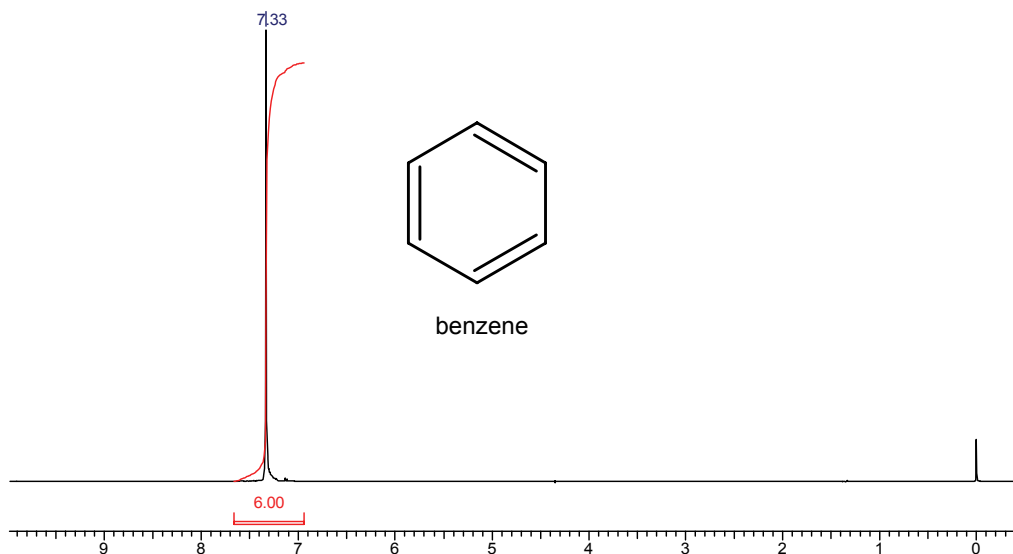


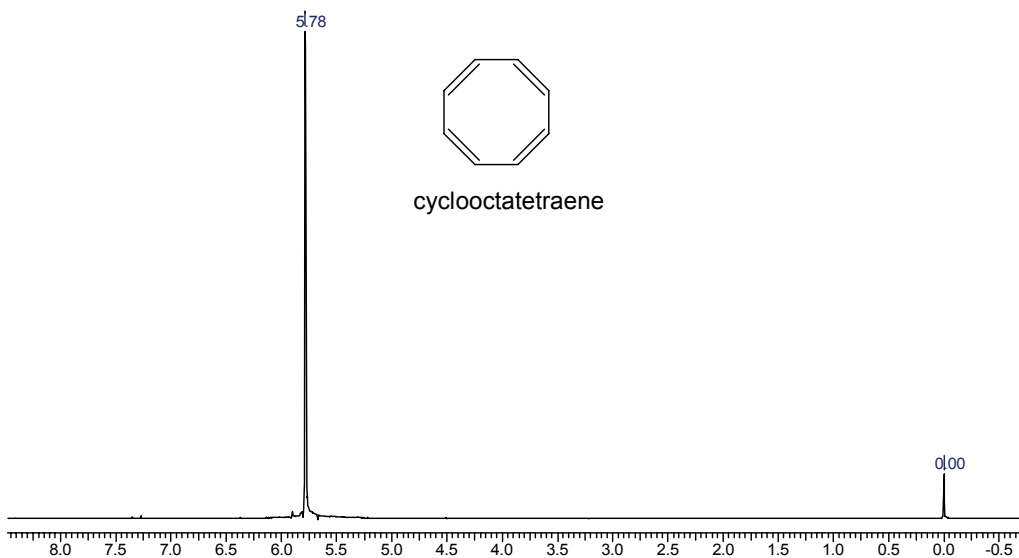
## NMR Spectroscopy of Aromatic Compounds (#1e)

