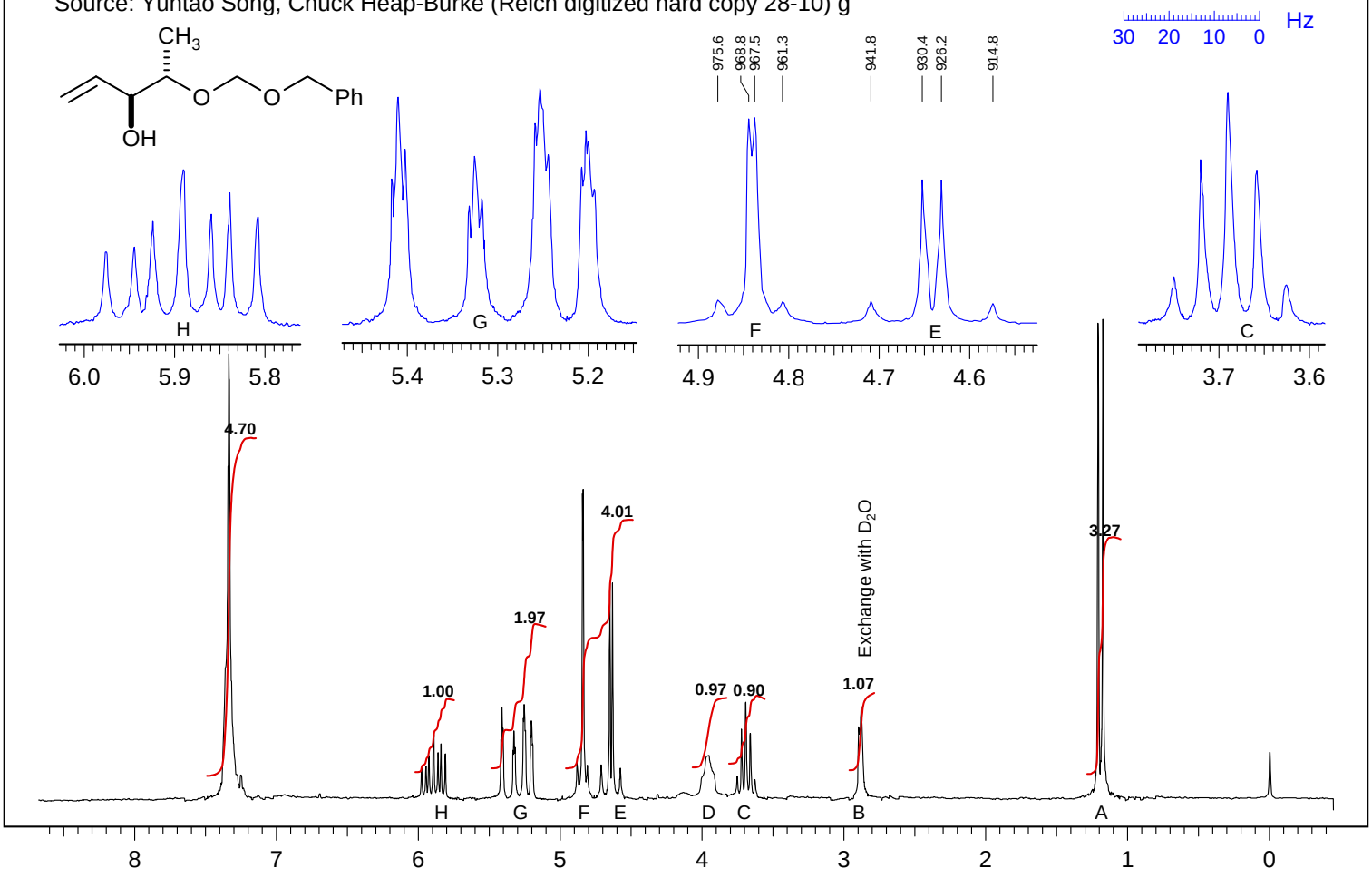
Problem R-06D ($C_{13}H_{18}O_3$)

