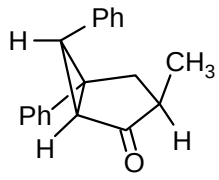
Problem R-11J ($C_{19}H_{18}O$)

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

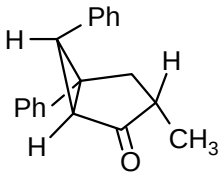
Source: Drew Weber/Zimmerman (Reich digitized hard copy) g



Problem R-11K ($C_{19}H_{18}O$)

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

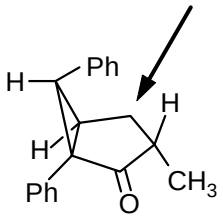
Source: Drew Weber/Zimmerman



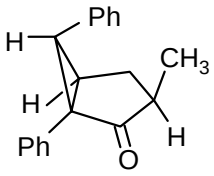
PLT ex-2-2011-12-gq.plt

Problem R-11J and K ($C_{19}H_{18}O$). You are given 200 MHz ^{1}H NMR spectra of two **stereoisomers** of a compound which differ at one stereocenter only (i. e., **1** and **2**, or **6** and **8**), the possibilities are **1** to **8** below. Your task is to make both a structural and a stereochemical assignment. Explain the basis of your assignment below, taking care to clearly identify the signals you are using.

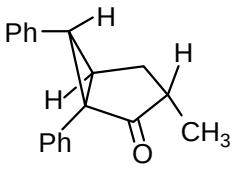
(a) What spectral features allow you to distinguish the two structural types (**1** to **4** versus **5** to **8**)?



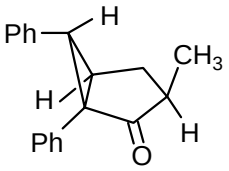
1 _____



2 _____

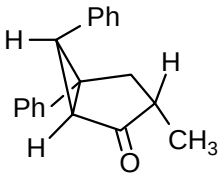


3 _____

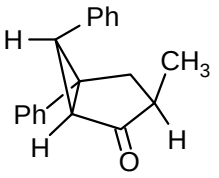


4 _____

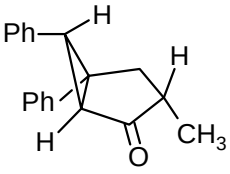
(b) What spectral features allow you to distinguish the pair of isomers? Write the spectrum number (**R-11J** or **R-11K**) in the appropriate blank.



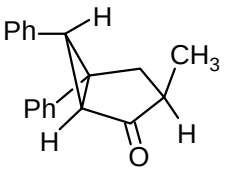
5 _____



6 _____



7 _____



8 _____

(c) Just to show you understand the spectra, give just the chemical shifts of the two protons at the CH_2 group (marked with an arrow in **1**).

