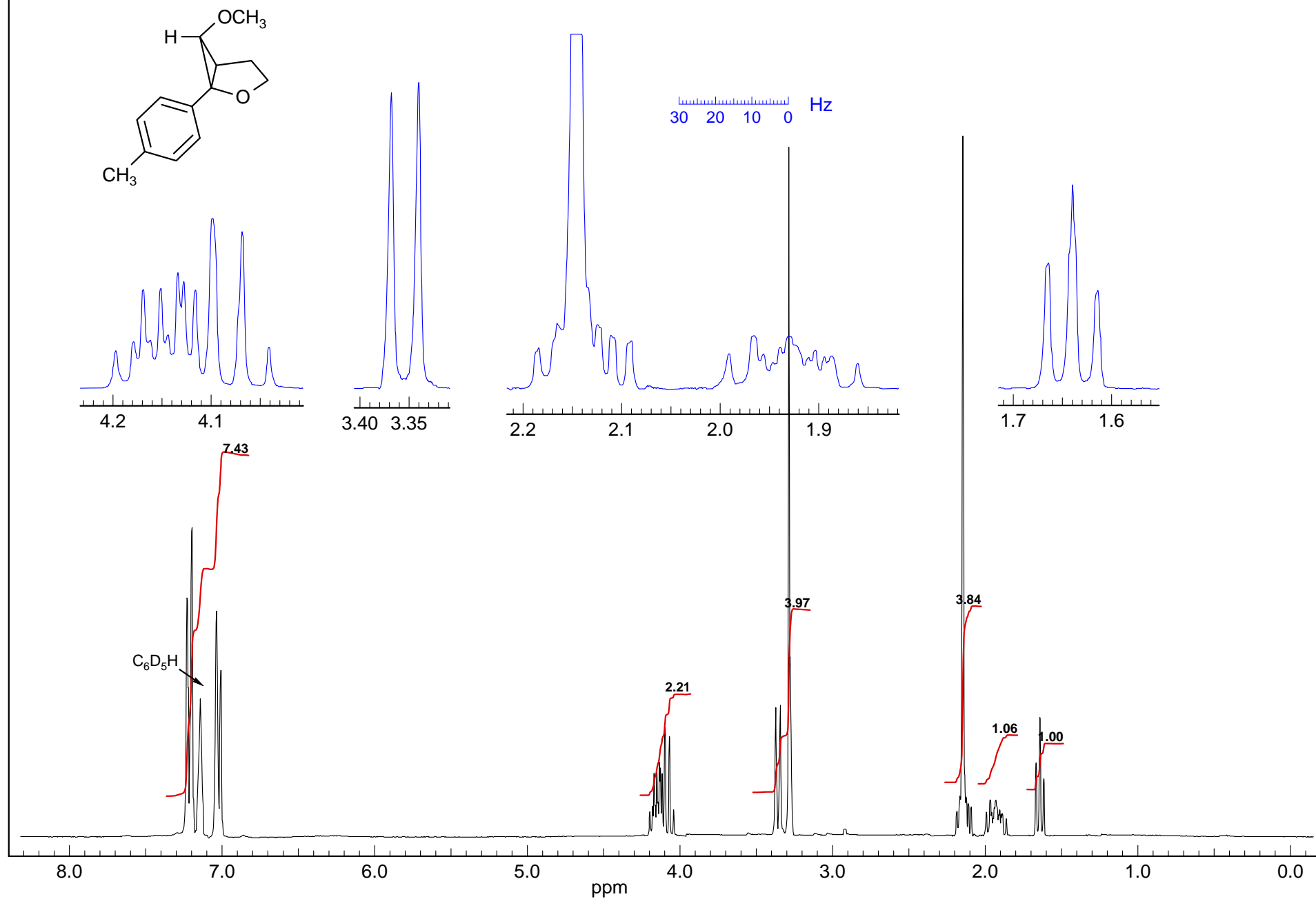


**Problem R-09L** ( $C_{13}H_{16}O_2$ )

270 MHz  $^1H$  NMR spectrum in  $C_6D_6$