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

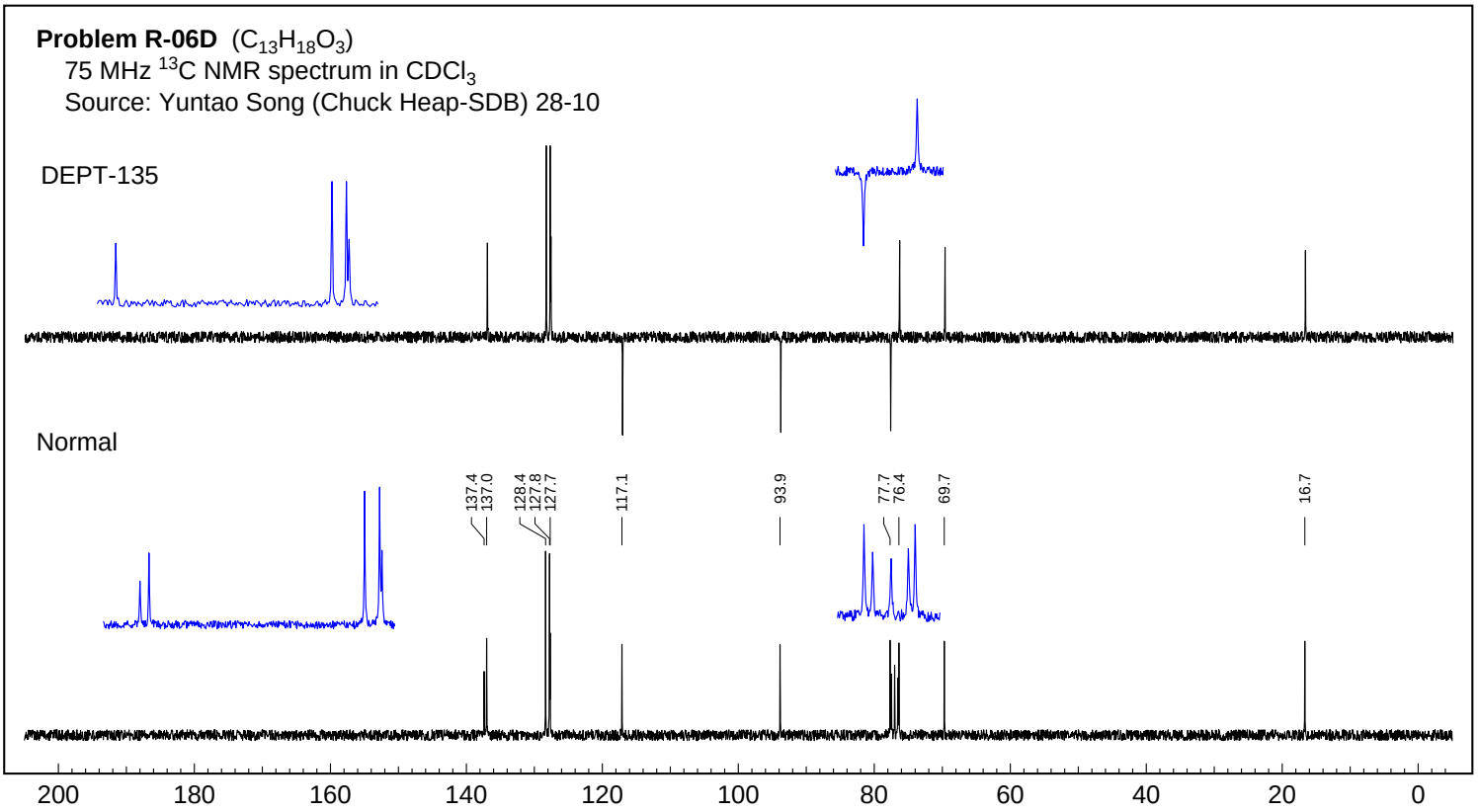
Source: Yuntao Song, Chuck Heap-Burke (Reich digitized hard copy 28-10) g



