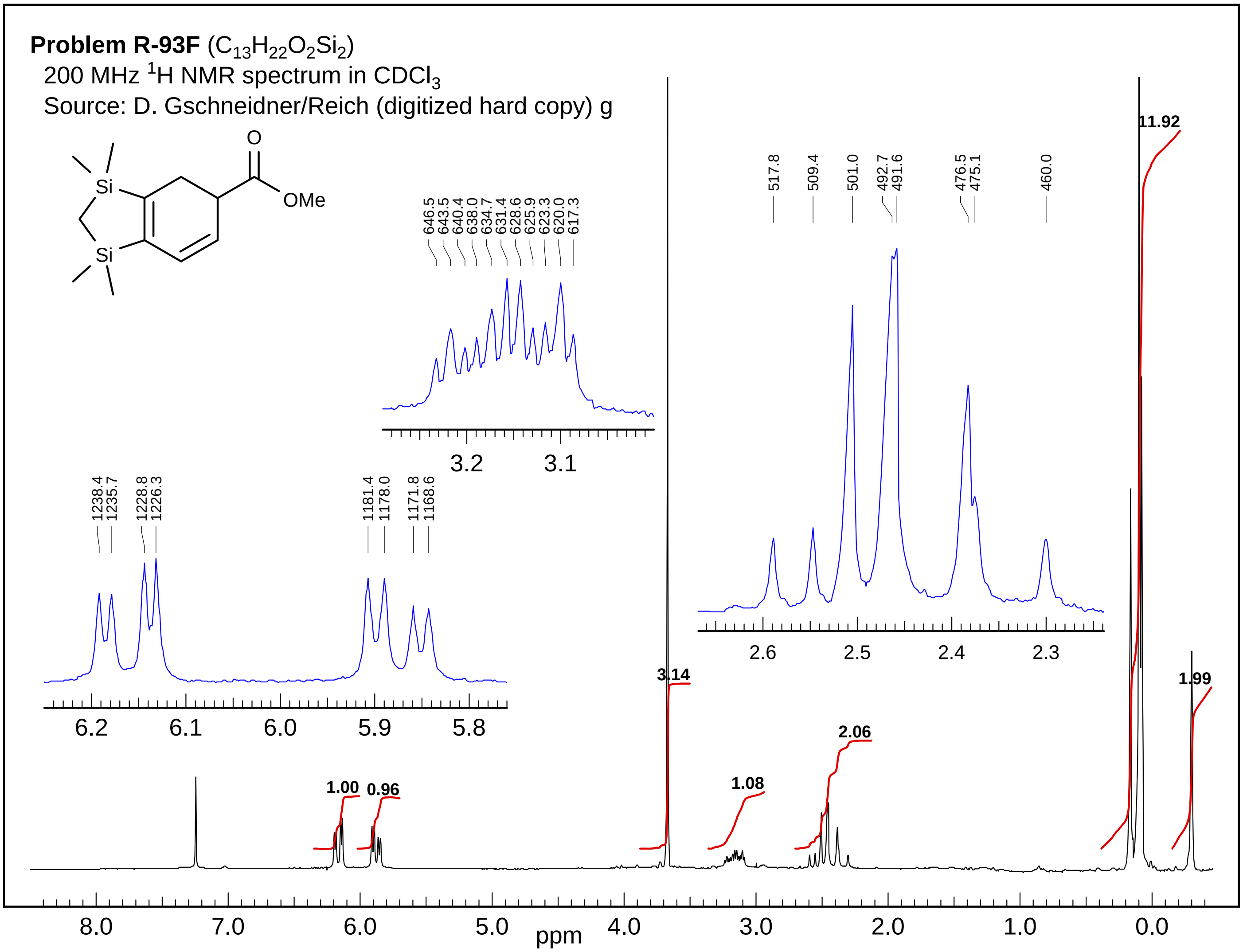
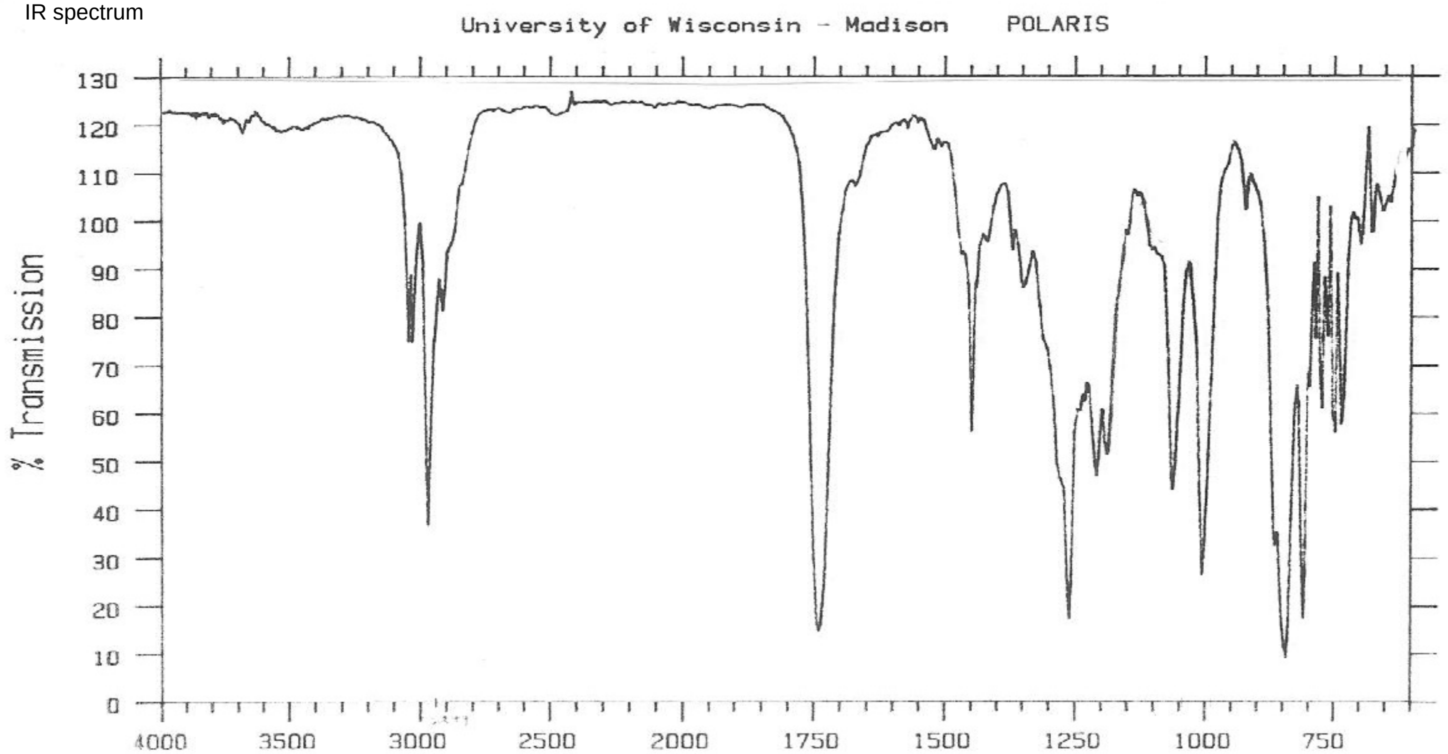
Problem R-93F ($C_{13}H_{22}O_2Si_2$)
200 MHz ^{1}H NMR spectrum in $CDCl_3$
Source: D. Gschneidner/Reich (digitized hard copy) g



