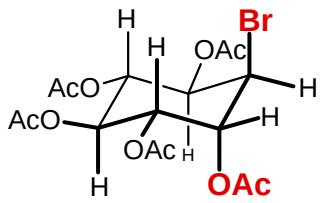
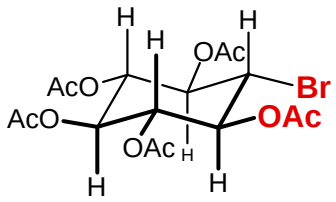
Problem R-11L ($C_{16}H_{21}BrO_{10}$)
270 MHz ^{1}H NMR spectrum in $CDCl_3$
Source: Ieva Reich (digitized hard copy) g



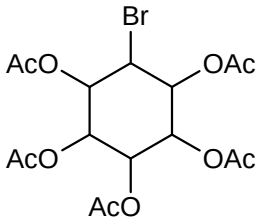
PLT ex-2-2011-12-gq.plt

Problem R-11M ($C_{16}H_{21}BrO_{10}$)
270 MHz ^{1}H NMR spectrum in $CDCl_3$
Source: Ieva Reich (digitized hard copy) g

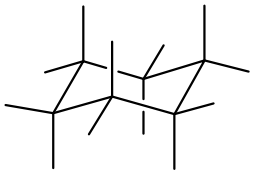


PLT ex-2-2011-12-gq.plt

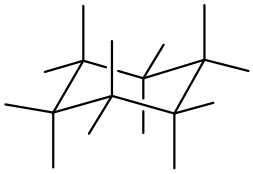
Problem R-11L and R-11M. From the 270 MHz ^{1}H NMR spectra of two stereoisomeric bromo pentaacetoxy cyclohexanes assign stereochemistry and conformation ("interpret" means give δ, *J* and multiplicity).



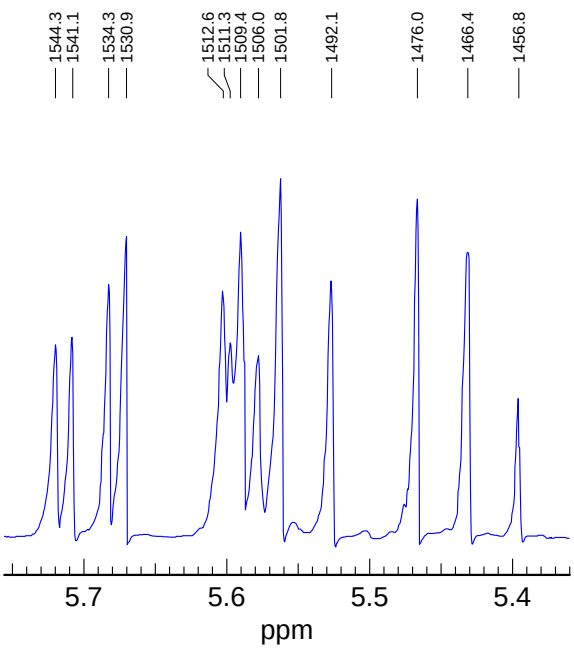
(a) Interpret the signal at δ 4.5 in **R-11L**. Suggest possible part structures. Circle the proton at δ 4.5



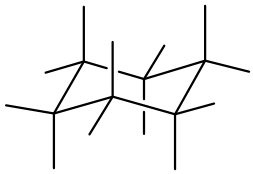
(b) Interpret the signal at δ 5.2 in **R-11L**. Suggest possible part structures. Circle the proton at δ 5.2.



(c) Identify other significant multiplets in the expansion (δ 5.3 - 5.8) on the right (**R-11L**), draw coupling trees, and identify part structures. HINT: these are all first order



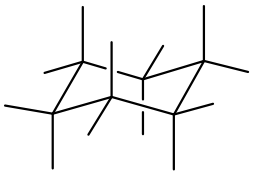
(d) Complete the structure for **R-11L** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.