Problem R-06D ($C_{13}H_{18}O_3$)

75 MHz ^{13}C NMR spectrum in $CDCl_3$

Source: Yuntao Song (Chuck Heap-SDB) 28-10

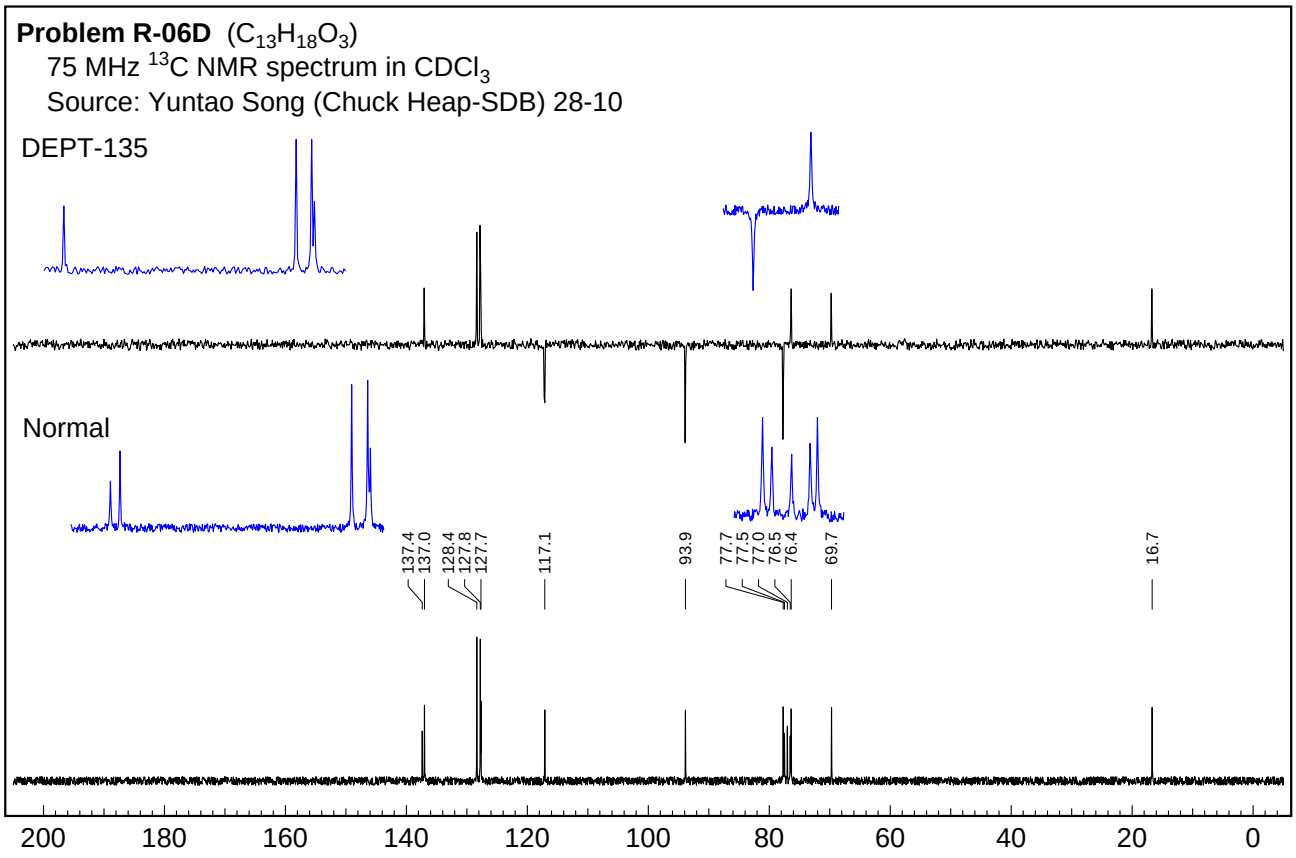


PLT ex-1-2006-07-gq.plt

Problem R-06D ($C_{13}H_{18}O_3$). Determine the structure (or part structure) of **R-06D** from the ^1H and ^{13}C NMR spectra provided. **The compound contains a Ph-CH_2-O-CH_2-O- group**.

