Chemistry 605 (Reich)

THIRD HOUR EXAM

Wed. May 15, 2013

Question/Points

R-12L_____/20
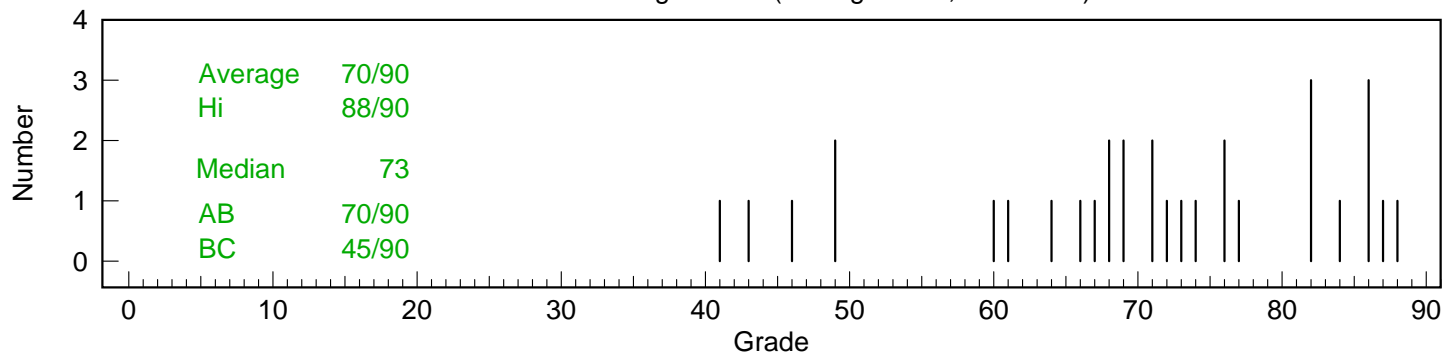
R-12M_____/15

R-12N_____/25
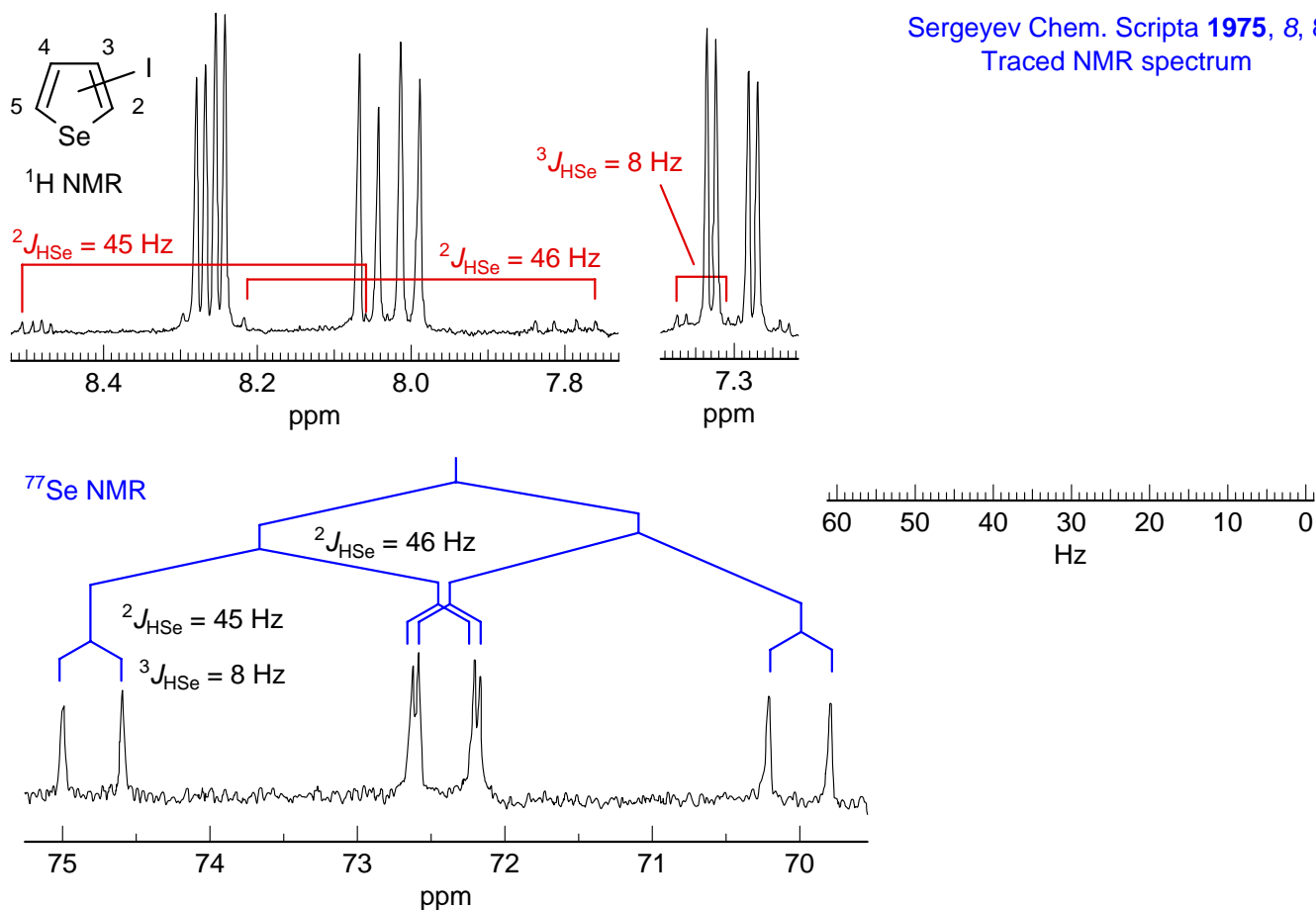
R-12O_____/10

R-12P_____/20

Total _____/90

Name_____

If you place answers anywhere else except in the spaces provided, (e.g. on the spectra
or on extra pages) clearly indicate this on the answer sheets.

Distribution from grade list (average: 70.1; count: 31)

Average	70/90
Hi	88/90
Median	73
AB	70/90
BC	45/90

Problem R-12L. The 100 MHz ^{1}H and 19.15 MHz ^{77}Se NMR spectra of a mono-iodo selenophene are shown below. Both spectra are at the same Hz scale.

^{1}H NMR

$^2J_{HSe}$ = 45 Hz

$^2J_{HSe}$ = 46 Hz

$^3J_{HSe}$ = 8 Hz

8.4   8.2   8.0   7.8   7.3
