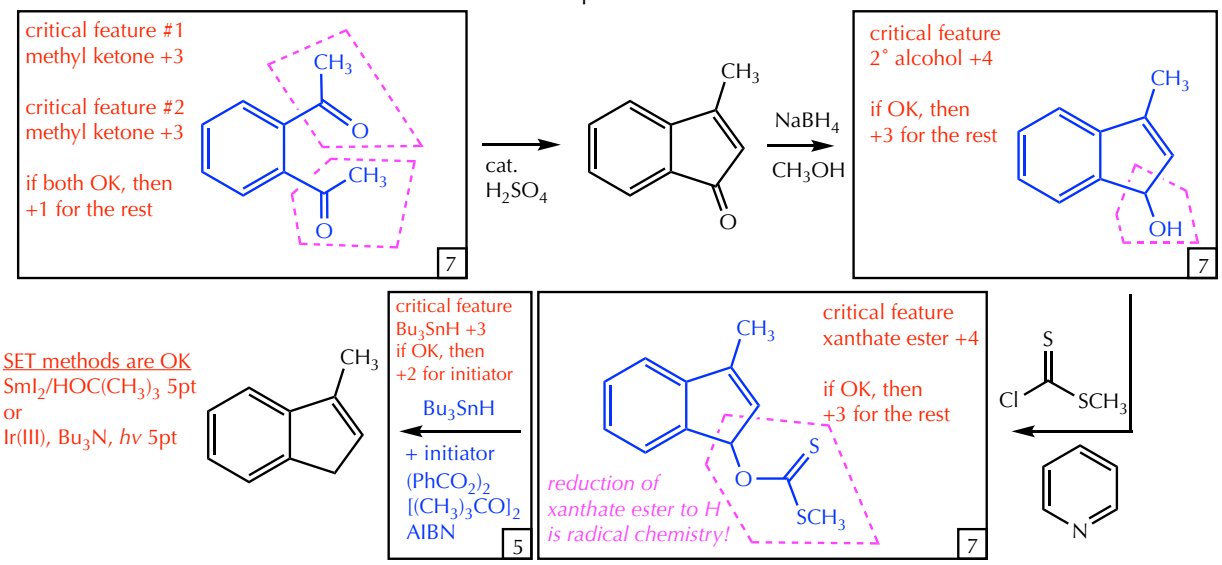
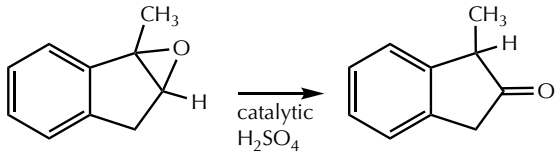
Question I (54 points) Name: _____

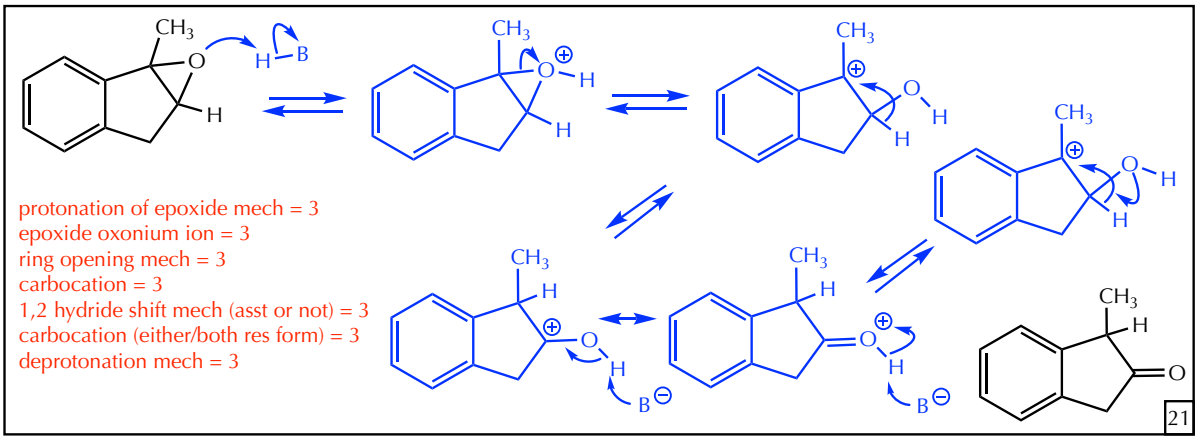
A. Complete the following reaction sequence (in part: *Org. Process Res. Dev.* **2022**, *26*, 1960), which begins with an ***intramolecular aldol condensation***. You do not need to provide stereochemical information.