R-11L

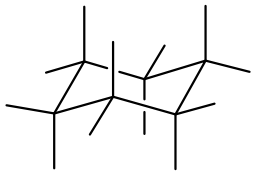
(e) What do the signals at δ 2 tell you about the structure of **R-11M** (compare them to the δ 2 signals of **R-11L**).

(f) Assign and interpret the signal at δ 4.0 in **R-11M**. Suggest possible part structures.



(g) Analyze the rest of the NMR spectrum of **R-11M**. Point out significant features of the spectrum which can be used to assign stereochemistry. HINT: there are some second-order effects in the multiplet δ 5.1 - 5.5.

(h) Complete the structure of **R-11M** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.

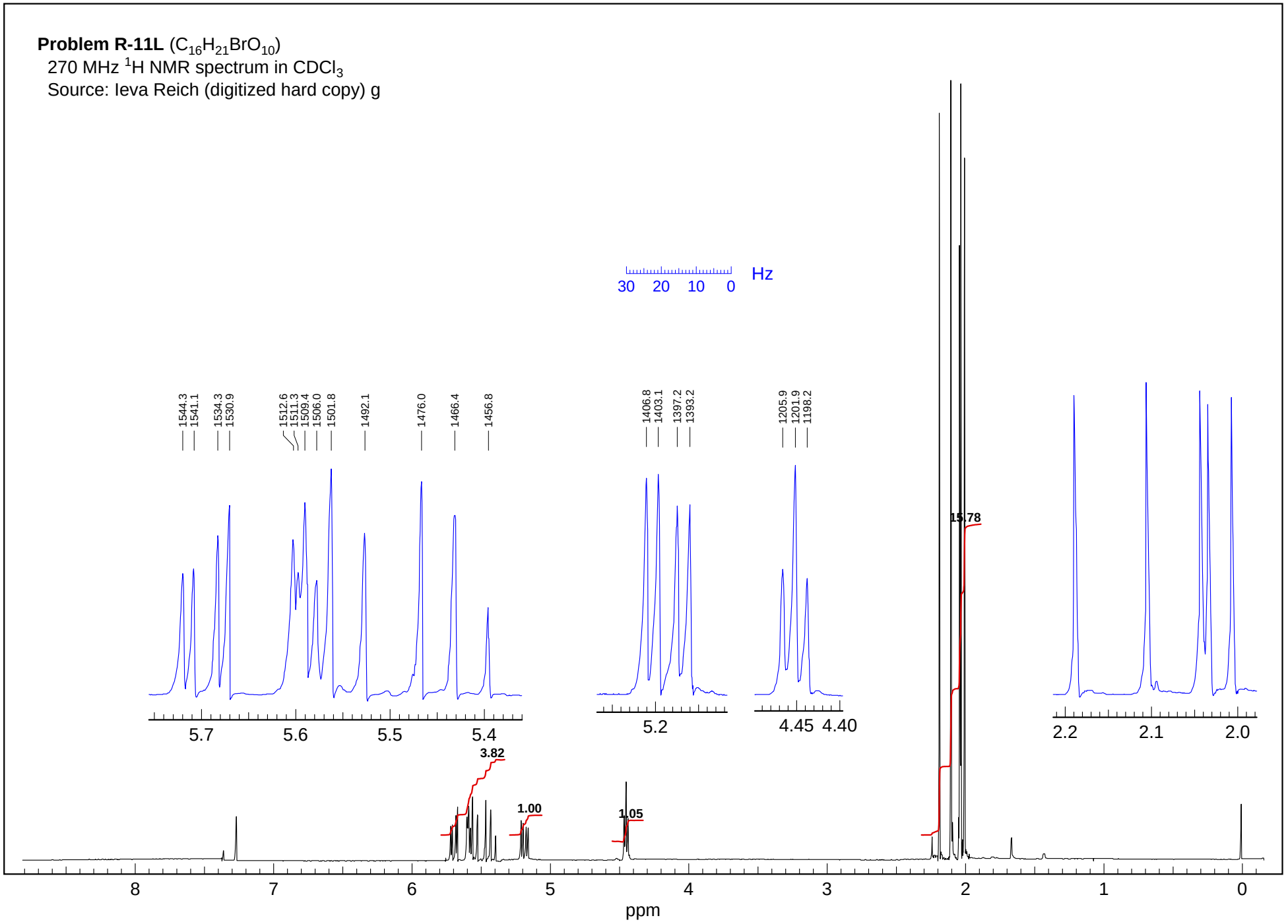


R-11M

Problem R-11L ($C_{16}H_{21}BrO_{10}$)

