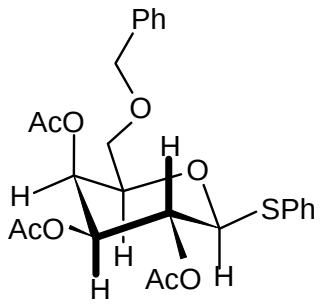
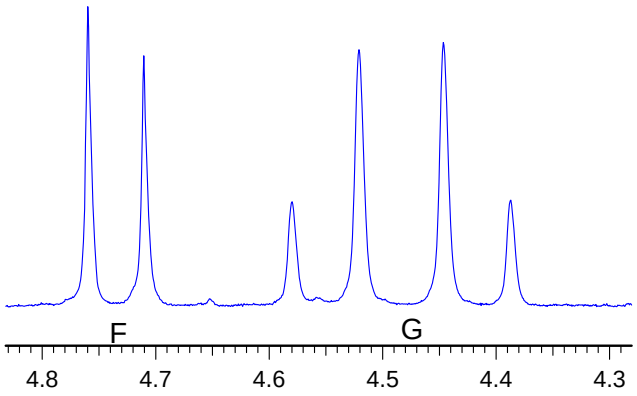
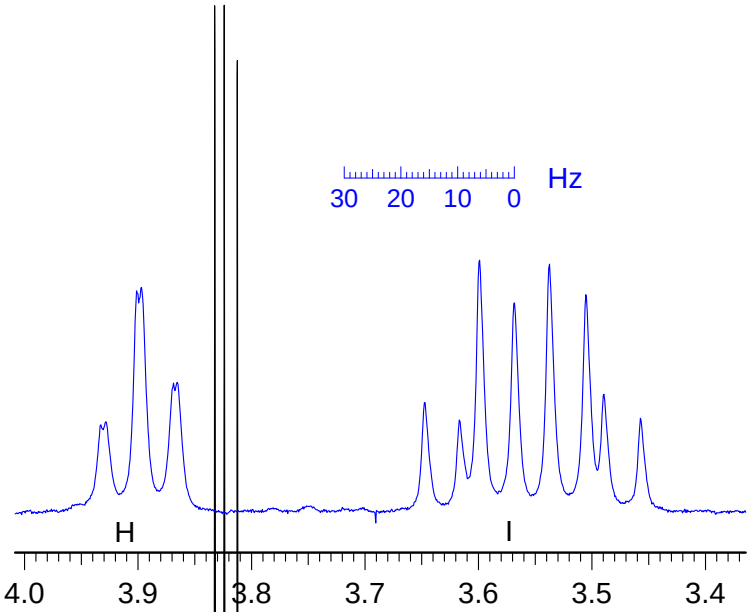
Problem R-12J ($C_{25}H_{28}O_8S$)

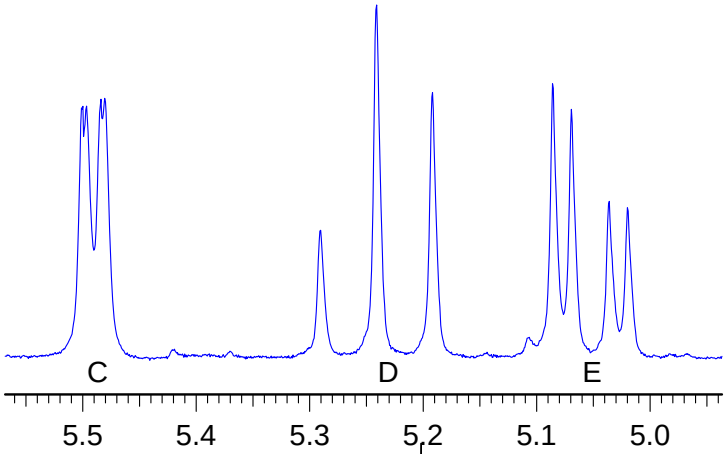
200 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: D. Manning/K. Dantzman/Kiessling g





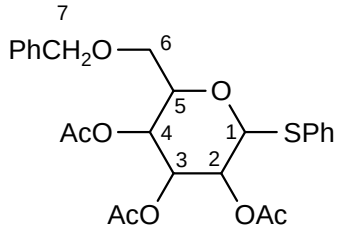




PLT ex-2-2012-13-gq.plt

Problem R-12J ($C_{25}H_{28}O_7S$). In this problem you are given the gross structure of a sugar. Your task is to determine the stereochemistry of the four substituents (three OAc, SPh, CH_2OCH_2Ph) around the ring by analysis of the ^1H NMR spectrum.

(a) Analyze the multiplets **C**-**H**. Report your results in the standard format: δ 9.3, dt, J = 14, 6 Hz, 3H. Indicate what structural information each signal provides, and a possible assignment (use the numbering on the structure). You may use first order analysis for this part.



