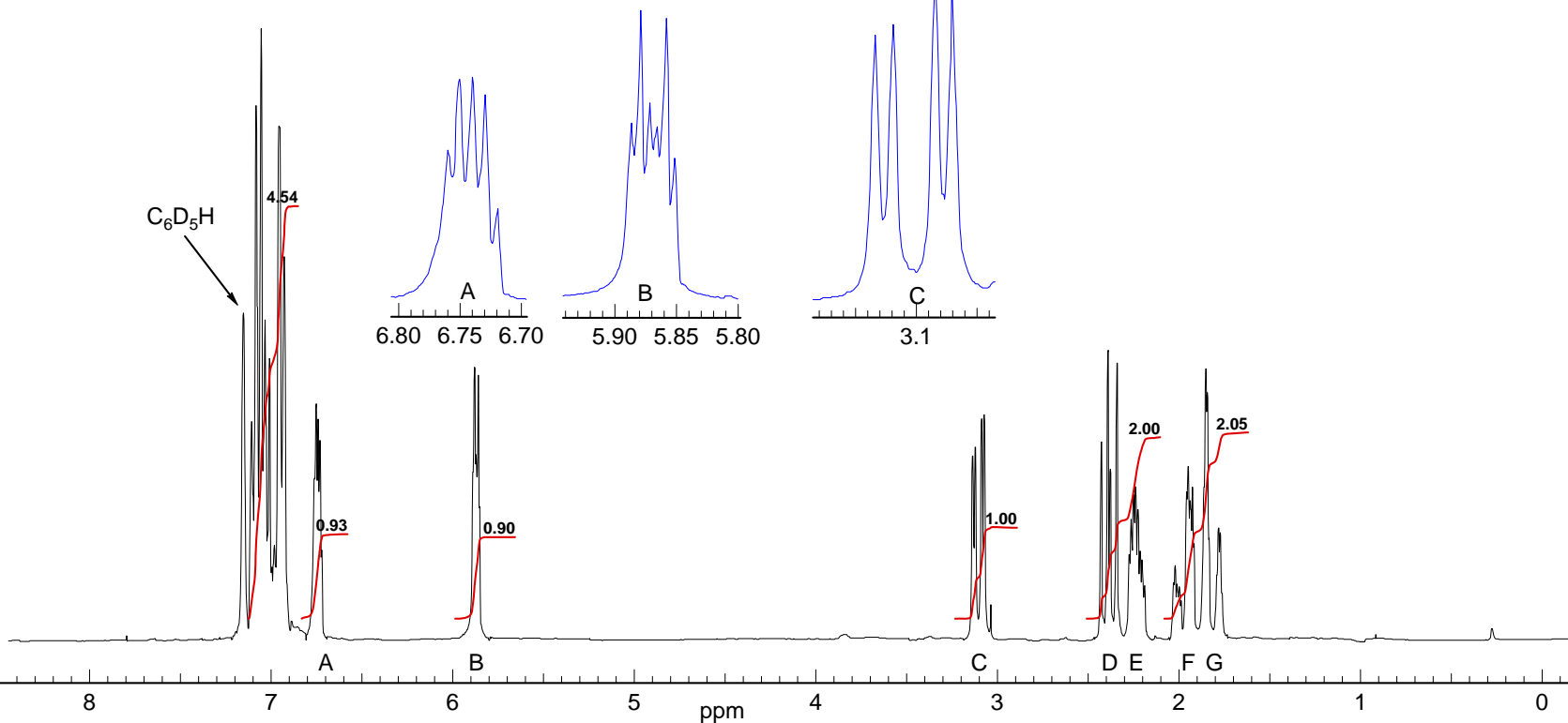
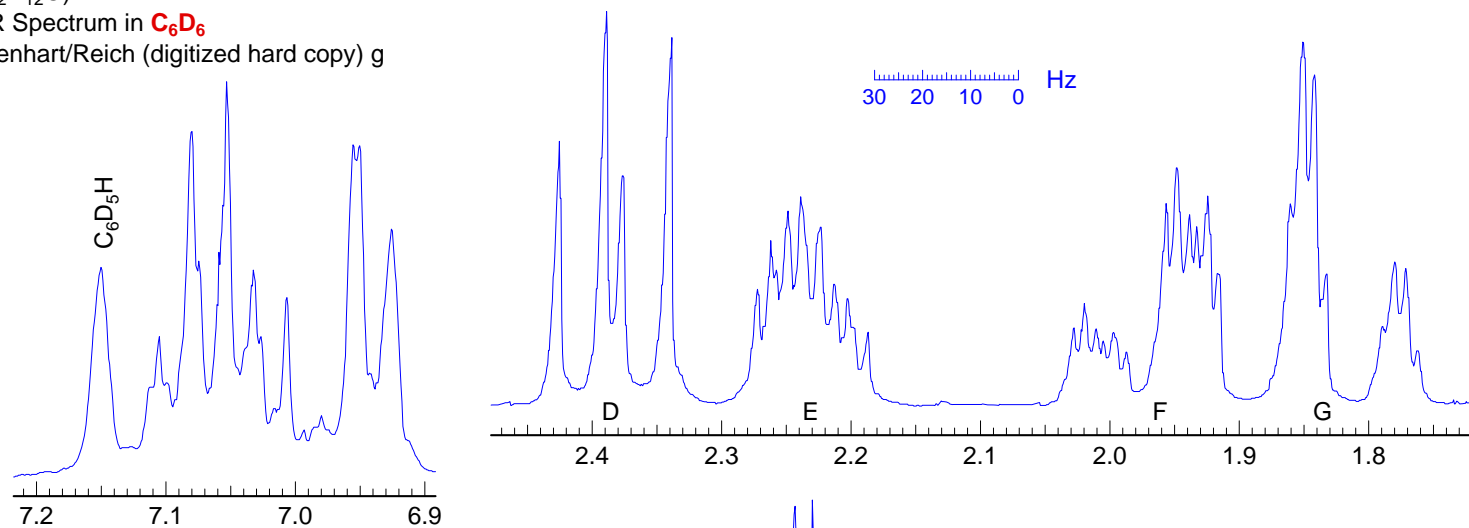
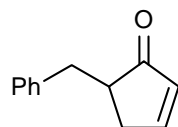


