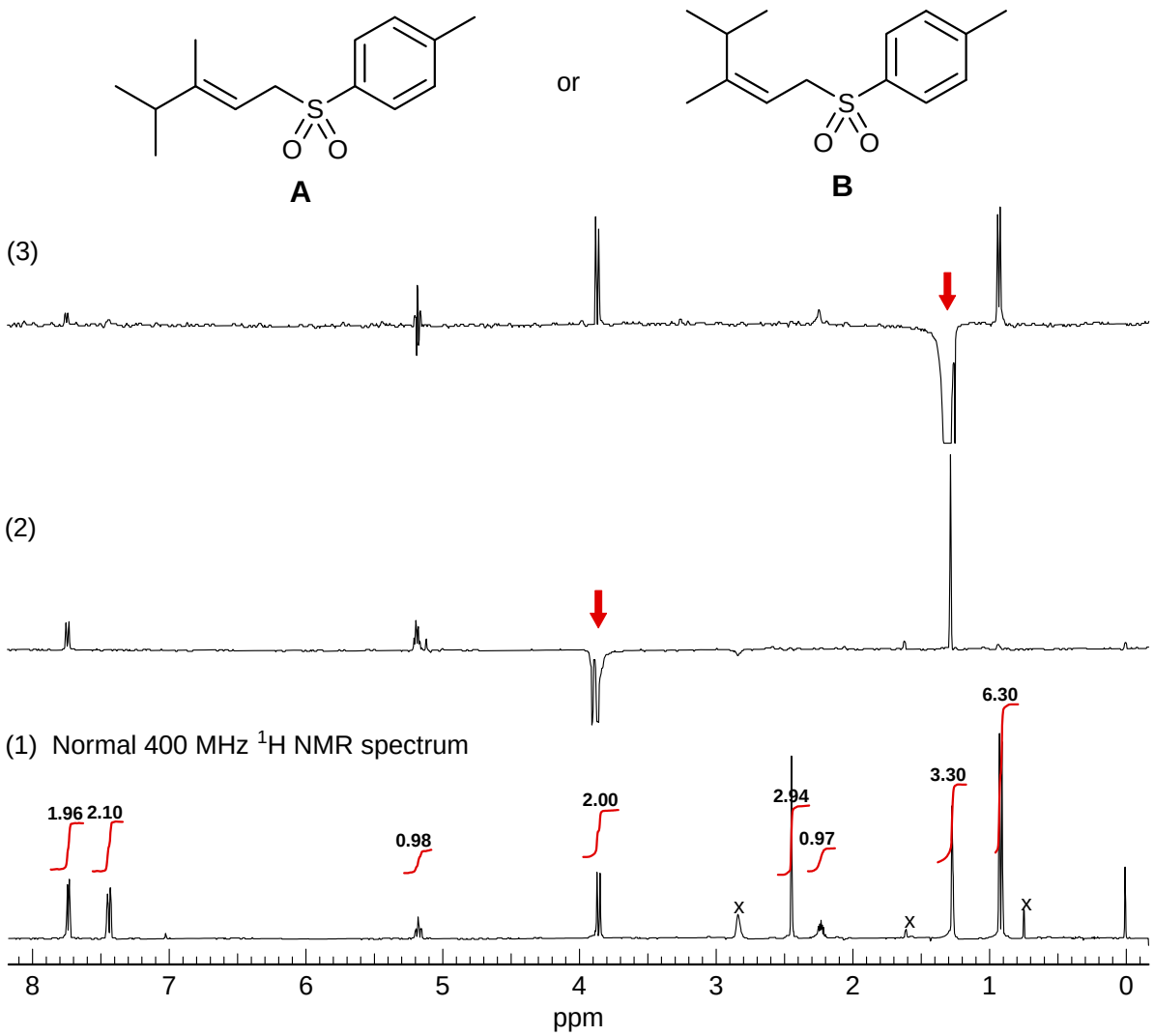
**Problem R-09P** ($C_{14}H_{20}O_2S$). Spectrum (1) is a normal 400 MHz $^1$H NMR spectrum of one of the isomers shown. Impurity peaks are marked with x. Spectra (2) and (3) are difference spectra, in which the normal spectrum is subtracted from the spectrum obtained by preirradiating for a few seconds at the frequency shown by the arrow (Source: Clennan, E. L.; Yang, K. *J. Org. Chem.*, **1992**, *57*, 4477)




(a) What kind of experiment is being done here?

(b) Which of the isomers is the correct structure (**A** or **B**)?_____ Explain briefly, but be specific.

(c) Assign the protons by writing chemical shifts on the correct structure.

