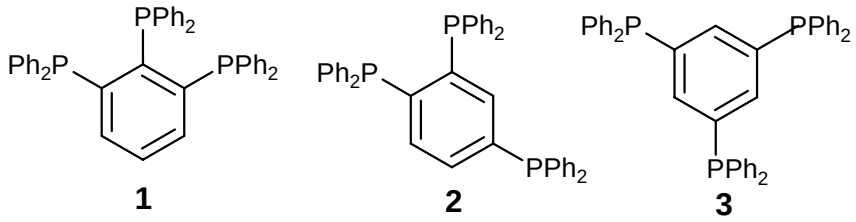
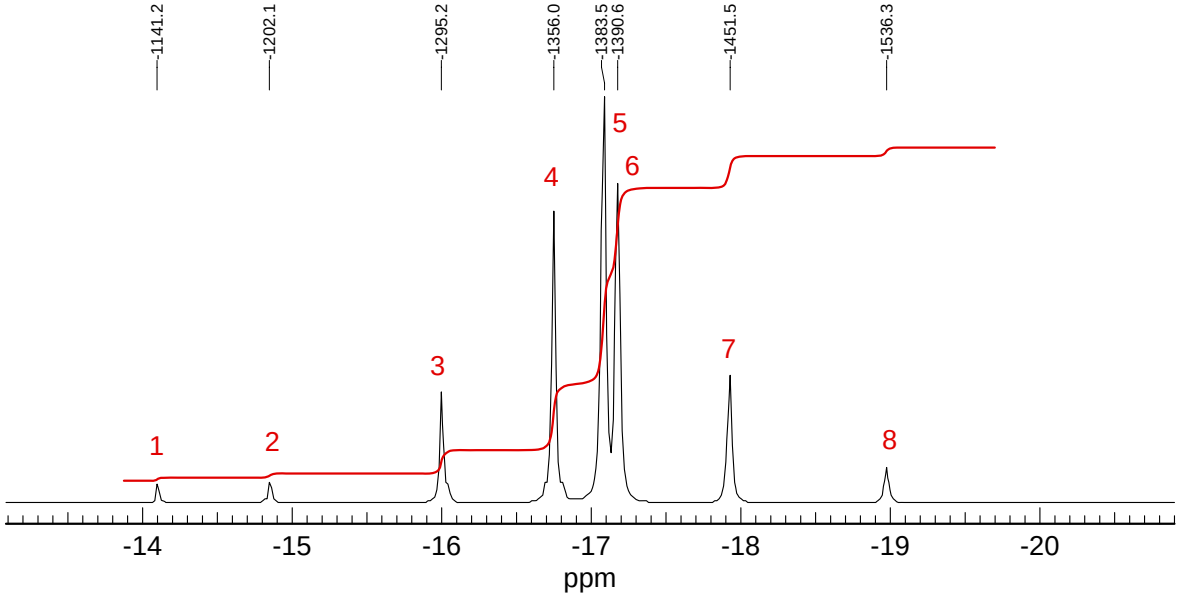
20

Problem Set 12 - 2014 - Answer

Problem R-10K ($C_{42}H_{33}P_3$). The proton decoupled ^{31}P NMR spectrum below is of one of the compounds **1**, **2** or **3**.

Problem R-10K $C_{42}H_{33}P_3$
80.96 MHz ^{31}P {^1H} NMR spectrum.
(Source: Peter H. M. Budzelaar)





(a) Which of the structures is correct? ____**1**____. Explain briefly.

5 **3** Should show just a singlet, **2** should show three shifts (AMX or ABX), each a dd. Neither one fits the spectrum

1 would show an AX_2 or AB_2 pattern, this clearly fits

(b) What kind of pattern is this (e.g. AA'BB') ____AB_2____. Analyze the spectrum to obtain all pertinent coupling constants and chemical shifts, and report them below.

4

$\nu_A = \nu_3 = -1295.2$ Hz, $\delta_A = -16.0$

5 $\nu_A = (\nu_5 + \nu_7) / 2 = -1417.6$ Hz, $\delta_B = -17.51$

$J_{AB} = (\nu_1 - \nu_4 + \nu_6 - \nu_8) / 3 = 120.2$

(c) What is the proton NMR frequency on this spectrometer? ____200____

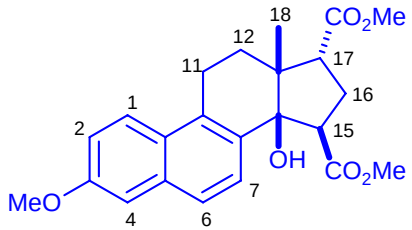
4

$$\frac{\gamma_H}{\gamma_P} \times 80.96 = 199.95 \text{ MHz}$$

Problem R-28B ($C_{23}H_{26}O_5$)
600 MHz ^{1}H NMR in $CDCl_3$
Source: C. Fry (A18)/Wilds