(a) DBE____

(b) Interpret the ^{13}C NMR spectrum. Use the Normal and DEPT-135 spectra to help in the analysis. Identify what kind of carbon each signal corresponds to and write possible part structures (you may wish to examine all the data before completing this section).



Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)

16.69 _____

69.70 _____

76.36 _____

77.68 _____

93.85 _____

117.09 _____

127.68 _____

127.77 _____

128.36 _____

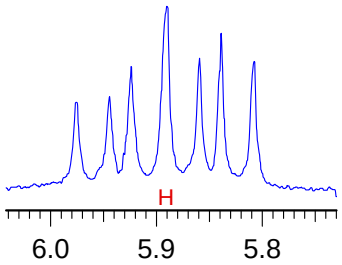
137.01 _____

137.38 _____

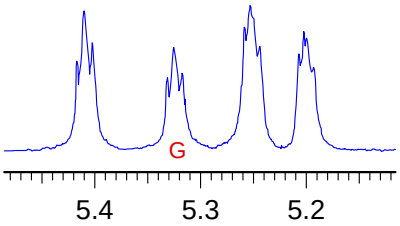
(c) When D_2O was added to the sample, the signal B disappeared and D became a clean triplet. What does this tell you about these peaks?

(d) What can you learn from the signals A and C (part structures)?

