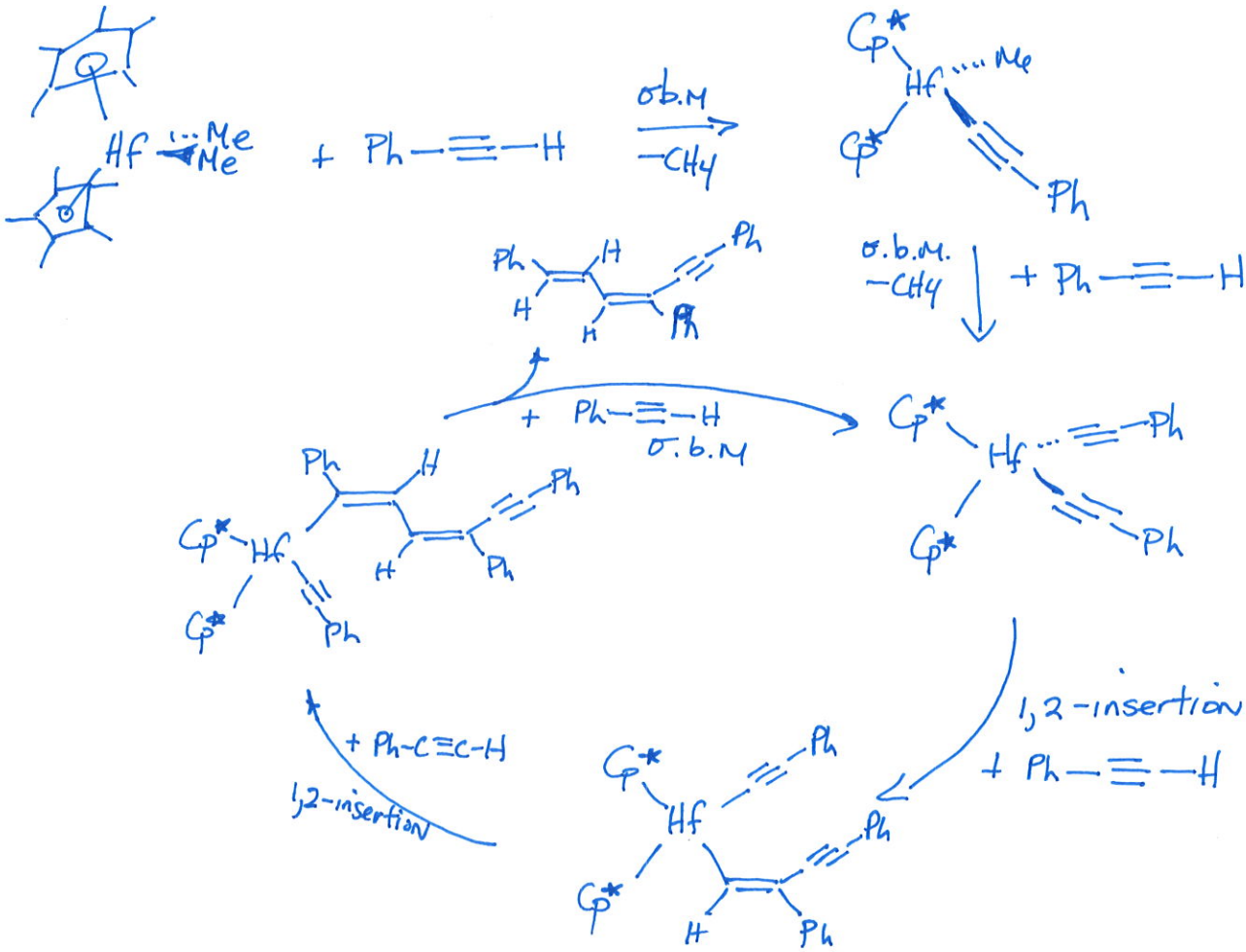
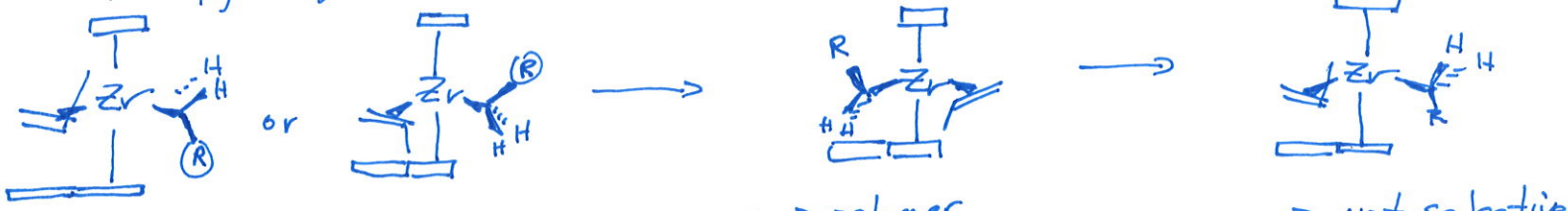
Chem 4000
Assignment #3
Answer Key.

