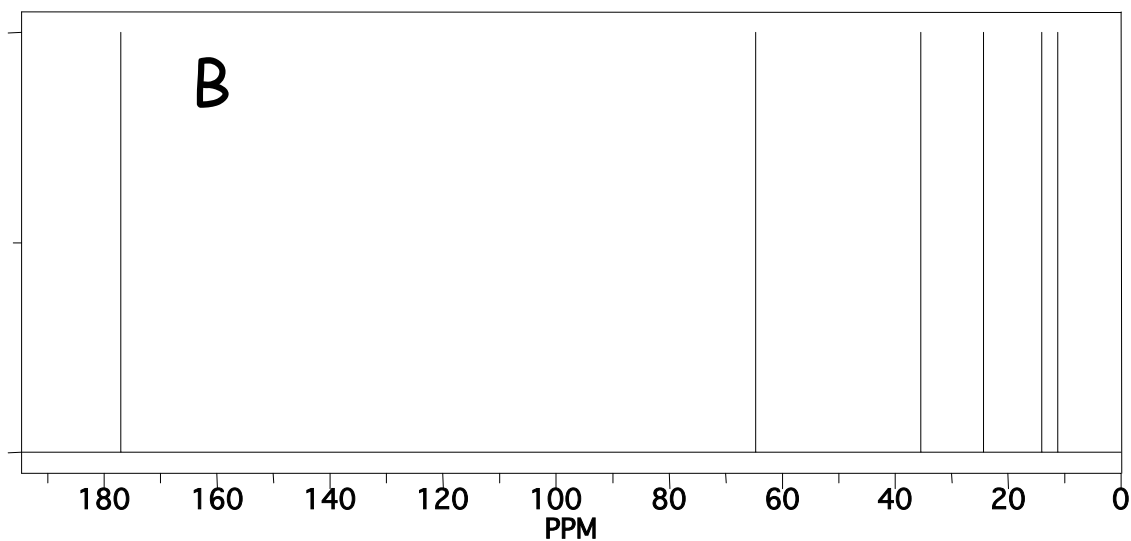
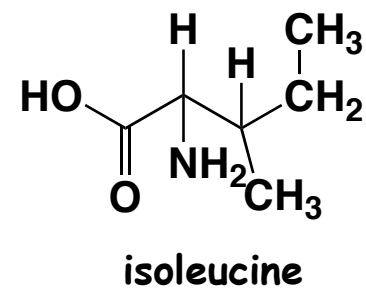
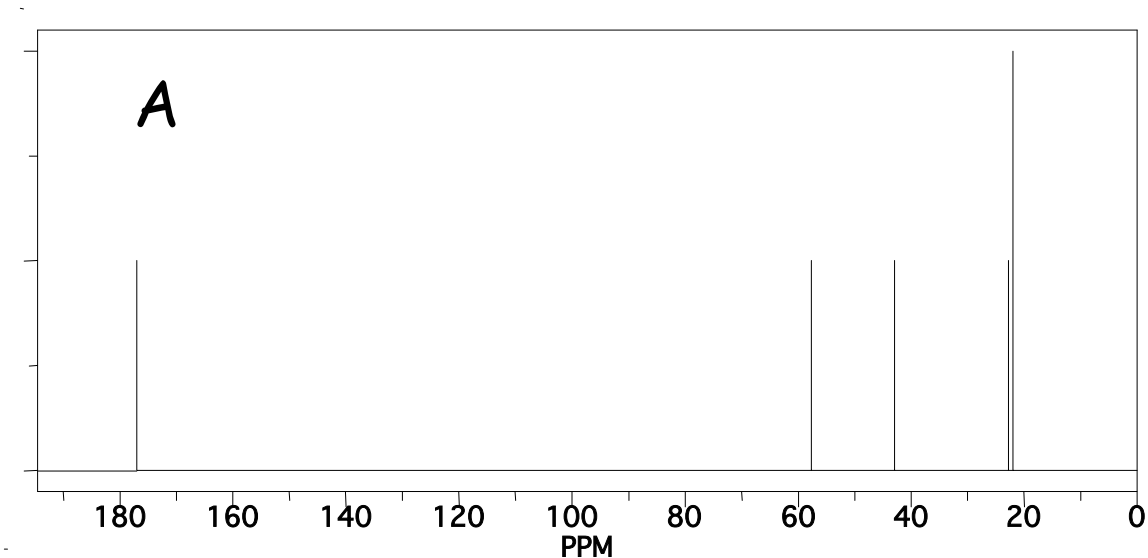
These are the position of the signals of carbon atoms (<sup>13</sup>C) in ppm. We think of the position of a NMR signal in ppm in the same way we viewed the frequency of IR signals. The <sup>13</sup>C NMR signals are characteristic of certain types of carbon atoms in molecules.

