Chem 12B Midterm 2

Instructor: Richmond Sarpong
March 22nd 2018
8:10-9:30 am, 100 Lewis

You have **80 minutes** to complete this exam. Please write you answers clearly only on the pages indicated *and be as detailed as possible*. Nothing written outside the numbered pages will be graded. There should be ~~8~~ 7 total pages in this exam.

Name: key _____

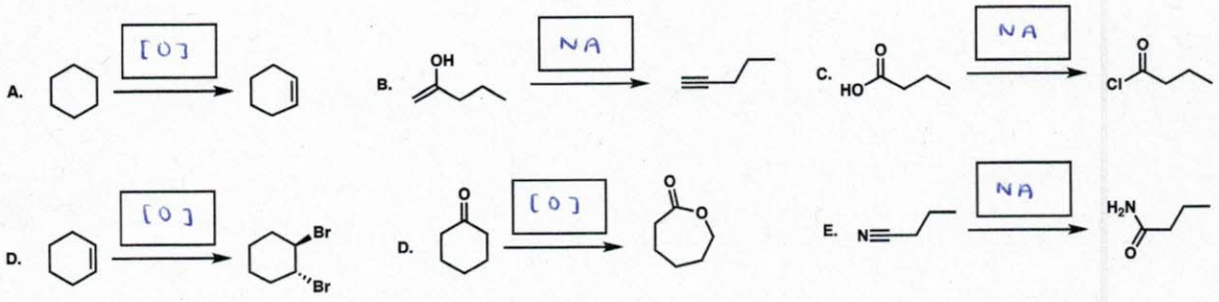
UID: _____

GSI Name: _____

Question	Score
1	_____ (12 points)
2	_____ (10 points)
3	_____ (10 points)
4	_____ (17 points)
5	_____ (12 points)
6	_____ (19 points)
7	_____ (20 points)

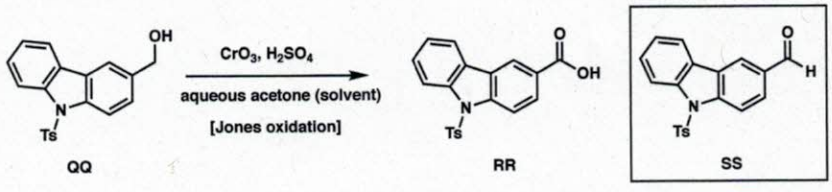
Total _____*(100)*

Question 1 (12 points):
Indicate in the boxes that are provided whether the following transformations are net oxidations (with "[O]"), net reductions (with "[H]") or neither (with "NA") (2 pts each; 12 pts total):

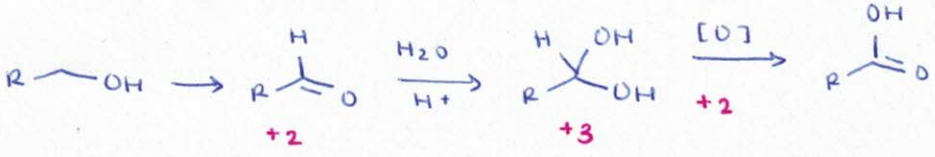


Question 2 (10 points):

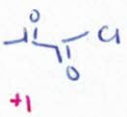
(a) Explain why **QQ** is converted to **RR** under the indicated conditions using up to four structures and three sentences. (7 pts total)



Jones oxidation conditions lead to formation of aldehyde SS, which is hydrated. The hydrate is then oxidized again to the carboxylic acid (RR).



(b) The Swern oxidation can be used instead of the Jones oxidation to convert **QQ** to **SS** in Part (a) above. Provide conditions for the Swern oxidation (3 pts).

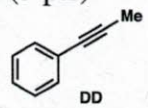
DMSO, Et_3N (or base), 

+1 +1 +1

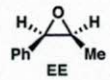
(other "dehydrating agents" may also be suggested although technically not a Swern: PCl_3, $POCl_3$, etc.)