1.



2.a) This catalyst will afford hemiisotactic polypropylene, as every second coordination/insertion is random and every other coordination/insertion is selective (via coordination to the Si-face of propylene).



→ polymer can point up or down ∴ ⇌ binds through either re or si face → Not specific

→ polymer points away for ligand (up) ∴ ⇌ binds selectively to si face (isospecific

→ Not selective

hemiisotactic

random → si → random → si → random → si →

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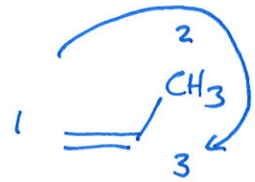
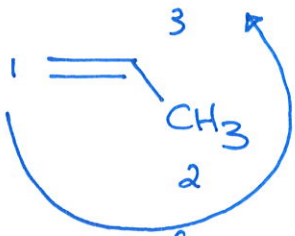
2b)

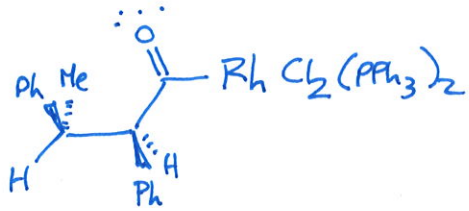


re-face

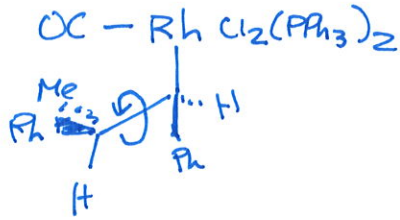


si-face

3.

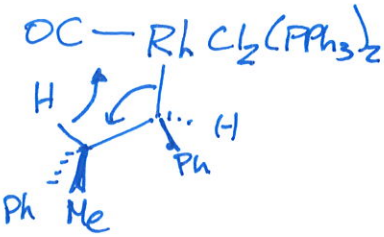


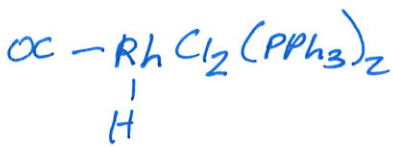
1,1-deinsertion → retention of configuration



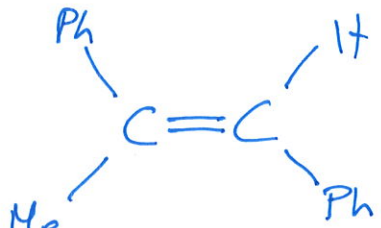
β-H elimination → atoms must be syn co-planar ∴ first rotation about C-C

β-H elimination





+



E olefin exclusively.

