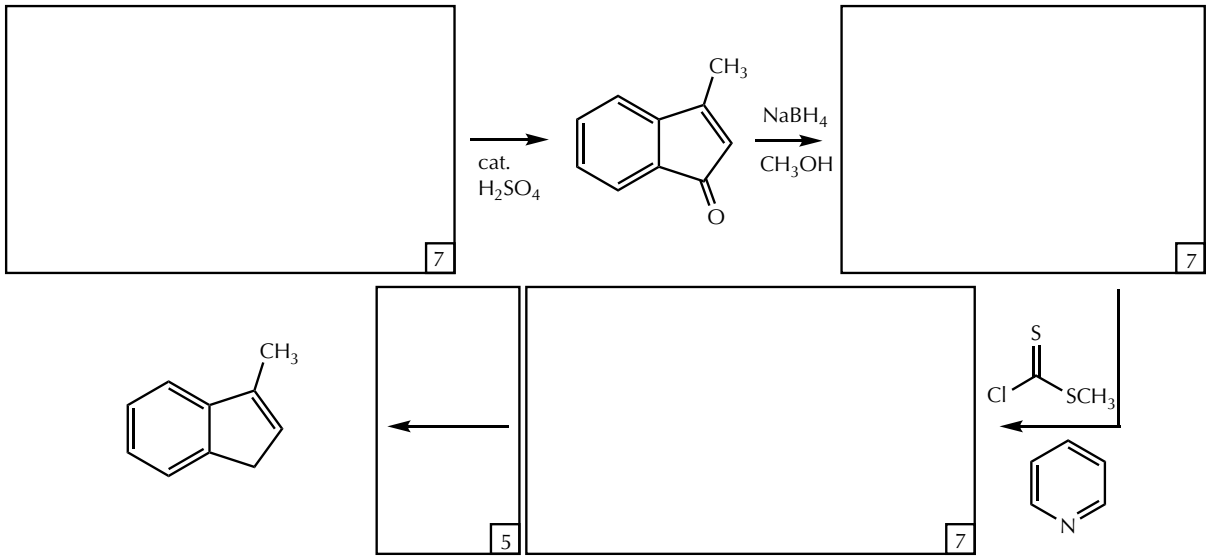
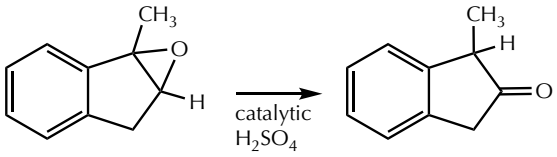
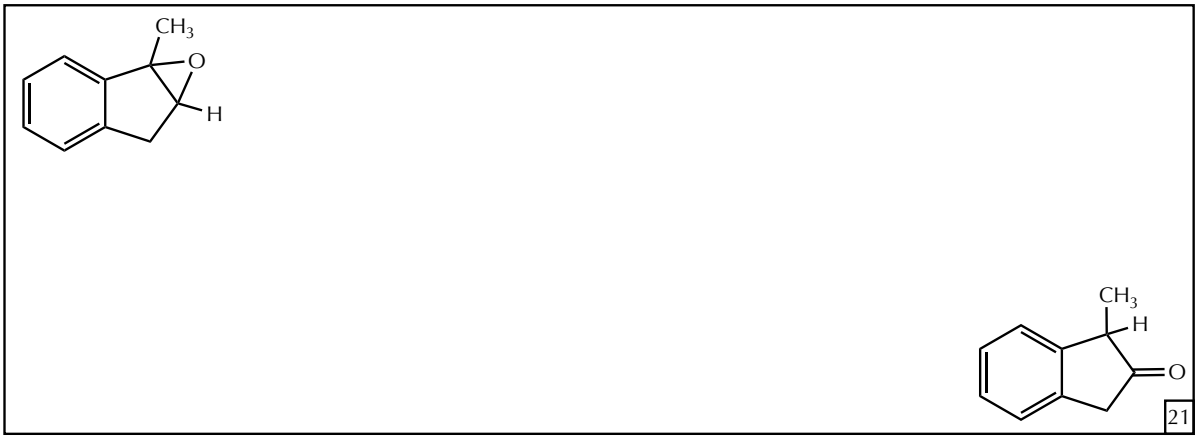
Question I (54 points) Name: _____

A. Complete the following reaction sequence (in part: *Org. Process Res. Dev.* **2022**, *26*, 1960), which begins with an ***intramolecular aldol condensation***. You do not need to provide stereochemical information.