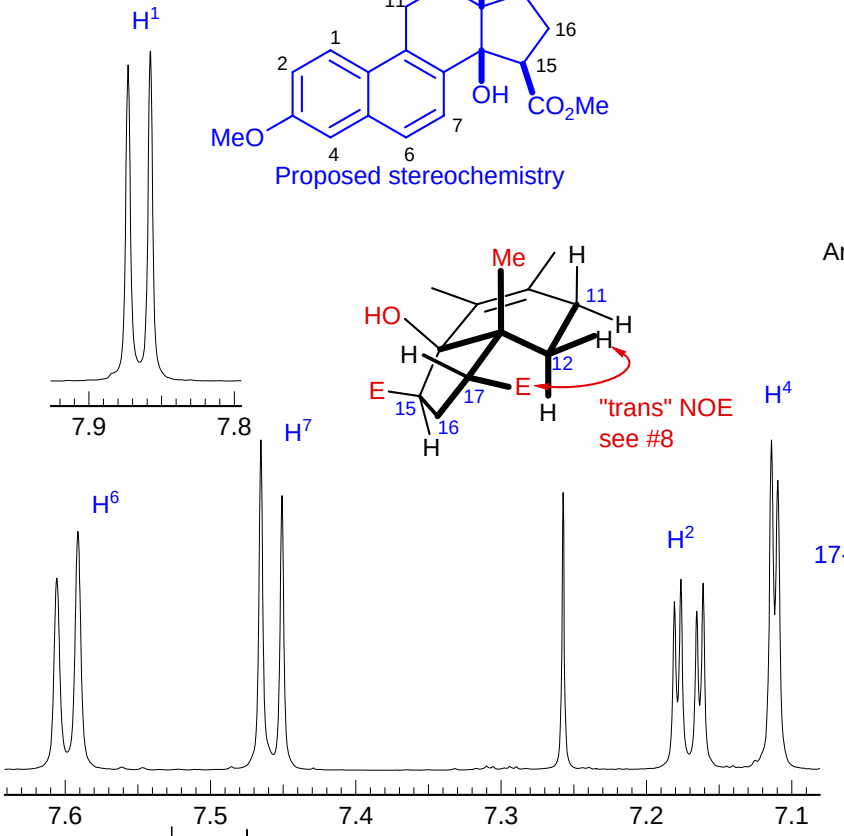
Answer

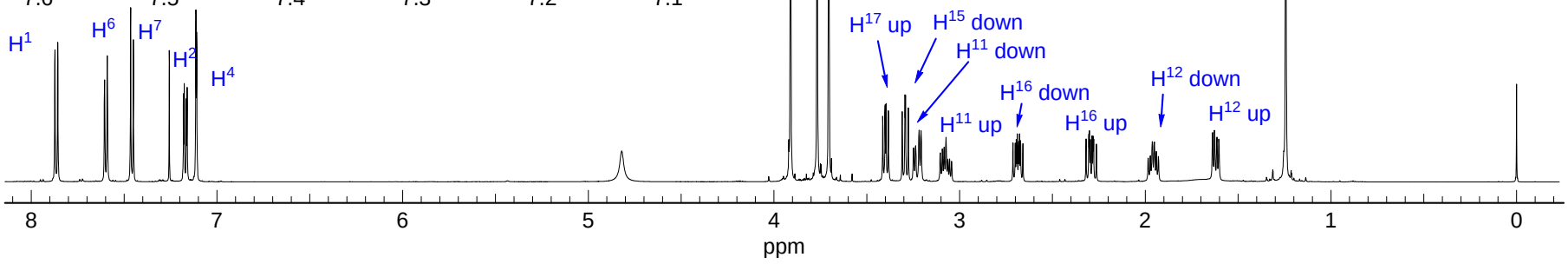
Interpret the NOE difference experiments on the compound below shown on the next two pages. The protons were partially assigned in Problem R-28A. Use the information to complete the assignment and establish the relative stereochemistry at the four asymmetric centers around the cyclopentane ring. Are there any remaining ambiguities?