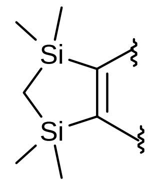
IR spectrum



PLT pr-087-to-95.plt

Problem R-93F ($C_{13}H_{22}O_2Si_2$). A partial structure of **R-93F** is given below:

(a) DBE ___. (b) Analyze important features of the IR spectrum.



(c) Analyze each of the signals in the NMR spectrum. Report δ, *J*, multiplicity, and number of hydrogens (e.g., δ 1.3. dq, *J* = 7, 3 Hz, 2H). Give any part structure the signal identifies.

6.1 ____________________________

5.9 ____________________________

3.6 ____________________________

3.2 ____________________________

2.5 ____________________________

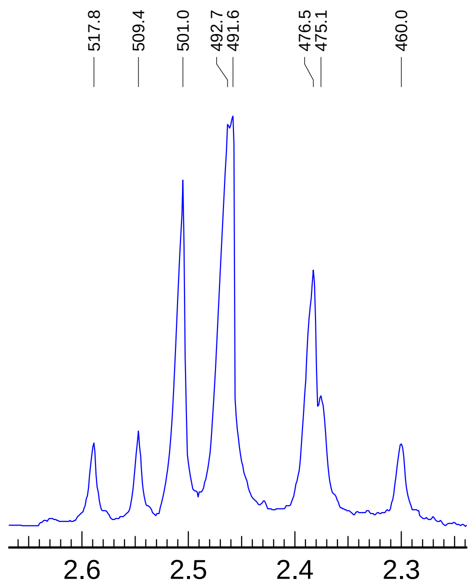
0.1 ____________________________

(d) Draw the structure of **R-93F**. Label the protons.

(e) The coupling constants for the signals near δ 6 are somewhat unusual. Explain, using stereochemical or conformational arguments, if appropriate.

(f) What kind of pattern is the multiplet at 2.5?

(g) Do a complete analysis of this multiplet. Obtain coupling constants and chemical shifts.