The  $^1\text{H}$  NMR of the amino acid valine is given below. Assign the protons of valine to the signals (a, b, c, d and e) in the NMR spectrum.

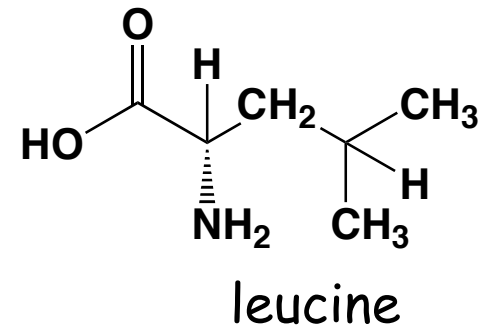
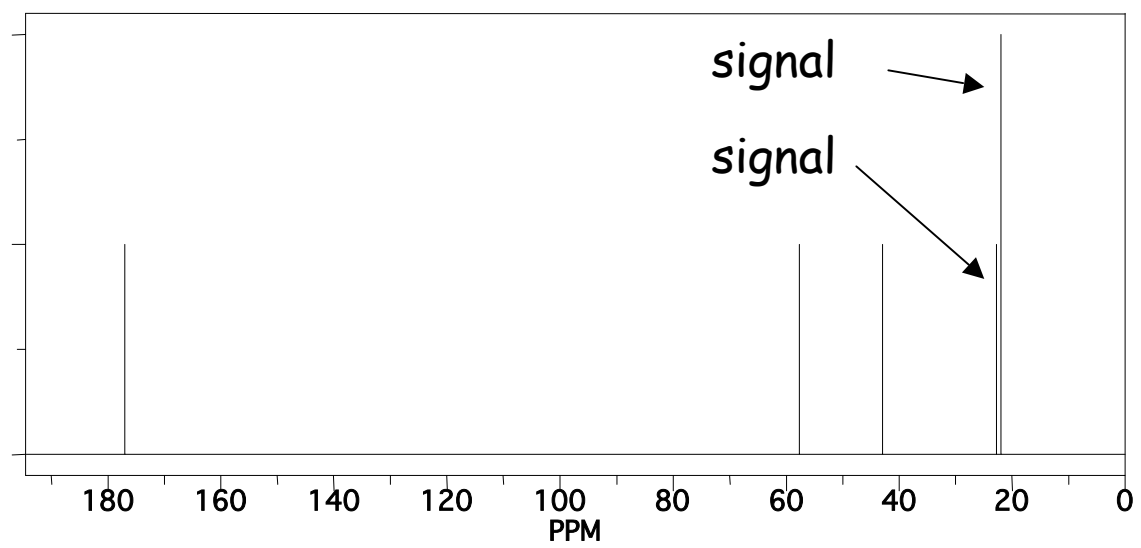
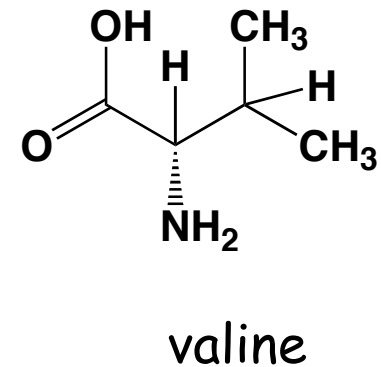
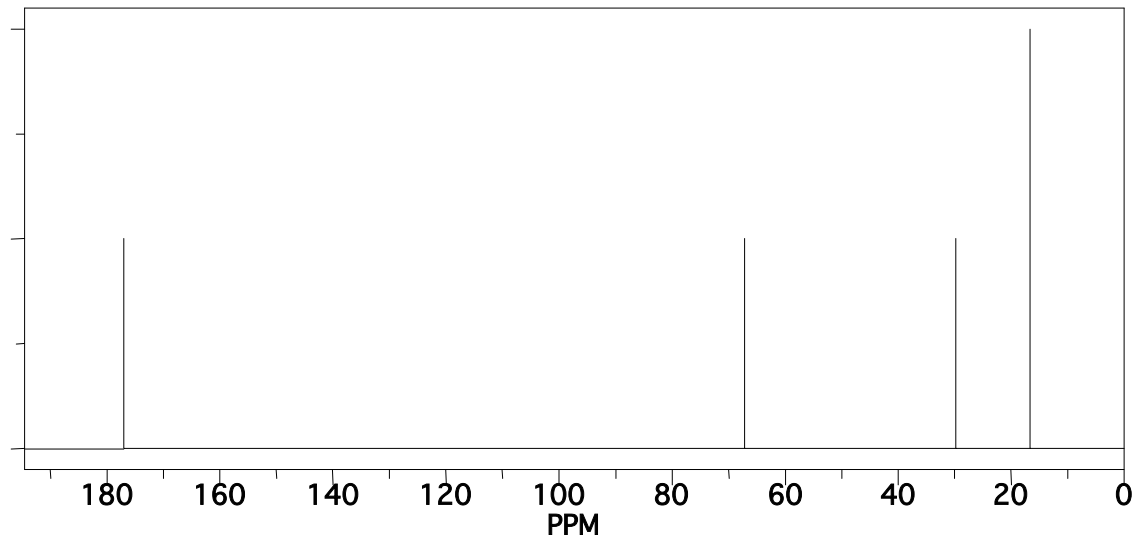