Proposed stereochemistry

"trans" NOE
see #8

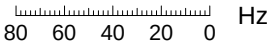




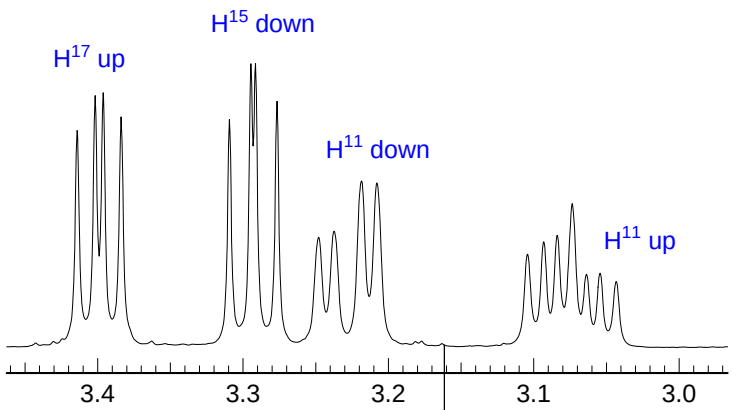
Ar-OMe

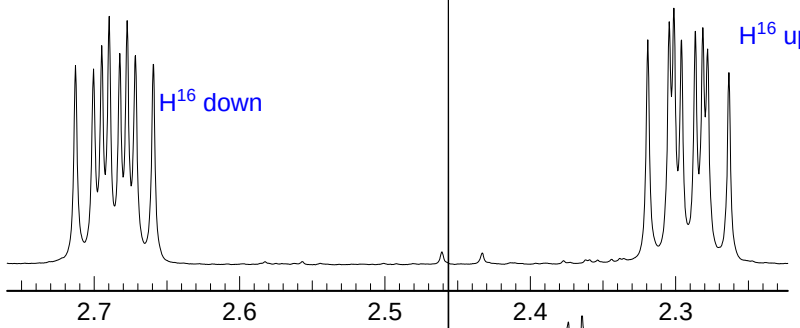
17-CO_2Me

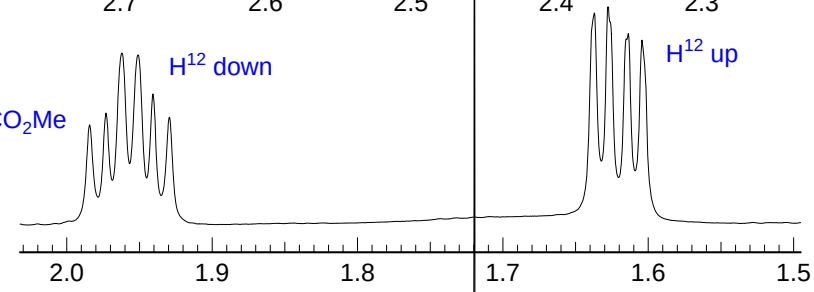
15-CO_2Me

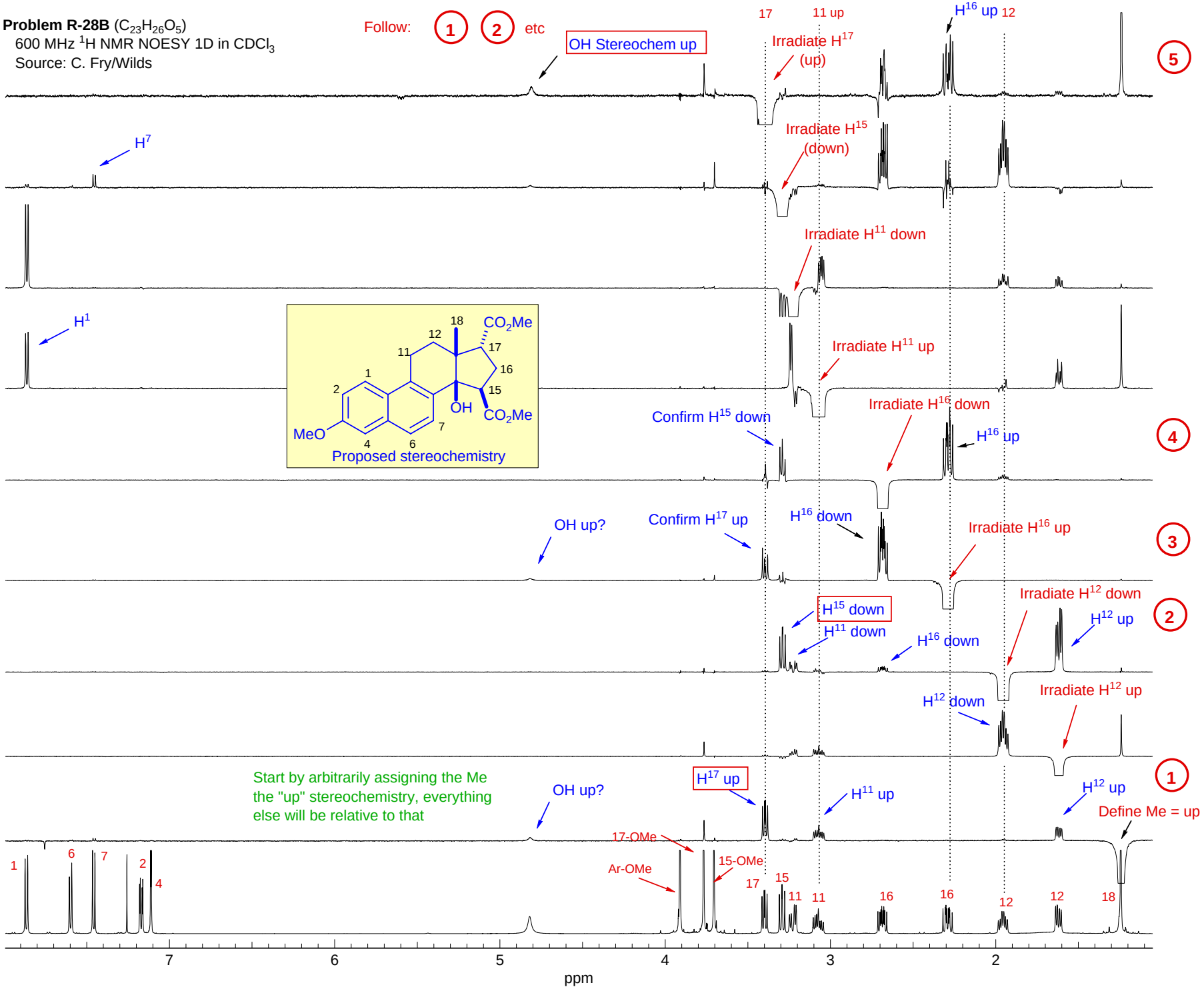


20 Hz/cm



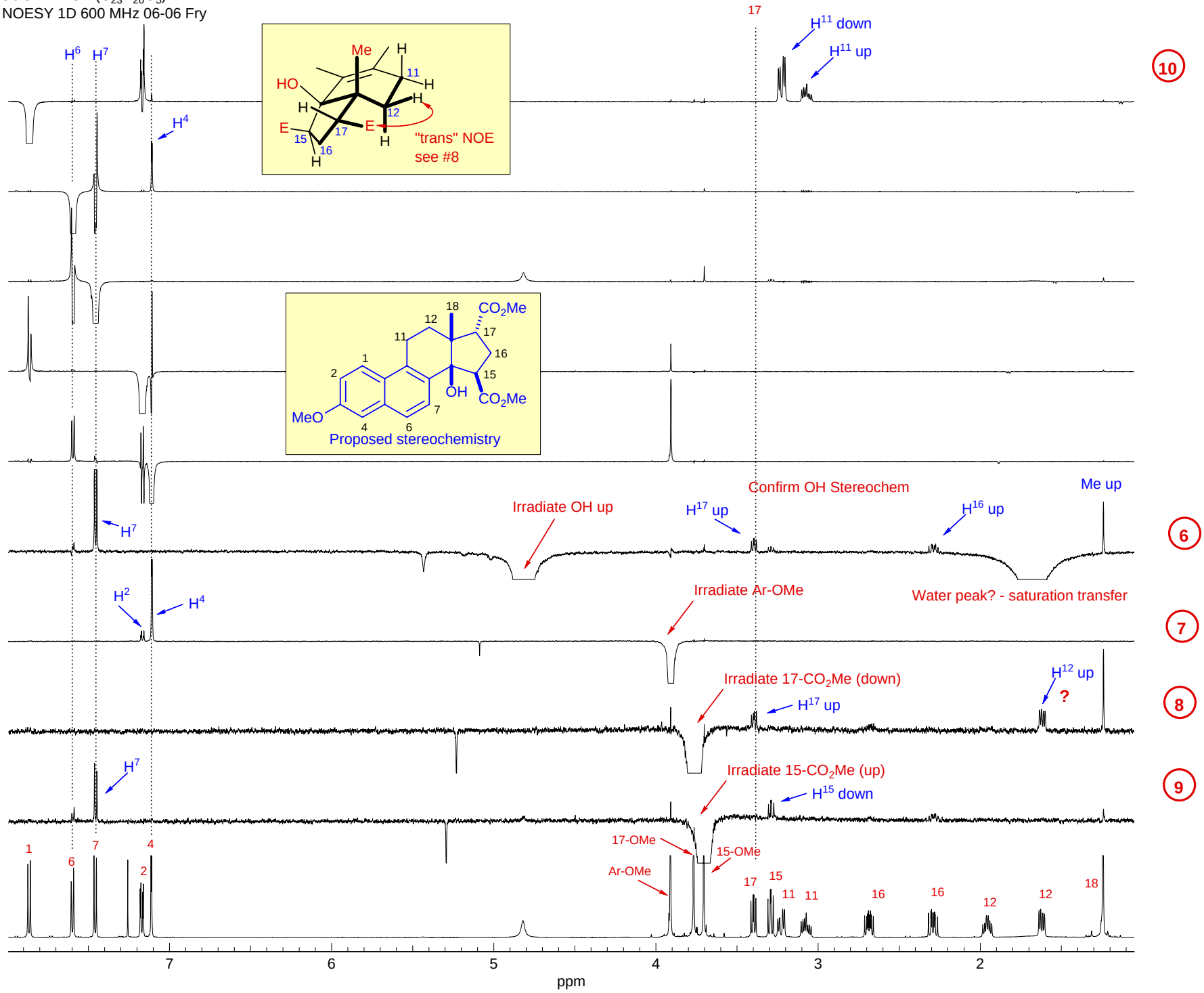




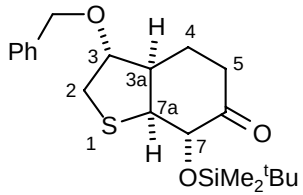

Problem R-28B (C23H26O5)
600 MHz 1H NMR NOESY 1D in CDCl3
Source: C. Fry/Wilds
Follow: 1 2 etc
OH Stereochem up
17
11 up
H16 up 12
Irradiate H17 (up)
5
Irradiate H15 (down)
