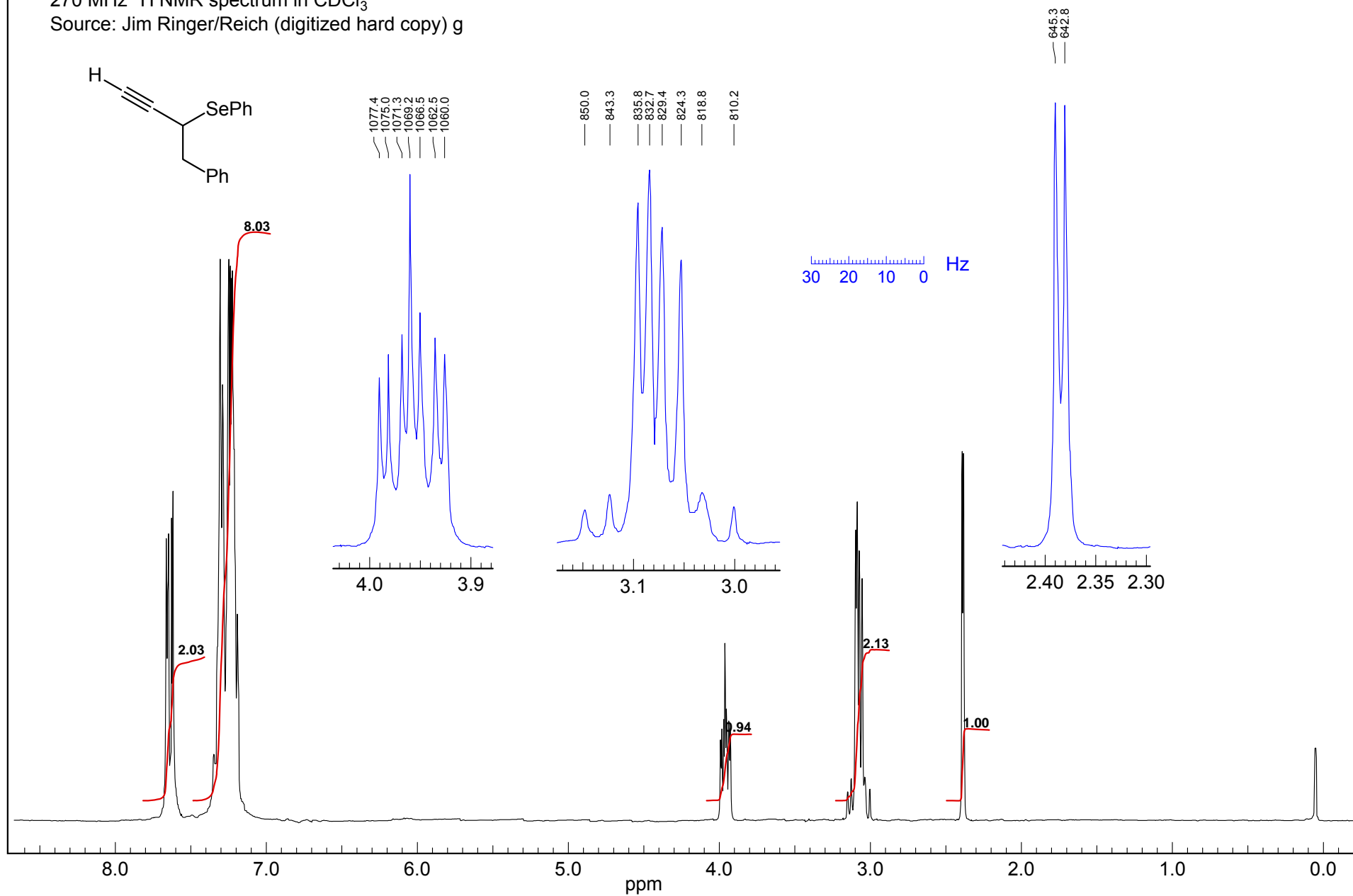