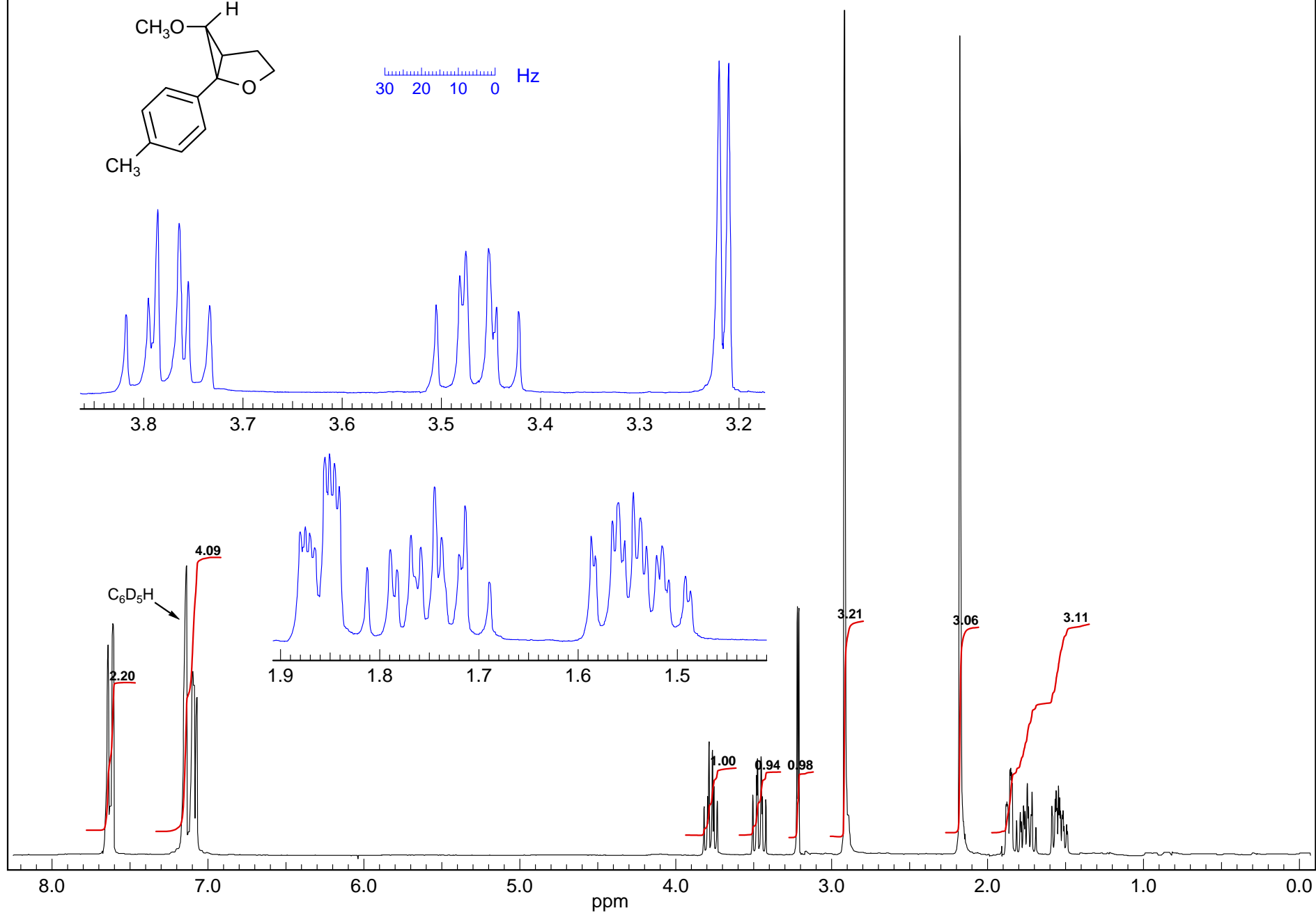
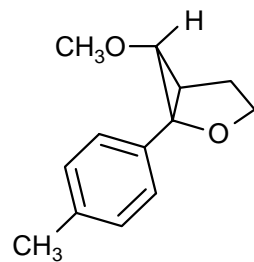
Source: Nora Hornung/Casey (Reich digitized hard copy) g