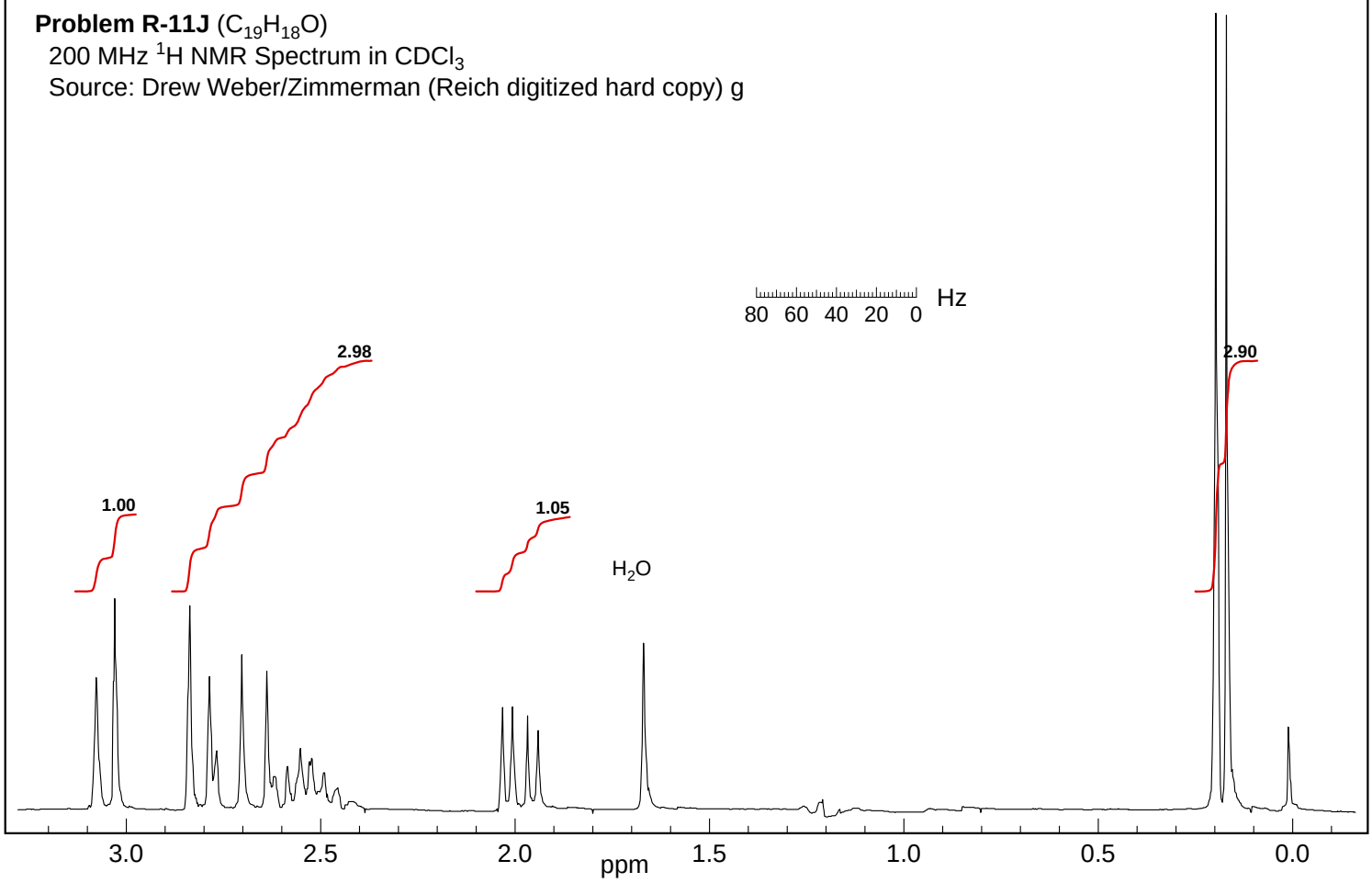
R-11J _____, _____

R-11K _____, _____

Problem R-11J ($C_{19}H_{18}O$)