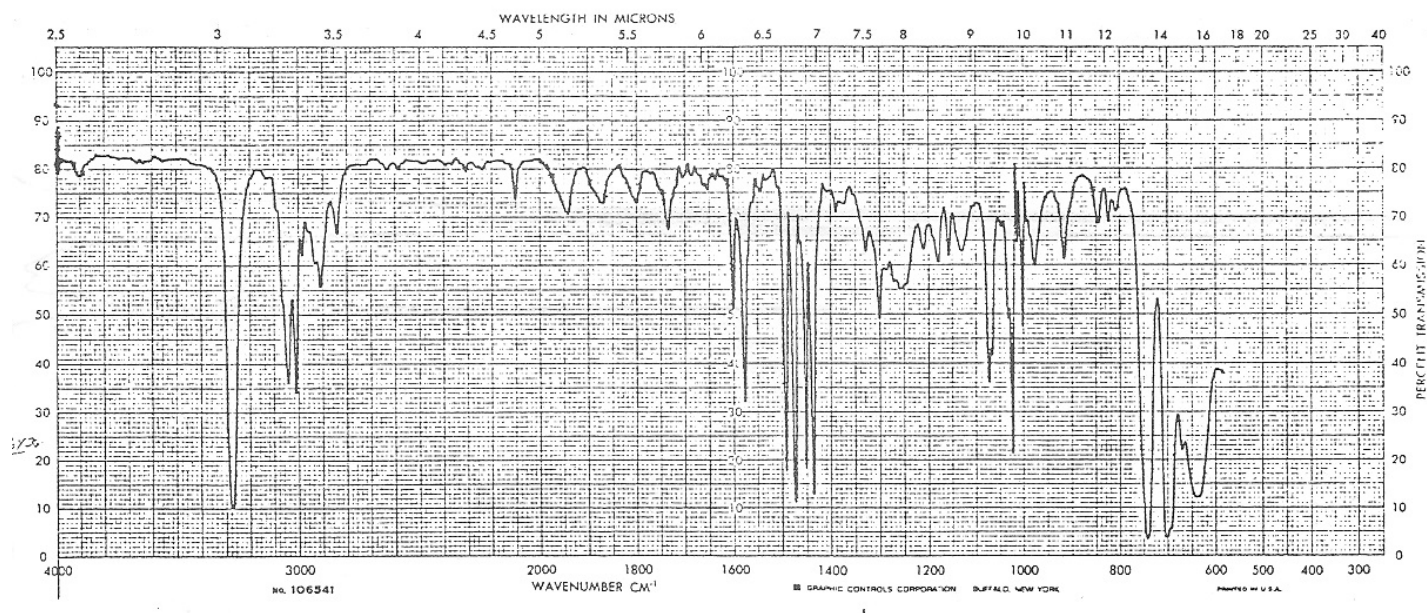
Problem R-89E (C₁₆H₁₄Se)