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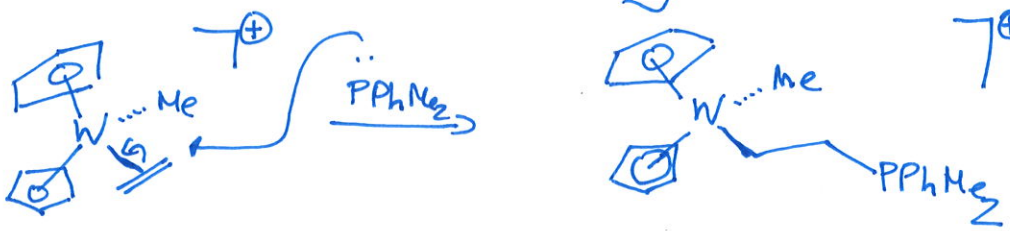
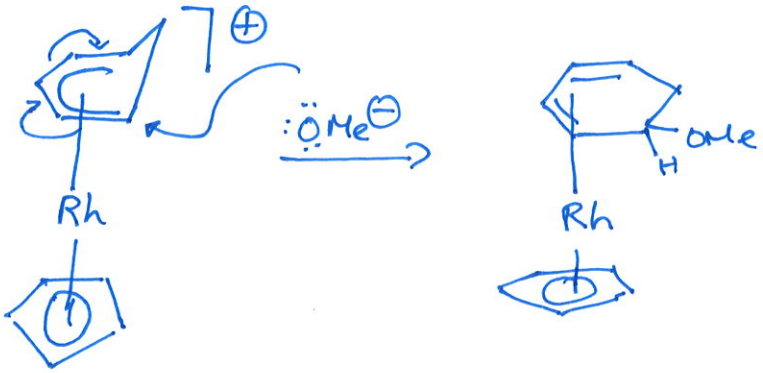
DGM Rules
→ Reactions w/ nucleophiles
Rule 1: Even > Odd

4.





Rule 2: Open > Closed

Rule 1: Even > Odd
2: Open > Closed
3: Terminal > Internal for even polyenes

Rule 1 Even > Odd
2 Open > closed
3 Internal > Terminal for odd polyenes.

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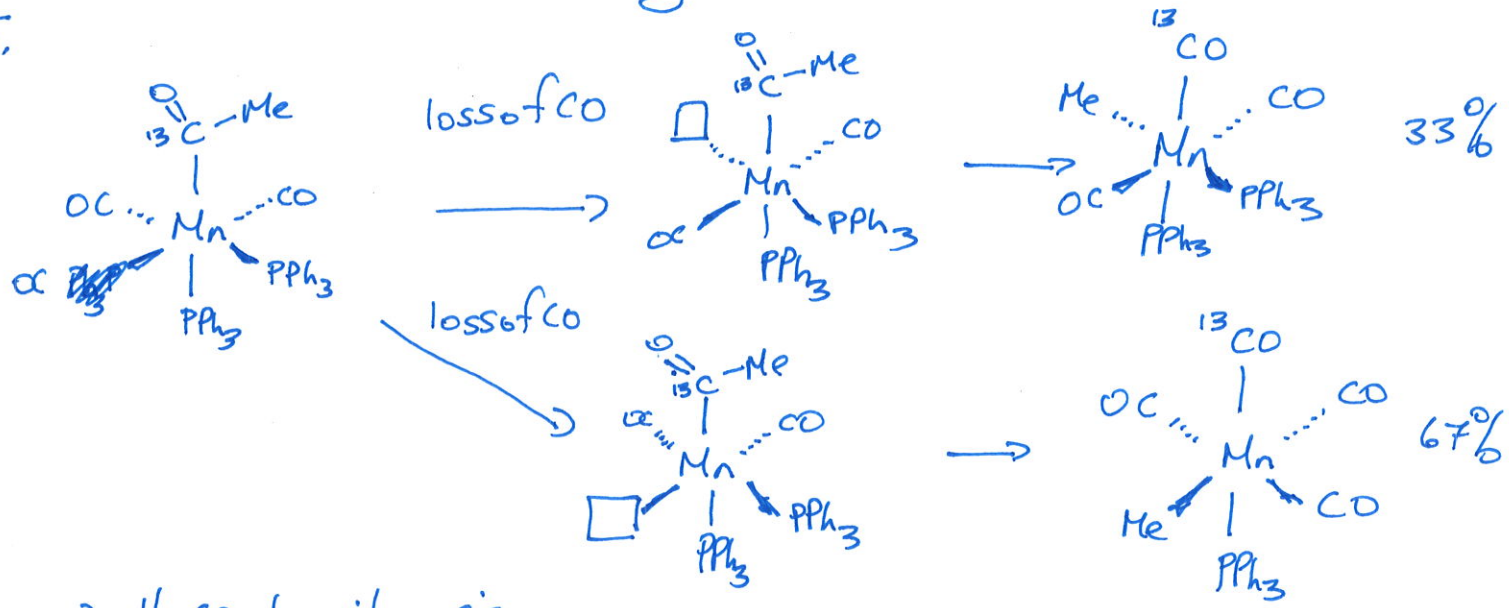
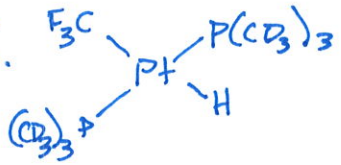
5.