PLT pr-087-to-95.plt

Problem R-93F ($C_{13}H_{22}O_2Si_2$)
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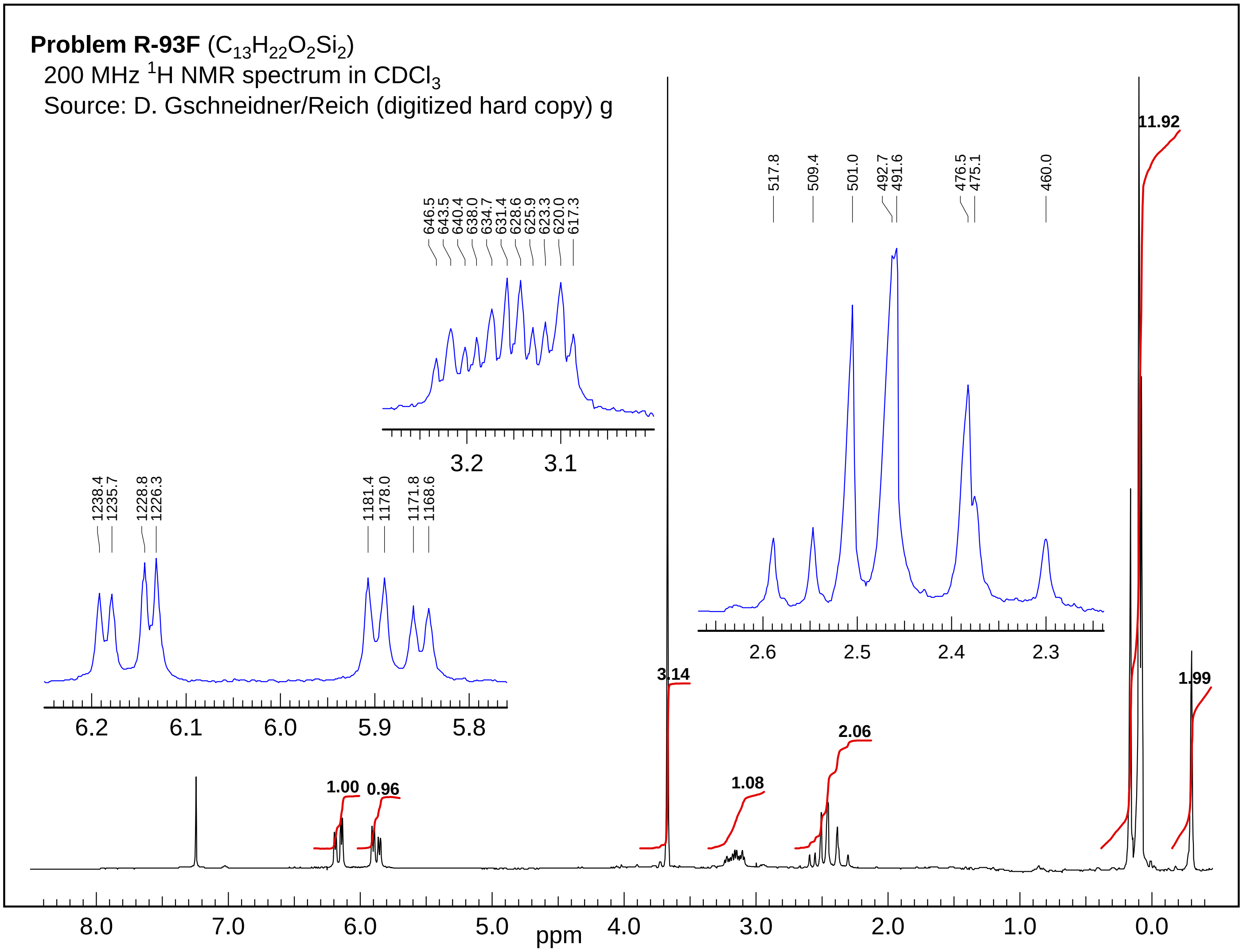
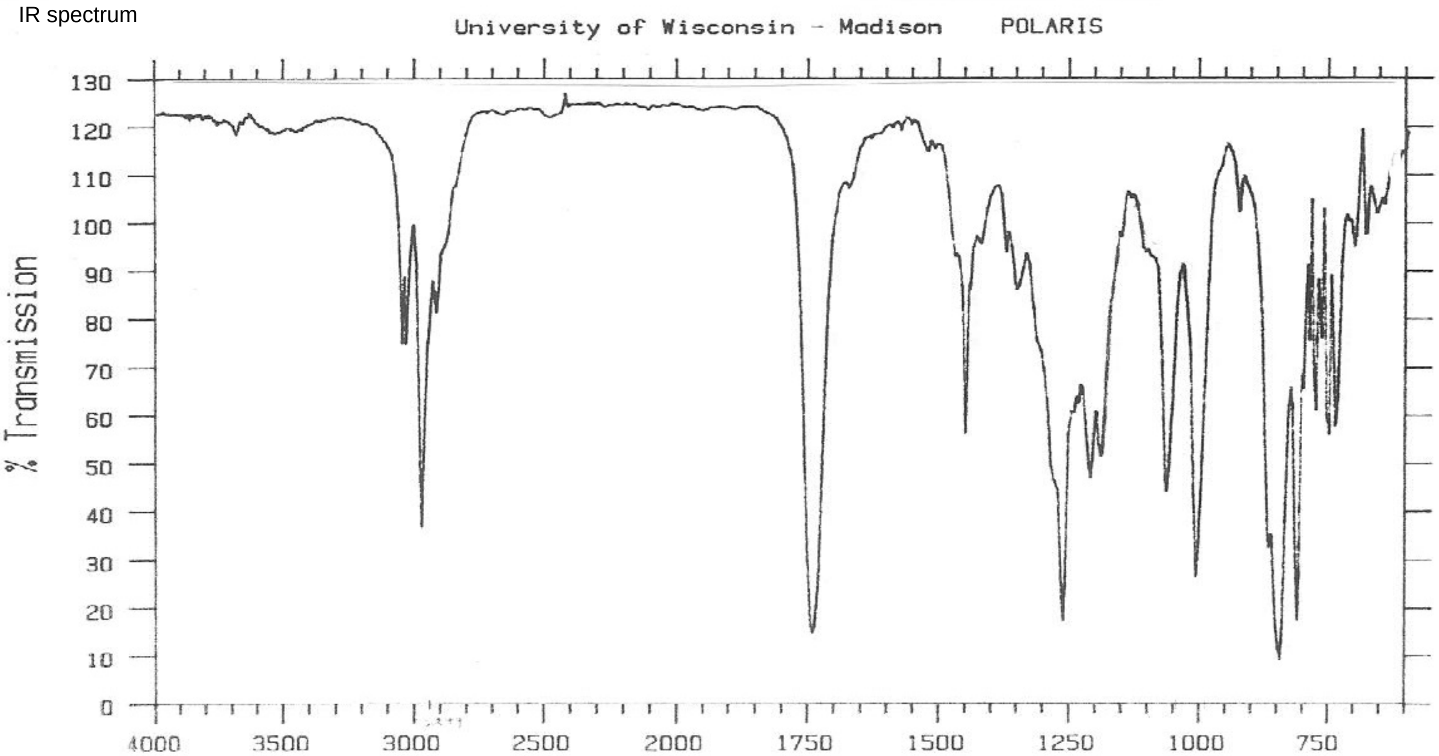


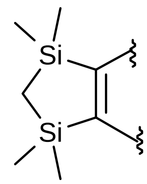
IR spectrum



PLT pr-087-to-95.plt

Problem R-93F ($C_{13}H_{22}O_2Si_2$). A partial structure of **R-93F** is given below:

(a) DBE 5. (b) Analyze important features of the IR spectrum.