ppm   ppm

^{77}Se NMR

$^2J_{HSe}$ = 46 Hz

$^2J_{HSe}$ = 45 Hz

$^3J_{HSe}$ = 8 Hz

60 50 40 30 20 10 0
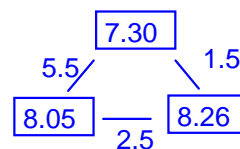Hz

75   74   73   72   71   70
ppm

(a) Interpret the ^{1}H NMR spectrum, including the various small peaks (e.g., those at δ 7.8 and 8.5). Report δ and all coupling constants in the standard format.

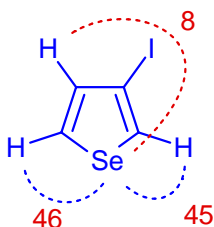δ 7.30, dd, J = 5.5, 1.5 Hz. Se satellites: $^3J_{HSe}$ = 8 Hz

δ 8.05, dd, J = 5.5, 2.5 Hz. Se satellites: $^2J_{HSe}$ = 46 Hz

δ 8.26, dd, J = 2.5, 1.5 Hz. Se satellites: $^2J_{HSe}$ = 45 Hz
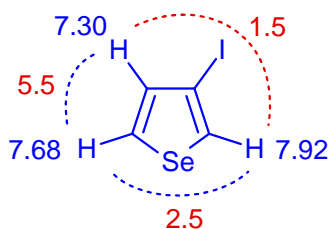
7.30
5.5 / 1.5
8.05 — 8.26
2.5

(b) Interpret the ^{77}Se NMR spectrum. Report all coupling constants. Draw a "coupling tree" on the spectrum.