→ all CO ligands cis to COMe ∴ equal likelihood of loss (statistically 2:1 greater likelihood of 2 chemically equivalent CO). Perhaps slightly greater than expected loss of those 2 CO since they are both cis to COMe + 2 PPh_3 while remaining CO is cis to COMe + 1 PPh_3.

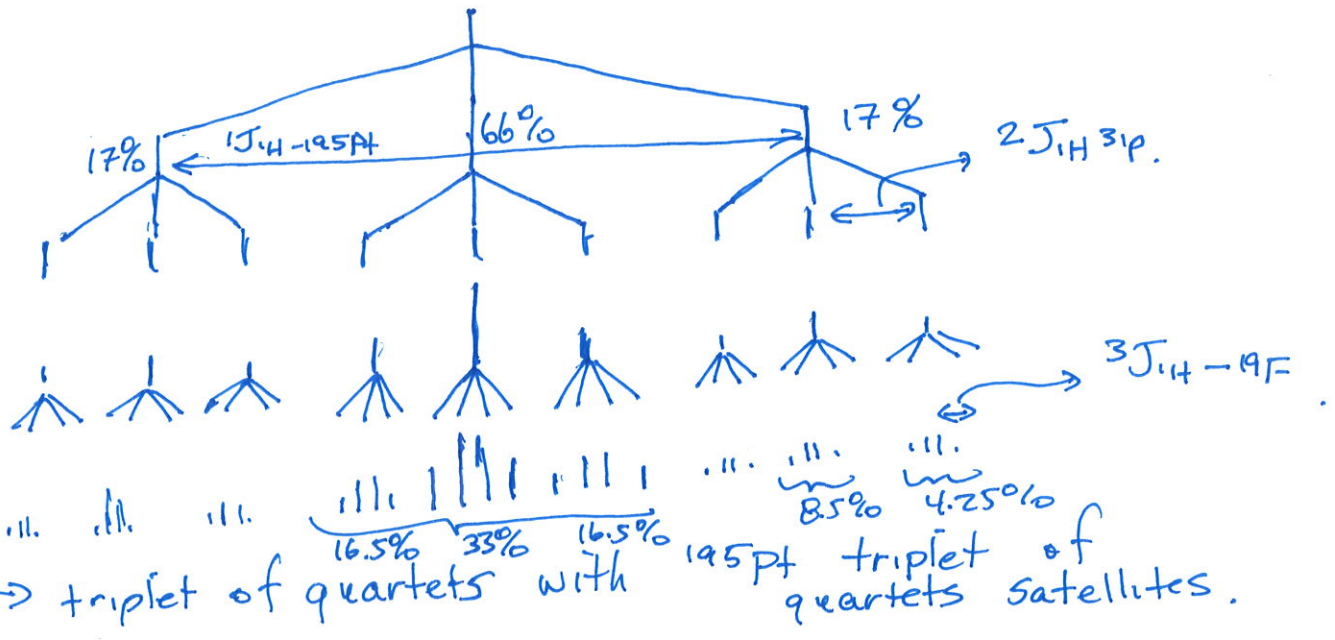
6.