H7
Irradiate H11 down
H1
Irradiate H11 up
Proposed stereochemistry
Confirm H15 down
Irradiate H16 down
H16 up
4
OH up?
Confirm H17 up
H16 down
Irradiate H16 up
3
H15 down
Irradiate H12 down
H11 down
H12 up
H16 down
2
H12 down
Irradiate H12 up
Start by arbitrarily assigning the Me the "up" stereochemistry, everything else will be relative to that
OH up?
H17 up
H11 up
H12 up
Define Me = up
1
17-OMe
Ar-OMe
15-OMe
1 6 7 2 4
17 15 11 11 16 16 12 12 18
7 6 5 4 3 2
ppm

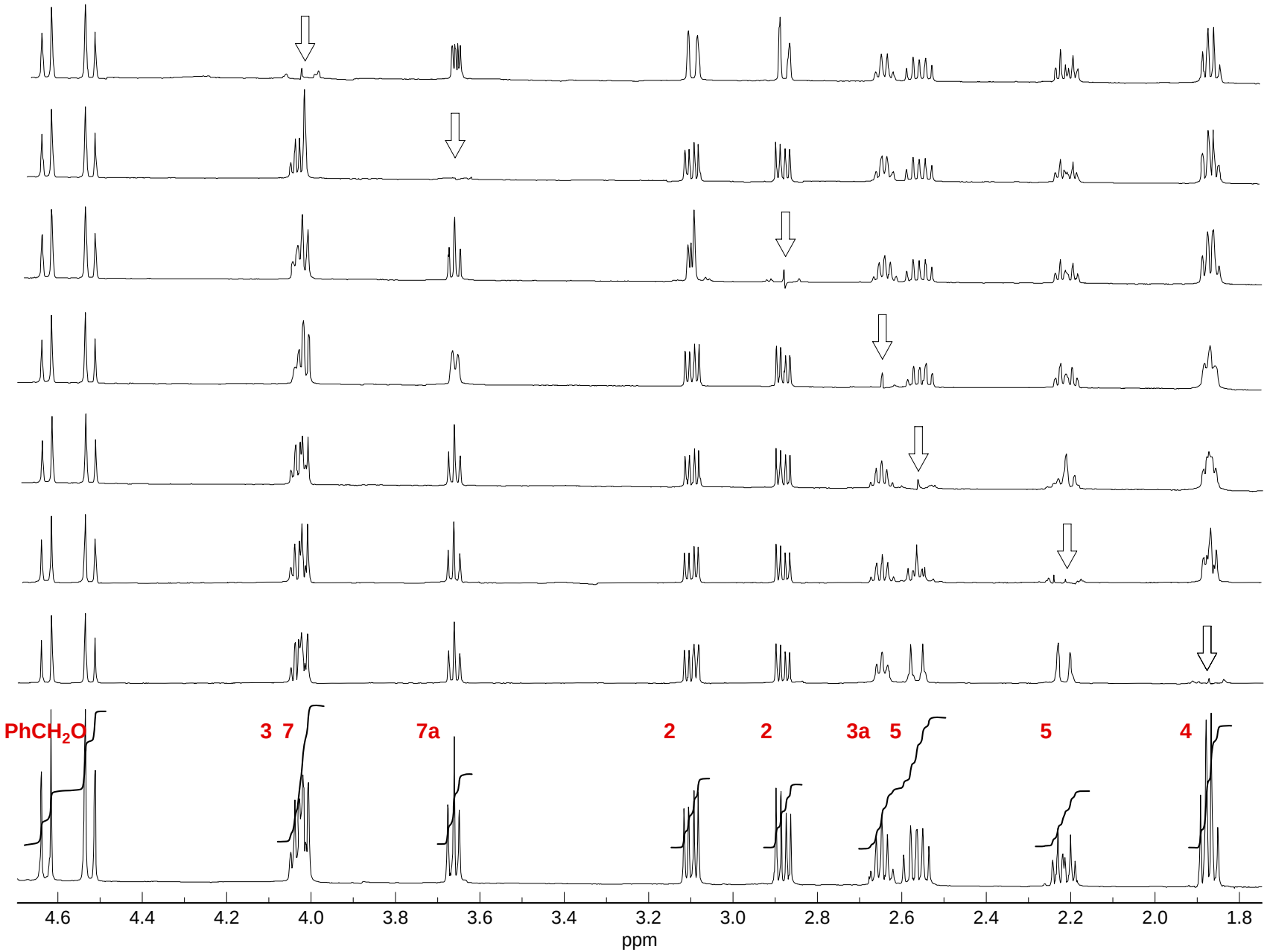
Problem R-28B ($C_{23}H_{26}O_5$)