δ 72.4, ddd, J =46, 45, 8 Hz

H   I   8
H   Se   H
46   45

(c) Draw the structure of **R-12L** below, briefly give your reasoning.

7.30   1.5
H   I
5.5
7.68 H   Se   H 7.92
2.5

The two large Se-H couplings require I to be at the 3 position (if know that ^2J >> ^3J - see examples under Selenophene in HDATA). This substitution also fits the proton couplings
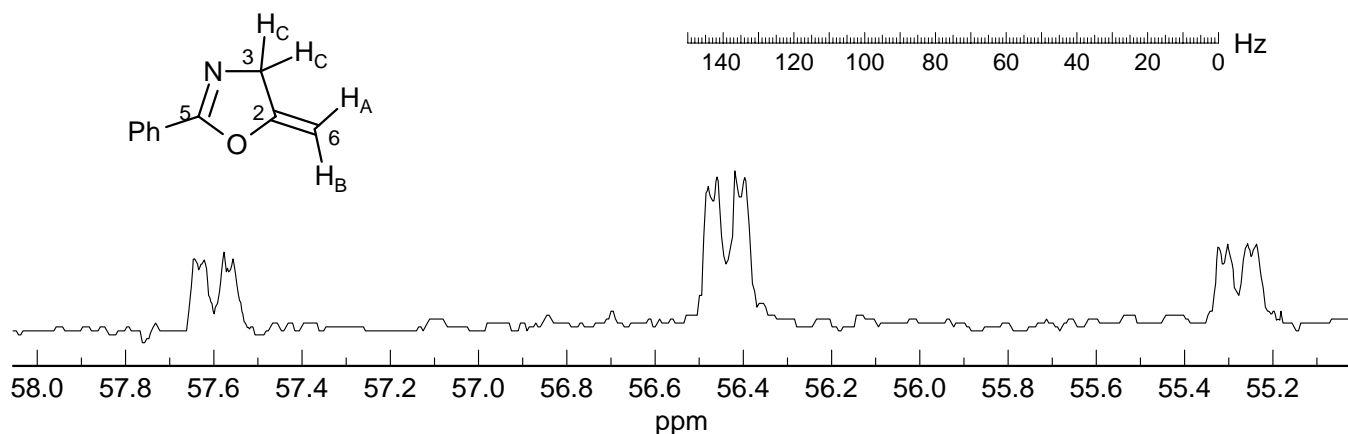
Chemical shift arguments also favor this structure - the two most downfield protons have the large Se-H coupling

Problem R-12M ($C_{10}H_{09}NO$). You are asked to interpret the coupled ^{13}C NMR spectrum of an oxazoline.

(a) Which carbon are we looking at? <u>C^3</u>

2

(b) Analyze the spectrum, report all coupling constants in the standard format ($^nJ_{X-Y} = 00.0$ Hz).

