CHEM 3331 (Richardson) Second Hour Exam – October 18, 2016

Your Name Key

Student ID _____

Recitation (check one)

- O 1:00 Monday w/ Thomas Carey
- O 2:00 Monday w/ Thomas Carey
- O 3:00 Monday w/ Matthew Farmer
- O 9:00 Tuesday w/ Ryan McCaffrey
- O 11:00 Tuesday w/ Ryan McCaffrey
- O 1:00 Tuesday w/ Ryan McCaffrey
- O 2:00 Tuesday w/ Patrick Nordeen
- O 3:00 Tuesday w/ Matthew Farmer

Question	Score	Out of
1		30
2		25
3		30
4		15
5		10 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.

1												13	14	15	16	17	18
1 H 1.008	2																2 He 4.0026
3 Li 6.94	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.97	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (294)

* Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
# Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

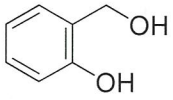
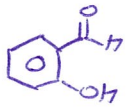
pKa Values

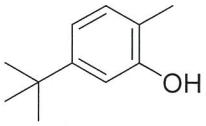
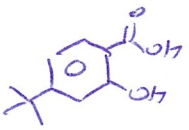
HI	-10	CH_3COOH	4.7	Phenol	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	Alcohol (ROH)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

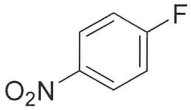
Average: 72.4
St. Dev: 23.0
Max: 107.5
Min: 11

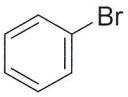
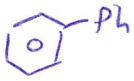
 Name_____

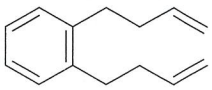
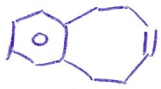
1) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (30 pts; 3 pts each)

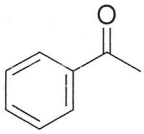
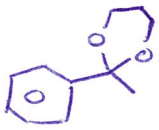
a.  MnO_2 

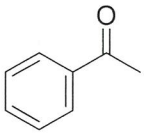
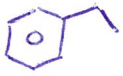
b.  $KMnO_4$ 

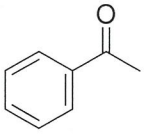
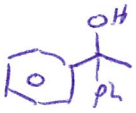
c.  NaOMe 

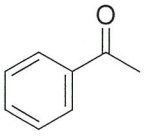
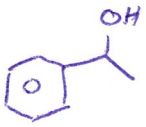
d.  $PhB(OH)_2$, $Pd(PPh_3)_4$, NaOH 

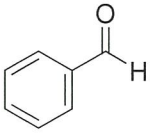
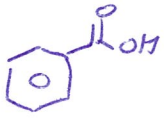
e.  Grubbs 2nd gen cat. 

f  HO–OH, H^+, 4AMS  ← 6-mem. ring, not 5.

g.  H_2NNH_2, KOH, Δ 

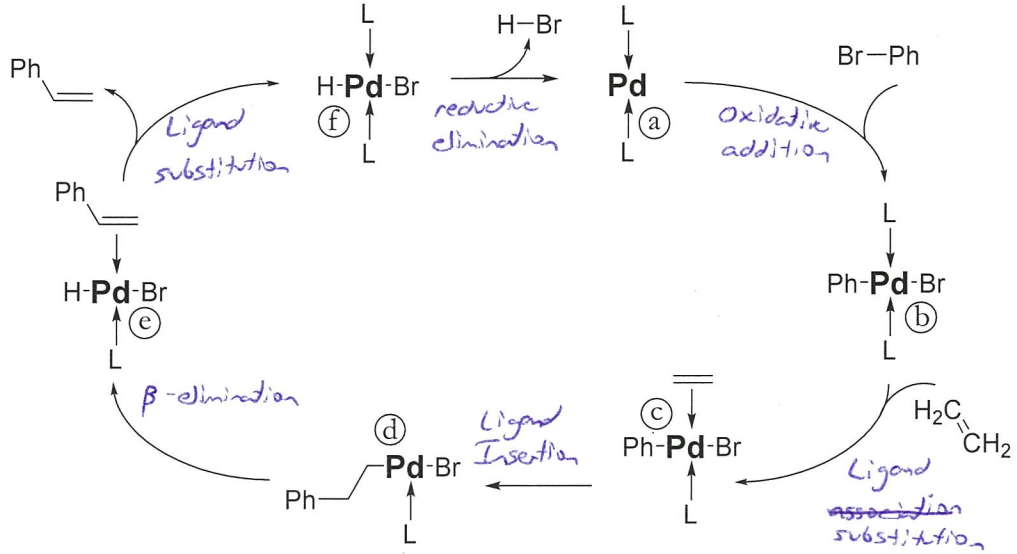
h.  1) Ph MgBr, 2) H_3O^+ 

i.  $NaBH_4$, MeOH 

j.  $Ag(NH_3)_2^+$ 

 Name_____

2) The mechanism for the Heck reaction is shown below. (25 pts total)



a. Label each arrow with the name for the step occurring at the transition metal. (6 pts)

b. For each Pd species (a through f) list the oxidation state, unshared electrons, and electron count at the transition metal. (9 pts)