270 MHz ¹H NMR spectrum in CDCl₃

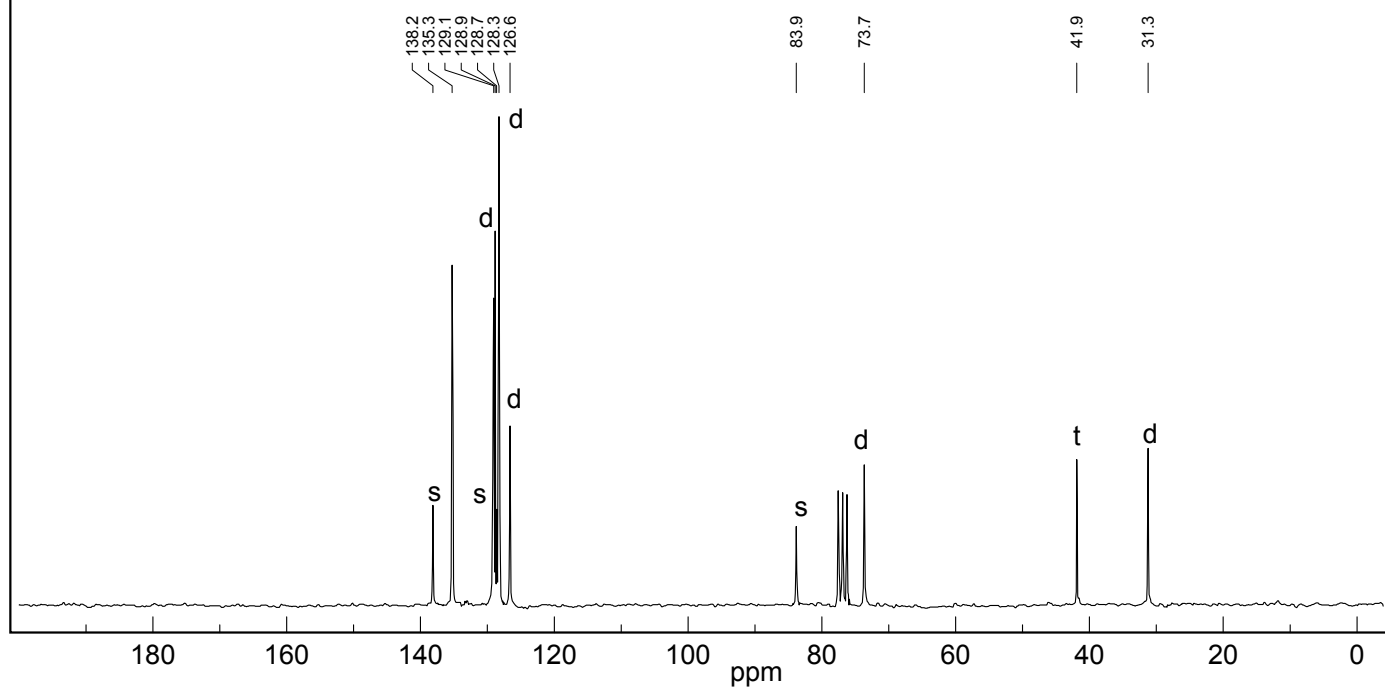
Source: Jim Ringer/Reich (digitized hard copy) g



Problem R-89E ($C_{16}H_{14}Se$)
 Infrared Spectrum neat.
 (Source: Jim Ringer/Reich 11/19)



Problem R-89E ($C_{16}H_{14}Se$)
 50.1 MHz ^{13}C NMR Spectrum in $CDCl_3$
 (Source: Jim Ringer/Reich 11/19)



Problem R-89E ($C_{16}H_{14}Se$) This problem requires you to determine the structure and do a detailed analysis of two of the multiplets. R-89E contains a PhSe group (selenium is divalent, like sulfur). For each part, explain what the signals tell you about the structure of R-89E.

(a) DBE ____

(b) Report your analysis of the IR spectrum. List the data, and any conclusions you drew from it.

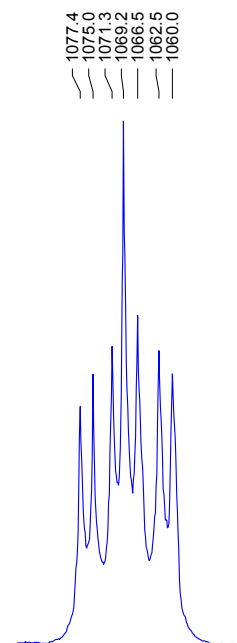
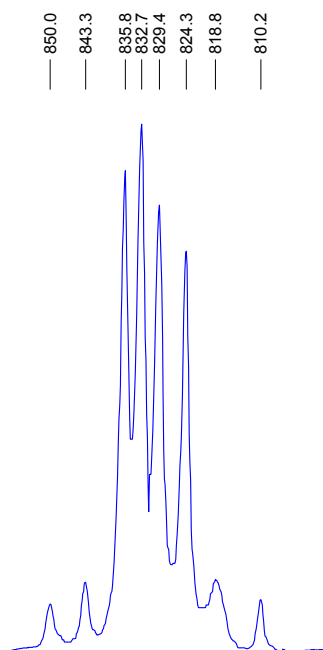
(c) Report your analysis of the ^{13}C NMR spectrum below. List the data, and any conclusions you drew from it.