The answer is at the end of the ppt

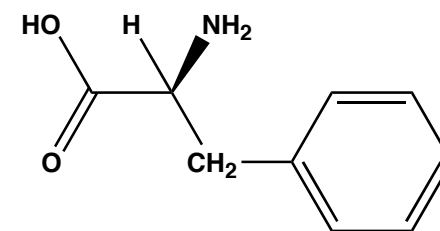
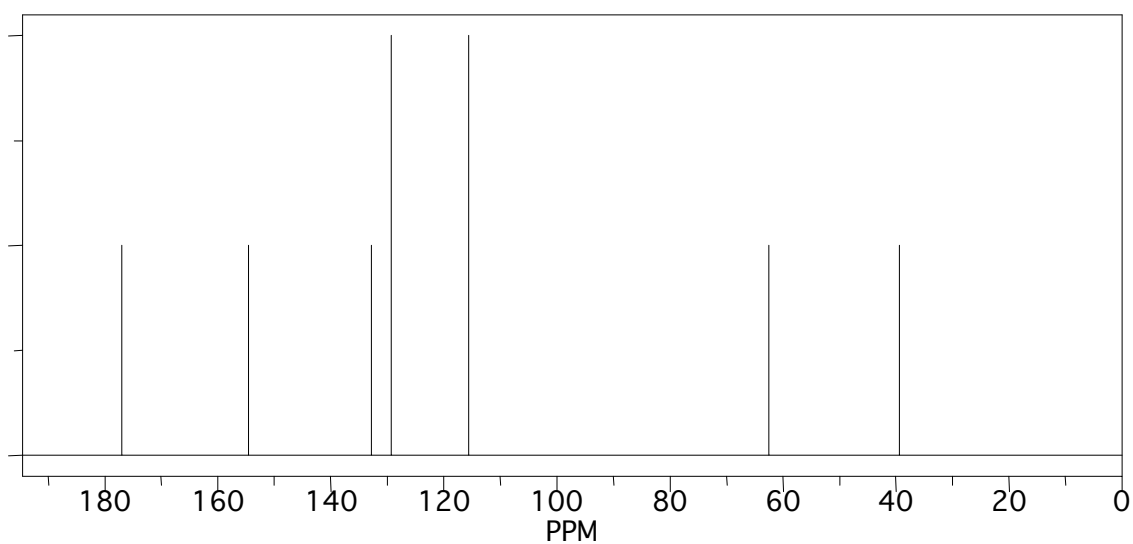
Leucine and isoleucine are isomers.  
 Two  $^{13}\text{C}$  NMR spectra A and B are shown below.  
 One is leucine the other is isoleucine. Which is which?