### $^1\text{H}$ NMR Spectroscopy of Aromatic Compounds

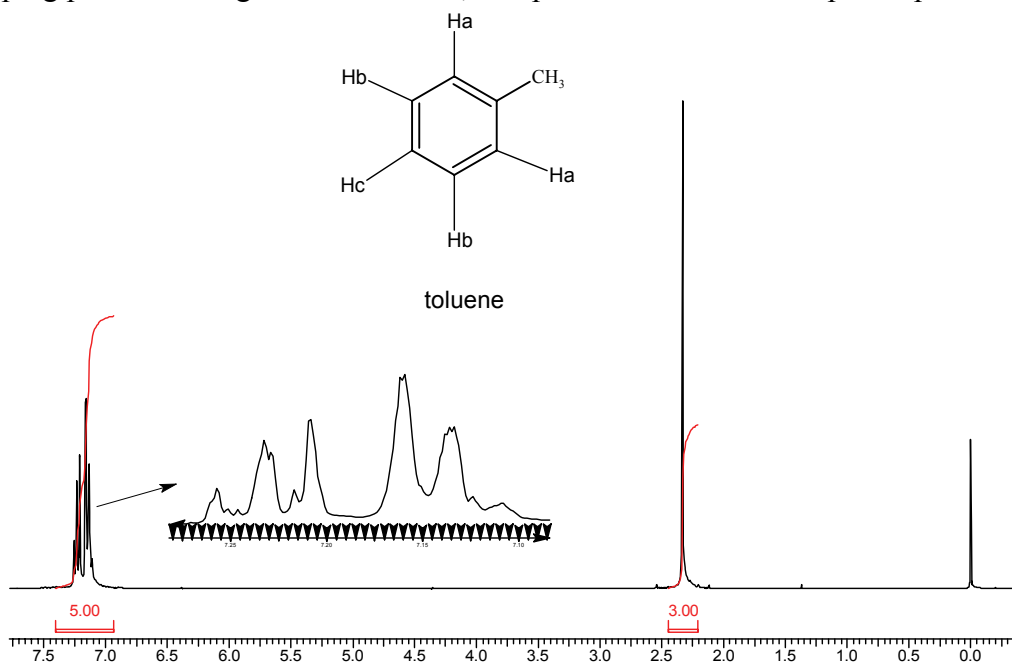
Erich Hückel's study of aromaticity in the 1930s produced a set of rules for determining whether a compound is aromatic. According to the Hückel criteria, a molecule must be cyclic, nearly planar, possess a p orbital on each carbon, and have  $4n + 2 \pi$  electrons, where  $n$  is an integer. These factors allow one to label a molecule as "aromatic," giving the molecule some special reactive characteristics that will be discussed in detail in your Chemistry 302 lecture. For now, the classic example of an aromatic compound is benzene, seen below with its  $^1\text{H}$  NMR spectrum.



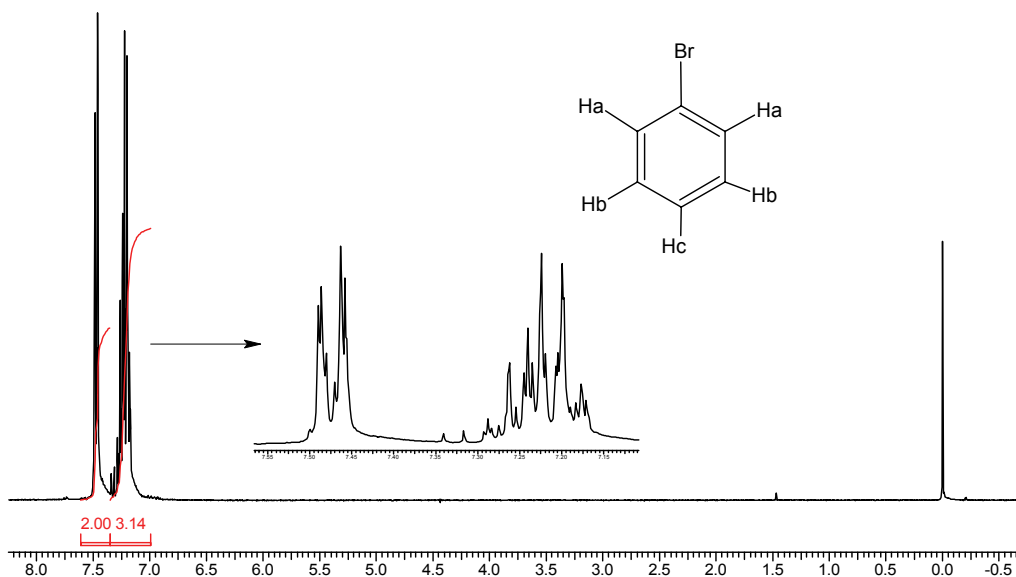
In aromatic compounds like benzene, the protons on the aromatic ring are shifted downfield. For example, the six protons in benzene are magnetically and chemically equivalent and appear at 7.33 ppm. This is farther downfield than alkene protons, which appear between 4.5-6.5 ppm. NMR serves as a useful tool to determine whether a compound is aromatic. For example, the protons in cyclooctatetraene ( $\text{C}_8\text{H}_8$ ), which is shown below, appear at 5.78 ppm indicating it is in the typical alkene region, not the aromatic region near 7 ppm.