^1H: $^1J_{^1H-^{195}Pt}$ $2nI+1 \rightarrow 2(1)(\frac{1}{2})+1=2$ 34% of time.

$^2J_{^1H-^{31}P}$ $2nI+1 \rightarrow 2(2)(\frac{1}{2})+1=3$

$^3J_{^1H-^{19}F}$ $2nI+1 \rightarrow 2(3)(\frac{1}{2})+1=4$.



→ triplet of quartets with ^{195}Pt triplet of quartets satellites.

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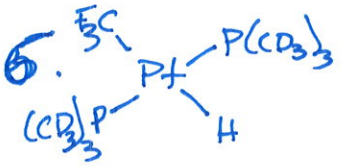
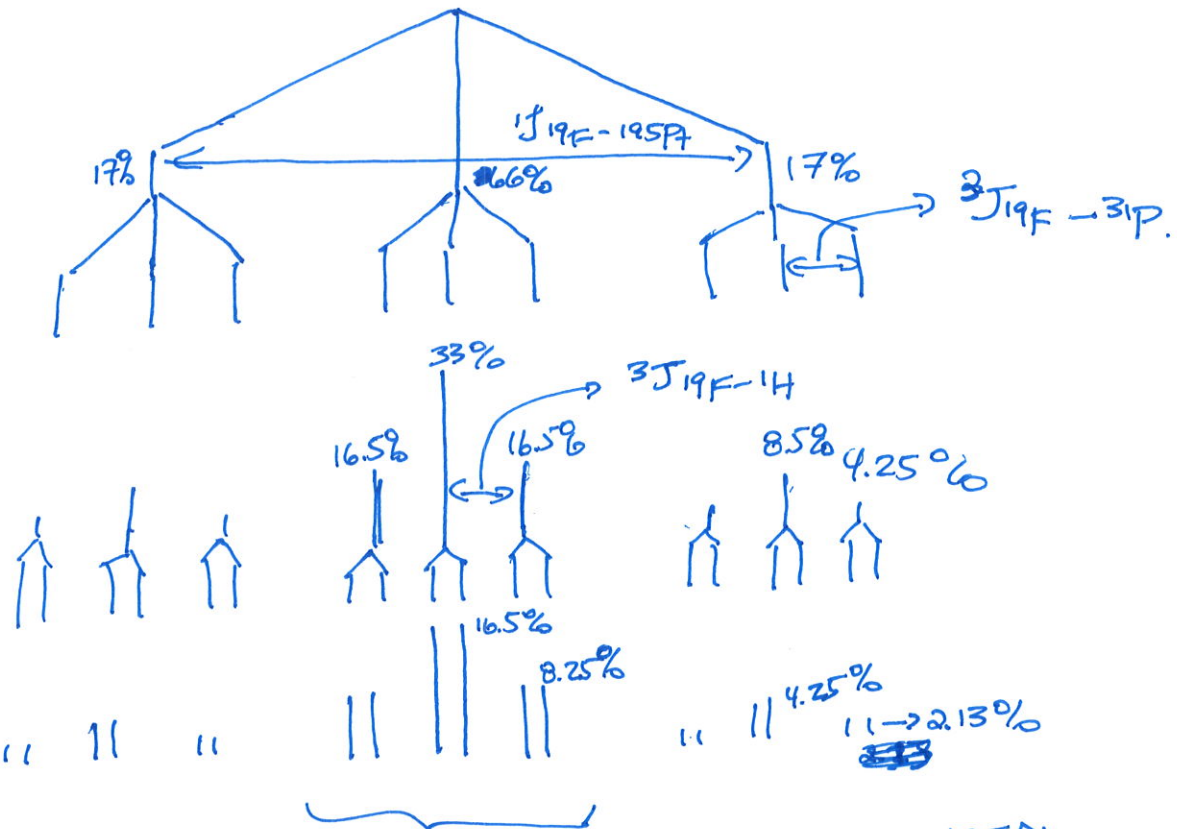
6. 