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

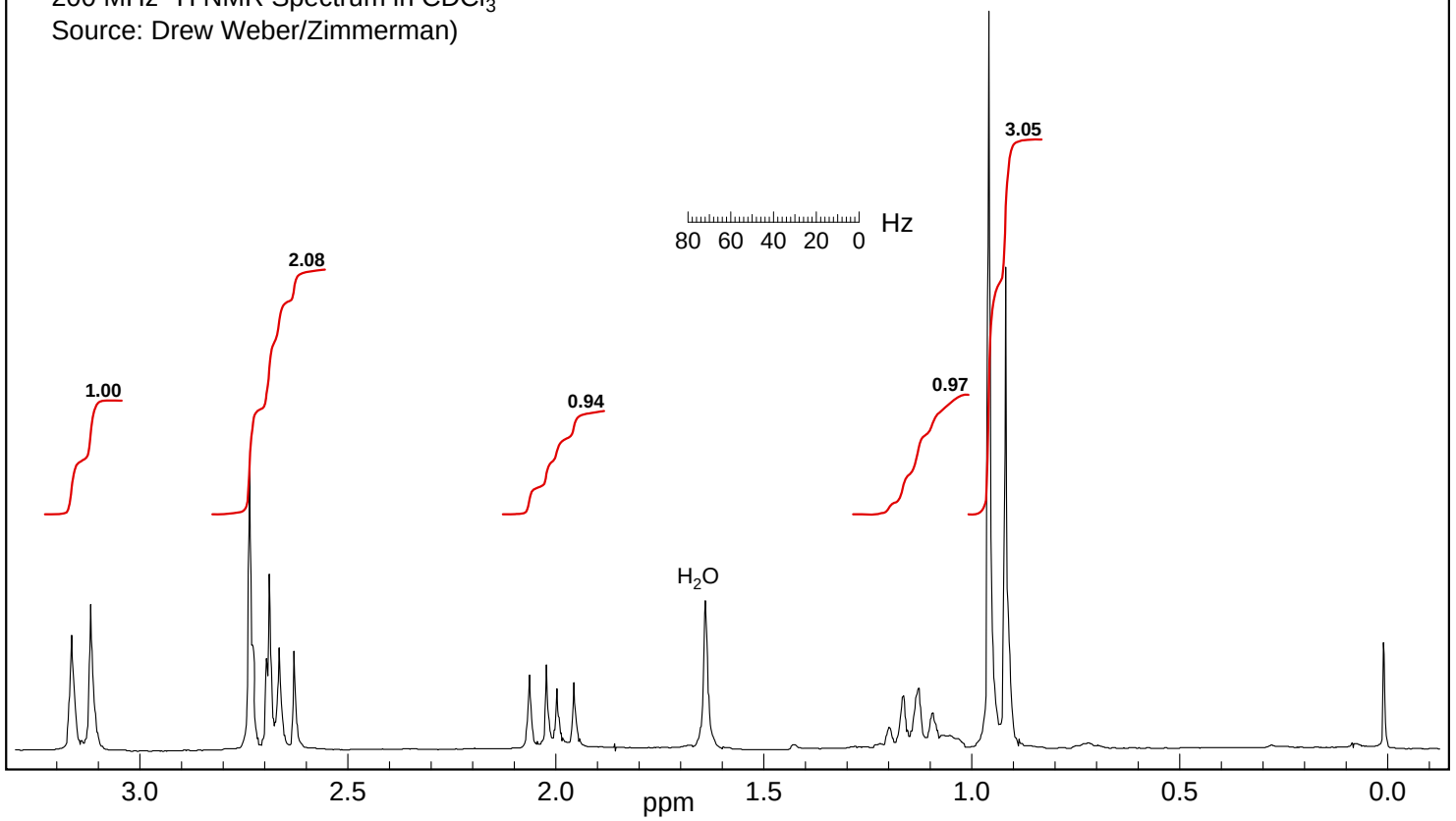
Source: Drew Weber/Zimmerman (Reich digitized hard copy) g



Problem R-11K ($C_{19}H_{18}O$)

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

Source: Drew Weber/Zimmerman)

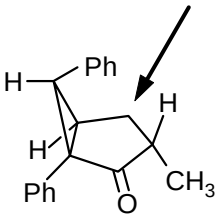


PLT ex-2-2011-12-gq.plt

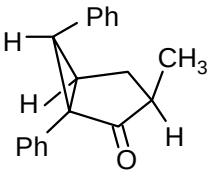
15

Problem R-11J and K ($C_{19}H_{18}O$). You are given 200 MHz ^{1}H NMR spectra of two **stereoisomers** of a compound which differ at one stereocenter only (i. e., **1** and **2**, or **6** and **8**), the possibilities are **1** to **8** below. Your task is to make both a structural and a stereochemical assignment. Explain the basis of your assignment below, taking care to clearly identify the signals you are using.