If a hydrogen atom on the benzene ring is replaced with a different substituent, such as a methyl group, some of the hydrogens become magnetically inequivalent. For example, in the compound toluene, there are three different kinds of hydrogens on the benzene ring. The hydrogens neighboring the methyl ( $H_a$ ) are magnetically inequivalent to the hydrogens two carbons away from the methyl ( $H_b$ ) and the hydrogen directly across the ring from the methyl group ( $H_c$ ).  $H_a$ ,  $H_b$ , and  $H_c$  all couple to each other and have  $J$  values that correlate with the number of bonds between coupling protons.  $H_a$  and  $H_b$  are *ortho* to one another (adjacent);  $J_{ortho} = 6-10$  Hz.  $H_a$  and  $H_c$  are *meta* to one another (two carbons apart);  $J_{meta} = 1-3$  Hz. Although there is not an example in this molecule, if two protons are three carbons apart, they are *para*;  $J_{para} = 0-1$  Hz. As you can see, the  $J$  value decreases as the number of bonds between hydrogens increases. The peak for the aromatic protons is a complex multiplet as a result of the many  $J$  values and overlapping peaks. With greater resolution, it is possible to see these separate peaks.

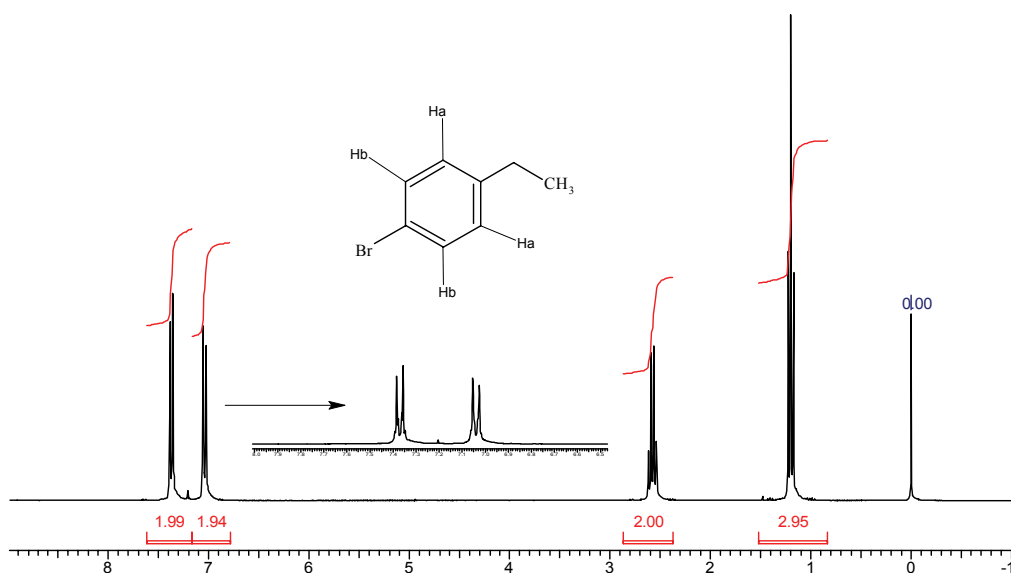


If the monosubstituted benzene contains an electron-withdrawing group such as Br, Cl or  $OCH_3$ , the protons adjacent to the electron-withdrawing group will be shifted slightly downfield of the other aromatics, producing separate peaks. The NMR of bromobenzene is shown below. Notice the peaks that are shifted downfield (7.4-7.5 ppm). These  $H_a$  couple to  $H_b$  ( $J_{ortho} = 6-10$  Hz) which results in a doublet. The doublet is further split by coupling to  $H_c$  with a very small  $J$  value ( $J_{para} \sim 0-1$  Hz).