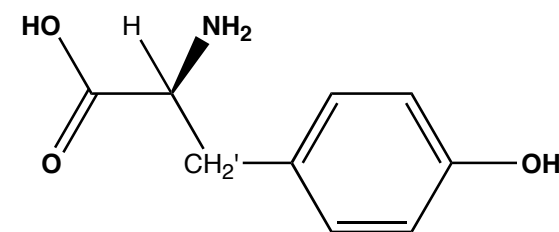
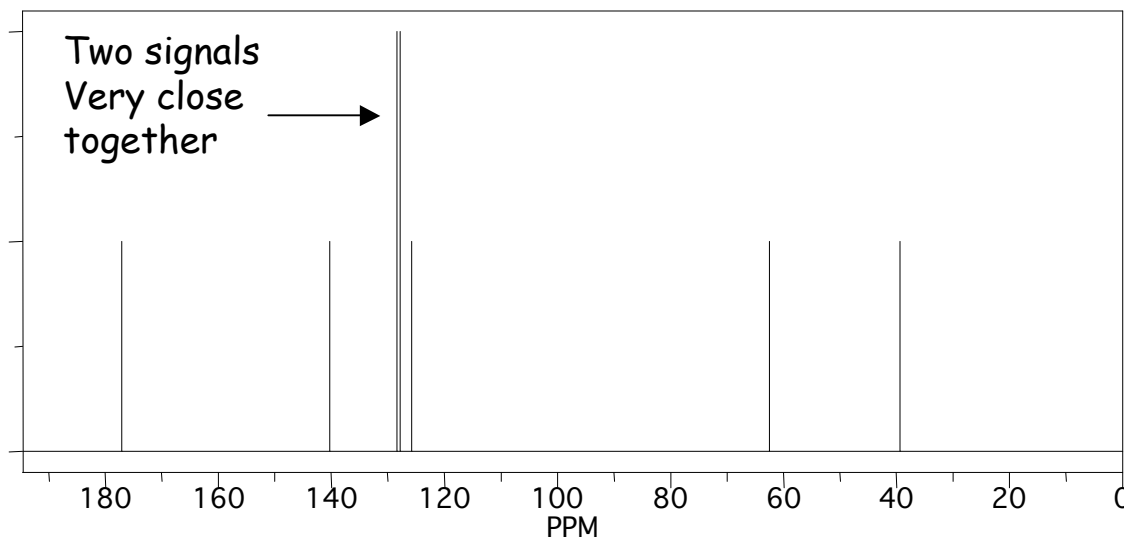
The  $^{13}\text{C}$  NMR spectrum of valine and leucine are shown.  
Which is valine and which is leucine?



The  $^{13}\text{C}$  NMR spectrum of phenylalanine and tyrosine (both possess aromatic rings) are shown. Which is phenylalanine and which is tyrosine?