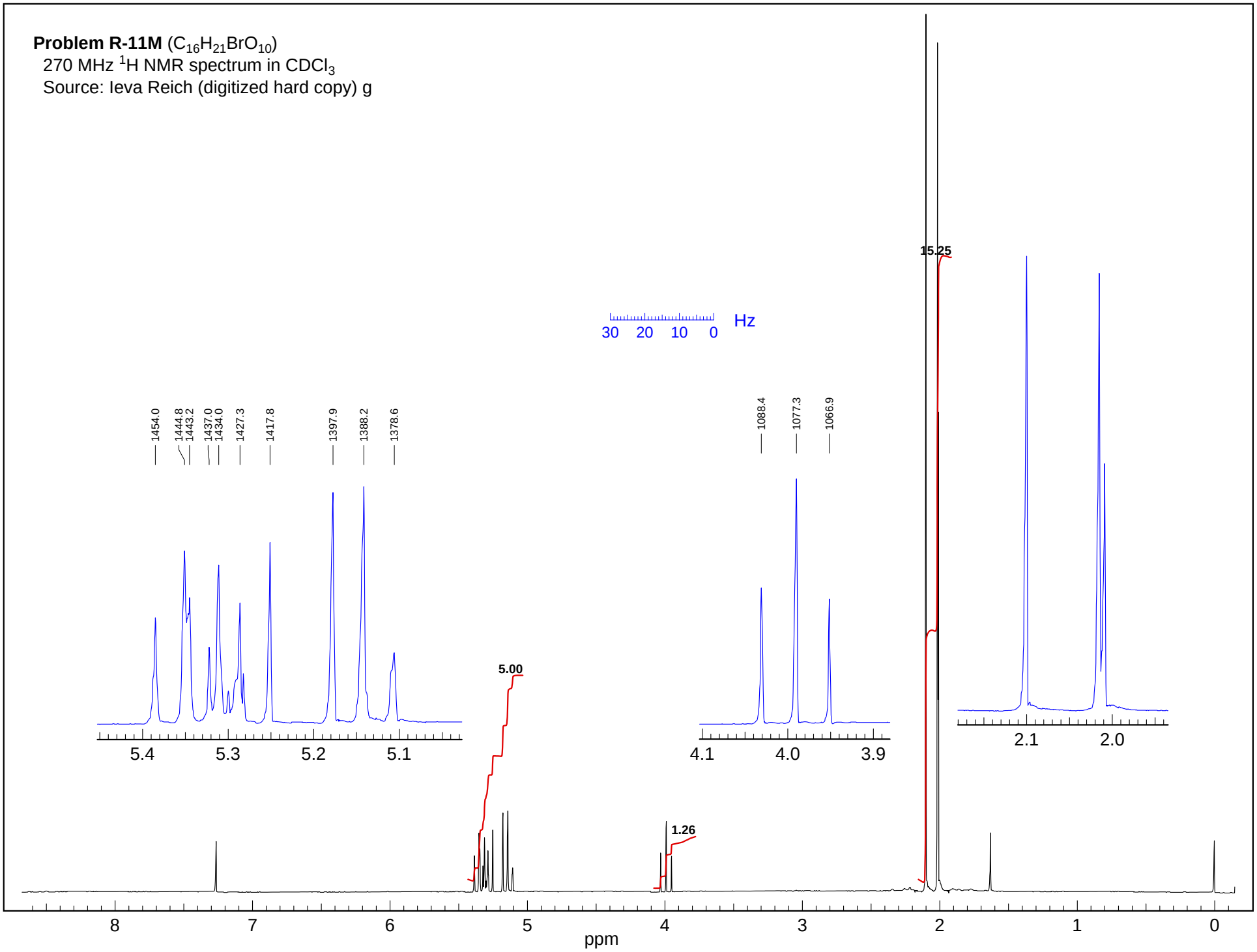
270 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: Ieva Reich (digitized hard copy) g