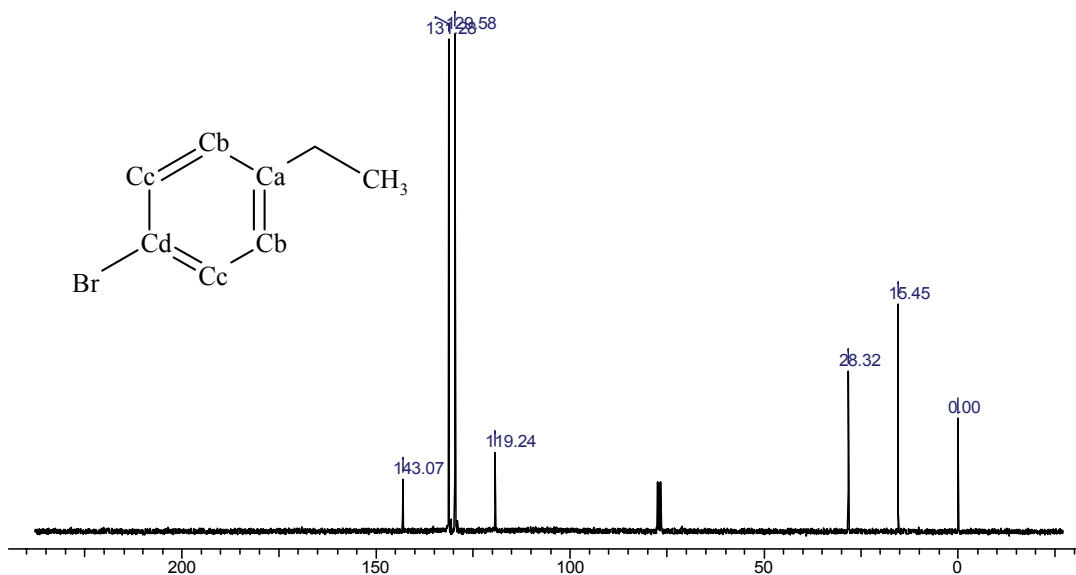
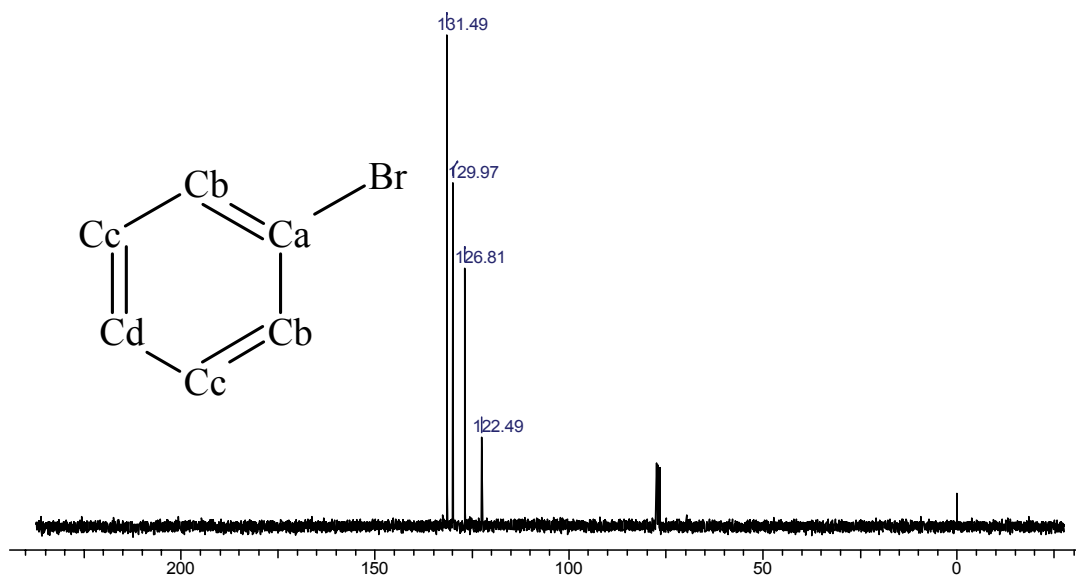
For disubstituted benzenes, the aromatic peaks are often separated as with bromobenzene. There are a few exceptions. For instance, the compound *para*-dimethylbenzene will have only a singlet in the aromatic region because all of the hydrogens are magnetically equivalent due to the symmetry in the molecule. This will be true of any *para*-disubstituted benzene having two identical substituents. However, *ortho*-dimethylbenzene will have separated aromatic peaks.