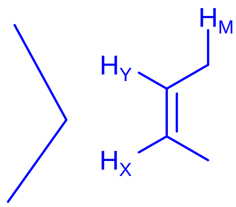
This has 2 DBE, leaving 3 DBE for rest of molecule

1740 cm^{-1} C+O, probably unconjugated ester
No OH - absence of 3500 cm^{-1}
No triple bond - probably

(c) Analyze each of the signals in the NMR spectrum. Report δ, *J*, multiplicity, and number of hydrogens (e.g., δ 1.3. dq, *J* = 7, 3 Hz, 2H). Give any part structure the signal identifies.

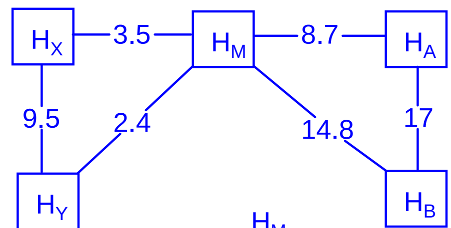
6.1 Y part of ABMXY
δ 6.16, dd, *J* = 9.5, 2.4 Hz, 1H

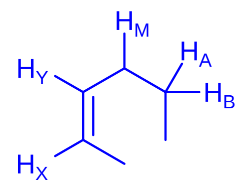
5.9 X part of ABMXY
δ 5.87, dd, *J* = 9.5, 3.5 Hz, 1H



A and B are coupled to each other, probably cis vinyl H, each coupled to one other proton

Coupling constant analysis:





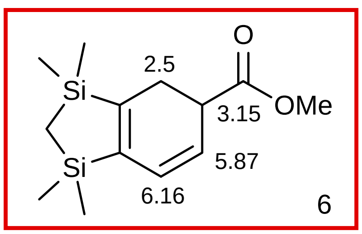
3.6 δ 3.65, s, 3H -OCH_3

3.2 δ 3.15, ddt, *J* = 14.8, 8.7, 3 Hz, M part of ABMXY
Really a dddd since the center peak of the small triplets are clearly broadened, meaning two different *J*

2.5 δ 2.4, 2.5, 2H, AB part of ABMXY,
J_{AB} = 16.5 Hz, J_{AM} = 7.6, J_{BM} = 15.8 Hx

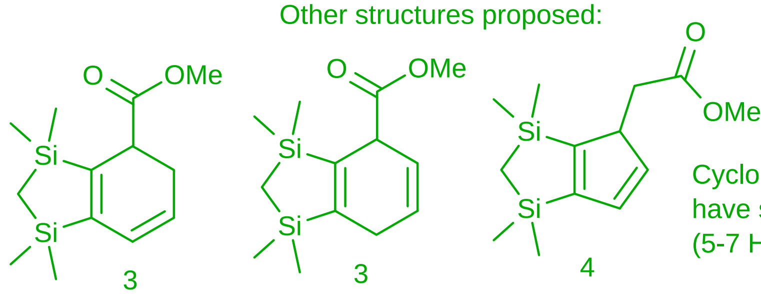
0.1 These are the four diastereotopic Si-CH_3 groups

(d) Draw the structure of **R-93F**. Label the protons.



6

Other structures proposed:



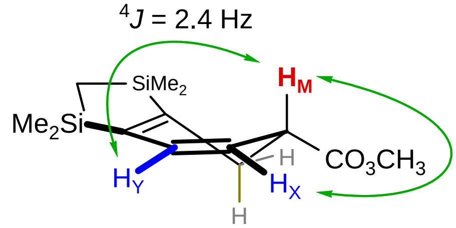
3 3 4

Cyclopentenes have smaller ^3J (5-7 Hz)

(e) The coupling constants for the signals near δ 6 are somewhat unusual. Explain, using stereochemical or conformational arguments, if appropriate.