(e) Analyze the 1-proton multiplet H at δ 5.9 (shown below). Draw a coupling tree on the multiplet below, and report coupling constants (in the standard form: e.g., δ 3.9, tq, J = 12, 4 Hz, 1H). Show any part structure you could obtain from the signal. You may use first-order analysis.



(f) Analyze the signals labeled G (two protons at δ 5.3), reproduced below. Show couplings with (coupling tree) and report J values and a part structure. You may use first order analysis.



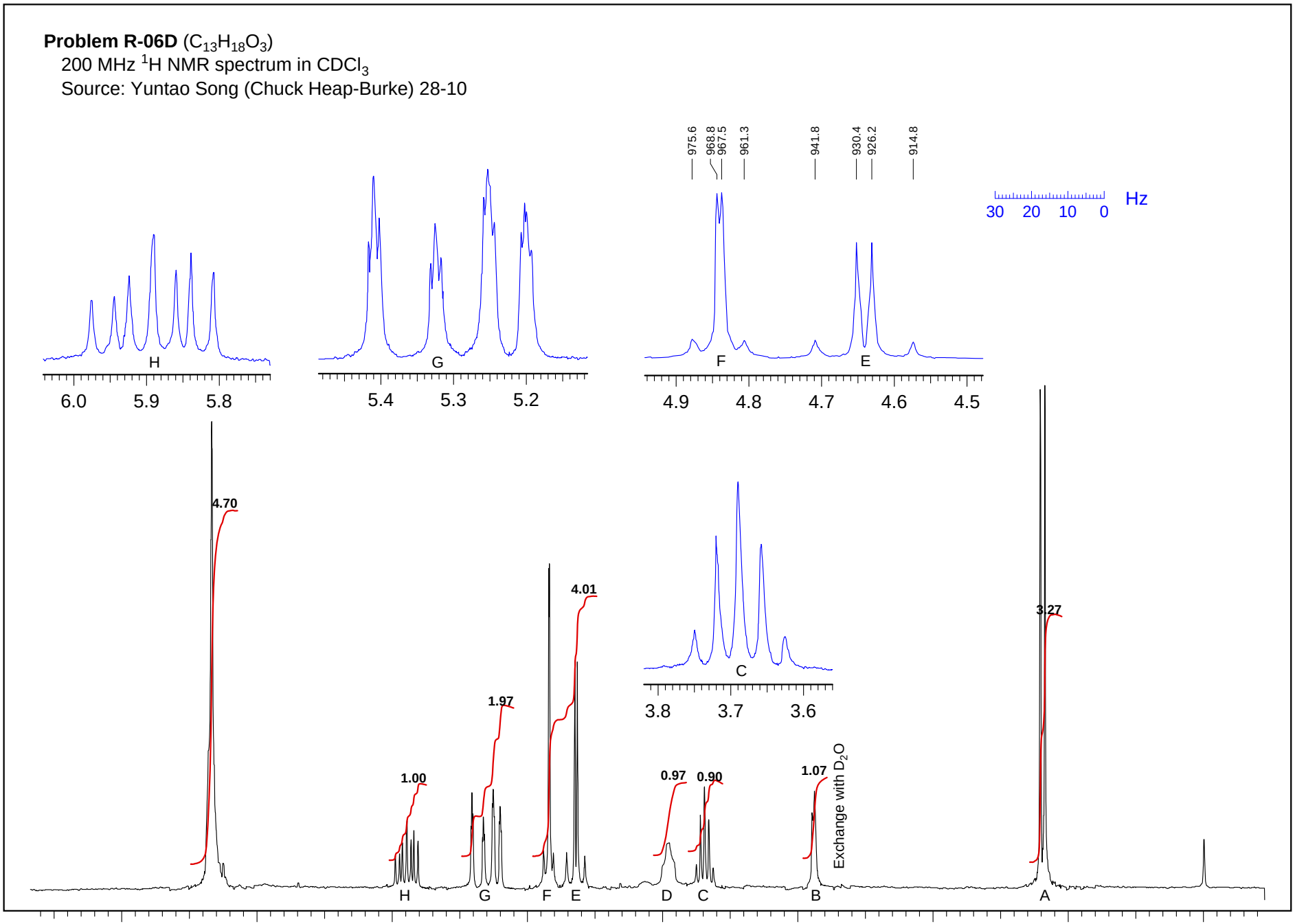
(g) Assign the signals E and F and explain their appearance. What kind of multiplets are these? Do an accurate calculation of the chemical shifts and couplings for multiplet E (frequencies are given on the spectrum).