An important splitting pattern that identifies a specific type of substituted benzene is that of a *para*-disubstituted benzene having two substituents with different electron-withdrawing effects. An example is shown below with *para*-bromoethylbenzene. The distinctive pattern is the pair of doublets, which can be widely spaced or close together depending on the groups on the ring. This pair of doublets is only seen with a *para*-disubstituted benzene, not *ortho*- or *meta*-disubstituted benzenes. The latter display much more complex patterns.



### <sup>13</sup>C NMR Spectroscopy of Aromatic Compounds

As with other <sup>13</sup>C NMR spectra, aromatic compounds display single lines for each unique carbon environment in a benzene ring. Aromatic carbons appear between 120-170 ppm. The <sup>13</sup>C NMR spectra of bromobenzene and *p*-bromoethylbenzene are shown below for comparison. There are four different carbon environments in bromobenzene, and four different peaks. Similarly, for *p*-bromoethylbenzene, four environments appear but the pattern of the peaks is quite different and more separated. Note that one of the carbons appears much farther downfield at 143 ppm.



DEPT spectra can also be obtained for aromatics; as with earlier examples, CH's appear as upright singlets in the DEPT-90 and DEPT-135. Quaternary carbons appear in the proton decoupled spectra but not in DEPT spectra.

## Postlab

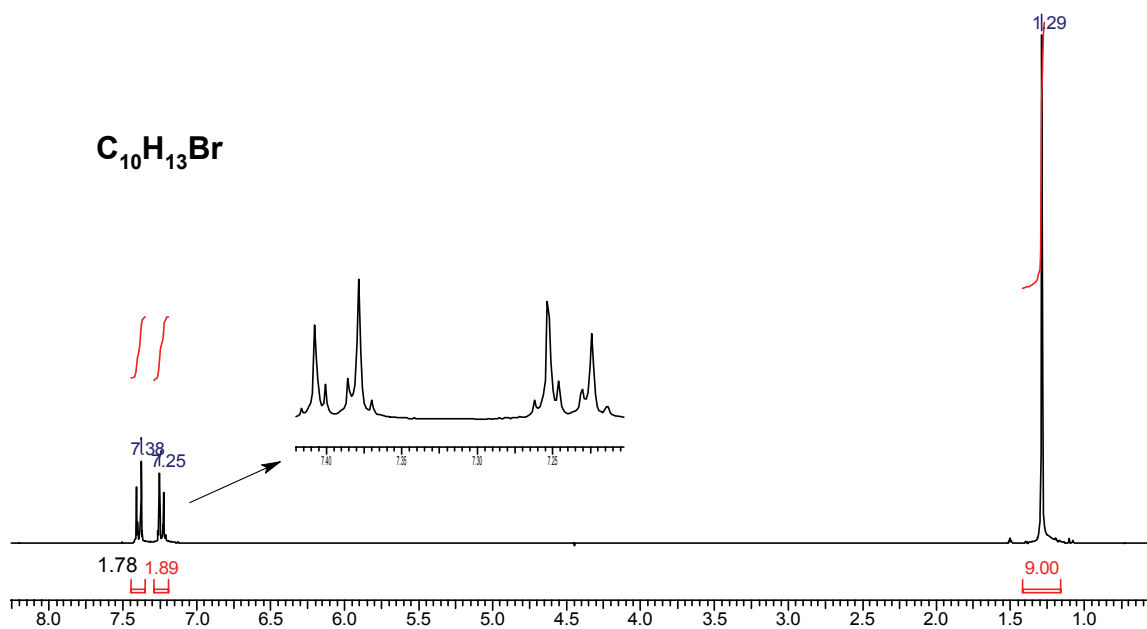
You should complete the following assignment in your lab notebook along with the other spectroscopy assignments. A table of  $^1\text{H}$  chemical shifts is located on page 43.