**15**

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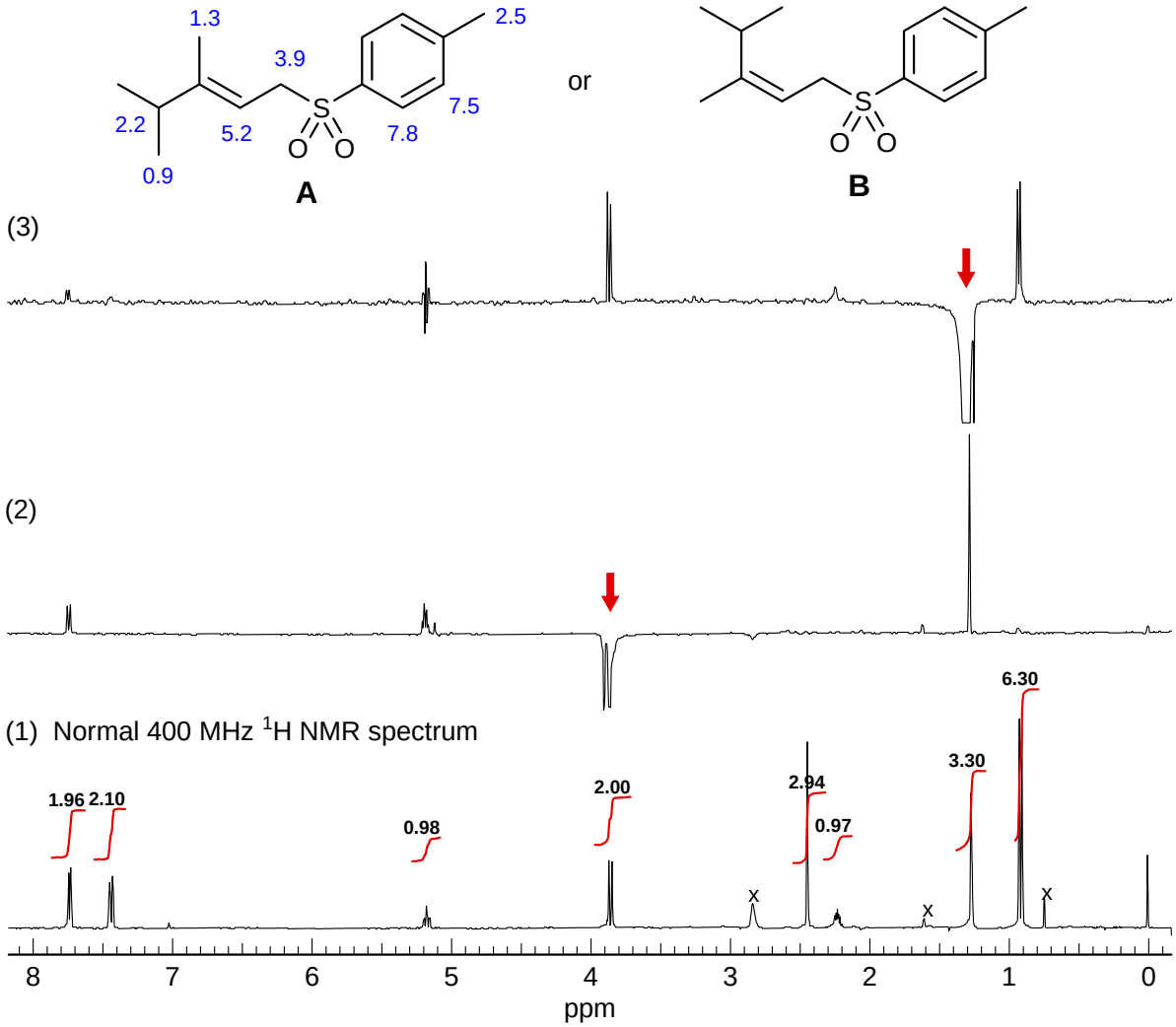


(a) What kind of experiment is being done here?

2 Proton-proton NOE difference experiment

(b) Which of the isomers is the correct structure (**A** or **B**)? **A** Explain briefly, but be specific.

5 Irradiation of the methyl group at δ 1.3 (spectrum 3) causes an NOE enhancement of the $CH_2$ doublet δ 3.9 - thus these must be cis, hence structure A. Conversely, irradiation at δ 3.9 (spectrum 2) causes NOE enhancement of the vinyl proton at δ 5.2, the ortho protons δ 7.8, and (most importantly), the methyl signal at δ 1.3, also consistent only with structure A

(c) Assign the protons by writing chemical shifts on the correct structure.

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