Question 3 (10 points):

(a) Propose a synthesis of **EE** from **DD** (show reagents) given that a Lindlar reduction and other reactions of your choosing are involved (5 pts)



DD

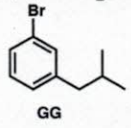


EE

DD → (or $CaCO_3$) PdI_{BaSO_4}, H_2, quinoline (Lindlar) → Ph, Me → mCPBA (epoxidation) → EE

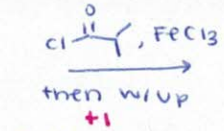
+3 +2

(b) Propose a synthesis of **GG** from benzene (show reagents) (5 pts)



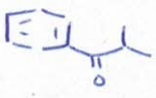
GG

Both are o/p directors, so need to make one a meta director



+1

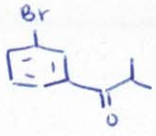
Friedel-Crafts Acylation



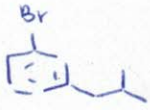
m-director

$FeBr_3$, Br_2

+2

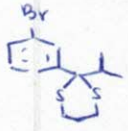


+2 H_2NNH_2, KOH, Δ — Wolff-Kishner



Clemmensen proposal -1 (could result in loss of bromine)

Also, could make

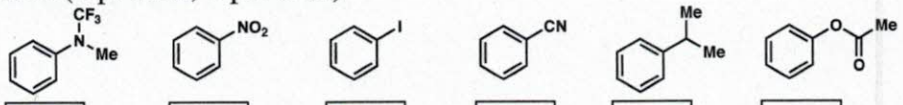


, then PdIC, H_2

Again, Br could be lost -1

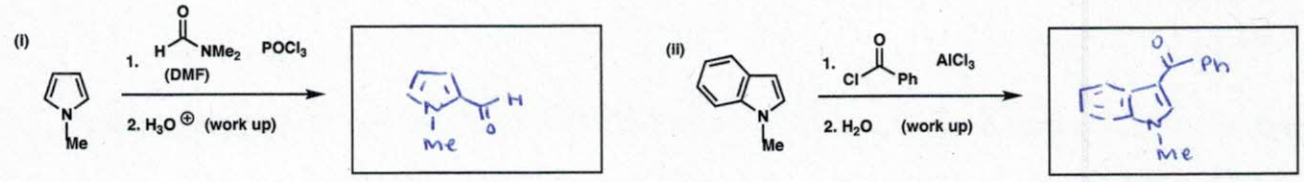
Question 4 (17 Points):

(a) Indicate which of the following substituents would direct ortho/para (with "o/p") or meta (with "m") in the boxes provided (1 pt each; 6 pts total)

