Písemná zkouška	**Multinukleární NMR spektroskpie**	**Jméno:**	
Body:	**C6800**	**Datum:**	
Max. 100 bodů	**Jaro 2009**	**Varianta A**	

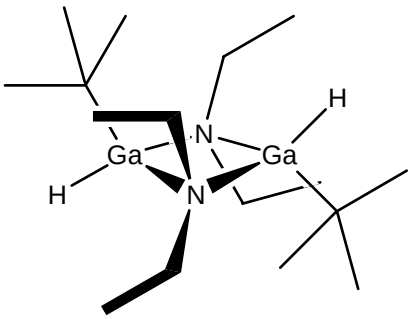
1. (10 pts) The reaction of Ph_3SnLi with $H_3Si\text{-}O\text{-}SO_3C_4F_9$ provided a salt $Li(O\text{-}SO_3C_4F_9)$ and a compound **A**, that displayed in the ^1H NMR spectrum a multiplet in the aromatic region (7.0-7.5 ppm) and another signal at 3.66 ppm.

a) Draw the structure of the product **A** and assign the symmetry point group label.
b) Describe in detail the appearance of the signal at 3.66 ppm.
c) Describe the expected signals of other NMR active nuclei in the molecule **A** (not for C_6H_5).

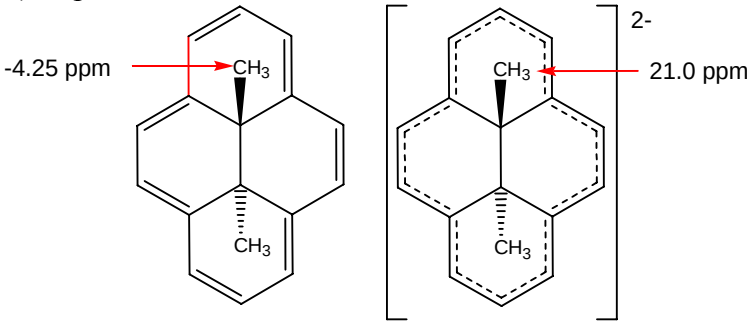
HINT: A typical value of $^1J_{SiH}$ for silyl-germyl hydrides, such as $(GeH_3)_xSiH_{4-x}$, is 200 Hz. Coupling constants $^2J_{SnH}$ with values of around 60 Hz were found in $HSi(SnMe_3)_3$ and $HSiR_2'SnR_3$ compounds.

2. (10 pts) Consider the following molecule:

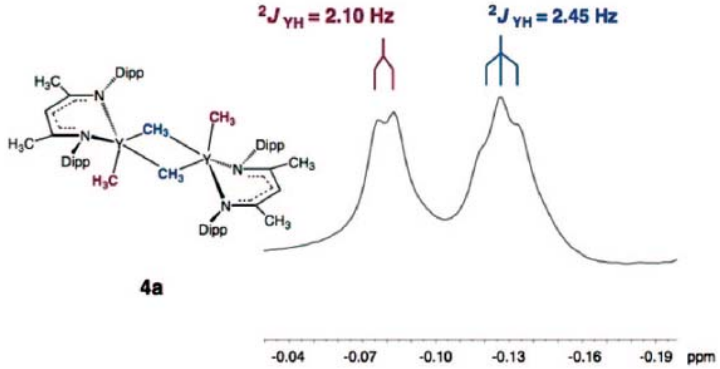
a) Find all symmetry elements and sketch them in the picture.
b) Assign the symmetry point group label to this molecule.
c) Draw schematically the ^1H NMR spectrum of this compound. Important is the number of signals, number of lines in the multiplets, intensities of the lines. The actual order of signals on the ppm scale is not important, CH_2 are at a lower field than CH_3.



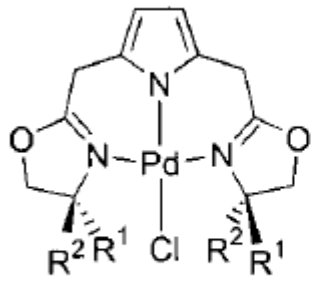
3. (10 pts) Consider the following molecule:
a) Assign the symmetry point group label.
b) Label the spin systems of the methine hydrogens using the spin system notation.
c) Give their approximate values of the chemical shift.
d) Explain the values of the chemical shift –4.25 and 21.0 ppm of the methyl groups.



4. (10 pts) Assign the signals in the ^{1}H NMR spectrum of compound **4a** to the particular CH_3 group and explain your assignment – chemical shift and coupling multiplicity.