PLT ex-2-2011-12-gq.plt

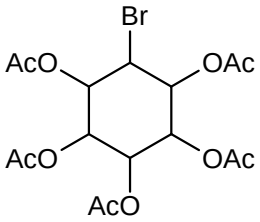
Problem R-11M ($C_{16}H_{21}BrO_{10}$)
270 MHz ^{1}H NMR spectrum in $CDCl_3$
Source: Ieva Reich (digitized hard copy) g



PLT ex-2-2011-12-gq.plt

30

Problem R-11L and R-11M. From the 270 MHz ^{1}H NMR spectra of two stereoisomeric bromo pentaacetoxy cyclohexanes assign stereochemistry and conformation ("interpret" means give δ, *J* and multiplicity).

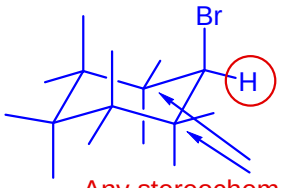


(a) Interpret the signal at δ 4.45 in **R-11L**. Suggest possible part structures. Circle the proton at δ 4.45

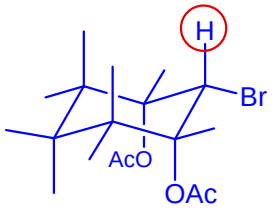
4

δ 4.45, t, J = 3.9 Hz (really a dd) - the chemical shift suggests a CHBr proton, the small couplings must be ee or ae:

Curphy-Morrison:
α Br 2.2, α OAc: 3.45 ppm



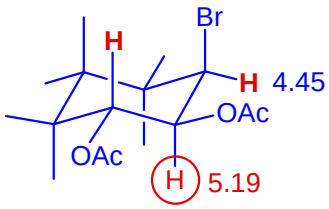
Any stereochem here



Less likely, but possible

(b) Interpret the signal at δ 5.19 in **R-11L**. Suggest possible part structures. Circle this proton.

4



δ 5.19, dd, J = 9.8, 3.9

- must be an axial proton (10 Hz J) with one neighboring eq and one ax

- probably coupled to δ 4.45 proton (the one at 5.7 has a smaller J, and leaning suggests it is coupled to the t at 5.59)

(c) Identify other significant multiplets in the expansion (δ 5.3 - 5.8) on the right (**R-11L**), draw coupling trees, and identify part structures. HINT: these are all first order

6

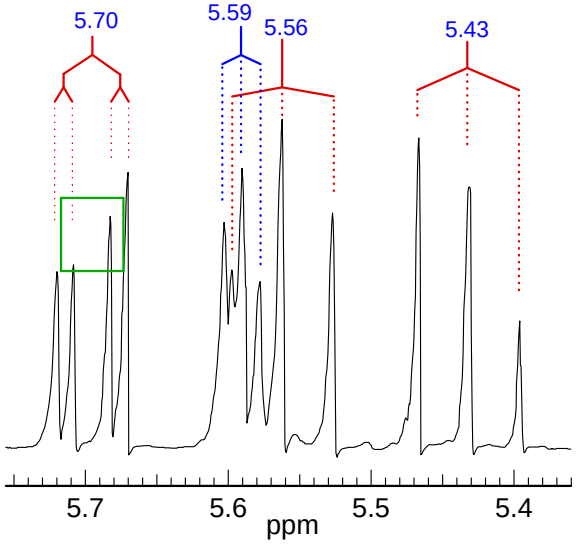
δ 5.43, t (J = 10), axial proton, axial on both sides