These formulas may help you:

Oxidation state of metal atom = # of X-type ligands + charge on metal

n = # of unshared electrons = valence electrons in neutral metal – oxidation state

Electron count = # of valence electrons in neutral metal – charge on metal + # of X-type ligands + 2•(# of L-type ligands)

ⓐ Oxidation state = 0, Unshared electrons = 10, Electron count = 14

ⓑ Oxidation state = +2, Unshared electrons = 8, Electron count = 16

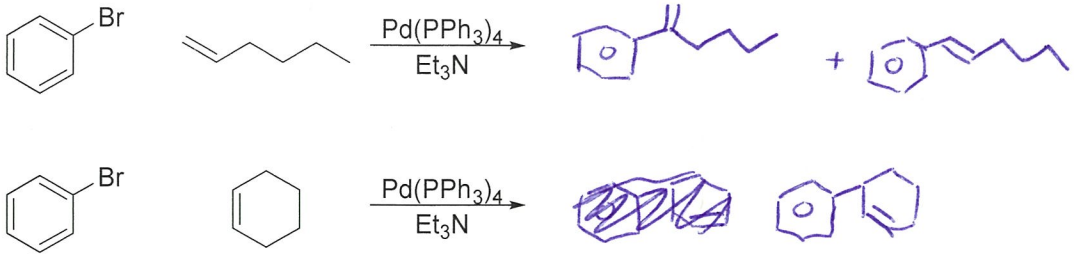
ⓒ Oxidation state = +2, Unshared electrons = 8, Electron count = 16

ⓓ Oxidation state = +2, Unshared electrons = 8, Electron count = 14

ⓔ Oxidation state = +2, Unshared electrons = 8, Electron count = 16

ⓕ Oxidation state = +2, Unshared electrons = 8, Electron count = 16

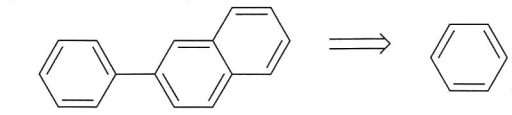
c. Show the product(s) of the following reactions. (10 pts)

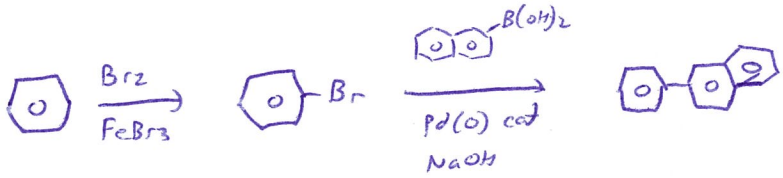


 Name_____

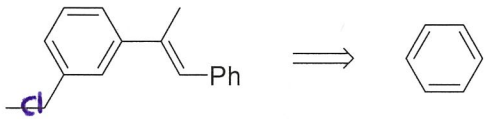
3) Find a way to synthesize the desired product from the given starting material plus any other reagents. If more than one step is necessary, show the product of each step. You do not need to show mechanisms or the specific structure of transition metal catalysts. (30 pts; 10 pts each)

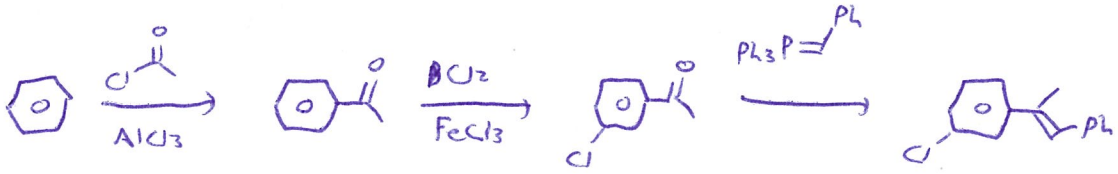
a.