tdd, J = 146, 8, 3

$^1J_{C-H}$ = 146 Hz

5

$^3J_{C-H}$ (trans) = 8 Hz
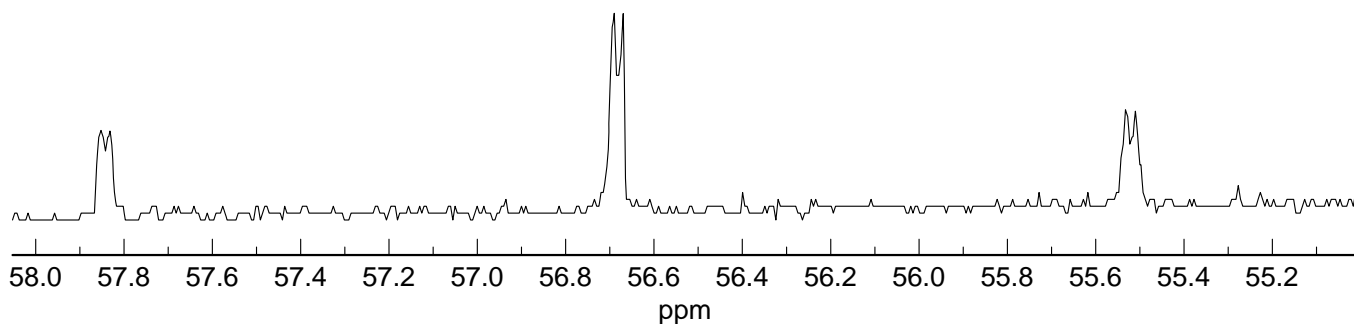
$^3J_{C-H}$ (cis) = 3 Hz

(c) The spectrum below is of the same compound with one H replaced by D. Where is the deuterium? Place it on the structure, and explain briefly.

Only the small cis $^3J_{C-H}$ remains in the deuterated compound, so the trans proton must have been replaced by deuterium. The C-D coupling would be only about 1.3 Hz. so is not detectable at this resolution.
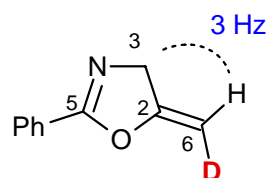
5

(d) What is the proton NMR frequency of the spectrometer they were using? <u>497 MHz</u>

3

1 ppm = 125 Hz in the ^{13}C NMR spectrum, so the ^{13}C frequency is 125 MHz. Thus the proton frequency is 125x(100/25.14) = 497.2 MHz

Problem R-12N. Analyze the ^{1}H decoupled 32.4 MHz ^{31}P NMR spectra of a palladium-phosphine complex shown on the next page (Bartsch, R.; Carmichael, D.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Sillett, G. J. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1615).

(a) Identify all signals in the low temperature spectrum (-75 °C), and report approximate coupling constants using the form: δ ____ , $^X J_{1\text{-}2} =$____ Hz. Use the numberings shown on the structure. For each signal briefly give your reasoning for the assignment.

4

This is the P closest to the two PEt$_3$ groups, so expect triplet splitting. The dtd (J = 502, 49, 22 Hz) at δ -17 is the only signal that shows a triplet, so this must be P^1, which should also be coupled to both P^2 And P^3, as observed.

P^1 $\quad$ δ -17, $^1J_{P1\text{-}P2}$ = 502 Hz, $^2J_{P1\text{-}P4/5}$ = 49 Hz, $^2J_{P1\text{-}P3}$ = 20 Hz

4

P^2 should also show the large ^1J to P^1, so it must be the dd (*J* = 500, 45 Hz) at δ 18. P^1 and P^2 form an <u>ABXY$_2$</u> system, would need to do an AB quartet calculation to get accurate chemical shifts
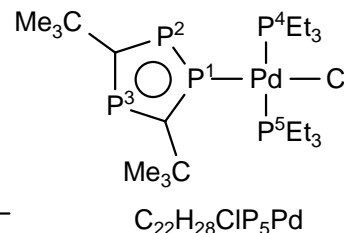
P^2 $\quad$ δ 18, $^1J_{P1\text{-}P2}$ = 500 Hz, $^2J_{P1\text{-}P3}$ = 40 Hz

3

P^3 is coupled to both P^1 and P^2 (dd, J = 46, 25 Hz), so it has to be the δ 112 signal

P^3 $\quad$ δ 112, $^2J_{P3\text{-}P2}$ = 40 Hz, $^2J_{P3\text{-}P1}$ = 20 Hz

3

This is the signal with double area at δ -122, d, J = 48 Hz

P^4, P^5 $\quad$ δ -122, $^1J_{P4/5\text{-}P1}$ = 46 Hz

(b) Identify the process which is responsible for the changes in the NMR spectrum at the higher temperatures (-30 °C and +50 °C). The signal at -122 ppm in the +50 °C spectrum is a triplet. Draw a structure or an equation.