δ 5.56, t (J = 10), axial proton, axial on both sides

δ 5.59, t (J = 3.3), equatorial proton

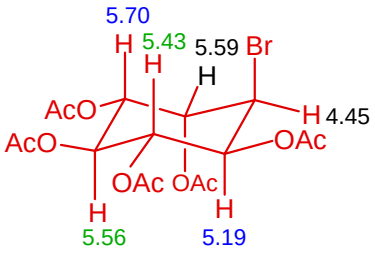
δ 5.70, dd (J = 10, 3.3), axial on one side, equatorial on other

5.43 and 5.56 are coupled to each other - hence adjacent



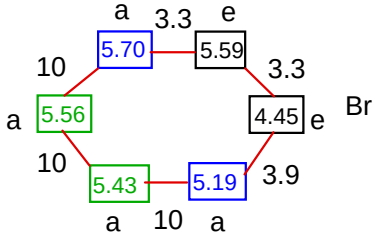
(d) Complete the structure for **R-11L** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.

4



R-11L

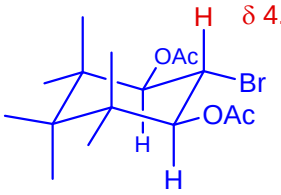
The two adjacent triplets with large *J* (5.43 and 5.56) means that there must be four adjacent axial hydrogens. The other two protons (4.45, 5.59) must be equatorial (triplets with J <4 Hz)



(e) What do the signals at δ 2 tell you about the structure of **R-11M** (compare them to the δ 2 signals of **R-11L**).

3 The CH_3-C(=O) signals are in a 2:2:1 ratio, so there is likely a symmetry element in the molecule (there are 5 different ones in R-11L)

(f) Assign and interpret the signal at δ 4.0 in **R-11M**. Suggest possible part structures.



3 δ 4.0, t (J = 10.7), 1H

From the shift, this must the CHBr proton. The 10.7 Hz triplet means the proton is axial, and so are both flanking protons

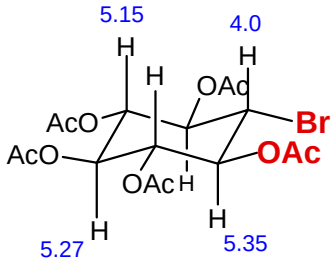
(g) Analyze the rest of the NMR spectrum of **R-11M**. Point out significant features of the spectrum which can be used to assign stereochemistry. HINT: there are some second-order effects in the multiplet δ 5.1 - 5.5.

δ 5.15, t (J = 9 Hz), 2H

δ 5.35, probably a dd J = 10.8, 9.2 Hz) 2H

3 There is a third proton at ca 5.27 (1H), which shows some second order effects (it is probably coupled to the overlapping 5.35 proton), but is basically also a triplet with J = 10. Thus all protons are of the axial type, The 5.27 can't be an equatorial proton, because that will cause 2 other protons to have one small coupling.

(h) Complete the structure of **R-11M** below by placing bromo and acetoxy groups with the appropriate stereochemistry on the structure.



R-11M

3 This has a plane of symmetry, so there are only 4 kinds of CH protons (in a 1:2:2:1 ratio) and 3 kinds of acetate Me (in a 2:2:1 ratio).

Problem R-11L ($C_{16}H_{21}BrO_{10}$)

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

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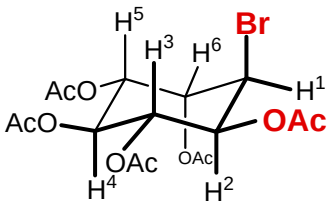

