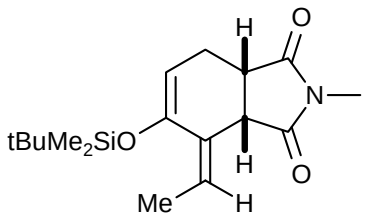
Problem R-84P ($C_{17}H_{27}NO_3Si$)

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

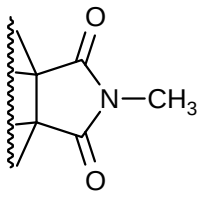
Source: Martha Kelly/Reich (digitized hard copy) 9/14 g



PLT pr-080-to-86.plt

Problem R-84P. The compound $C_{17}H_{27}NO_3Si$ whose 270 MHz ^1H NMR spectrum ($CDCl_3$) is shown has part structures:

$-OSi(CH_3)_2C(CH_3)_3$



(a) DBE____

(b) Identify additional part structures from the NMR spectrum. Give chemical shifts and coupling constants.

(c) Irradiation of the signal at δ 5.7 leads to an increase in area of the signal at δ 3.5 of 24%. However, irradiation of the signal at δ 1.9 leads to no change of the signal at δ 3.5. What experiment is being done here, and what does it tell you about the structure of **R-84P**?

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

(e) Explain the origin of the closely spaced doublet at δ 0 (the sample contains no tetramethylsilane).

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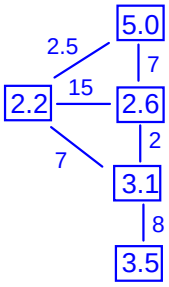
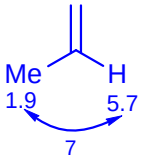
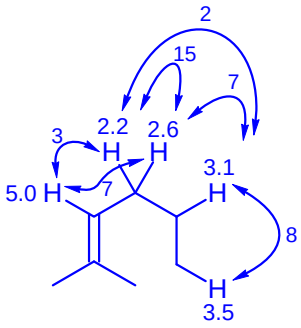
(a) DBE **6**

(b) Identify additional part structures from the NMR spectrum. Give chemical shifts and coupling constants.

	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

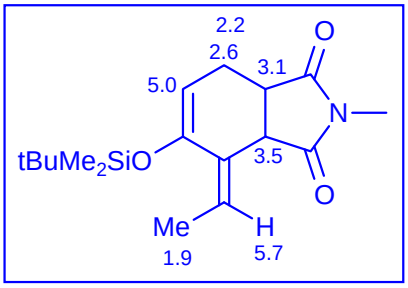




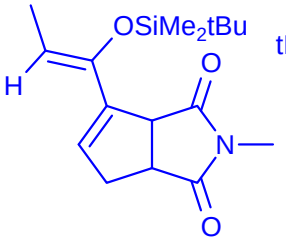


2.2, 2.6 (15 Hz leaning)
3.2, 3.5 (8 Hz leaning)

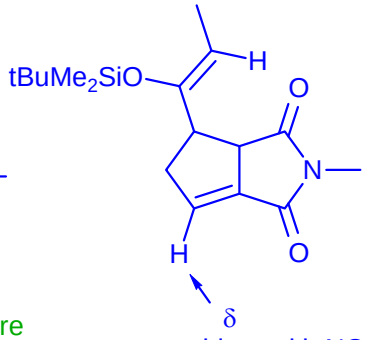
(c) Give a complete structure of **R-84P** below and make a note of any additional structural ambiguities (if any) that remain. Assign signals.



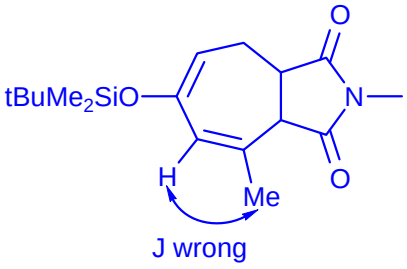
Actual structure



Pretty good alternative structure problem with NOE



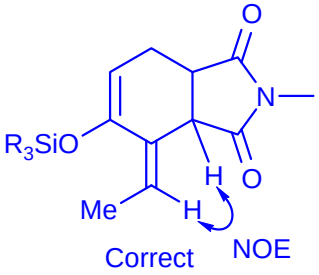
problem with NOE



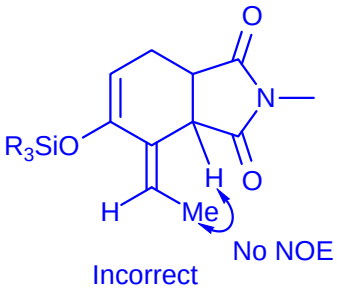
J wrong

(d) Irradiation of the signal at δ 5.7 leads to an increase in area of the signal at δ 3.5 of 24%. However, irradiation of the signal at δ 1.9 leads to no change of the signal at δ 3.5. What experiment is being done here, and what does it tell you about the structure of **R-84P**?