1. How many separate peaks would be observed in the  $^{13}\text{C}$  spectra of the following compounds?

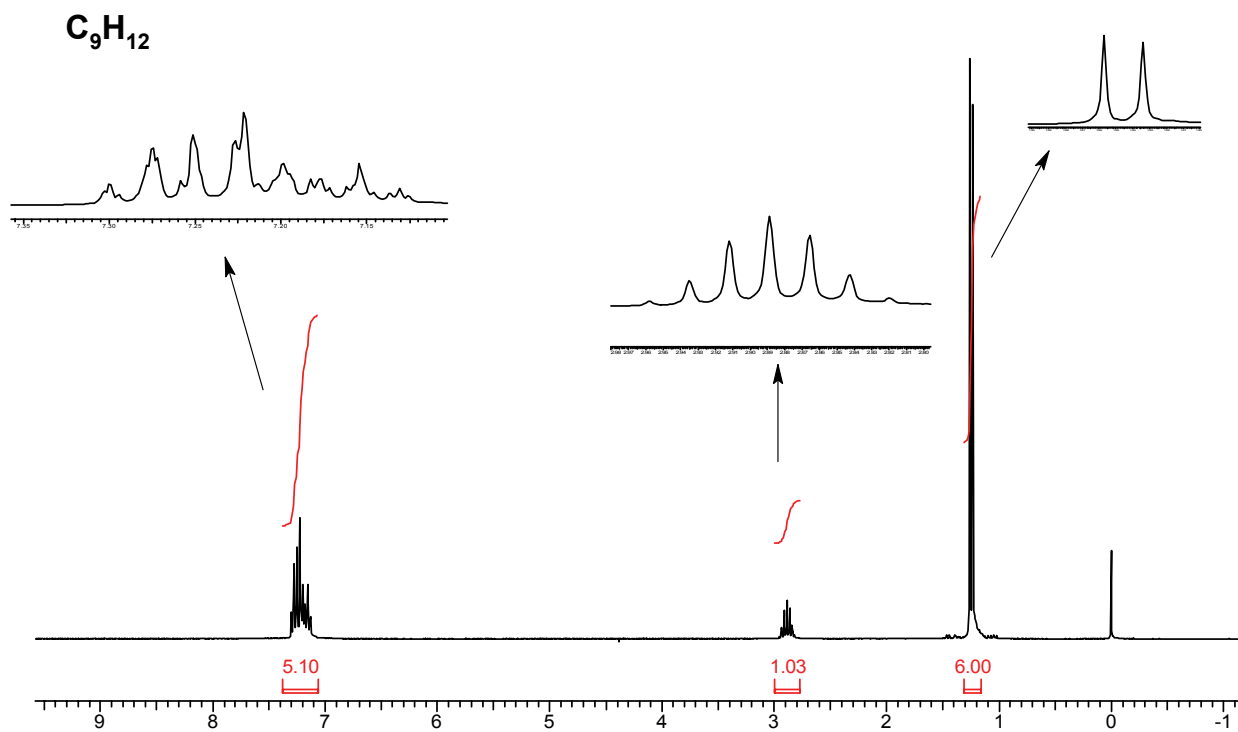
- 1,2-dinitrobenzene
- 1,3-dinitrobenzene
- 1,4-dinitrobenzene

2. Propose structures for the compounds that would be expected to generate the following  $^1\text{H}$  NMR spectra. Calculate the degree of unsaturation of each compound and assign the protons to their respective peaks.

A.



B.



C.