C

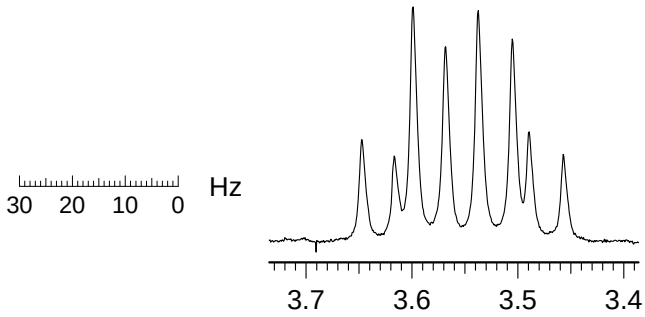
D

E

F

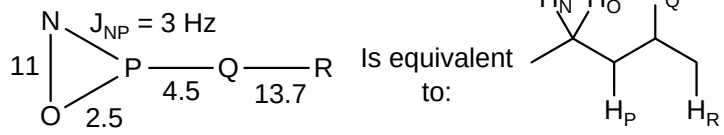
G

H

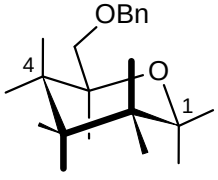


(b) Do a qualitative analysis of the signal **I** reproduced above to show you understand the pattern. Draw a coupling tree, and report the data below.

(c) Indicate the proton connectivity which your analysis provides, using a scheme such as the one below. Describe how you identified the starting point for your assignment (proton **R** in the example below).



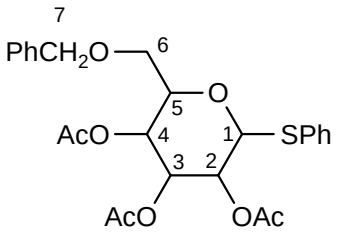
(d) Draw the complete structure of R-12J by adding appropriate substituents to the structure below. Comment on how you identified the stereochemistry at C-1 and C-4.



25

Problem R-12J ($C_{25}H_{28}O_8S$). In this problem you are given the gross structure of a sugar. Your task is to determine the stereochemistry of the four substituents (three OAc, SPh, CH_2OCH_2Ph) around the ring by analysis of the ^1H NMR spectrum.

(a) Analyze the multiplets **C**-**H**. Report your results in the standard format: δ 9.3, dt, J = 14, 6 Hz, 3H. Indicate what structural information each signal provides, and a possible assignment (use the numbering on the structure). You may use first order analysis for this part.



1 **C** H^4 δ 5.50, dd, J = 3.2, 1 Hz, 1H
small coupling is to E. Since E is ax, C must be eq

δ 5.25, t, J = 10 Hz, 1H

1 **D** H^2 Axial proton, with both axial neighbors. Must be H^2 - one coupling to F, other to E

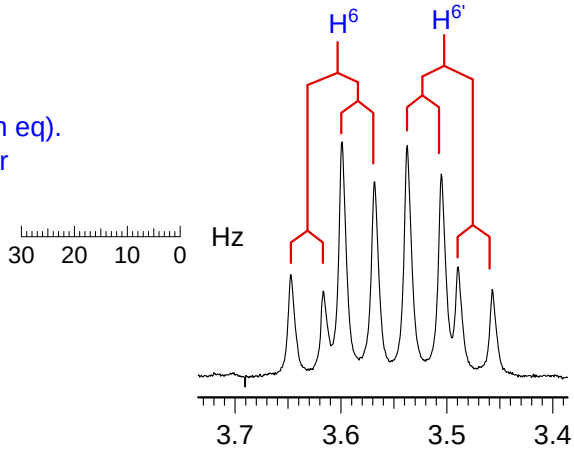
δ 5.05, dd, J = 10, 3.2 Hz, 1H

1 **E** H^3 From 10 Hz coupling to D, we know E is axial, small 3 Hz coupling is to C, so C is equatorial

1 **F** H^1 δ 4.73, d, J = 10 Hz, 1H
This is only doublet seen, so must be H^1, and it is axial (SPh eq).
Coupled to D, since this is the only possible coupling partner

3 **G** H^7 ABq, δ 4.54, 4.42. JAB= 11.5 Hz, 2H
This is the CH_2 of the benzyl group

1 **H** H^5 δ 3.90, td, J = 6, 1 Hz, 1H
This is H^5 - triplet coupling is to H^6, $H^{6'}$, doublet to H^4

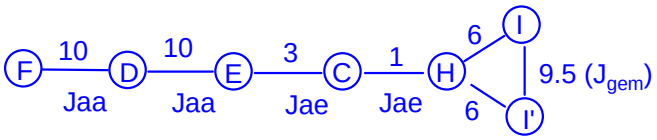


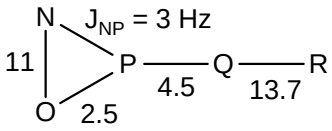
(b) Do a qualitative analysis of the signal **I** reproduced above to show you understand the pattern. Draw a coupling tree, and report the data below.