The Pd migrates back and forth between P^1 and P^2, so their chemical shifts are averaged, and both P^3 and P^4/P^5 become triplets, equally coupled to both. Since the two coupling constants are fairly close (expect the P^4/P^5 coupling to be (49+0)/2 = 25, and P^3 coupling to be (40+20)/2 = 30 Hz in size, the P^1/P^2 signal becomes an approximate quartet.

8

The exchange is intramolecular, since the coupling between P^1/P^2 and P^4/P^5 is maintained in the high temperature spectrum
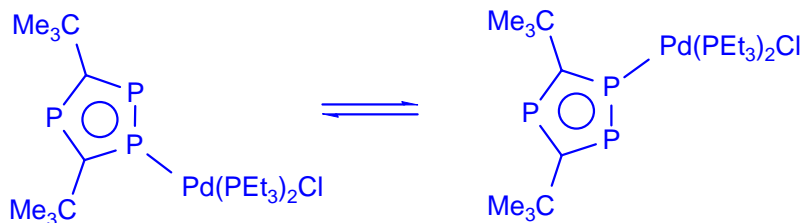
(c) What is the proton frequency (MHz) of the spectrometer which was used for these spectra?

3

32.4x(100/40.49) = 80 MHz

Problem R-12N. 32.4 MHz ^{31}P-{^{1}H} NMR spectra.
Solvent toluene-d$_8$
(Source: *Chem. Commun.* **1988**, 1615)

Me$_3$C

P^2

P^{4}Et$_3$

P^1 — Pd — Cl

P^3

P^{5}Et$_3$

Me$_3$C

P^1, P^2

+50 °C
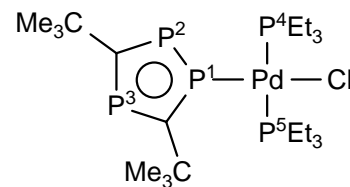
Hz scale for main spectra
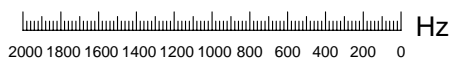
Hz

2000 1800 1600 1400 1200 1000 800 600 400 200   0

-30 °C

-120 -125 -130

$^2J_{12}$ = 502 Hz

Hz scale for expansions

Hz

2000 1800 1600 1400 1200 1000 800   600   400   200   0
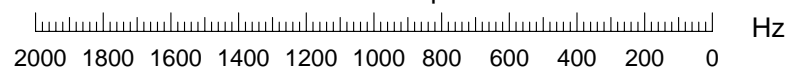
115 110

40   30   20   10   0   -10   -20   -30
ppm

-120-125

2.00

P^4, P^5

-75 °C

0.88

P^3

0.96

P^2

0.97

P^1

120   100   80   60   40   20   0   -20   -40   -60   -80   -100   -120   -140

ppm

Problem R-12O ($C_{16}H_{21}ClNOPPt$). Shown below are partial ^1H NMR spectra of a platinum complex at several field strengths. All three spectra are at the same Hz scale. Only the signal for H_A is shown (source: *Magn. Res. Chem.* **1985**, *23*, 671).

^1H NMR Spectra

30 20 10 0 Hz

400 MHz

250 MHz

90 MHz

27 Hz

4.5 Hz

6 Hz

2 Hz

(a) Explain the small outer peaks of the multiplet.