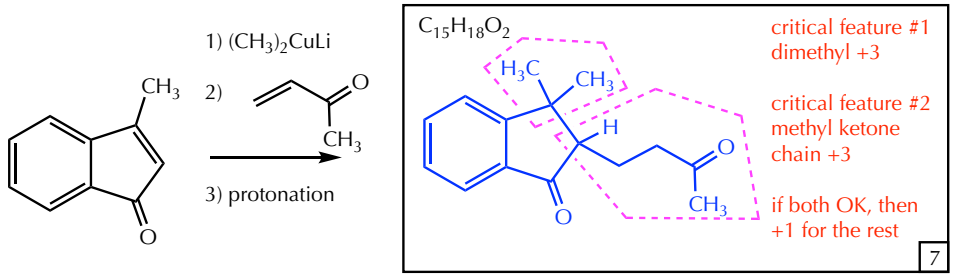
B. When the epoxide derived from the product in part A, above, is treated with an acid catalyst, a rearrangement to a ketone is observed. Using HB/B⊖ as your generic Brønsted acid/base, as needed, provide the complete, curved arrow mechanism for this transformation, in which a carbocation intermediate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



note that the question specifies a rearrangment in the mechanism, particularly with a carbocation specified also - which is not a deprotonation to give an enol (common error)



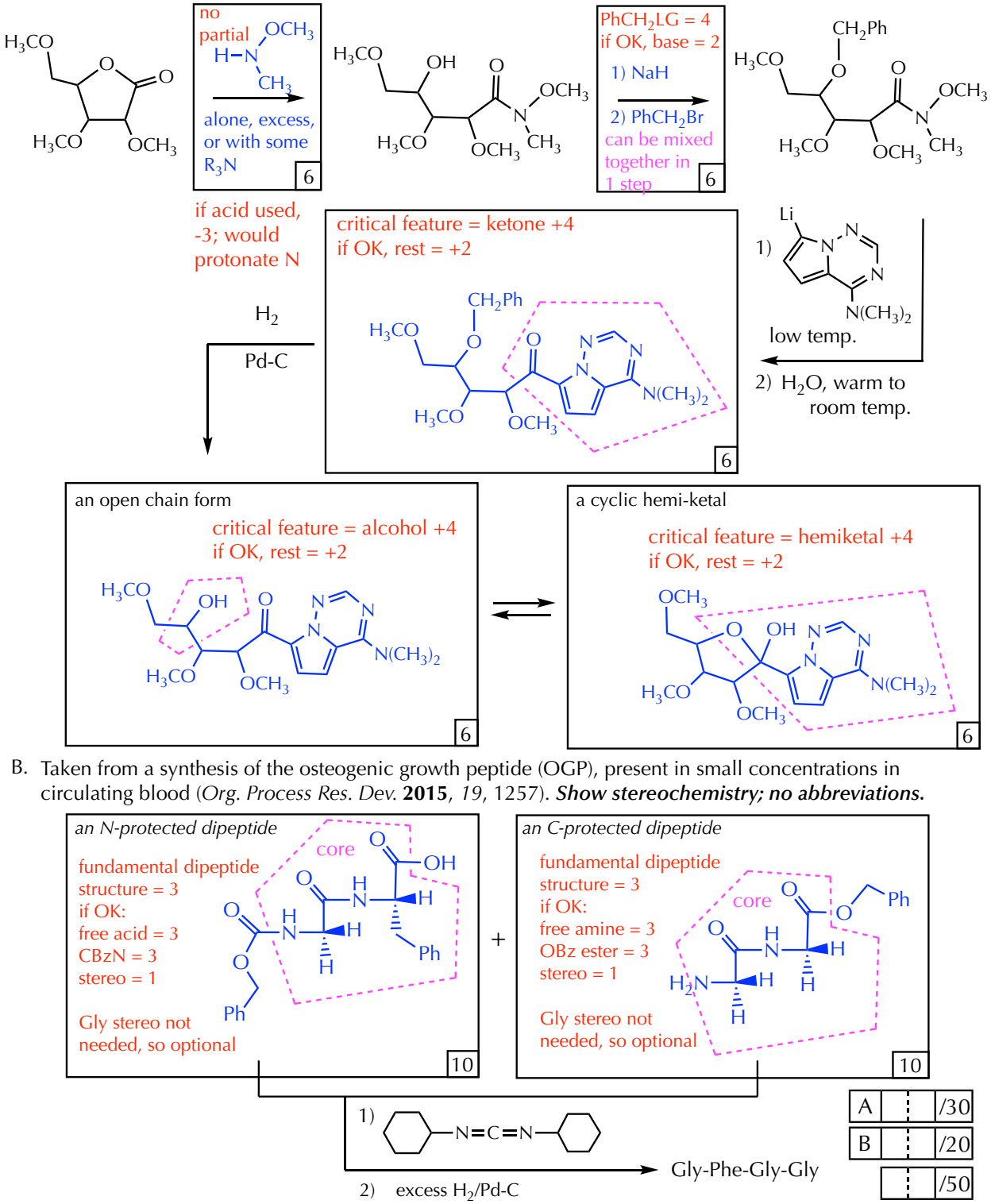
C. Complete the following transformation, which is carried out on the aldol condensation intermediate from part A.



