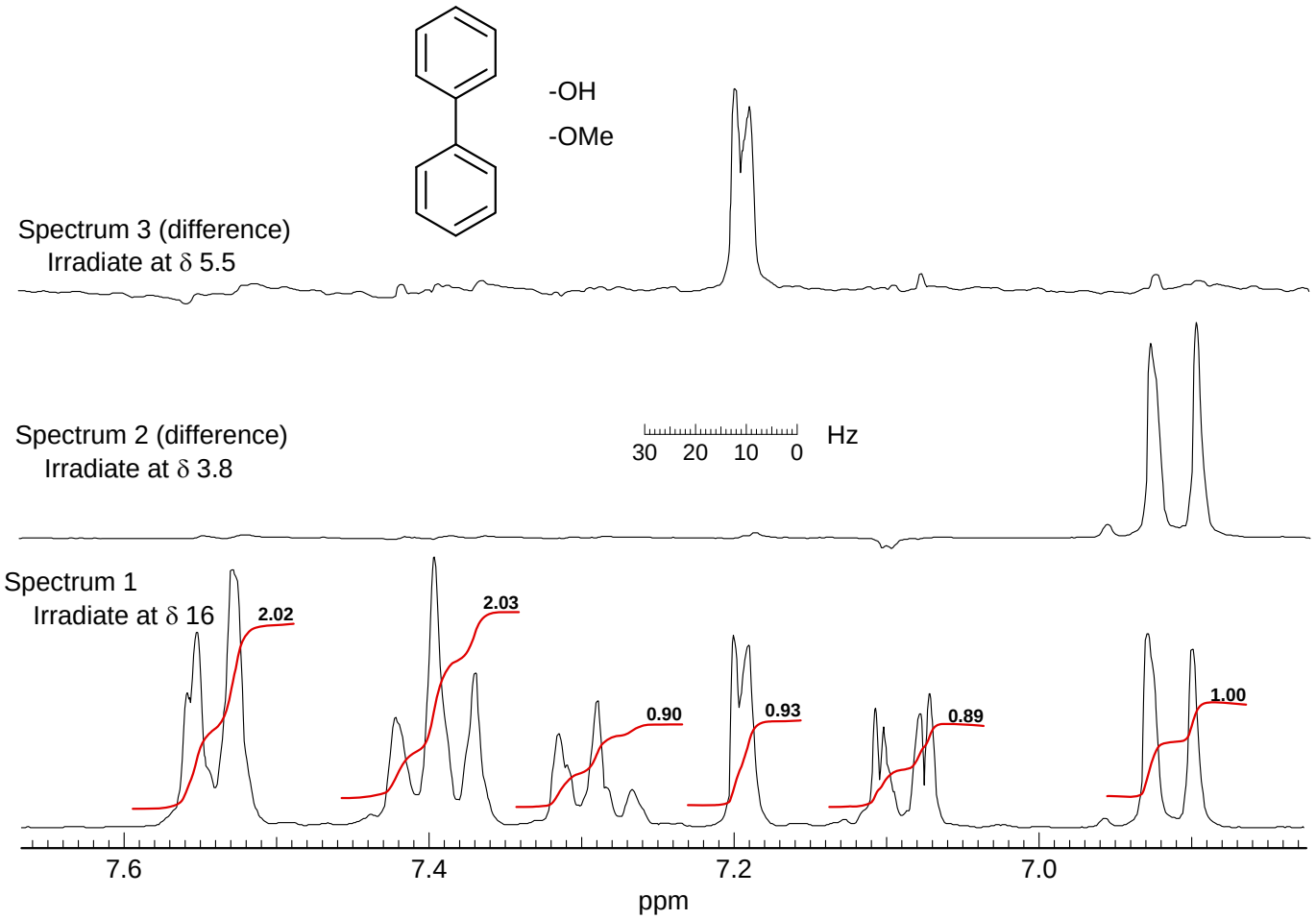
Problem R-10L ($C_{13}H_{12}O_2$). Determine the structure of a methoxy hydroxybiphenyl from the 300 MHz ^{1}H NMR spectra (E. W. Huber, R. A. Parker, *J. Org. Chem*., **2000**, *55*, 1274).