H_X and H_Y are almost equally coupled to H_M (3.5 and 2.4 Hz), even though one is ^3J and the other ^4J. This is because the conformation with H_M axial is ideal for the long-range (^4J) allylic coupling, but poor for the vicinal (^3J) coupling, with the dihedral angle near 90°. In fact it is possible that the assignments to H_X and H_Y given here might be reversed, with ^4J larger than ^3J.

^4J = 2.4 Hz



^3J = 3.5 Hz

(f) What kind of pattern is the multiplet at δ 2.5?

This is the AB part of an ABMXY pattern

(g) Do a complete analysis of this multiplet. Obtain coupling constants and chemical shifts.

$c_- = (5+3)/2 = 496.3$, $c_+ = (6+4)/2 = 484.6$ Hz

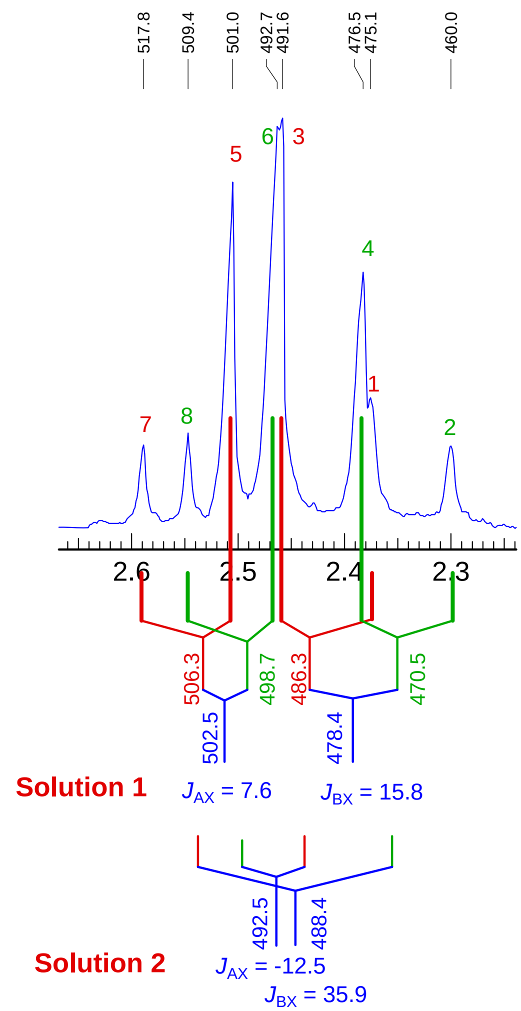
$\Delta\nu_{ab-} = \Delta\delta_- = \mathrm{sqrt}((7-1)(5-3)) = 20.0$ Hz

$c- \pm \Delta\delta_-/2 = 506.3, 486.3$ Hz

$\Delta\nu_{ab+} = \Delta\delta_+ = \mathrm{sqrt}((8-2)(6-4)) = 28.3$ Hz

$c_+ \pm \Delta\delta_+/2 = 498.7, 470.5$ Hz

	Solution 1	**Solution 2**
J_{AB}	16.5	16.5
J_{AM}	7.6	-12.5
J_{BM}	15.8	35.9
ν_A	502.5	492.5
ν_B	478.4	488.4
$\Delta\nu_{AB}$	24.2	4.1
δ_A	2.65	2.63
δ_B	2.59	2.61



Intensity Calculation (D_+ = 6-2, D_- = 7-5)

Solution 1	**Solution 2**
$\Phi1+ = 0.5 \arcsin(J_{AB}/2D+) = 15.2$	$\Phi_2+ = \Phi1 = 15.2$
$\Phi1- = 0.5 \arcsin(J_{AB}/2D-) = 19.5$	$\Phi_2- = 90 - \Phi1- = 70.5$
$i_{10} = i_{11} = 0.994$	$i_{10} = i_{11} = 0.323$
$i_{14} = i_{15} = 0.006$	$i_{14} = i_{15} = 0.676$

The intensity calculations are not too definitive here because of the complexity of the M peak due to coupling with X and Y. However, the magnitude of one of the Solution 2 *J* values (35.9 Hz) is simply too large for an H-H coupling, and the sign of *J* is also wrong - all ^3J are positive, and one of the Solution 2 couplings is negative. Thus Solution 1 is correct.