5 AB of an ABXYZ.. system (H^6): $\delta_A = 3.6$, $J_{AB} = 9.5$, $J_{AX} = 6$ Hz
$\delta_B = 3.5$, $J_{BX} = 6$ Hz

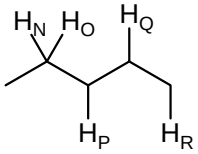
These are the diastereotopic protons at C^6

(c) Indicate the proton connectivity which your analysis provides, using a scheme such as the one below. Describe how you identified the starting point for your assignment (proton **R** in the example below).

3 



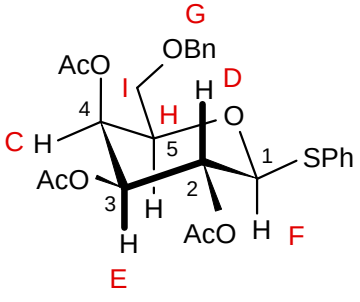
Is equivalent to:



(d) Draw the complete structure of R-12J by adding appropriate substituents to the structure below. Comment on how you identified the stereochemistry at C-1 and C-4.

F is the only one coupled to only other proton so must br F. It must be axial to get large 10 Hz coupling to D, which must be C^2

9 C^4 proton (C) must be equatorial since C^3-H (E) and C^5-H (H) are axial, and there is a small coupling to each



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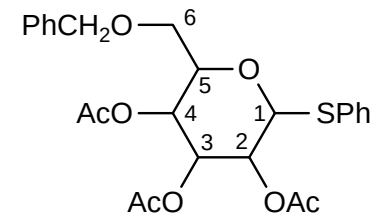

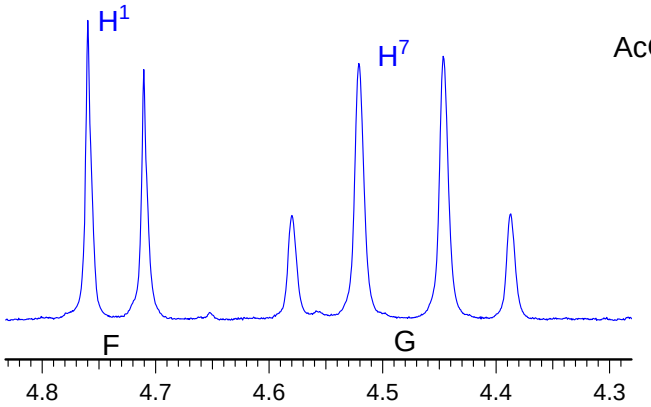

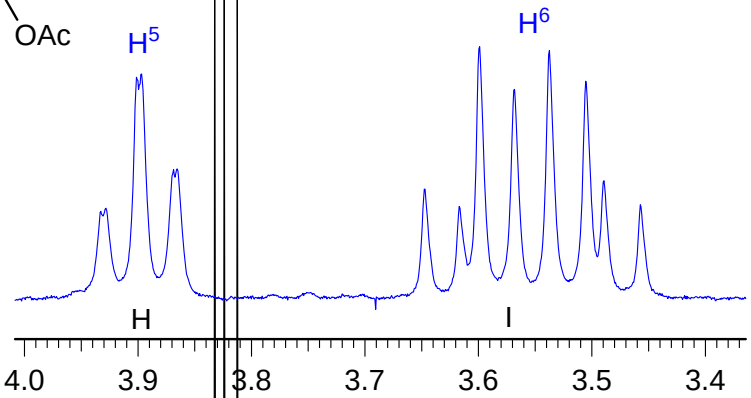

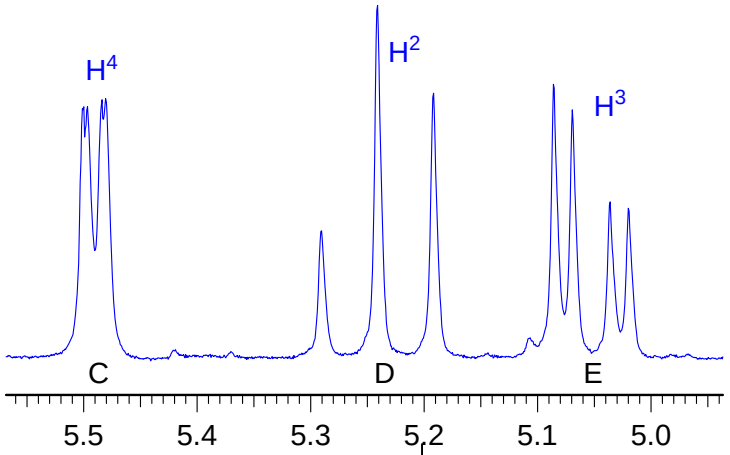

1.55

α SPh 1.60

α OR 2.10

β OAc 0.00

Calc: 5.25

Obs: 4.7

PLT ex-2-2012-13-gq.plt