(h) Draw the structure of **R-06D**. If more than one structure is possible, show them, and circle the one you think fits the data best and give your reasons for choosing it. Place labels on the protons (A, B, C etc) to identity their NMR signals.

Problem R-06D ($C_{13}H_{18}O_3$)

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

Source: Yuntao Song (Chuck Heap-Burke) 28-10

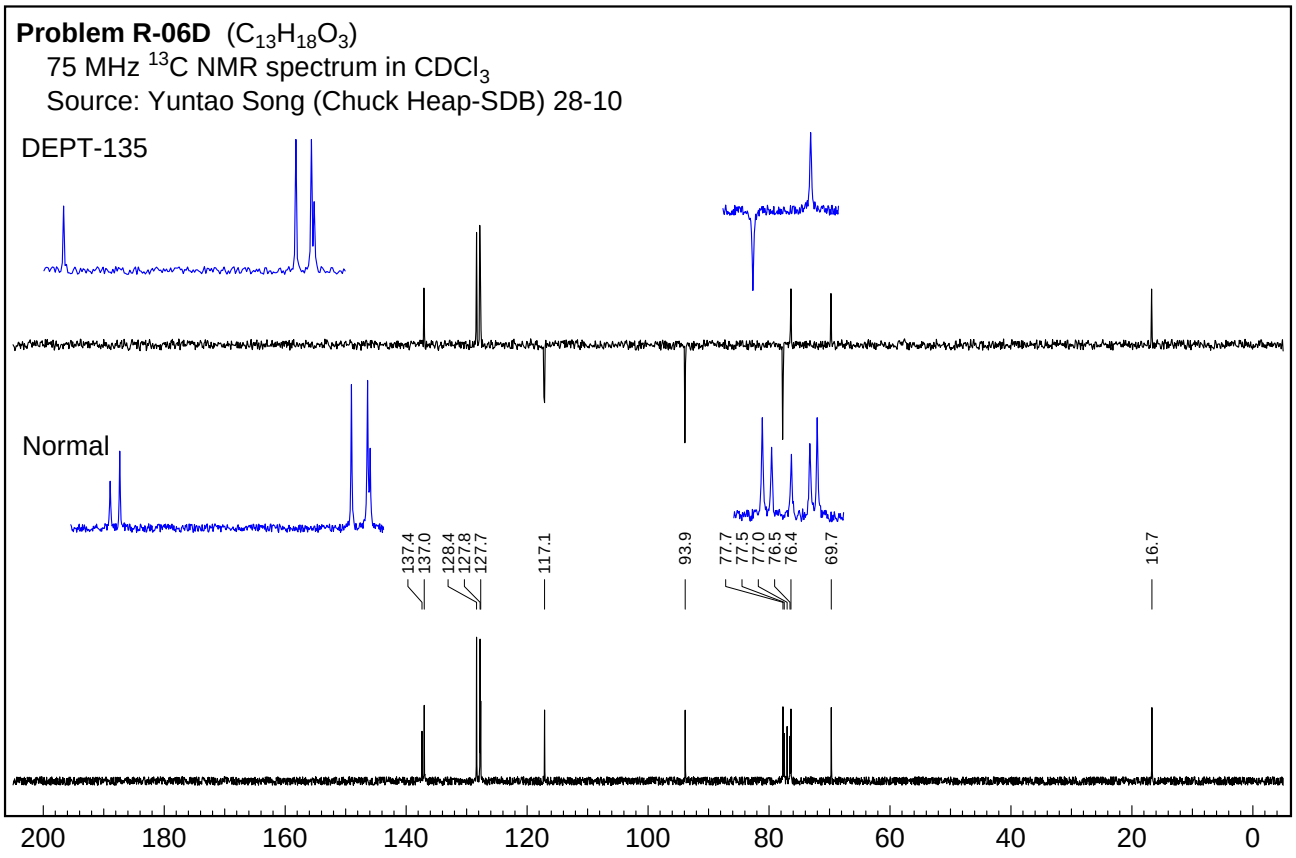


PLT ex-1-2006-07-gq.plt

Problem R-06D ($C_{13}H_{18}O_3$). Determine the structure (or part structure) of **R-06D** from the ^1H and ^{13}C NMR spectra provided. **The compound contains a Ph-CH_2-O-CH_2-O- group**.

1 (a) DBE 5 Ph has 4 DBE, thus one double bond/ring in rest of molecule

(b) Interpret the ^{13}C NMR spectrum. Use the Normal and DEPT-135 spectra to help in the analysis. Identify what kind of carbon each signal corresponds to and write possible part structures (you may wish to examine all the data before completing this section).



Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)

16.69 CH_3

69.70 CH-O

5 76.36 CH-O

77.68 CH_2-O

93.85 O-CH_2-O (possibly C=CH_2)

117.09 CH_2=C

127.68 sp^2 CH (p Ph-C)

127.77 sp^2 CH (2C) (m or o Ph-C)

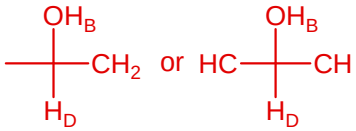
128.36 sp^2 CH (2C) (m or o Ph-C)

137.01 sp^2 CH (probably C=CH_2)

137.38 sp^2 C (ipso Ph carbon)

Only 17 C-H protons apparent in C-13, so most be OH

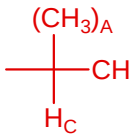
(c) When D_2O was added to the sample, the signal B disappeared and D became a clean triplet. What does this tell you about these peaks?



3 B is an OH signal, and it is coupled to a CH coupled to two other protons

Most common error - failure to consider second structure

(d) What can you learn from the signals A and C (part structures)?