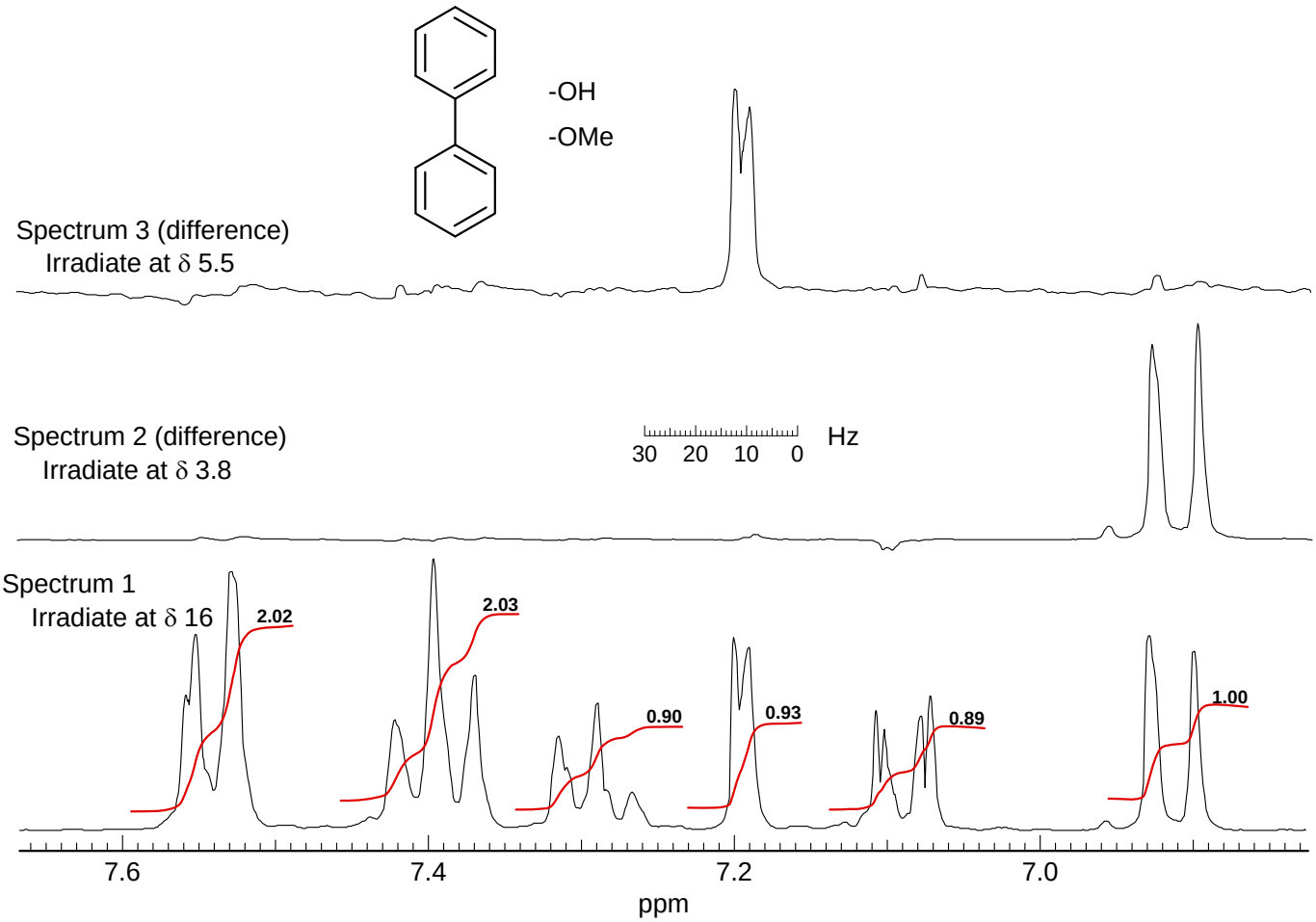
(a) From the multiplets in Spectrum 1 determine the substitution pattern of each ring of the biphenyl. Explain briefly.

(b) Spectrum 2 is a difference spectrum obtained by pre-irradiating at the frequency of the OMe protons (δ 3.8) and subtracting Spectrum 1 from it. Similarly, Spectrum 3 was obtained by irradiating at the frequency of the OH proton (δ 5.5) and subtracting Spectrum 1 from it. What kind of experiments are these?

What do these experiments tell you about the structure of the biphenyl? Draw the complete structure.

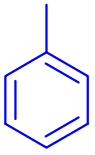
16

Problem R-10L ($C_{13}H_{12}O_2$). Determine the structure of a methoxy hydroxybiphenyl from the 300 MHz ^{1}H NMR spectra (E. W. Huber, R. A. Parker, *J. Org. Chem.*, **2000**, *55*, 1274).



(a) From the multiplets in Spectrum 1 determine the substitution pattern of each ring of the biphenyl. Explain briefly.

- δ 7.3-7.5 is shows characteristic peaks of a monosubstituted benzene

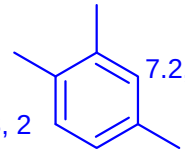


2H 7.55 ~doublet m

2H 7.55 ~triplet m

1H 7.3 ~triplet m

- the remaining peaks correspond to a 1,2,4-trisubsituted benzene



-OH
-OMe
-Ph

6

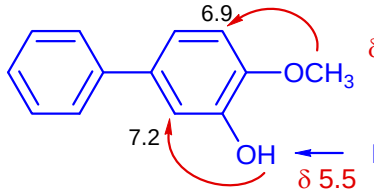
(b) Spectrum 2 is a difference spectrum obtained by pre-irradiating at the frequency of the OMe protons (δ 3.8) and subtracting Spectrum 1 from it. Similarly, Spectrum 3 was obtained by irradiating at the frequency of the OH proton (δ 5.5) and subtracting Spectrum 1 from it. What kind of experiments are these?

3

These are NOE difference experiments

What do these experiments tell you about the structure of the biphenyl? Draw the complete structure.

7



Irradiate here - only the wide doublet at δ 6.9 shows enhancement

Irradiate here - only the narrow doublet at δ 7.2 shows an NOE

All other structures would show different or more than one NOE

-Since each NOE experiment shows only one proton enhanced, OH and OMe must be ortho

-Since irradiation of OH enhances the small doublet, Ph must be meta to OH