(d) What kind of a multiplet is the signal at 4.0 δ ? _____. Report J values.

(e) What kind of multiplet is the signal at 3.1 δ ? _____. Do a first order analysis of this multiplet.

(f) Draw the structure of R-89E below. Label the structure with δ and J values.

(g) Do a complete analysis of the multiplet at 3.1 . As part of your answer, draw coupling tree(s) on the spectrum. Obtain coupling constants and chemical shifts. Use the peak positions in Hz given on the spectrum for your calculations. □



Problem R-89E ($C_{16}H_{14}Se$) This problem requires you to determine the structure and do a detailed analysis of two of the multiplets. R-89E contains a PhSe group (selenium is divalent, like sulfur). For each part, explain what the signals tell you about the structure of R-89E.

2 (a) DBE 10

(b) Report your analysis of the IR spectrum. List the data, and any conclusions you drew from it.

5
 3020, 3040 cm^{-1} - Aromatic CH stretch
 3280 cm^{-1} - can't be OH or NH, since no O or N, so must be $C\equiv C-H$ CH stretch
 2100 cm^{-1} - $-C\equiv C-$ stretch
 1570, 1600 cm^{-1} - Aromatic $C=C$ stretch
 700, 780 cm^{-1} - monosubstituted benzene

(c) Report your analysis of the ^{13}C NMR spectrum below. List the data, and any conclusions you drew from it.

Peak	Hz	ppm		Peak	Hz	ppm	
1	1562.98	31.260	CH_2	5	6332.10	126.642	C
2	2096.89	41.938	CH	6	6415.07	128.302	CH (2C ?)
3	3684.19	73.684	$C\equiv C-H$	7	6433.11	128.662	C
4	4192.85	83.857		8	6443.93	128.879	CH
				9	6454.76	129.095	CH
				10	6765.00	135.300	CH
				11	6909.30	138.186	CH

Aromatic C

(d) What kind of a multiplet is the signal at 4.0 δ ? ddd. Report J values.

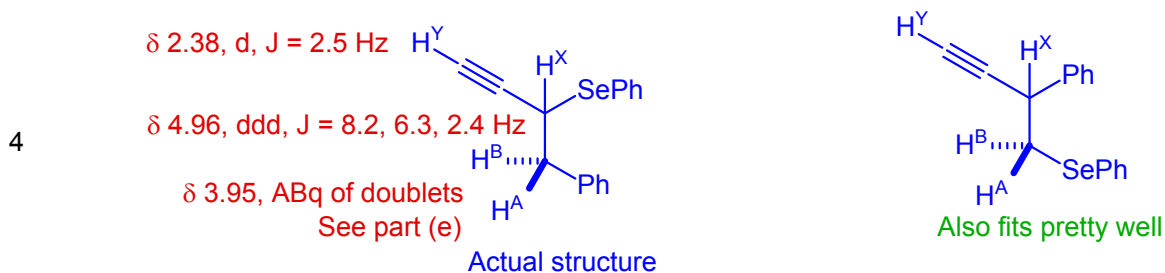
4 δ 4.96, ddd (apparent), J = 8.2, 6.3, 2.4 Hz (see coupling tree on next page). The J values a little doubtful because this is the X of an ABXY.

(e) What kind of multiplet is the signal at 3.1 δ ? AB of ABXY. Do a first order analysis of this multiplet.