**Problem R-275:** Determine the structure from the  $^1\text{H}$  NMR spectrum. Suggest an average conformation for the molecule from the coupling constants and chemical shifts.

**Problem R-275** ( $\text{C}_{12}\text{H}_{12}\text{O}$ )

270 MHz  $^1\text{H}$  NMR Spectrum in  $\text{C}_6\text{D}_6$

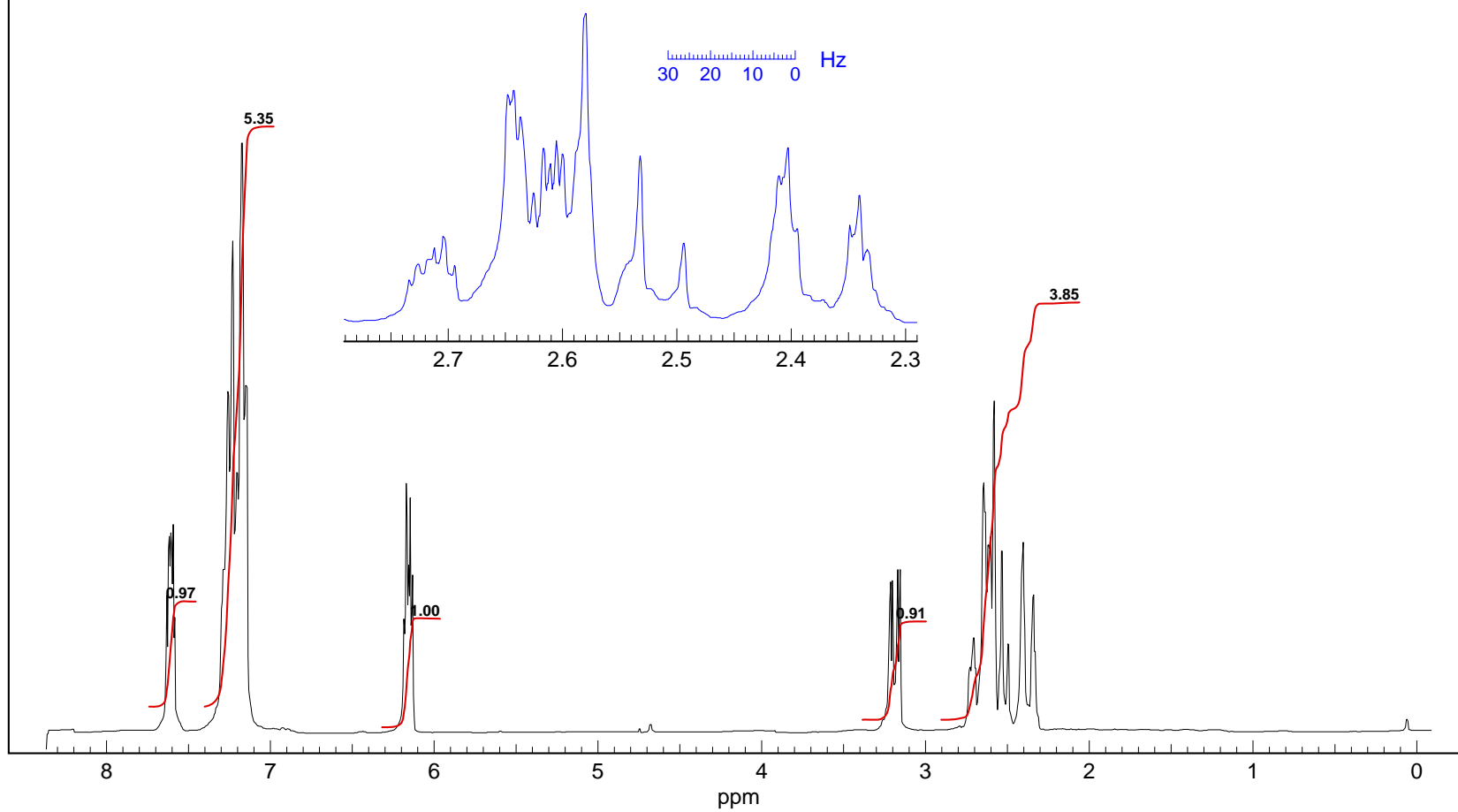
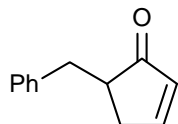
Source: E. K. Eisenhart/Reich (digitized hard copy) g



**Problem R-275** ( $C_{12}H_{12}O$ )

270 MHz  $^1H$  NMR Spectrum in  $CDCl_3$

Source: E. K. Eisenhart/Reich (digitized hard copy) g



# **Problem R-275** ( $C_{12}H_{12}O$ )

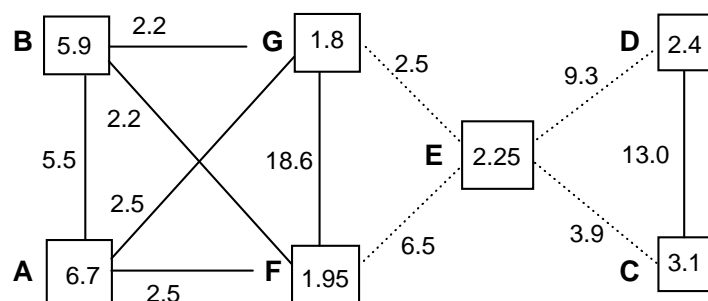
Because of second order effects resulting from several close-coupled protons, the spectrum in  $CDCl_3$  cannot be analyzed. In  $C_6D_6$  the spectrum is mostly first order, and allows complete analysis (see next page for ASIS analysis).