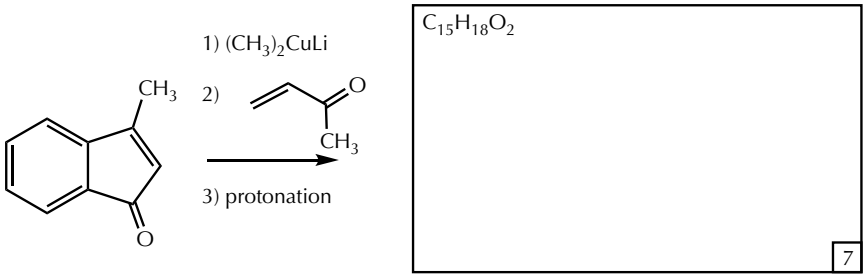


B. When the epoxide derived from the product in part A, above, is treated with an acid catalyst, a rearrangement to a ketone is observed. Using $HB/B^{\ominus}$ as your generic Brønsted acid/base, as needed, provide the complete, curved arrow mechanism for this transformation, in which a carbocation intermediate is anticipated.





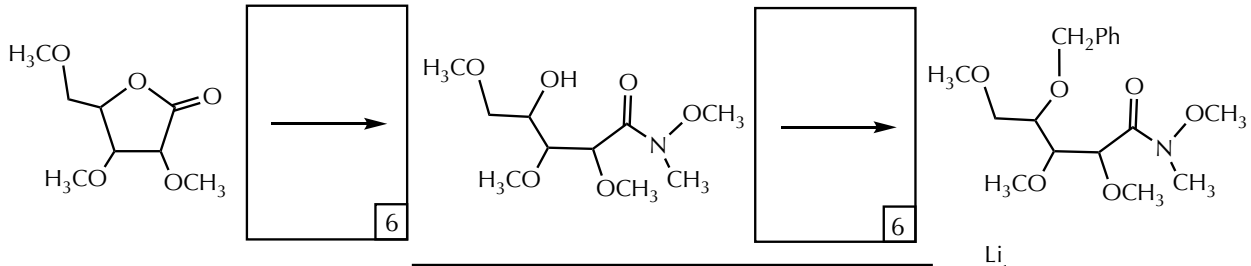
C. Complete the following transformation, which is carried out on the aldol condensation intermediate from part A.