NOESY 1D 600 MHz 06-06 Fry



Problem R-28C ($C_{21}H_{32}O_3SSi$). Use the 500 MHz ($CDCl_3$) homonuclear decoupled spectra below to assign the protons of the compound shown. Source: Mark Matulenko/Burke





Problem R-84P ($C_{17}H_{27}NO_3Si$)

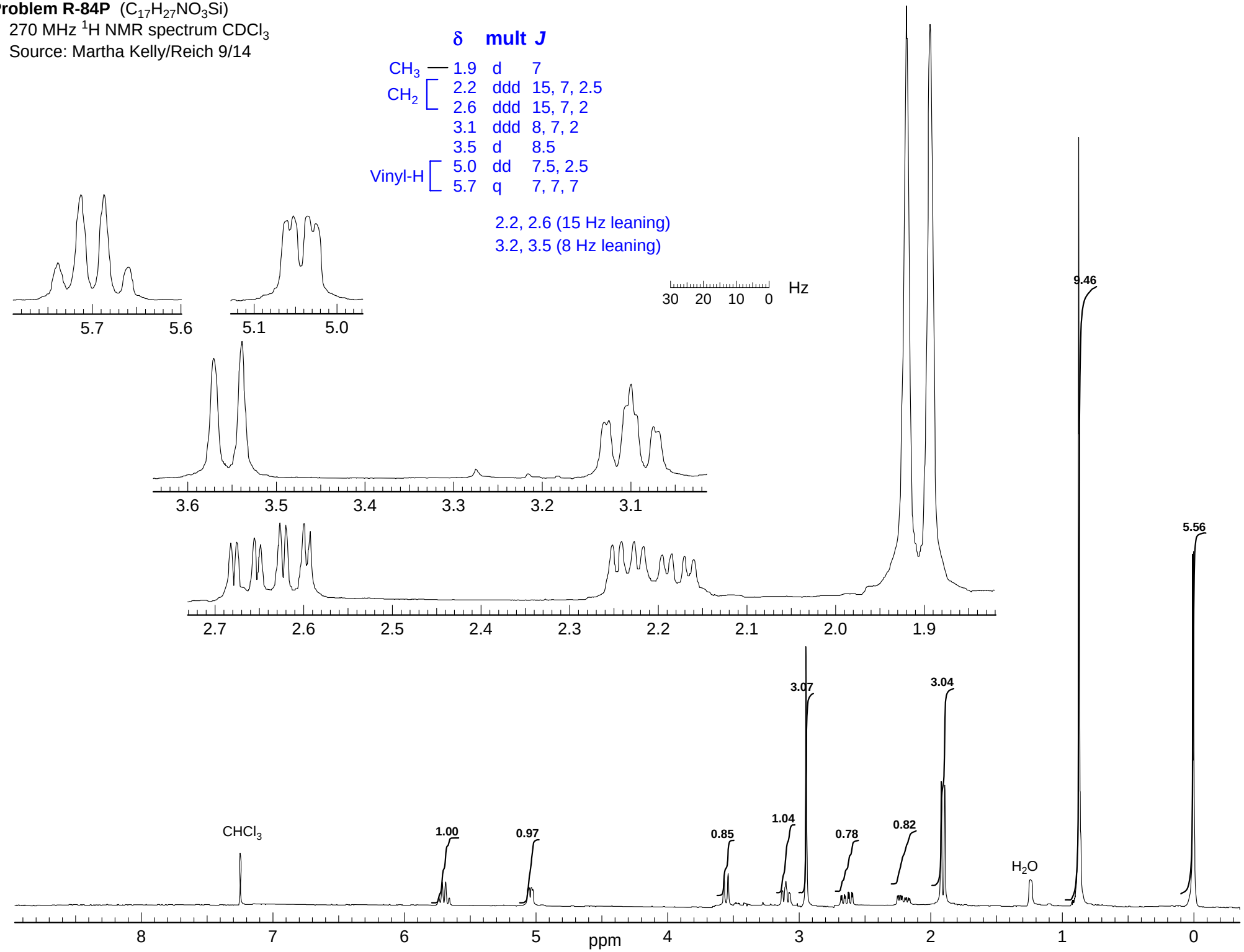
270 MHz ^{1}H NMR spectrum $CDCl_3$

Source: Martha Kelly/Reich 9/14

	δ	mult	*J*
CH_3	1.9	d	7
CH_2	2.2	ddd	15, 7, 2.5
	2.6	ddd	15, 7, 2
	3.1	ddd	8, 7, 2
	3.5	d	8.5
Vinyl-H	5.0	dd	7.5, 2.5
	5.7	q	7, 7, 7