Downfield: δ 3.1, dd, J = 14, 6.7; upfield δ 3.05, dd J = 14, 8.4 Hz

4 A proper ABX analysis gives J values of 9.0 and 5.9 (instead of 8.4 and 6.7 from "AMX" type of analysis). See part (g). As is usually the case, the first order analysis gives apparent coupling constants that are partially averaged. Note that analysis of the X-part gives the same slightly erroneous J values of X to A and B

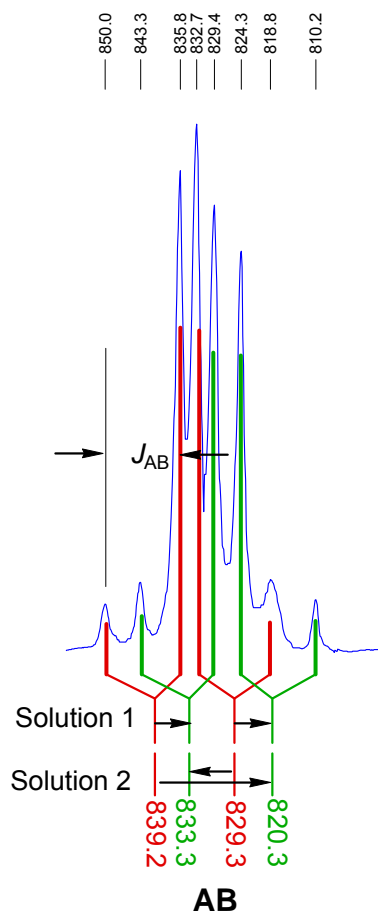
(f) Draw the structure of R-89E below. Label the structure with δ and J values.



(g) Do a complete analysis of the multiplet at 3.1 . As part of your answer, draw coupling tree(s) on the spectrum. Obtain coupling constants and chemical shifts. Use the peak positions in Hz given on the spectrum for your calculations. □

Although this is an ABXY system, the Y proton (alkyne H) is not coupled to the AB protons, and is far away from the X proton, so the AB part can be handled as an isolated ABX system.

14



Solution 1

$$J_{AB} = 14.1$$

$$J_{AX} = +5.9$$

$$J_{BX} = +9.0$$

$$\nu_A = 836.2 \text{ (}\delta \text{ 3.10)}$$

$$\nu_B = 824.8 \text{ (}\delta \text{ 3.05)}$$

$$\Delta\nu_{AB} = 11.4$$

$$i_{14} = i_{15} = 0.004$$

Solution 2

$$J_{AB} = 14.1$$

$$J_{AX} = +18.8$$

$$J_{BX} = -4.0$$

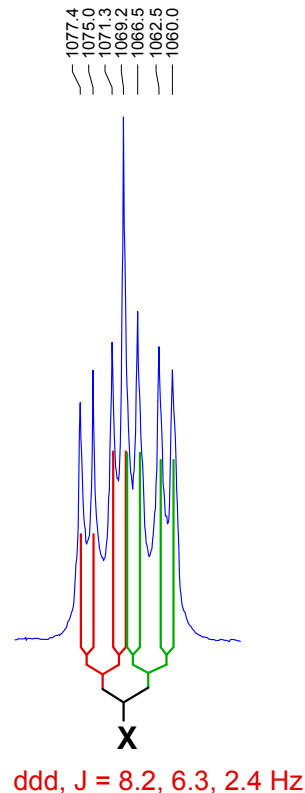
$$\nu_A = 829.7$$

$$\nu_B = 831.3$$

$$\Delta\nu_{AB} = -1.6$$

$$i_{14} = i_{15} = 0.391$$

Clearly, Solution 1 is correct, both because of the coupling constants (solution 2 has one negative 3J , not possible for this structure), and the size of one of the couplings (18.8 is very large for a vicinal coupling). In addition the X-part intensities are clearly those of solution 1 - solution 2 would have two extra signals (each doublets from coupling to Y) with 39% of the intensity of the largest peaks, which should be easily visible.



ddd, $J = 8.2, 6.3, 2.4$ Hz