This is a Nuclear Overhauser Effect (NOE) experiment. It tells us that the δ 5.7 and δ 3.5 protons are close in space (i.e., double bond stereochemistry is as shown), and that the proton at δ 5.7 causes a large part of the relaxation of δ 3.5. The protons at δ 1.9 are not very close to δ 3.5 proton.



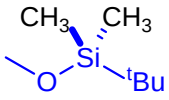
Correct



Incorrect

(e) Explain the origin of the closely spaced doublet at δ 0 (the sample contains no tetramethylsilane).

The molecule is chiral, and hence the gem-dimethyl groups on silicon are diastereotopic.



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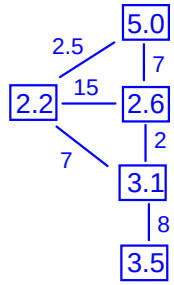

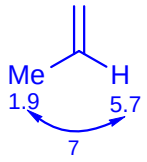

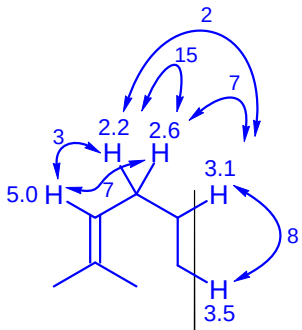

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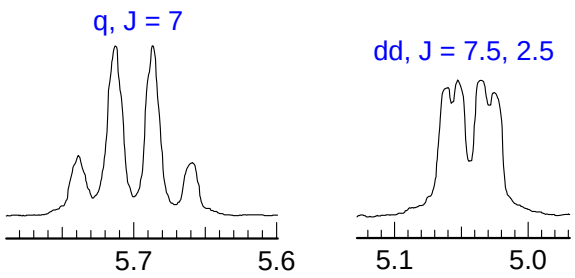

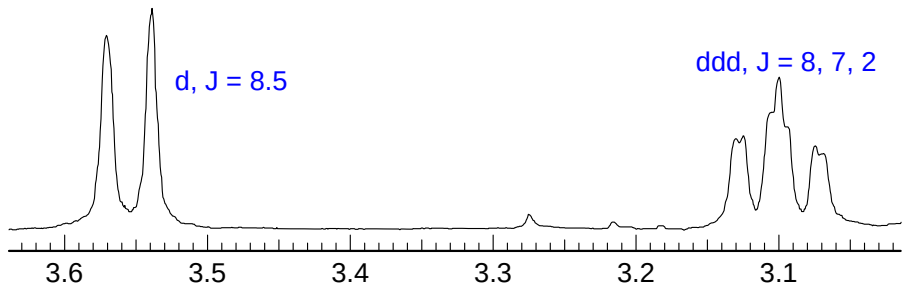

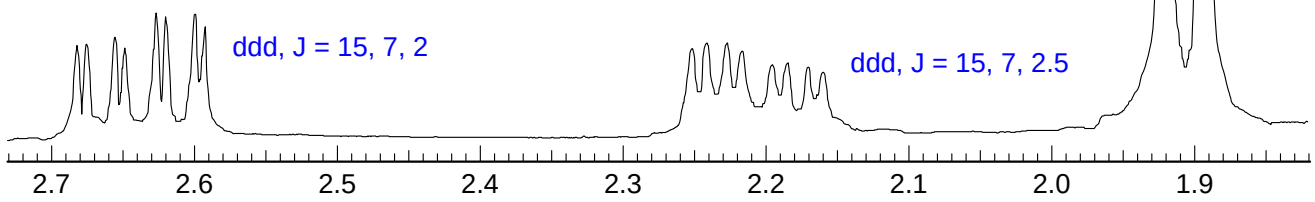

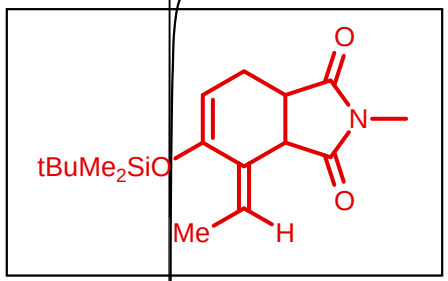

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