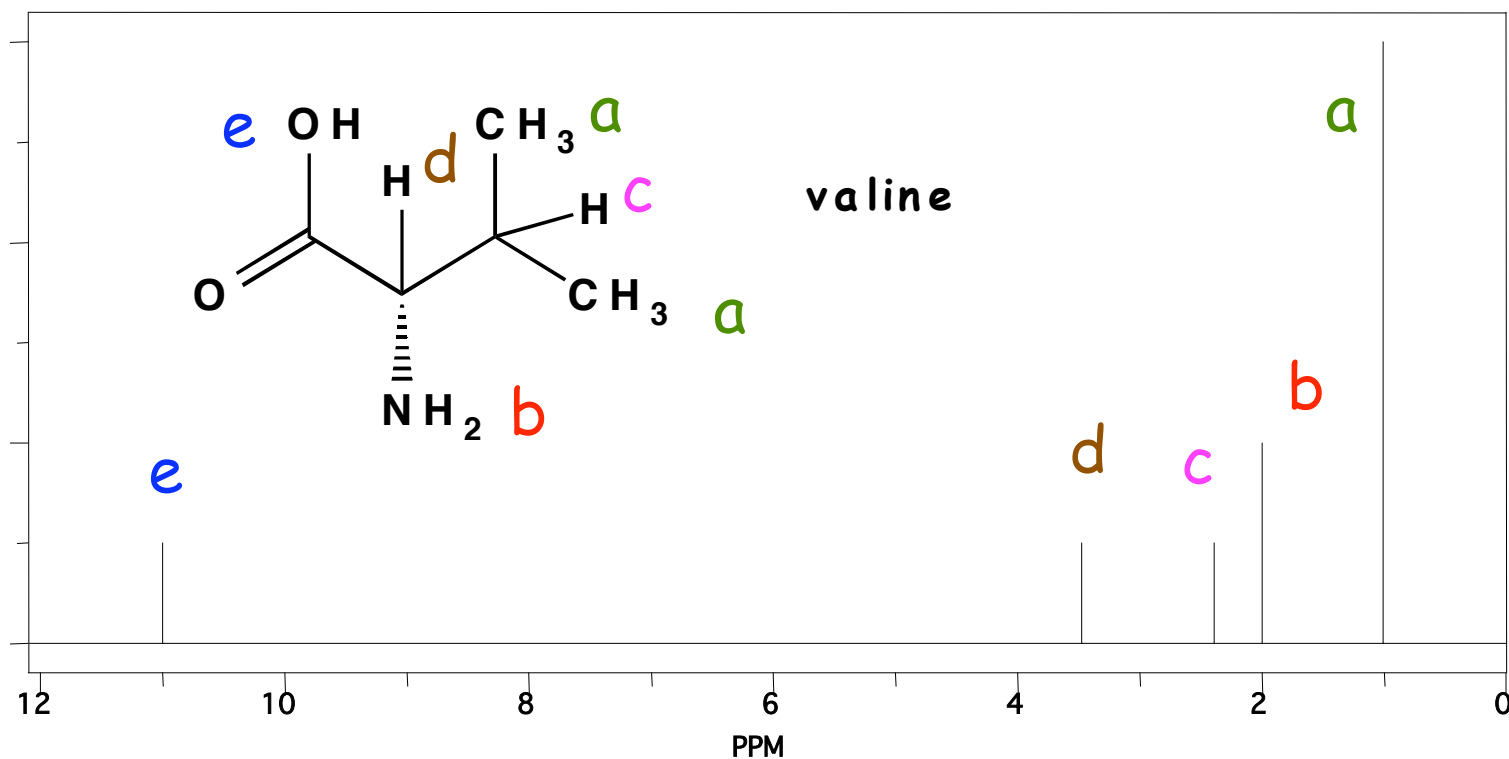


phenylalanine



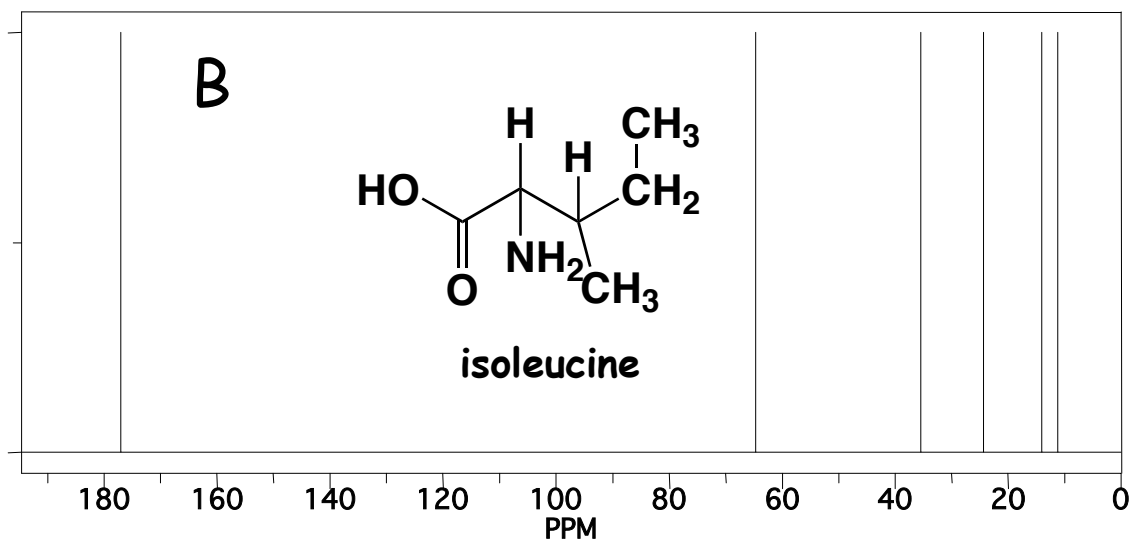
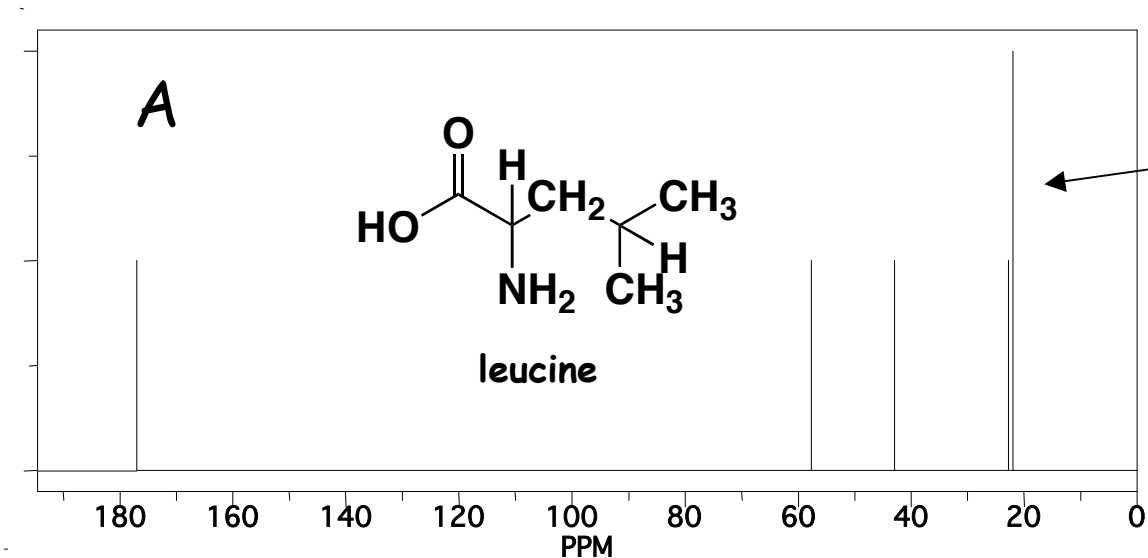
tyrosine

The  $^1\text{H}$  NMR of the amino acid valine is given below. Assign the protons of valine to the signals in the NMR spectrum.