^{19}F: $^{2}J_{^{19}F-^{195}Pt}$ $2nI+1 = 2(1)(\frac{1}{2})+1 = 2$ 34% of time

$^{3}J_{^{19}F-^{31}P}$ $2nI+1 = 2(2)(\frac{1}{2})+1 = 3$

$^{3}J_{^{19}F-^{1}H}$ $2nI+1 = 2(1)(\frac{1}{2})+1 = 2$

Assume $^{3}J_{^{19}F-^{31}P} > {}^{3}J_{^{19}F-^{1}H}$.



triplet of doublets with ^{195}Pt satellites.
triplet of doublets

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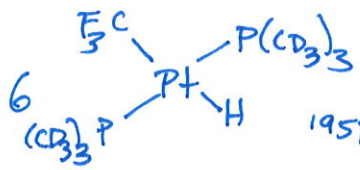
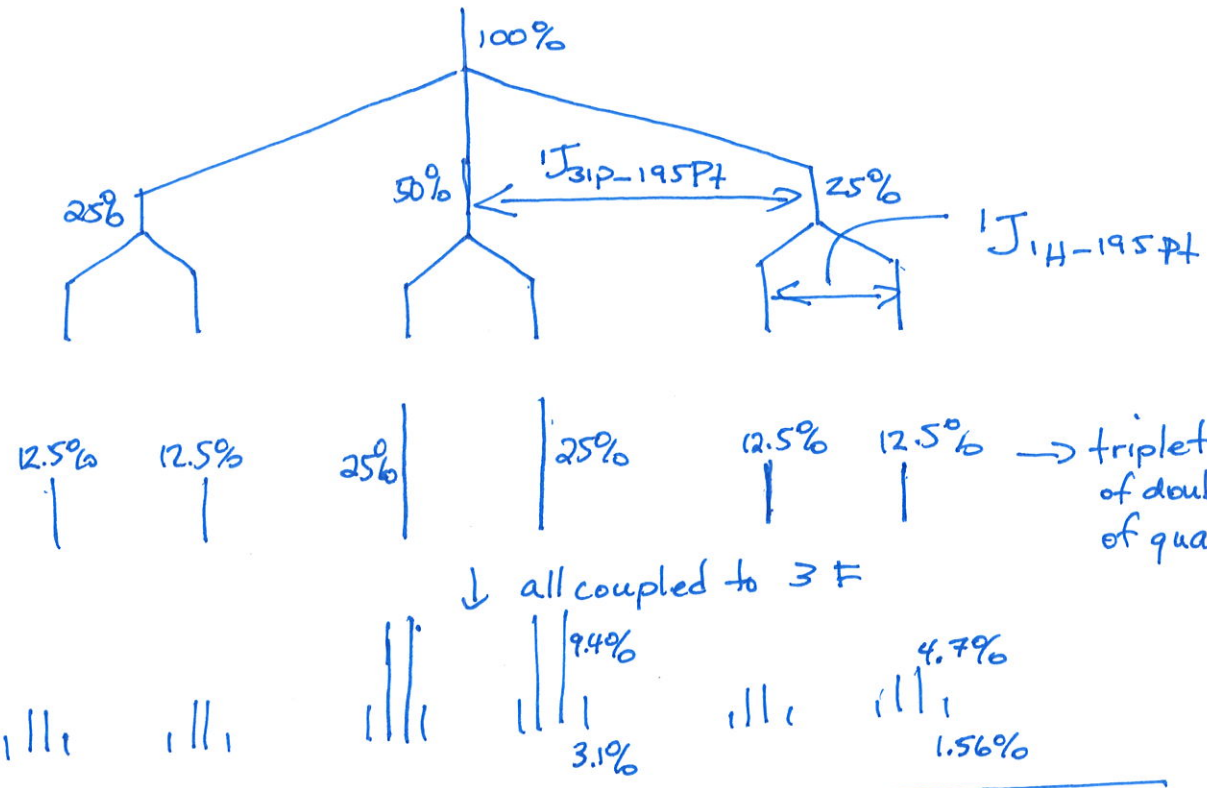