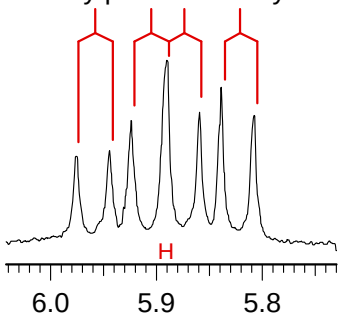


A is probably a CH_3-CH_C group, C is coupled to it, and to one additional proton

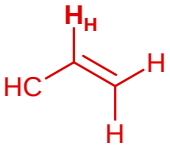
3 A: 1.18, d, J 7 Hz

C: 3.69, pentet, J= 6 Hz

(e) Analyze the 1-proton multiplet H at δ 5.9 (shown below). Draw a coupling tree on the multiplet below, and report coupling constants (in the standard form: e.g., δ 3.9, tq, J = 12, 4 Hz, 1H). Show any part structure you could obtain from the signal. You may use first-order analysis.

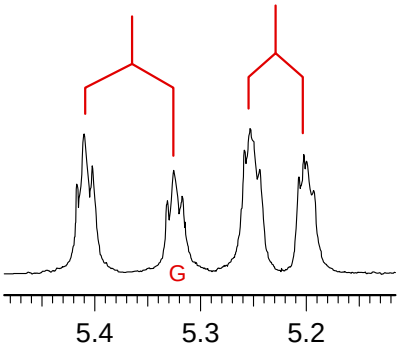


δ 5.89, ddd, J = 17, 10, 7 Hz



3 This is a very characteristic multiplet of a proton coupled cis (10 Hz) and trans (17 Hz) across adouble bond, plus one additional coupling (7 Hz)

(f) Analyze the signals labeled G (two protons at δ 5.3), reproduced below. Show couplings with (coupling tree) and report J values and a part structure. You may use first order analysis.



G are the two terminal $=CH_2$ protons, one coupled cis (10 Hz), the other trans (17 Hz) the additional

3 splittings are the ^2J between them, and a long range coupling

5.22, dt, J= 10, 1.5 or ddd, J= 10, 1.5, 1

5.36, dt, J = 16,5, 1.5

(g) Assign the signals E and F and explain their appearance. What kind of multiplets are these? Do an accurate calculation of the chemical shifts and couplings for multiplet E (frequencies are given on the spectrum).

Both E and F are AB quartets, corresponding to the diastereotopic O-CH_2-O (F) and Ph-CH_2-O (E)

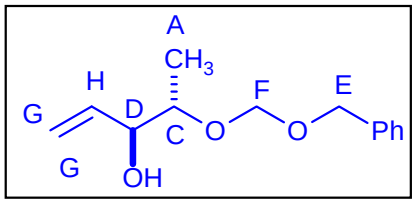
5 groups of the BOM protecting group. Molecule must have an asymmetric center.

J_{AB} = 11.4 Hz C = 928.3 Hz $\Delta\nu_{AB}$ = 10.7 Hz ν_A = 923.0 ν_B = 933.6 -1 for no δ

δ_A = 4.62 δ_B = 4.67 -2 for not diving υ_{AB} by 2

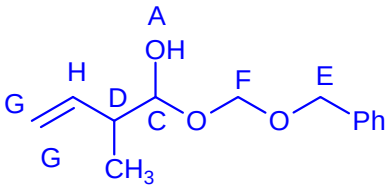
(h) Draw the structure of **R-06D**. If more than one structure is possible, show them, and circle the one you think fits the data best and give your reasons for choosing it. Place labels on the protons (A, B, C etc) to identity their NMR signals.

8

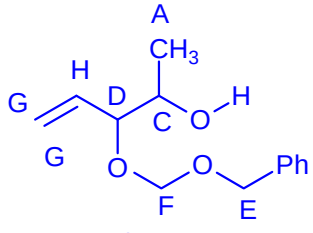


2 points for assignment

Stereochestry not easily assignable



6



6

+ about 10 other structures

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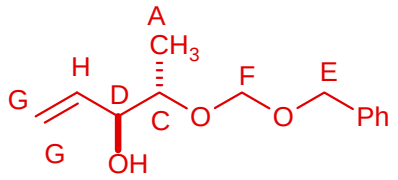

PLT ex-1-2006-07-gq.plt