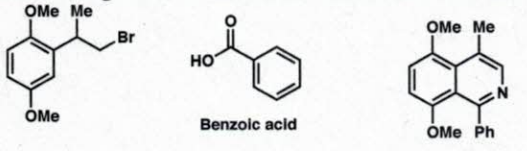


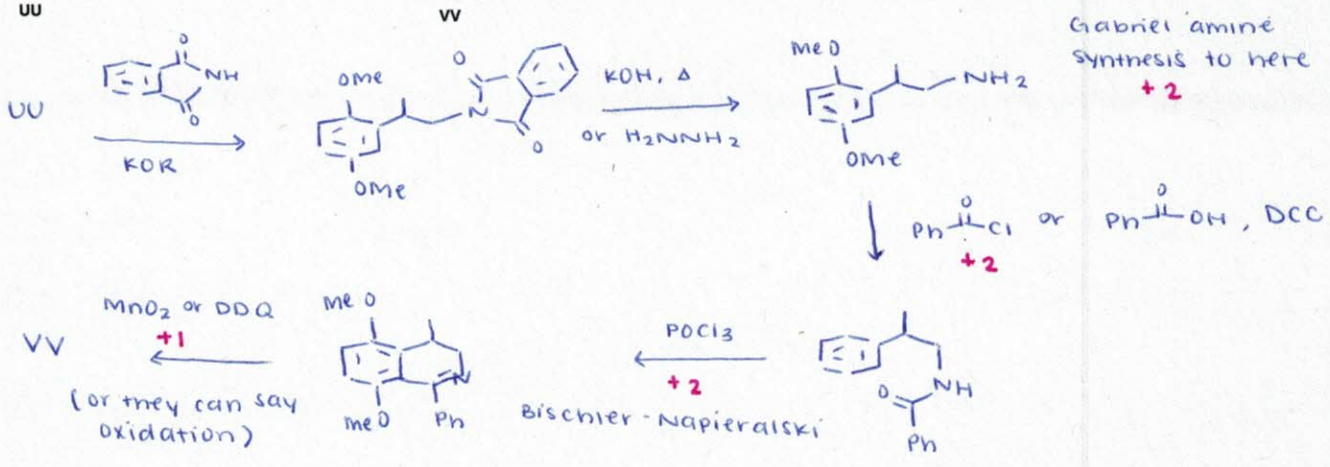
o/p	m	o/p	m	o/p	o/p

(b) Predict the outcome of the following reactions. Place your answers in the boxes provided (~~3~~ 2 pts each)



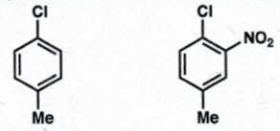
(c) Quinoline **VV** can be prepared from **UU** and benzoic acid. Provide a synthesis (show reagents) knowing that it involves a Gabriel amine synthesis and Bischler-Napieralski reaction (8 pts).





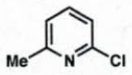
Question 5 (12 points):

(a) Rank the following chlorinated aromatic compounds in order of their reactivity with NaOMe (indicate the most reactive as 1). (1 pt each)

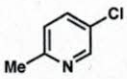


A: 4

B: 1



C: 2

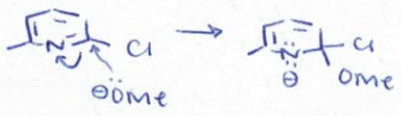


D: 3

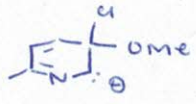
(b) Provide a rationalization for your relative ranking of **C** and **D** from Part (a) in three or less sentences and four or less structures (4 pts)

C can form a Meisenheimer complex (+2) that is stabilized by N-atom in the ring; not possible for D

for C



for D

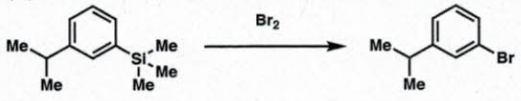


more stable b/c anion on nitrogen

carbon is not as electronegative as nitrogen and so not as stabilized

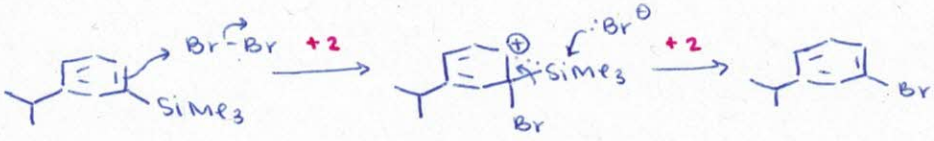
1 – +2

(c) Provide a mechanism for the following observation of *ipso* substitution (4 pts)