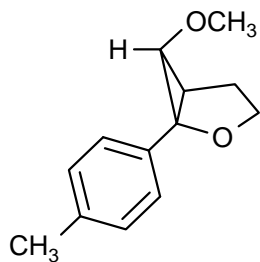
**Problem R-09M** ( $\text{C}_{13}\text{H}_{16}\text{O}_2$ )

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

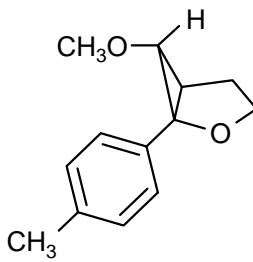
Source: Nora Hornung/Casey (Reich digitized hard copy) g



**Problem R-09L and R-09M** ( $C_{13}H_{16}O_2$ ). The 270 MHz  $^1H$  spectra are of the isomers below:



R-09\_\_



R-09\_\_

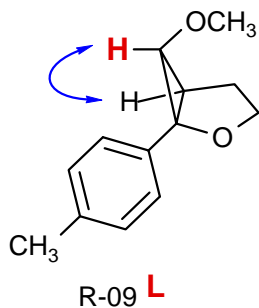
(a) Identify a key feature of the spectra which allows confident assignment of the stereochemistry. Explain and label the structures above appropriately. It is not necessary to analyze the spectra completely.

(b) Explain the differences in the chemical shift of the sharp singlet at  $\delta$  3.25 in **R-09L** and  $\delta$  2.9 in **R-09M**.

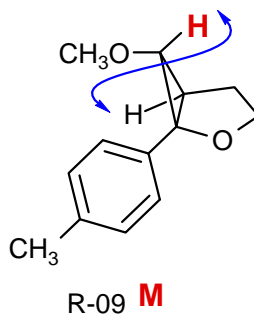
(c) Assign and interpret the signal at  $\delta$  1.65 (explain the coupling) in the spectrum of **R-09L**. Give the chemical shift of the corresponding signal in the spectrum of **R-09M**\_\_\_\_\_.

**Problem R-09L and R-09M** ( $C_{13}H_{16}O_2$ ). The 270 MHz  $^1H$  spectra are of the isomers below:

cis coupling  
should be larger  
( $\Theta = 0^\circ$ ):  $J = 7.5$   
Hz



trans coupling  
should be  
smaller:  $J = 3$   
Hz



(a) Identify a key feature of the spectra which allows confident assignment of the stereochemistry. Explain and label the structures above appropriately. It is not necessary to analyze the spectra completely.

The most reliable stereochemical feature is the  $^3J$  coupling cis and trans in the cyclopropane, with the expectation that  $J_{cis} > J_{trans}$ . Each isomer has an isolated doublet at ca  $\delta$  3.3 corresponding to the CH-OMe proton

8

R-09L has a d,  $J = 7.5$  Hz at  $\delta$  3.36, thus the two Hs are cis

R-09M has a d,  $J = 3$  Hz at  $\delta$  3.22, the two H s are trans

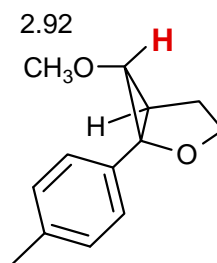
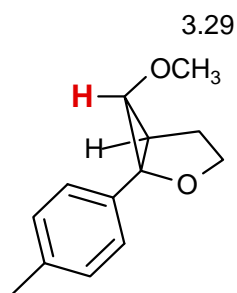
4 for chemical shift arguments

1-2 for others

(b) Explain the differences in the chemical shift of the sharp singlet at  $\delta$  3.25 in **R-09L** and  $\delta$  2.9 in **R-09M**.

Apparently, in R-09M the MeO group is over the shielding portion of the aromatic ring, so shifted upfield to  $\delta$  2.9 from its "normal" position - alkyl ethers like  $Me_2O$  are typically at  $\delta$  3.4-3.5.