3

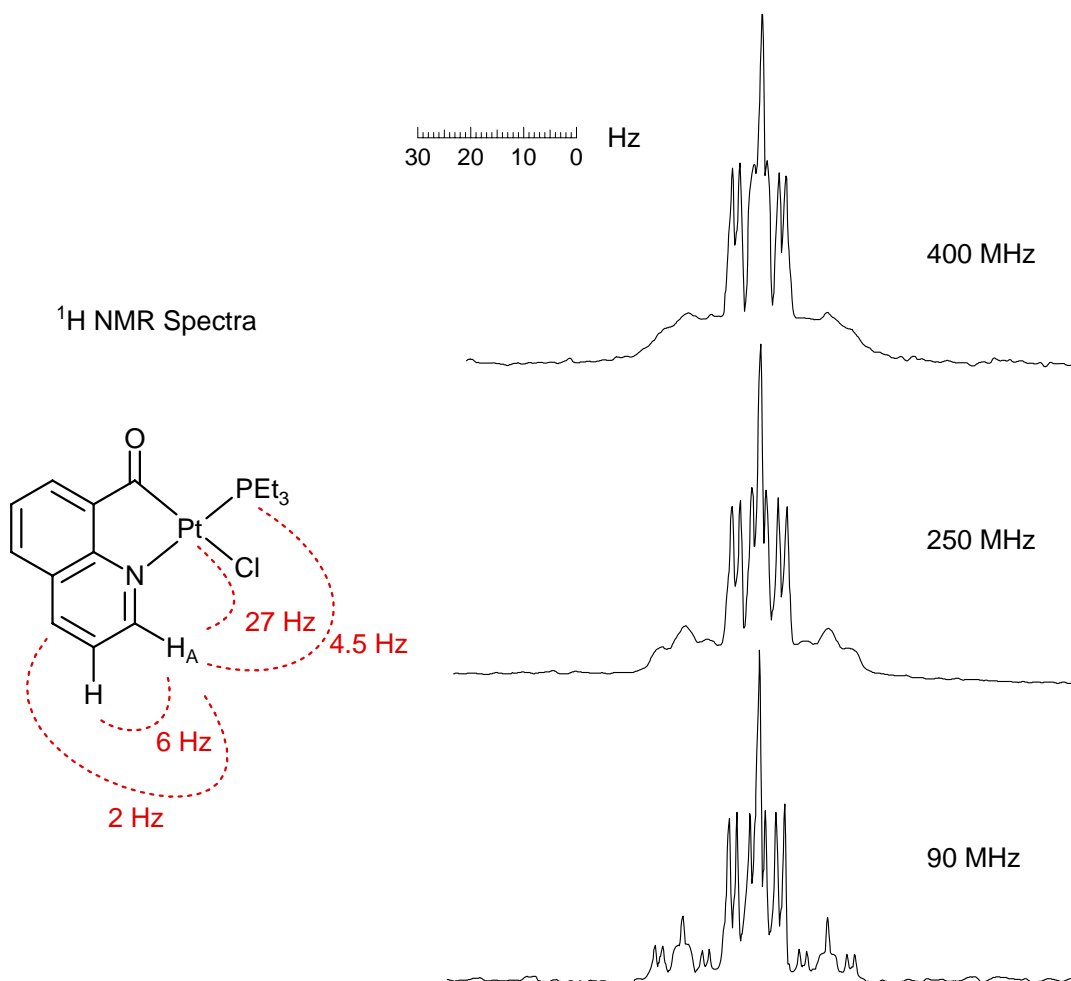These are ^{195}Pt satellites: $^3J_{Pt-H}$ = 27 Hz

^{195}Pt I= 1/2, 33.7% abundant

^{31}P I= 1/2, 100% abundant

(b) Analyze the multiplet. Give approximate coupling constants, report them in the form $^nJ_{XY}$ = _ Hz. Assign the couplings.

The central peak is a ddd, J = 6, 4.5, 2 Hz

6 Hz is ortho coupling ($^3J_{H-H}$)

4

4.5 Hz is coupling to P ($^4J_{H-P}$)

2 Hz is meta coupling ($^4J_{H-H}$)

(c) Why do the small outer peaks become broad at higher field strength? This is not a fluxional molecule, and there is no ligand exchange under these conditions.