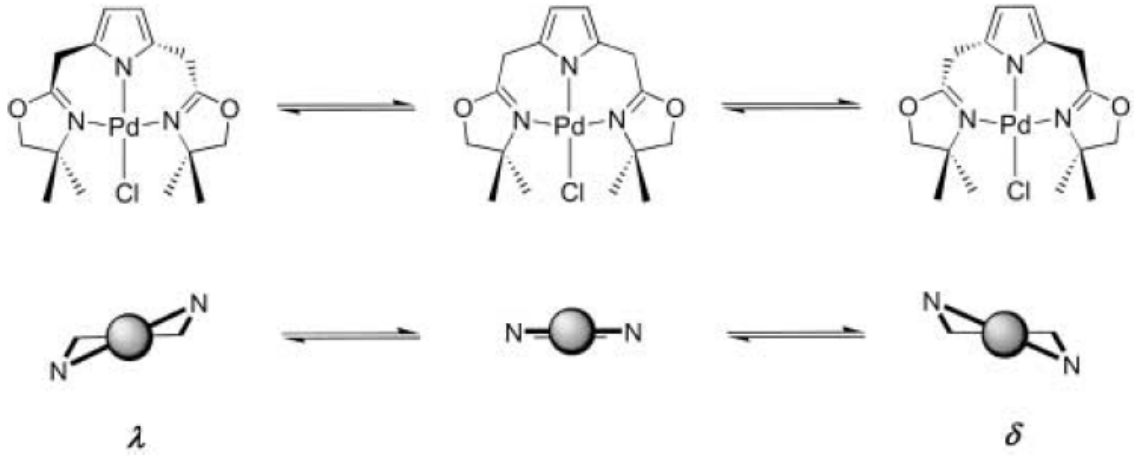
5. (10 pts) Label hydrogens in geminal groups in the molecules **4a, b, c** as **H**omotopic, **E**nantiotopic, **D**iastereotopic.



	R^1	R^2
4a	Me	Me
4b	H	*i*Pr
4c	H	*t*Bu

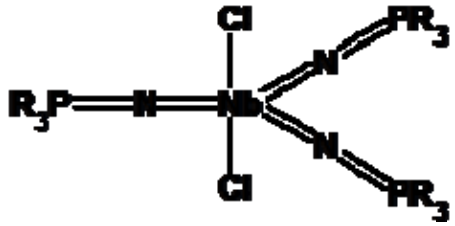
4 a-c

Based on this knowledge, propose a method to study the kinetics of the following interconversion of two enantiomeric helical conformers of **4a**. How would you measure the rate constant of this process.

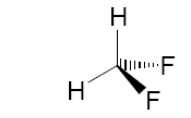


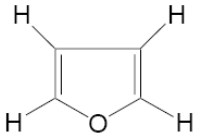
6. (10 pts) The 60 MHz ^{1}H NMR spectrum of an AB system gives the following four peaks (in Hz from TMS): 423, 418.5, 416, 411.5. Calculate:
a) δ_A and δ_B in ppm, and J_{AB} in Hz
b) The positions of the four peaks if the spectrum is acquired at 300 MHz (in both Hz and ppm).

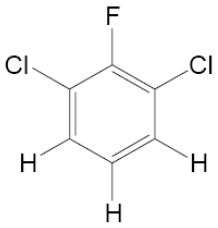
7. (10 pts) Draw the $^{31}P\{^{1}H\}$ NMR spectrum of the Nb complex (R = NMe_2, no P-N coupling observed):
a) Mark clearly with an arrow the position of the chemical shift δ = 17.9 ppm.
b) Label clearly $^{2}J_{NbP}$ = 279 Hz.

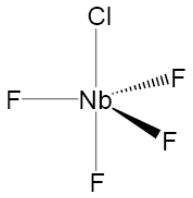


8. (10 pts) Consider magnetic and chemical equivalence: Label the spin systems using the spin system notation. Only take into account high abundance spin-1/2 nuclei (e.g. no C).

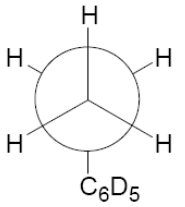




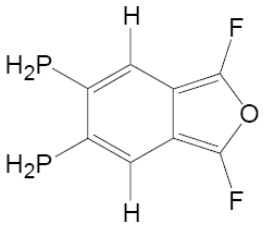




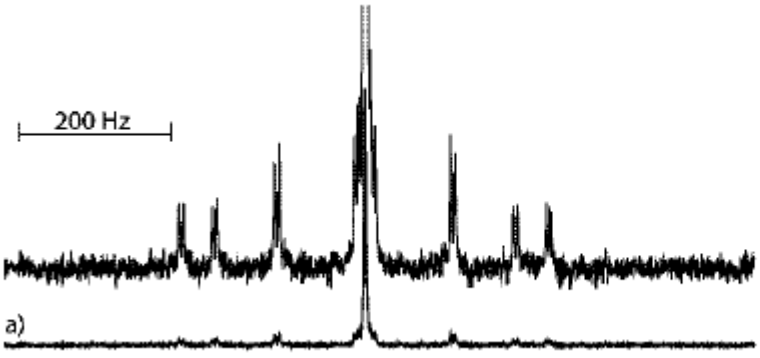
Trigonal bipyramid

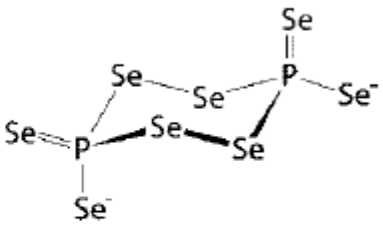


Mobile, negligible rotation barrier



9. (10 pts) The $P_2Se_8^{2-}$ anion is present in the solution as *chair* and *twist* conformers. Interconversion between the conformers at ambient temperature is slow on the NMR time scale. Consider for now only the *chair* conformer.
a) Give the symmetry point group of the anion.
b) Explain the satellite signals in the $^{31}P\{^{1}H\}$ NMR spectrum.





A: ^{31}P
X, Y, Z: ^{77}Se

10. (10 pts) How many resonances will you observe in a ^{14}N NMR spectrum of NH_4NO_3? Which resonance(s) will be sharp and which will be broad? Explain why.