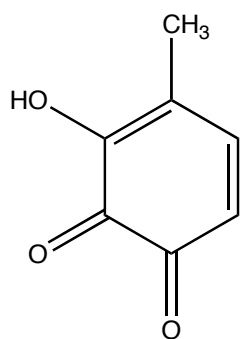
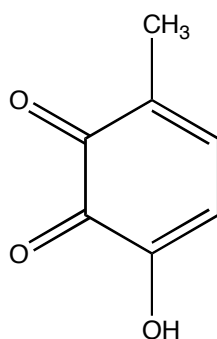
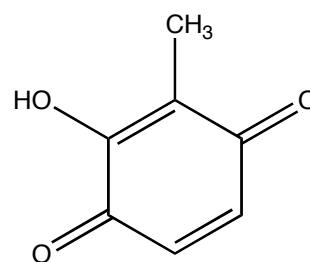


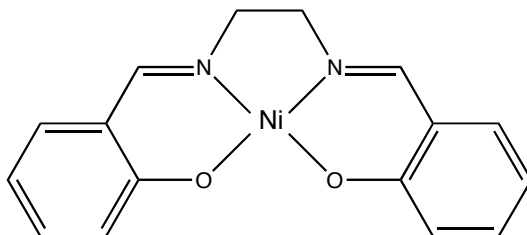
1. Consider the below 3 molecules, which might result from the oxidation of methylphenol.

**1****2****3**

You've got a reaction that makes one of these possible products stereoselectively (congratulations!) But, which one is it? In the NMR, there are aromatic protons in an AB quartet having chemical shifts of 7.0 and 7.4 ppm. Use computational models to decide which one you've made. Describe what you do and how you arrive at your conclusions. You *may* very well find useful a trip to [~cm8021pr/templates](#) on Calhoun to take a look at some files I have there called `tms.com`, `tms.out`, `tmsnmr.com`, and `tmsnmr.out`.

Would UV/Vis spectroscopy (in combination with theory) also have been useful to identify the isomer that you made? Here, too, describe what computational protocol you choose to answer this question and summarize your results.

2. The below molecule is a salen complex of nickel. What is the predicted standard reduction potential, relative to the Ag/AgNO₃ electrode, for reduction of Ni^{II}(salen) to Ni^I(salen) in acetonitrile? The experimental value is -2.1 V (see Miranda et al. *J. Org. Chem.* **2005**, 70, 8017).



To answer this question, compute molecular free energies for the neutral, singlet, Ni^{II} complex and the anionic, doublet, Ni^I complex at the SMD(acetonitrile)/M06-L/6-311+G(2df,p)//SMD(acetonitrile)/M06-L/6-31G(d) level. Note that this notation implies that each geometry is optimized at the SMD(acetonitrile)/M06-L/6-31G(d) level, so the thermal contributions to free energy will be taken from a frequency calculation at this level and *not* from a frequency calculation with the larger basis set (*don't try to do the larger frequency*). To save time, use a density-fitting basis set with the M06-L functional. The keyword for this is `auto` in *Gaussian09*. Thus, for each geometry optimization and frequency, you will have as keywords `M06L/6-31G(d)/auto`, and for each large basis single-point energy you will have `M06L/6-311+G(2df,p)/auto` in the keywords line. To use SMD solvation in acetonitrile, use the keywords `scrf=(smd,solvent=acetonitrile)`.

Note that the Ni^{II} complex belongs to the C_2 point group, but the Ni^I complex, unfortunately, has no symmetry. The frequency calculation on the C_1 open-shell Ni^I complex takes almost a full hour on Calhoun, so expect to do this frequency calculation as a separate job.

You may find it useful to know that the absolute potential of the normal hydrogen electrode is 4.28 V (the course textbook says 4.36 V, but that is an error).

If the computed value is not in perfect agreement with experiment, what may be contributing to the error (put differently, how might one do a “better” calculation)?

3. Here continues a problem that will carry over to the final exam. We add to the data at:

pollux.chem.umn.edu/8021/PES/

Your present task is to update your two structures on the potential energy surface (PES) with a calculation at the M06/6-31G(d) level (since there is no double slash, this implies re-optimizing the geometry). The most efficient way to do this will be to read in the force constants and geometry from your RHF frequency calculations (i.e., `fopt=(readfc) geom=checkpoint guess=read`) as keywords. *Nota bene*: if you were using `fopt=ts` at the RHF level, you will need to continue to use the `ts` keyword, of course (but you don't have to start with `calcfc — readfc` will work just fine). Once you have a reoptimized structure, do a new frequency calculation at the M06/6-31G(d) level and update your entry with the relevant energy, enthalpy, and free energy data.

Remember, the *energy* comes from the last instance of the SCF energy in the optimization, e.g.,

```
SCF Done: E(RM06) = -1729.65395114 A.U. after 21 cycles
```

and the *enthalpy* and *free energy* come from the frequency calculation, e.g.,

```
Sum of electronic and thermal Enthalpies= -3697.283578
Sum of electronic and thermal Free Energies= -3697.326262
```

Finally, compute the M06/6-31G(d) *aqueous* solvation free energy for your DFT structure using the SMD model in Gaussian09 (as a *single-point* calculation on the DFT optimized geometry). When the calculation completes, add the solvation free energy to the website data. Report only one position after the decimal place for the solvation free energy in units of kcal/mol (the solvation free energy is the difference between the M06 SCF energies in solution (found in the SMD output file) and in the gas phase (found in the M06 geometry optimization output file)).