3

^{195}Pt must be relaxing by the CSA mechanism (chemical shift anisotropy), whose effectiveness varies as B_o^2, so T_1 values become shorter at higher field, until the coupling in the satellites begins to be averaged out at 500 MHz. The central peak is not affected by this process (other Pt isotopes).

Problem R-12P ($C_8H_{12}O$). This question requires you to assign the protons of compound **R-12P** using the 300 MHz proton NMR spectra given. The spectrum shows the normal ^1H NMR, and two inserts which are difference spectra resulting from subtraction of the normal spectrum from one in which the large signal at δ 0.95 or at δ 1.4 was preirradiated for a second or so, and then the decoupler was turned off during acquisition of the FID. The assignment of these signals is shown on the structures. The integration of the insets has been expanded five times (5x) compared to the normal spectrum

(a) What kind of experiment is being performed here? What information does this experiment provide?

4

Homonuclear NOE difference experiment. One proton signal is irradiated until it is saturated, increase in area of other protons tells us which ones are close in space to the one being irradiated, provided that the irradiated proton is causing DD relaxation of the observed proton.

(b) For the NMR signals below assign each to one of the protons labeled H_a to H_f. Briefly summarize the evidence you used in making each assignment. Each of the signals corresponds to a single proton. The signals marked with an x are impurities.

13

δ 1.43 _____ H_f

Assigned by difference - just a doublet, coupled only to H_e. There must be a 90° dihedral angle with H_c and H_d

These should be together

δ 2.08 _____ H_b

2.08 and 2.28 should be the α-keto protons H_a and H_b. They are coupled to each other, and show a characteristic large geminal coupling of 17 Hz.

δ 2.28 _____ H_a

This signal shows an NOE effect when the endo Me group is irradiated (δ 0.95), so it must be H_a, other is H_b

These should be together

δ 2.43 _____ H_c

2.43 and 2.55 both show NOE effect when either Me group is irradiated, so they must be the H_c and H_d protons. 2.55 is just a dd, so must be H_d; H_c is complex, since it could be coupled to H_a, H_b, H_d, H_e, and H_f

δ 2.55 _____ H_d

δ 2.60 _____ H_e

This signal shows an NOE effect when the exo Me group is irradiated (δ 1.38), so it must be H_e, other is H_f (δ 1.43)

Are there any ambiguities in the assignments you have made?

None

(c) Comment on the chemical shift difference between the two methyl signals, as well as the protons H_e and H_f.
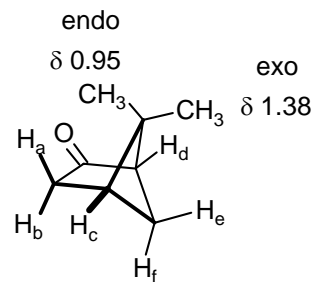
3

The endo methyl group (δ 0.95) and H_f may both be over the shielding cone above and below the C=O group, hence the unusual upfield shift.

Problem R-12P ($C_8H_{12}O$)

300 MHZ ^{1}H NMR Spectrum
Source: The XL Series NMR Spectra Collection Vol 1
Varian Associates 12/19

endo
δ 0.95

exo
δ 1.38

x5

Difference spectrum:
Irradiate at δ 1.38

Must be H_e - closest
proton to exo Me

x5

Difference spectrum:
Irradiate at δ 0.95

Common to both - must   Must be H_a - closest
be H_c and H_d proton to endo Me

x1

J = 18, next to ketone

These two are coupled to
each other with large J, thus
a, b or possibly e,f

endo   exo

80 60 40 20 0   Hz

x

Normal spectrum

x x x

H_f

H_e H_d H_c H_a H_b
2.60 2.55   2.43   2.28   2.08

2.8   2.6   2.4   2.2   2.0   1.8   1.6   1.4   1.2   1.0   0.8
ppm