Here are the coupling constants obtained by analysis of the  $C_6D_6$  spectrum

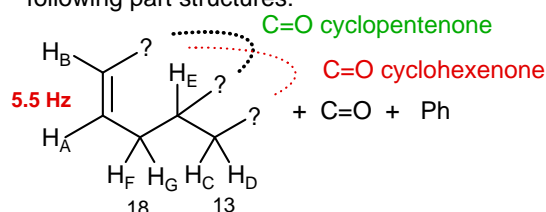
E is hard to analyze a priori, but all coupling to E can be identified from the "left-over"  $J$  values in the other multiplets

	A	B	C	D	E	F	G
$\delta$	6.7	5.9	3.1	2.4	2.25	1.95	1.8
	dt	dt	dd	dd	(dddd)	ddt	dq
$J$	5.5	5.5	13.0	13.0	(9.3)	18.6	18.6
	2.5	2.2	3.9	9.3	(6.5)	6.5	2.5
	2.5	2.2			(3.9)	2.4	2.5
					(2.5)	2.4	2.5

The coupling constants can be matched up as shown in the scheme below



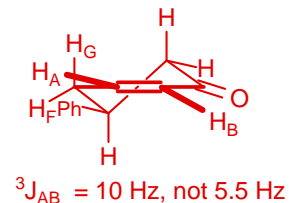
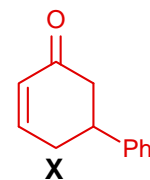
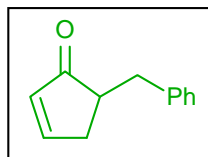
The chemical shifts and couplings lead to the following part structures:



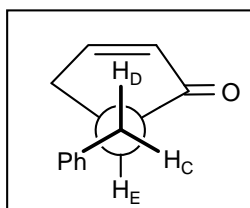
This defines all protons and carbons in the molecule. The three "?" position are filled by C=O and Ph.

Two structures fit the data:

The cyclohexenone would have a ca 10 Hz  $HC=CH$  coupling. Since it is only 5.5 Hz, must be the cyclopentenone



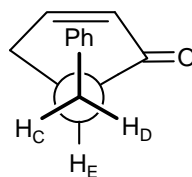
## **Conformation of benzyl:**



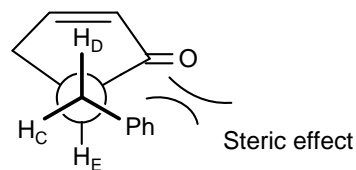
$J_{DE}$  large

$J_{CE}$  small,  $H_C$  downfield (C=O anisotropy)