2.2, 2.6 (15 Hz leaning)

3.2, 3.5 (8 Hz leaning)



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	3.1	ddd	8, 7, 2
	3.5	d	8.5
Vinyl-H	5.0	dd	7.5, 2.5
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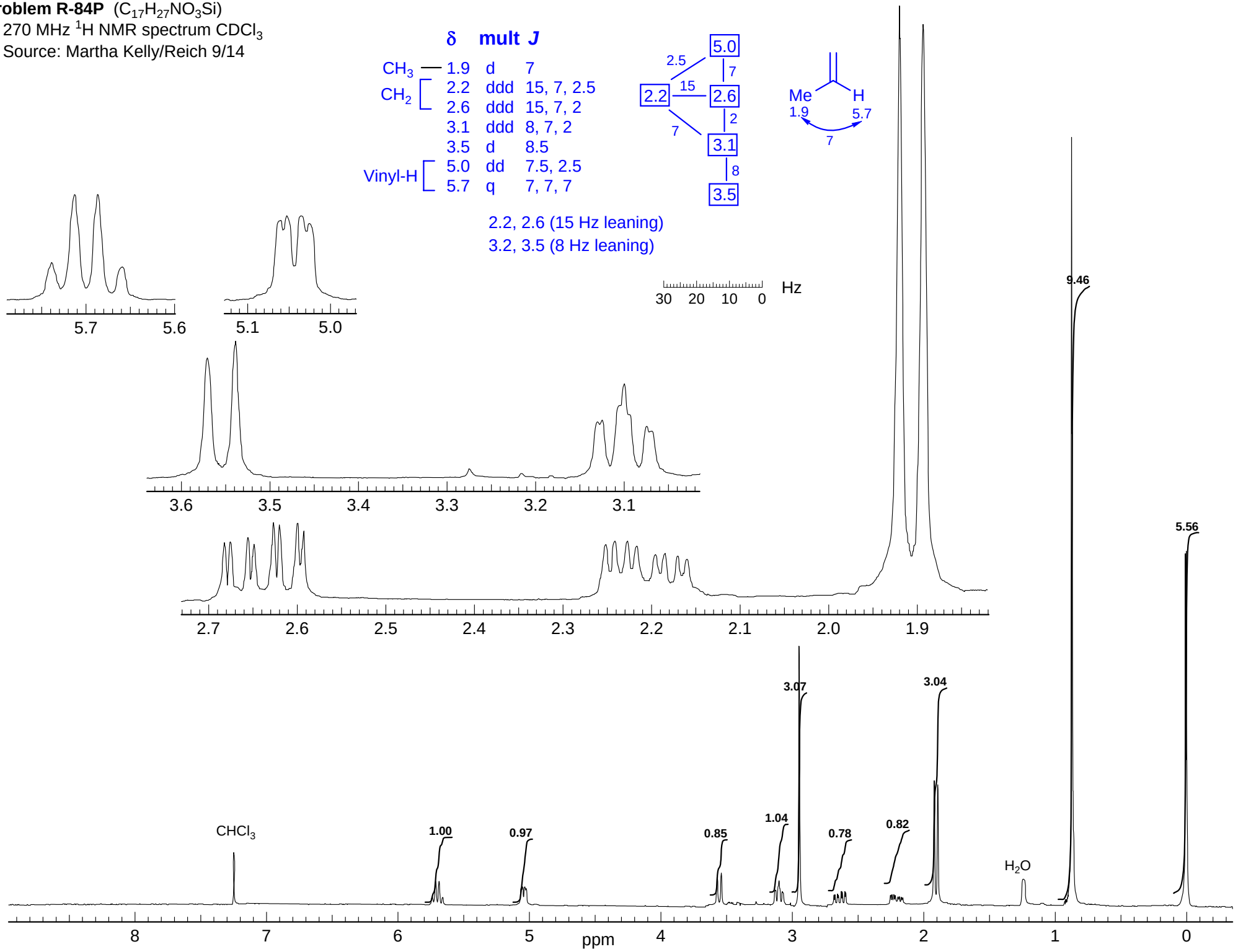

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	3.5	d	8.5
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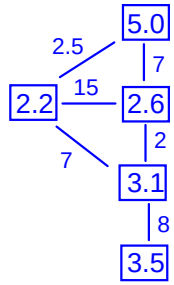