10



1 2

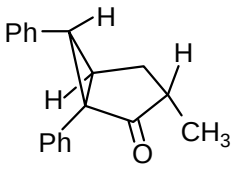


2 2

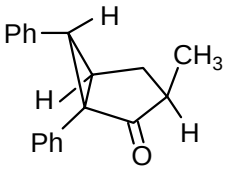
(a) What spectral features allow you to distinguish the two structural types (**1** to **4** versus **5** to **8**)?

Each spectrum has an isolated AB pattern at 2.7 and 3.1 J_{AB} = 10 Hz), and an $ABMX_3$ pattern, which is as expected for the compounds **5** - **8**. In compounds **1** - **4** the coupling pattern would be more complicated, since one of the cyclopropane protons would be coupled to the CH_2.

2



3 1

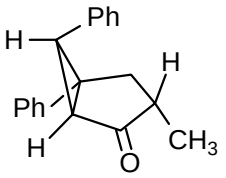


4 1

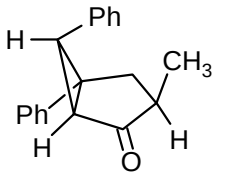
(b) What spectral features allow you to distinguish the pair of isomers? Write the spectrum number (**R-11J** or **R-11K**) in the appropriate blank.

The AB coupling of the cyclopropane protons is identical in both. The relatively large vicinal coupling (10 Hz) shows a cis relationship between them. Thus the two compounds must be **5** and **6**. The other coupling constants are quite similar, and do not provide much insight. However, there are some large chemical shift differences - in **R-11J** the Me doublet is unusually upfield (δ 0.2), and the CHMe multiplet normal (δ 2.5), whereas in **R-11K** the methyl is normal (δ 0.95), and the multiplet unusually upfield (δ 1.1). This can only be explained by large anisotropy effects of the phenyl group in compounds **5** and **6**.

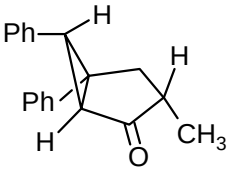
3



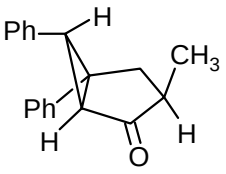
5 R-11K 5



6 R-11J 5

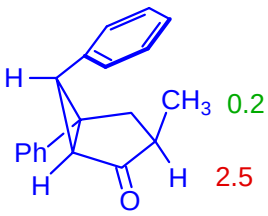


7 2

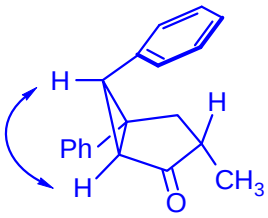


8 2

Both ^3J same: 10 Hz (i.e. cis)



6 (R-11J)



5 (R-11K)

Endo protons are both upfield

Normal

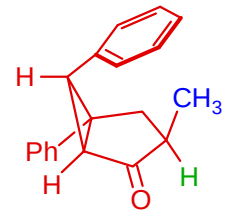
(c) Just to show you understand the spectra, give just the chemical shifts of the two protons at the CH_2 group (marked with an arrow in **1**).

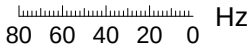
R-11J 2.0, 2.7

R-11K 2.0, 2.65

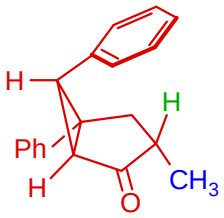
2

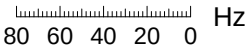
Problem R-11J ($C_{19}H_{18}O$)
200 MHz ^{1}H NMR Spectrum in $CDCl_3$
Source: Drew Weber/Zimmerman





Problem R-11K ($C_{19}H_{18}O$)
200 MHz ^{1}H NMR Spectrum in $CDCl_3$
Source: Drew Weber/Zimmerman





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