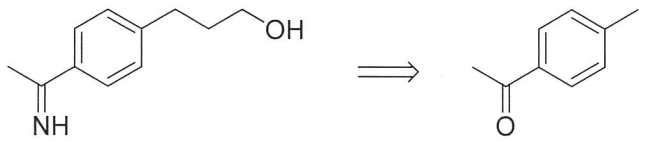


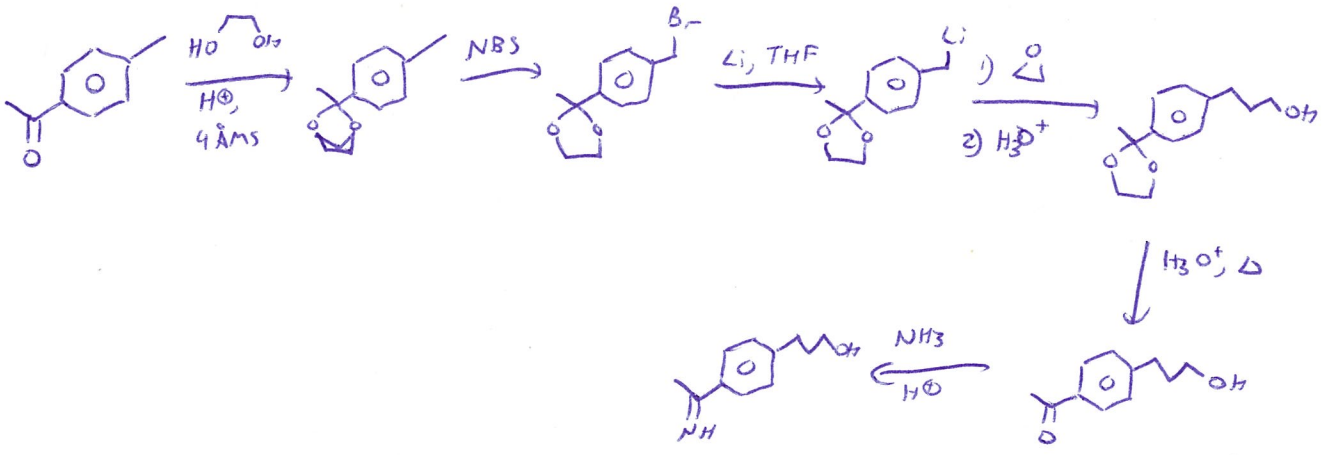
b.





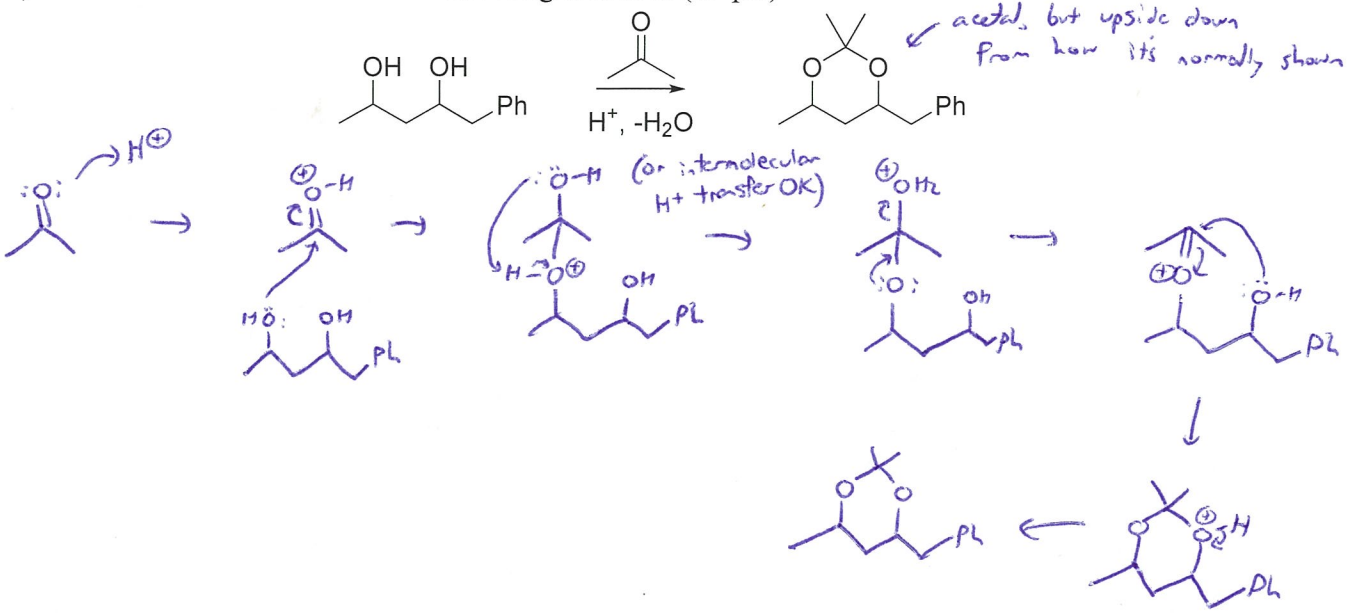
c.





 Name_____

4) Provide a mechanism for the following reaction. (15 pts)



5) Extra credit! Arrange each of the following groups of compounds in order of decreasing reactivity (1 = fastest, 5 = slowest) towards nucleophilic aromatic substitution with NaOMe. For the fastest reactant, show all the resonance forms in the intermediate and point out which ones are particularly stable. (10 pts e.c.)