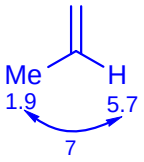

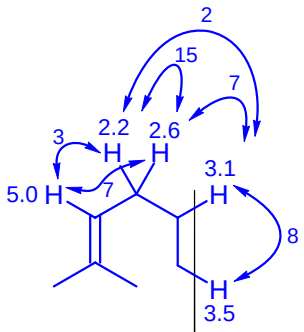

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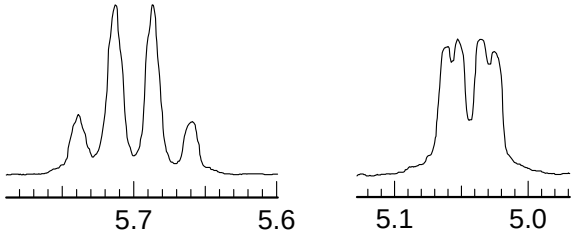
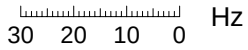
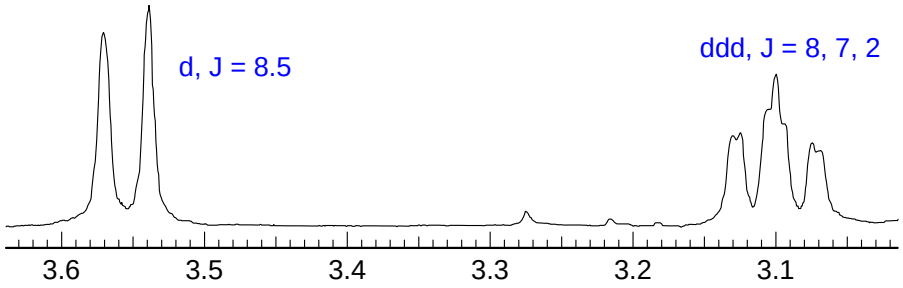
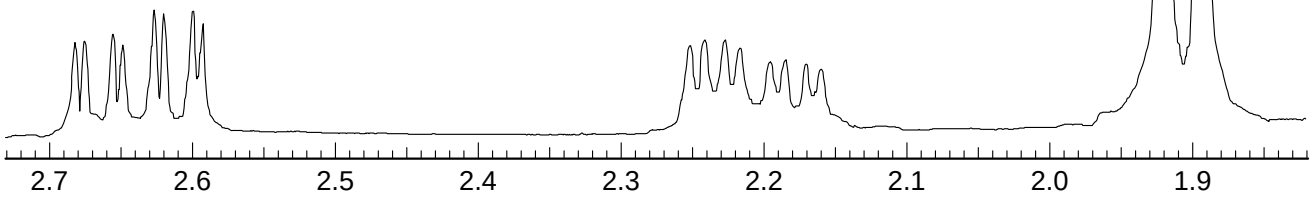
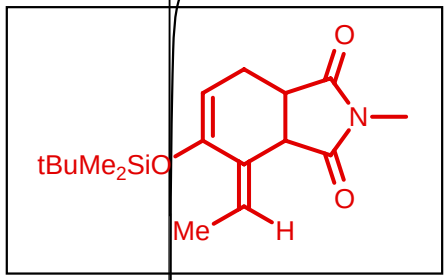
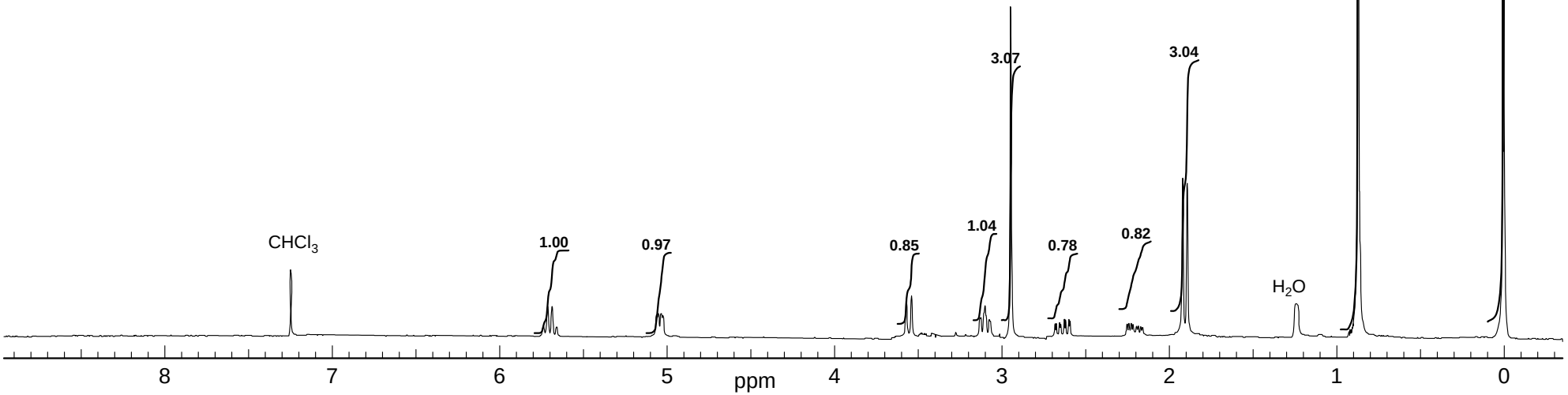




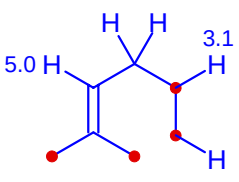


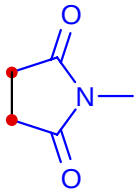


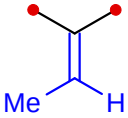


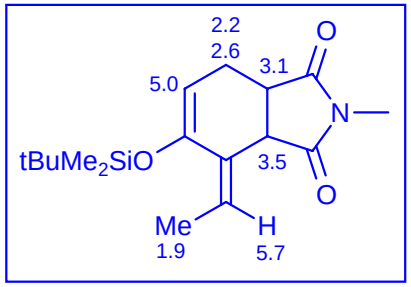


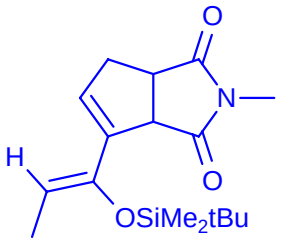
(c) Give a complete structure of **R-84P** below and make a note of any additional structural ambiguities (if any) that remain. Assign signals.