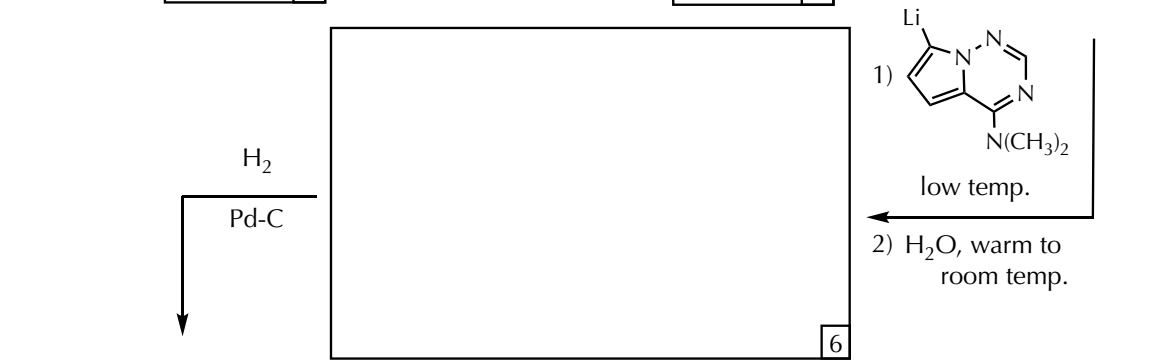


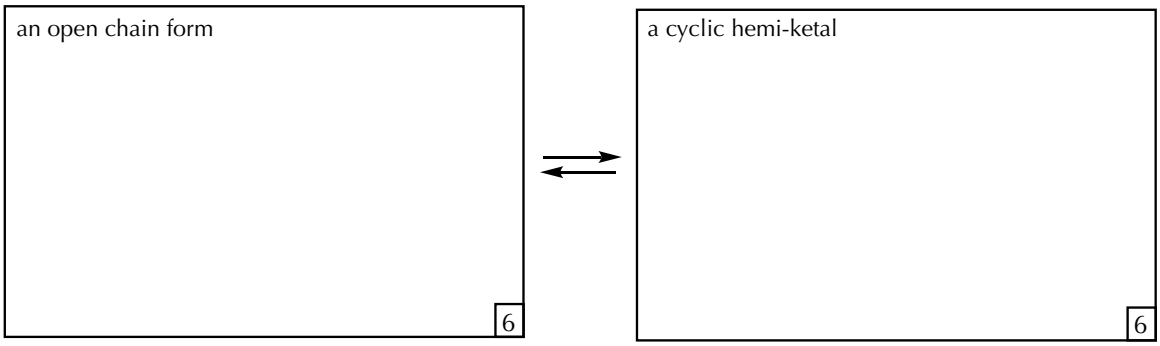
A		/26
B		/21
C		/07
		/54

Question II (50 points) Name: _____

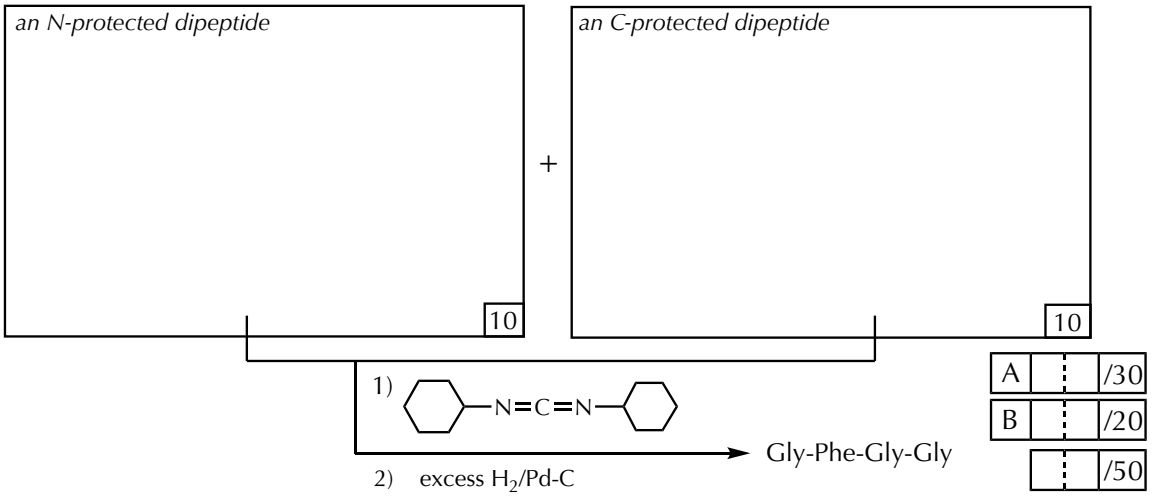
A. Complete the following reaction scheme that was used in a practical synthesis of remdesivir, the first and only FDA-approved antiviral drug for treating COVID-19 (*J. Org. Chem.* **2021**, *86*, 5065). Showing stereochemistry is not required.







B. Taken from a synthesis of the osteogenic growth peptide (OGP), present in small concentrations in circulating blood (*Org. Process Res. Dev.* **2015**, *19*, 1257). ***Show stereochemistry; no abbreviations.***

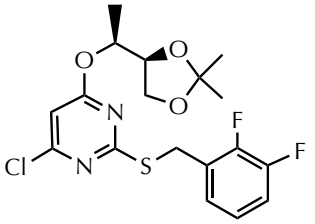


A		/30
B		/20
		/50

Question III (46 points) Name: _____

Complete the following transformations.