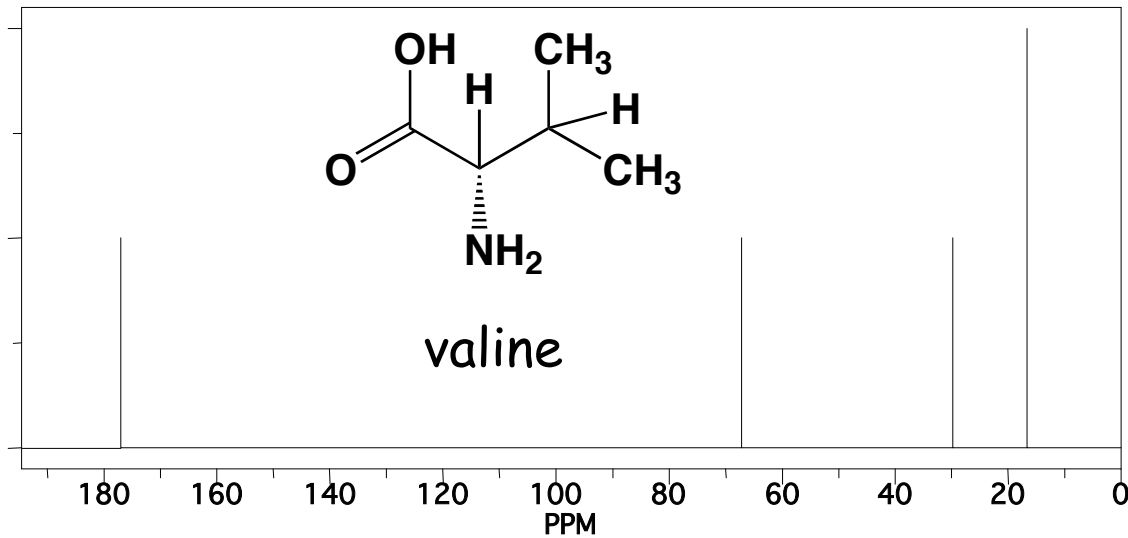




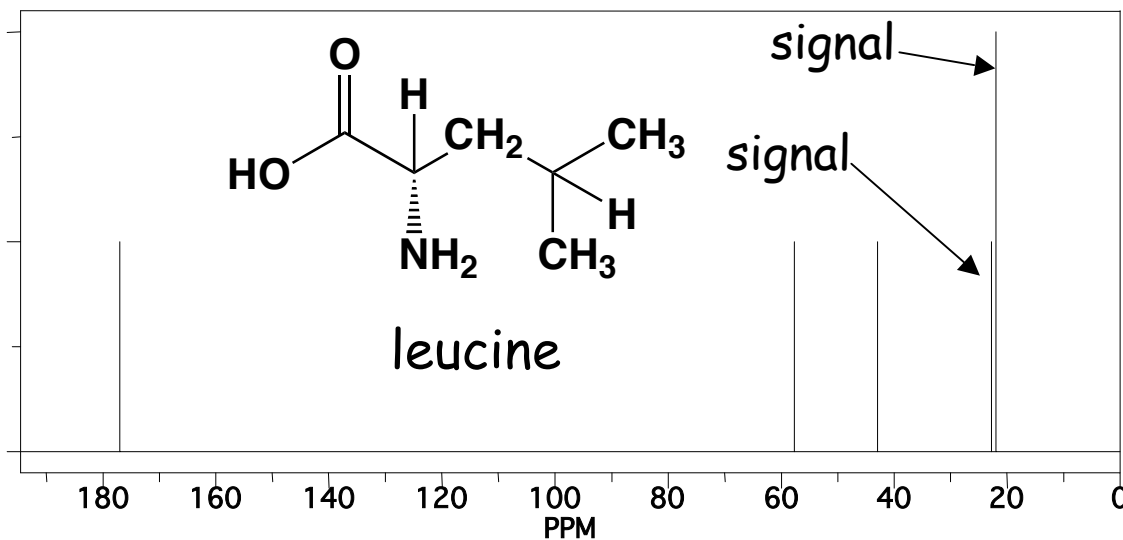
Leucine and isoleucine are isomers.  
 Two  $^{13}\text{C}$  NMR spectra A and B are shown below.  
 One is leucine the other is isoleucine. Which is which?



The  $^{13}\text{C}$  NMR spectrum of valine and leucine are shown.  
Which is valine and which is leucine?



An essential difference between valine and leucine is that leucine has one more carbon atom. In the bottom spectrum the  $\text{CH}_2$  carbon atom of leucine is just to the left of the  $\text{CH}_3$  carbon atom.



The  $^{13}\text{C}$  NMR spectrum of phenylalanine and tyrosine (both possess aromatic rings) are shown. Which is phenylalanine and which is tyrosine?

The most significant difference between the two structures is the OH on the benzene ring of the tyrosine. This substituent will cause the carbons of the benzene ring of tyrosine to be much more different chemically than those of phenylalanine. This difference will also be reflected in the differences in the separation of the carbon signal in the NMR