HH

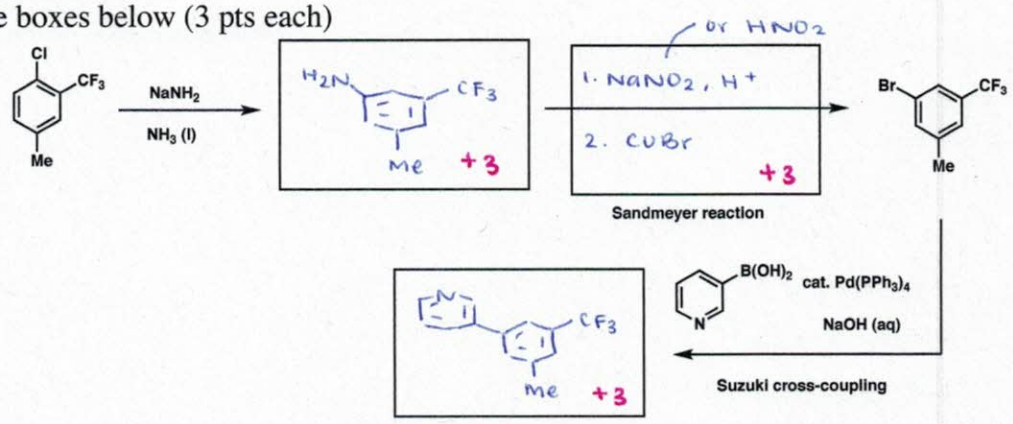
CC



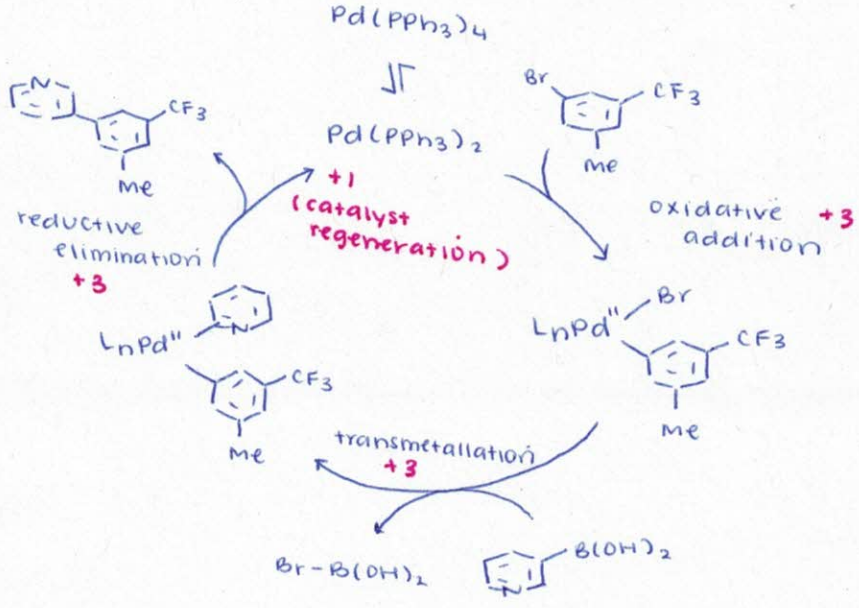
stabilization by silicon (β-silicon effect) (+2)

Question 6 (19 points)

(a) Fill in the boxes below (3 pts each)