(a) *Org. Process Res. Dev.* **2022**, *26*, 2337.



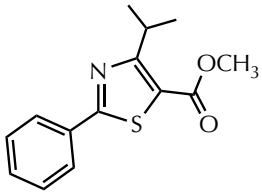
H_2O

catalytic mild acid

balance the equation; give the neutral/uncharged product(s)

6

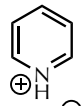
(b) *Org. Process Res. Dev.* **2022**, *26*, 10.



1) $LiAlH_4$

2) H_2O protonation

6



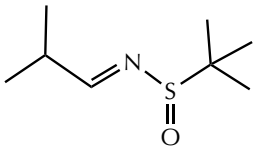
$ClCrO_3^-$

6

(c) *Org. Process Res. Dev.* **2022**, *26*, 2138.

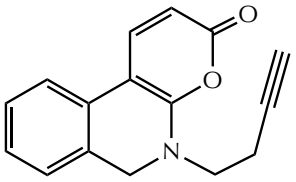
6 + 6

~ pH 6 buffer



+ H_2O

(d) *J. Org. Chem.* **1996**, *61*, 1650.



210 °C
8 hours

an intramolecular Diels-Alder reaction creates an intermediate that undergoes a retro-Diels-Alder reaction to lose carbon dioxide

+ CO_2 8

(e) arabinose is the C2 epimer of ribose

α-L-arabinofuranose

CH_3OH

catalytic TsOH

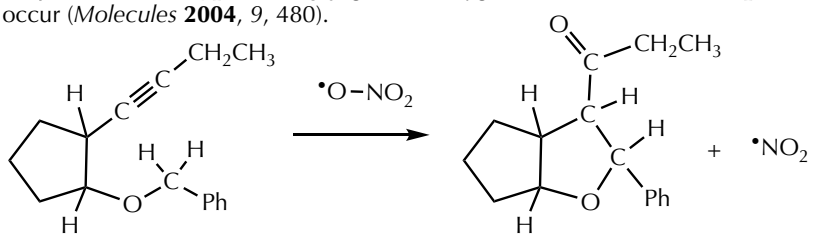
gives the β-anomer of the product

8

a		/06
b		/12
c		/12
d		/08
e		/08
		/46

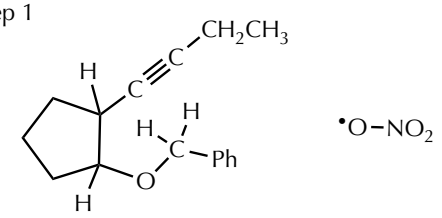
Question IV (48 points) Name: _____

A. The photochemical decomposition of $(NH_4)_2$ $[Ce(NO_3)_6]$ gives an oxygen atom radical: $^{\bullet}O\text{-}NO_2$. The following reaction is observed to occur (*Molecules* **2004**, *9*, 480).



The mechanistic steps are outlined here: provide the missing intermediates as well as the curved (fish-hook) arrows for each step.

step 1



5

the oxygen atom adds to the triple bond; its regioselectivity can be inferred from the product

step 2

9

the sp^2 carbon radical resulting from step 1 removes a hydrogen atom intramolecularly from the benzyl group

step 3

9

the benzylic carbon radical formed in step 2 undergoes an intramolcular addition reaction to give an oxygen-stabilized radical

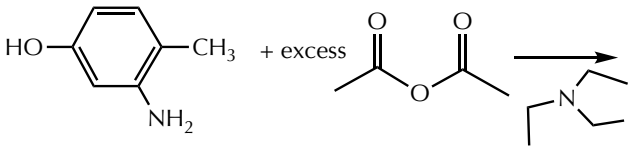
step 4

9

the oxygen-stabilized radical formed in step 3 gives a dissociation reaction resulting in the observed products (drawn above)