This fits best



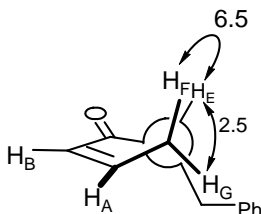
$J_{DE} \approx J_{CE}$



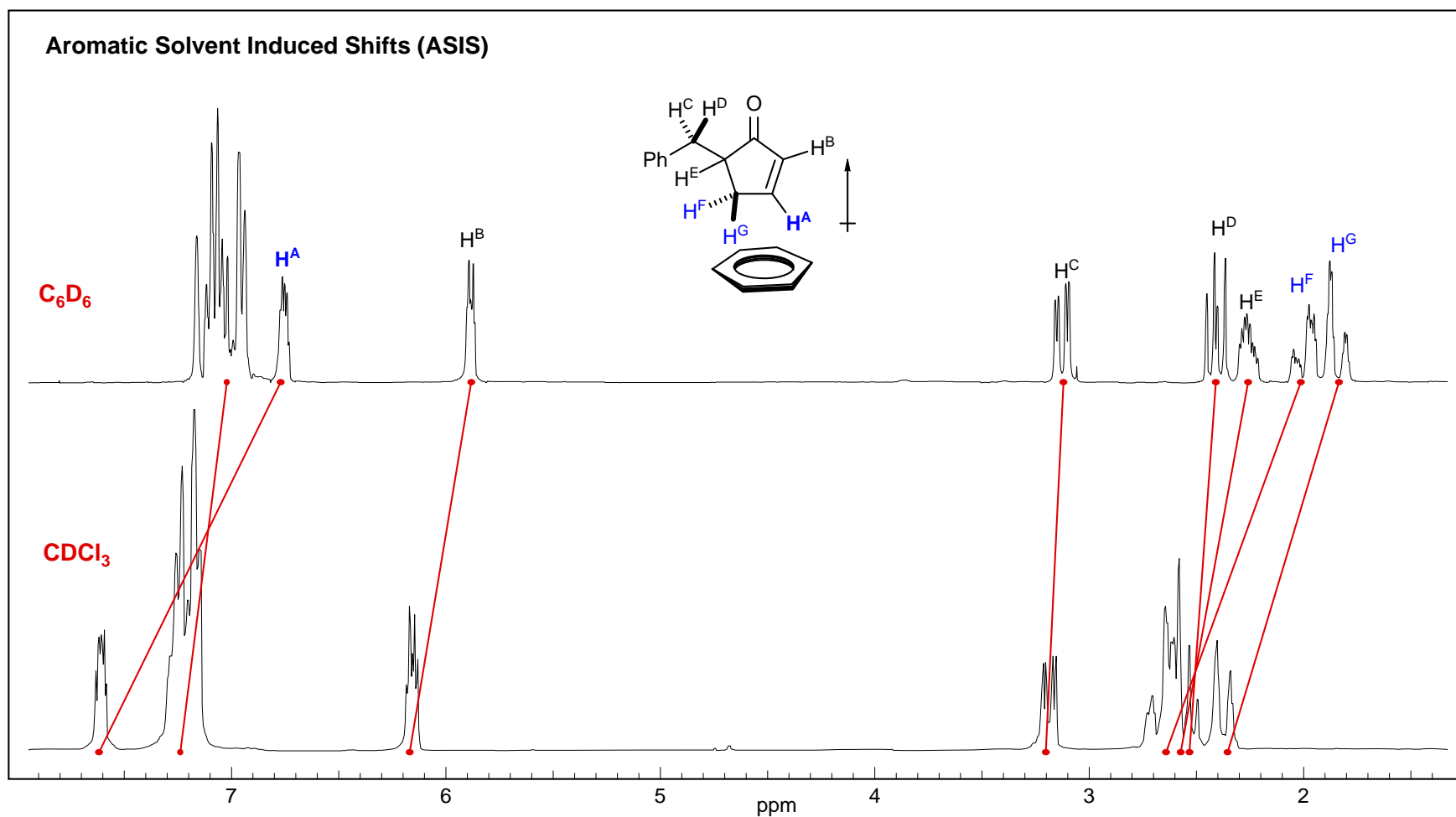
$J_{DE}$  large

$J_{CE}$  small

Chemical shift of  $H_C$ ?



# Aromatic Solvent Induced Shifts (ASIS)



The observed shifts fit well with the "transient pi complex" model for ASIS.  $H^A$  moves the most,  $H^F$  and  $H^G$  also move a lot;  $H^C$  and  $H^D$  move the least - they are furthest from the positive end of the enone dipole.

**Problem R-275:** Determine the structure from the  $^1\text{H}$  NMR spectrum. Suggest an average conformation for the molecule from the coupling constants and chemical shifts.

**Problem R-275** ( $\text{C}_{12}\text{H}_{12}\text{O}$ )

270 MHz  $^1\text{H}$  NMR Spectrum in  $\text{C}_6\text{D}_6$

Source: E. K. Eisenhart/Reich (digitized hard copy) g