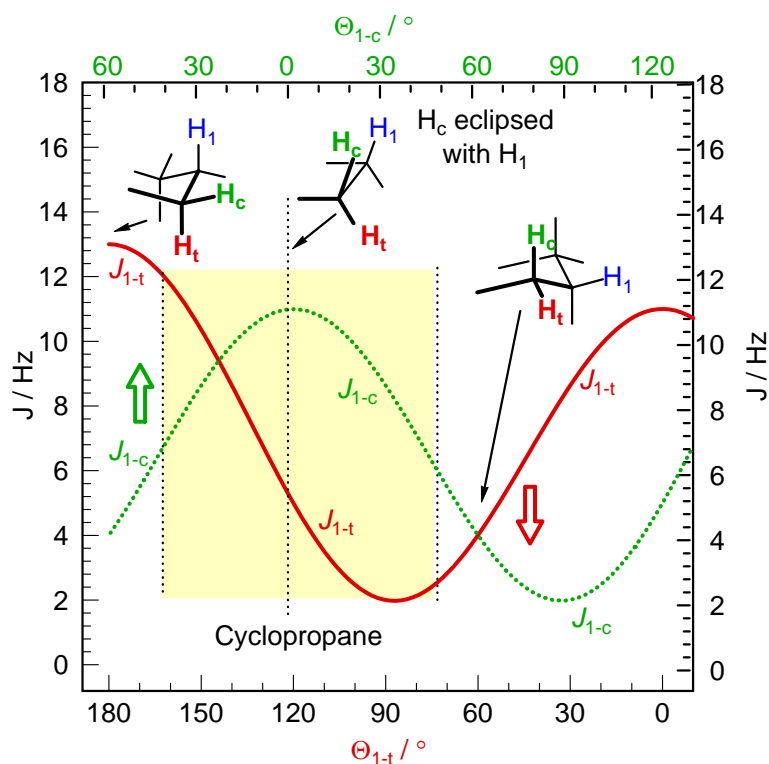
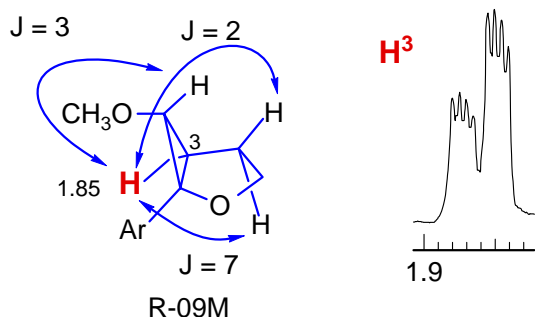
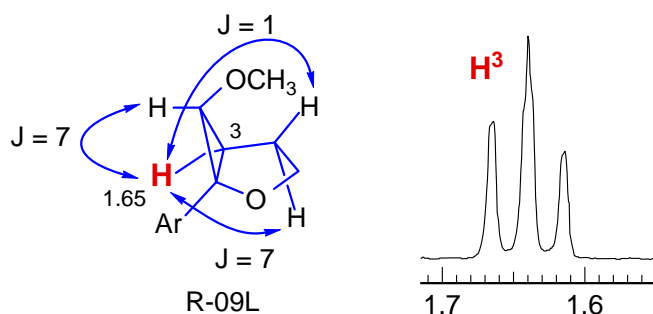
4



- 6 (c) Assign and interpret the signal at  $\delta$  1.65 (explain the coupling) in the spectrum of **R-09L**. Give the chemical shift of the corresponding signal in the spectrum of **R-09M** 1.86 . 2

This is roughly a t,  $J = 7$  Hz, although actually almost a ddd,  $J = 7, 6, 1$ , which can be assigned from its chemical shift (upfield of the other cyclopentane protons) and coupling. It must have a dihedral angle near  $90^\circ$  to one of the vicinal  $\text{CH}_2$  protons