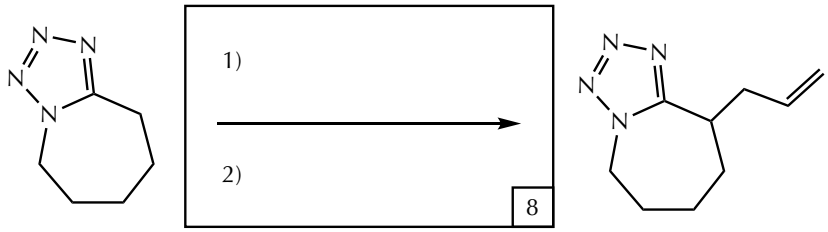
B. Complete the following transformations.

(a) *Org. Process Res. Dev.* **2022**, *26*, 10.



8

(b) *Org. Lett.* **2022**, *24*, 6722.



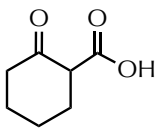
8

A		/32
B		/16
		/48

Question V (42 points)

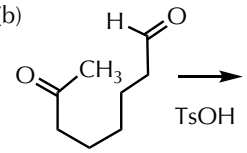
Name: _____

(a)



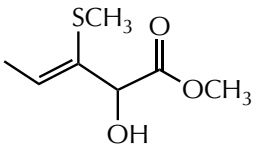
How many exchangeable proton under H/D exchange conditions? 3

(b)



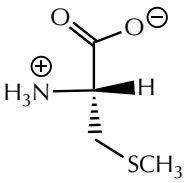
Number of possible intramolecular aldol condensations? 3

(c)



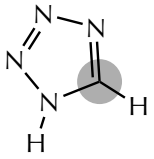
Position number of the alcohol group in the IUPAC name? 3

(d)



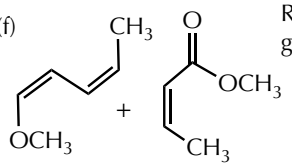
Stereochemical configuration [(*R*) or (*S*)] for methionine? 3

(e)



Oxidation number of the shaded atom? 3

(f)

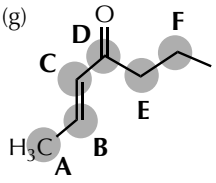


Relationship of the 2 CH_3 groups in the major product?

circle one

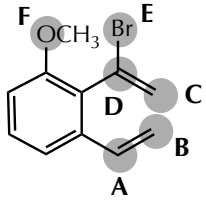
1,2-cis 1,2-trans
1,3-cis 1,3-trans 3

(g)



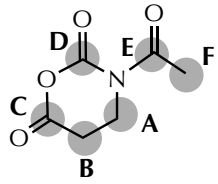
Site (**A**-**F**) of reactivity of this compound with an enol under acid conditions? 3

(h)



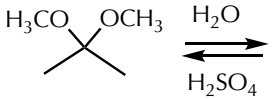
Site (**A**-**F**) of fastest reactivity with tributyltin radical? 3

(i)



Most reactive site (**A**-**F**) with methyl magnesium bromide? 3

(j)



Based on the entropy change, the K_{EQ} for this process is:

circle one

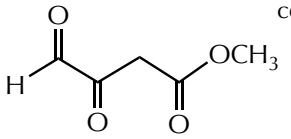
> 1 ~ 1 < 1
can't tell 3

(k)

L-mannose is the open chain form of an aldohexose

How many chiral diastereomers does L-mannose have? 3

(l)

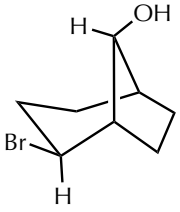


The IUPAC name for this compound would include:

circle one

trioxo dioxo oxo
no "oxo" 3

(m)

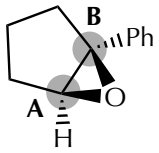


The position of the two groups, "OH" & "Br", are:

circle one

exo & exo *exo & endo*
endo & exo *endo & endo* 3

(n)



Site of fastest reaction with ammonia (NH_3)? 3

number of correct answers:	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
score:	3	6	9	12	15	18	21	24	27	30	33	36	39	42