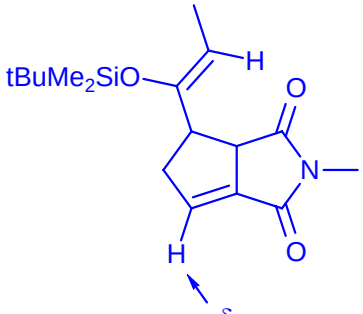




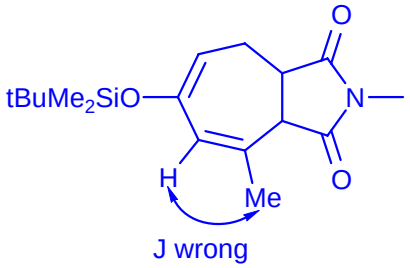




Pretty good alternative structure problem with NOE



δ problem with NOE



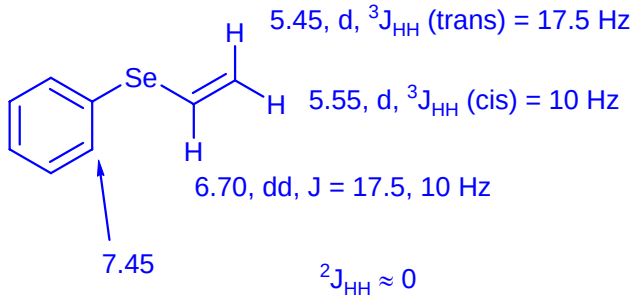
J wrong

22

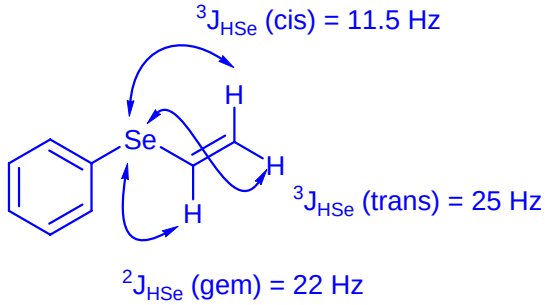
Problem R-10O. (C_8H_8Se) Determine the structure from the 270 MHz ^1H NMR spectrum.

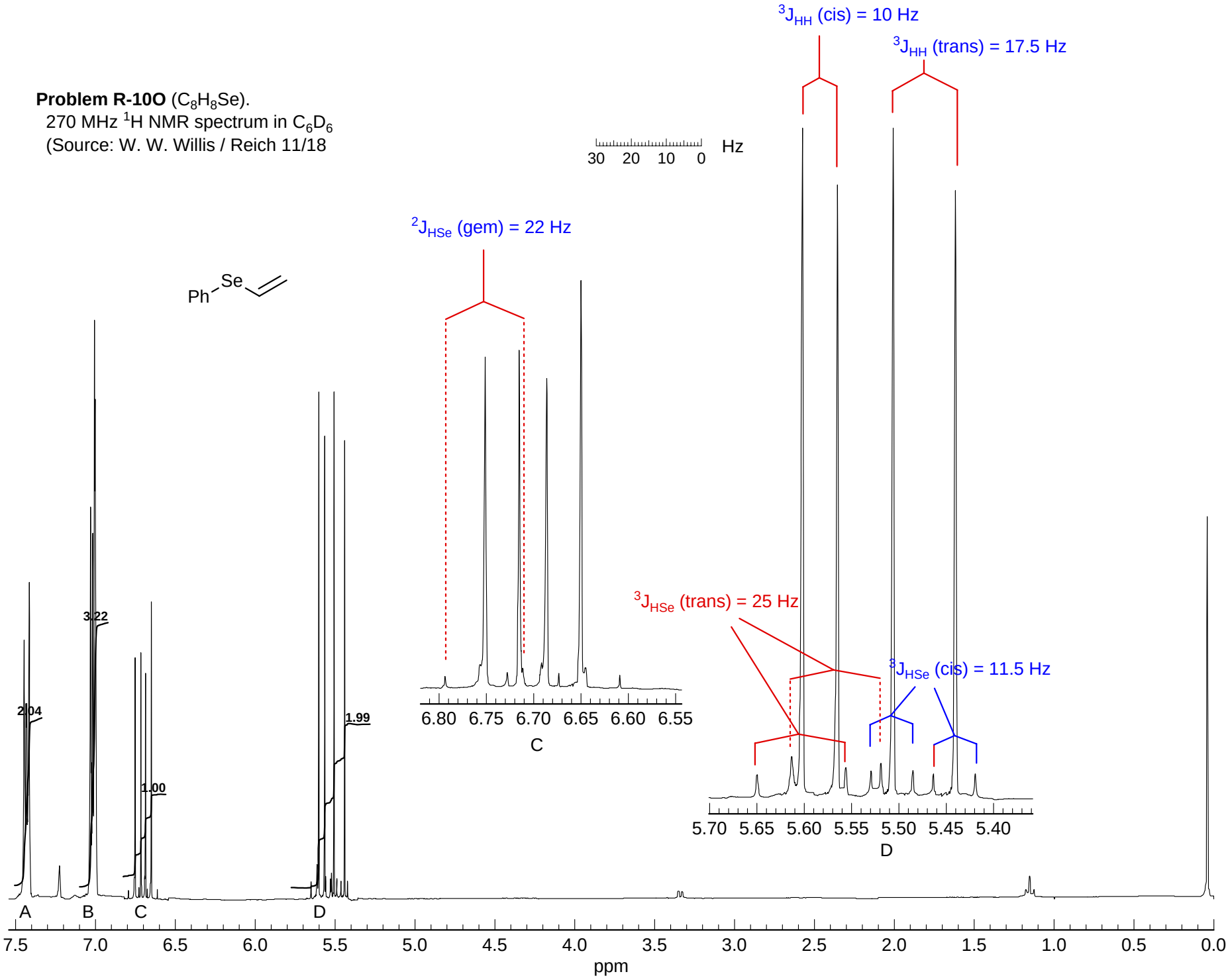
3 (a) DBE 5

(b) Determine the structure of **R-10O**. Mark the chemical shifts on a drawing of the molecule below.



(c) Obtain all of the coupling constants from the expansions of the multiplets C and D. Report them in the standard format ($^nJ_{X\text{-}Y}$ = 0.00 Hz). Clearly mark them on a drawing of the molecule, and on the spectra.



-4 for half/values

Problem R-10O (C_8H_8Se).
270 MHz ^1H NMR spectrum in C_6D_6
(Source: W. W. Willis / Reich 11/18