^{195}Pt: $^1J_{^{31}P-^{195}Pt}$ $2nI+1 \rightarrow 2(2)(\frac{1}{2})+1 = 3$

Assume $^1J_{^{31}P-^{195}Pt} >$ $^1J_{H-^{195}Pt}$ $^1J_{H-^{195}Pt}$ $2nI+1 \rightarrow 2(1)(\frac{1}{2})+1 = 2$

$^2J_{^{19}F-^{195}Pt}$ $2nI+1 \rightarrow 2(3)(\frac{1}{2})+1 = 4$.



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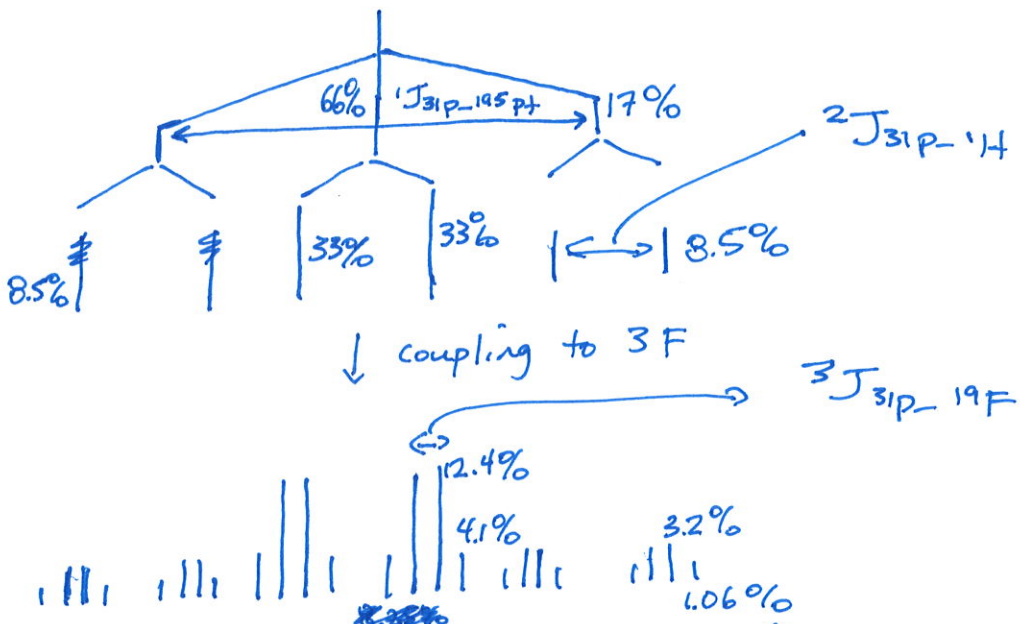
^{31}P: $^1J_{^{31}P-^{195}Pt}$ $2nI+1 \rightarrow 2(1)(\frac{1}{2})+1 = 2$ 34% of time

$^2J_{^{31}P-^1H}$ $2nI+1 \rightarrow 2(1)(\frac{1}{2})+1 = 2$

$^3J_{^{31}P-^{19}F}$ $2nI+1 \rightarrow 2(3)(\frac{1}{2})+1 = 4$



→ doublet of quartets with ^{195}Pt doublet of quartet satellites.