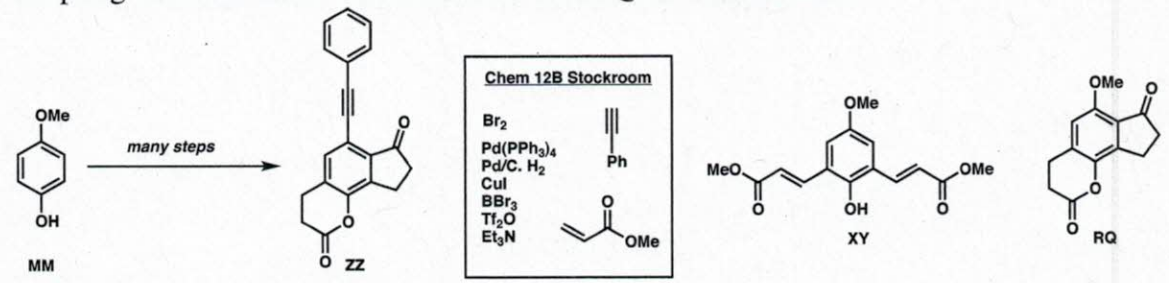


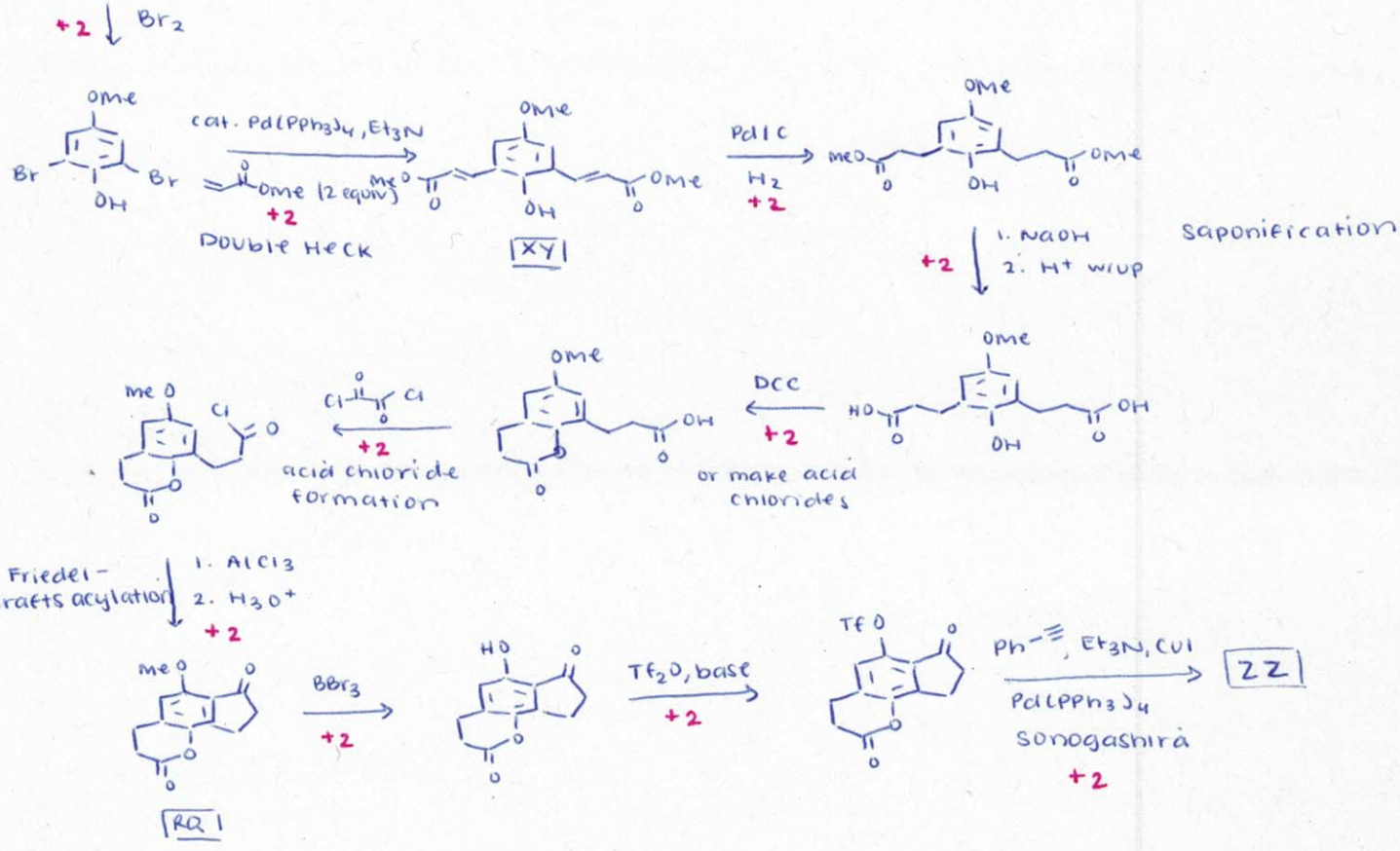
(b) Provide a mechanism for the Suzuki coupling step from Part (a) above. Be sure to label each elementary organometallic step in your mechanism (10 pts)



Question 7 (20 points):

Propose a synthesis of **ZZ** from **MM** using unlimited amounts of the materials provided from the Chem 12B stockroom and any other materials that you may deem necessary. Hints: Heck and Sonogashira coupling reactions are involved and **XY** and **RQ** are intermediates.





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