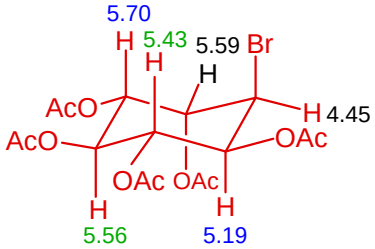

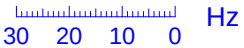

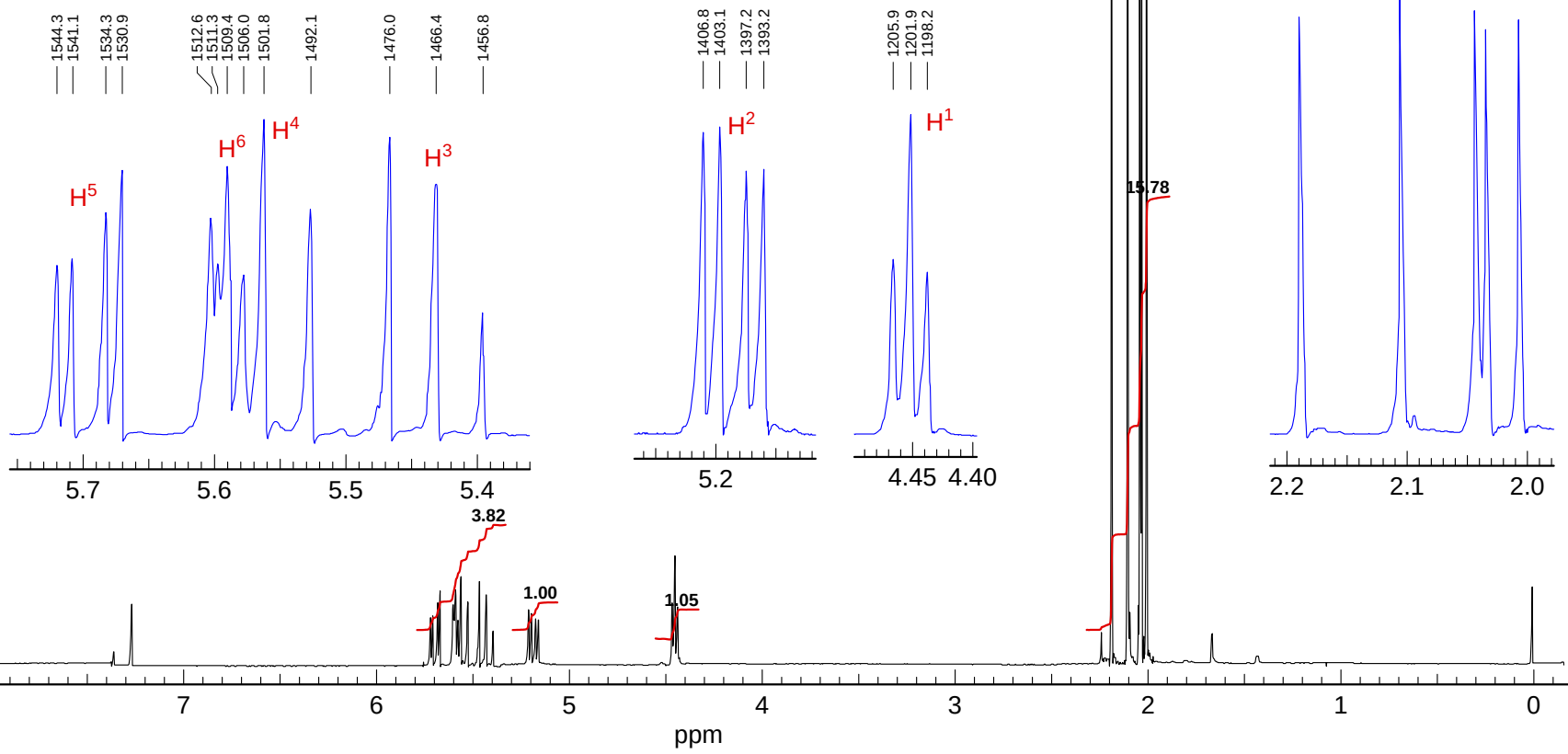

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Problem R-11M ($C_{16}H_{21}BrO_{10}$)
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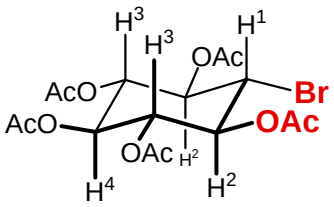

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