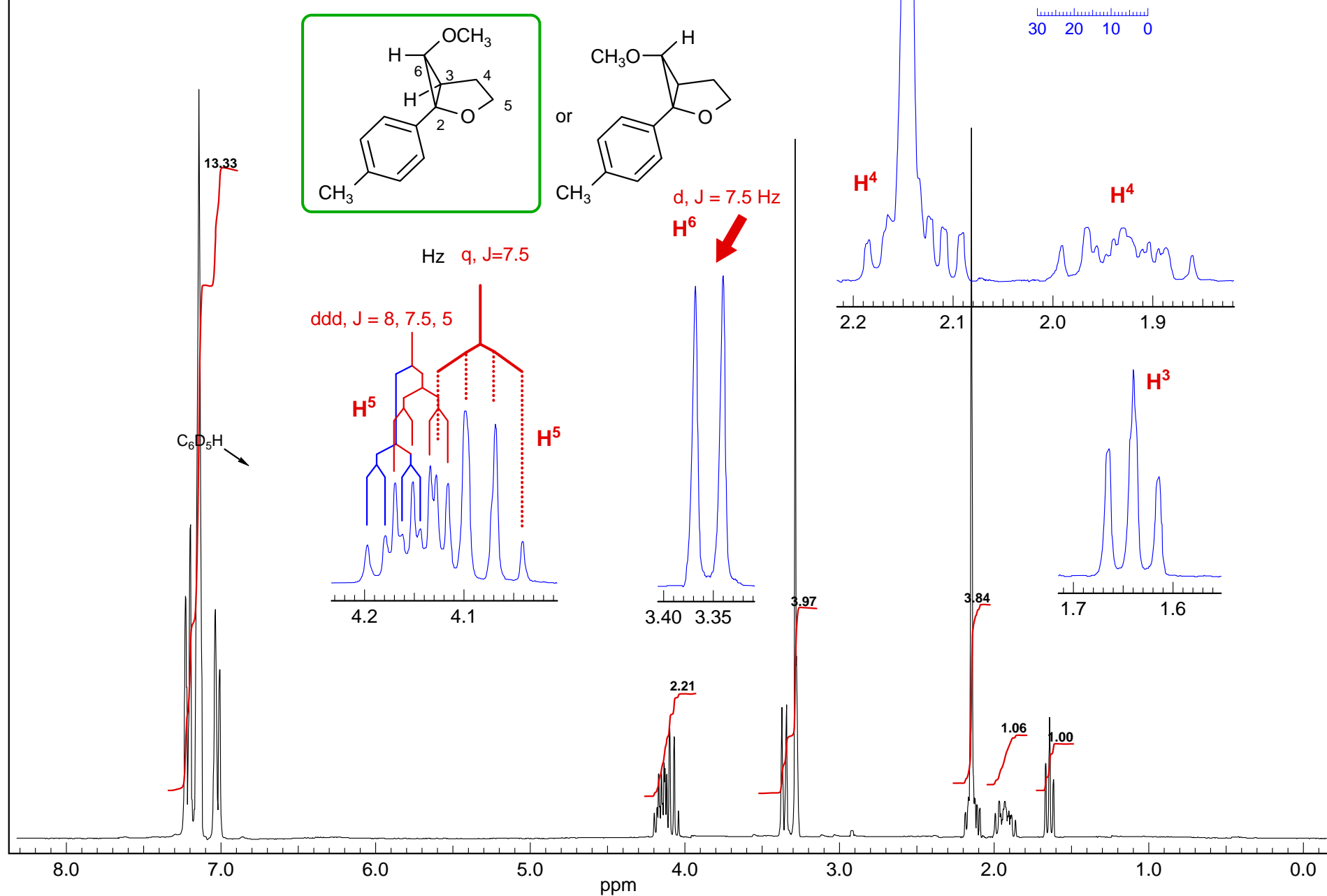
The corresponding proton in R-09M is at  $\delta$  1.86, ddd,  $J = 7.5, 3, 1.5$  Hz 4



**Problem R-09L** ( $C_{13}H_{16}O_2$ )

270 MHz  $^1H$  NMR spectrum in  $C_6D_6$

Source: Nora Hornung/Casey (Reich digitized hard copy) g



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

**H<sup>5</sup>** Since the couplings are nearly the same, the OCH<sub>2</sub> (C<sup>5</sup>) must be nearly eclipsed with the vicinal CH<sub>2</sub> (C<sup>4</sup>)

**H<sup>5</sup>**

**H** d, J = 3 Hz

dt, J = 8, 6

dt, J = 8, 6

3.8 3.7 3.6 3.5 3.4 3.3 3.2