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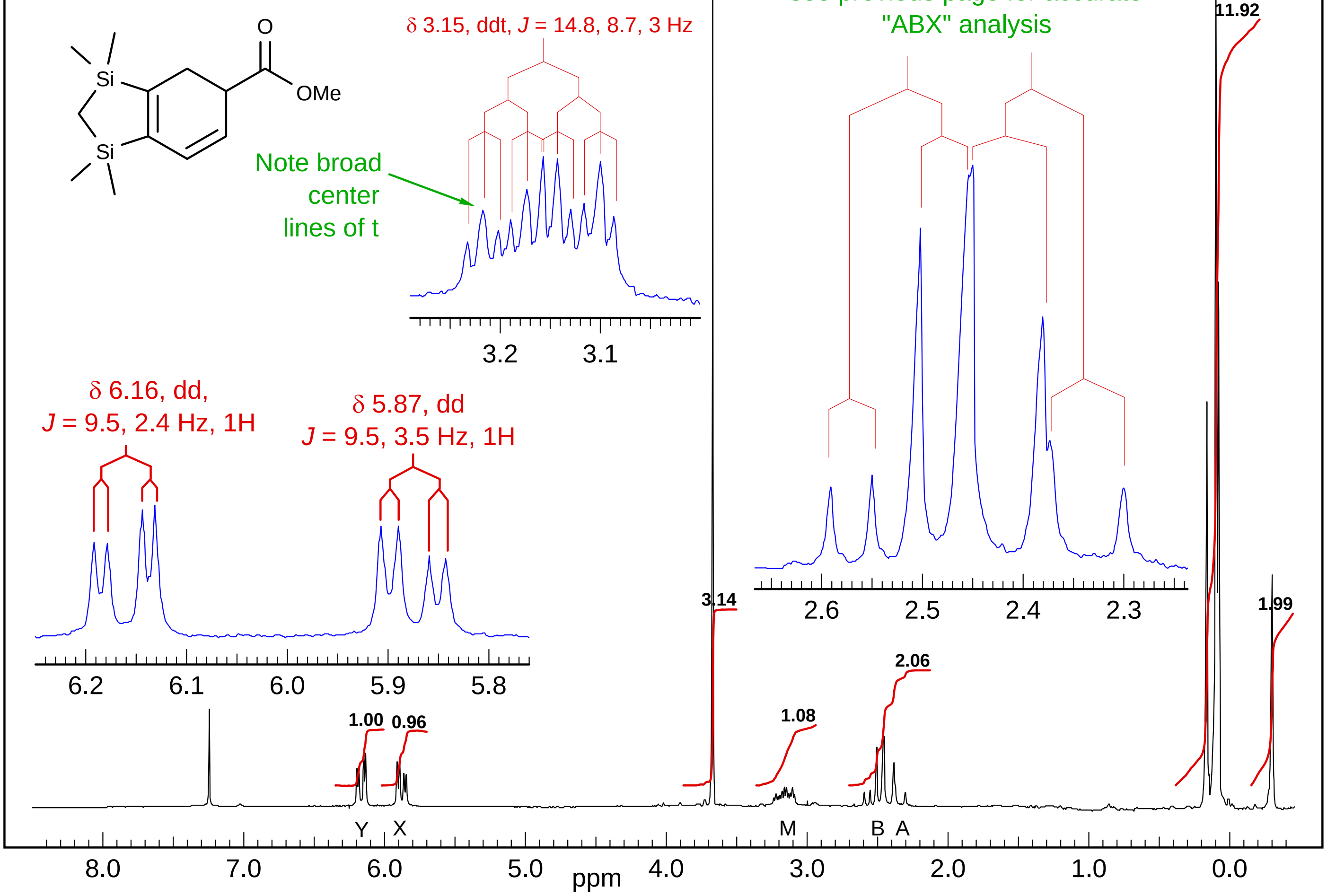

IR spectrum