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.



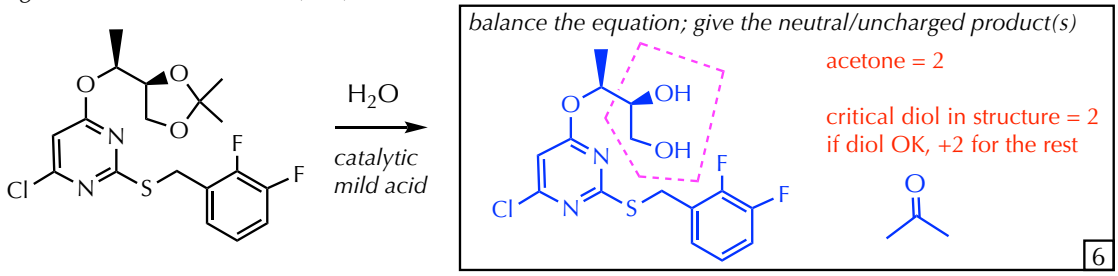
B. Taken from a synthesis of the osteogenic growth peptide (OGP), present in small concentrations in circulating blood (*Org. Process Res. Dev.* **2015**, *19*, 1257). ***Show stereochemistry; no abbreviations.***

A		/30
B		/20
		/50

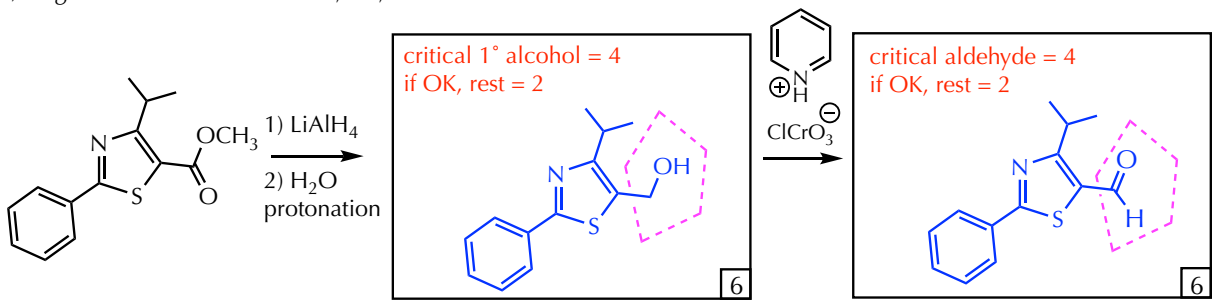
Question III (46 points) Name: _____

Complete the following transformations.

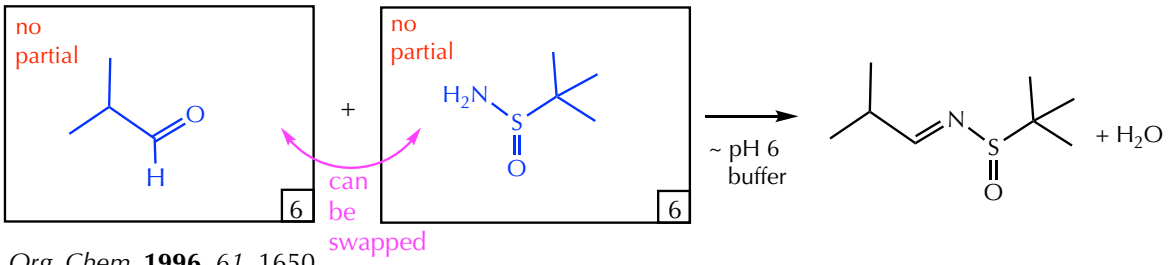
(a) *Org. Process Res. Dev.* **2022**, *26*, 2337.



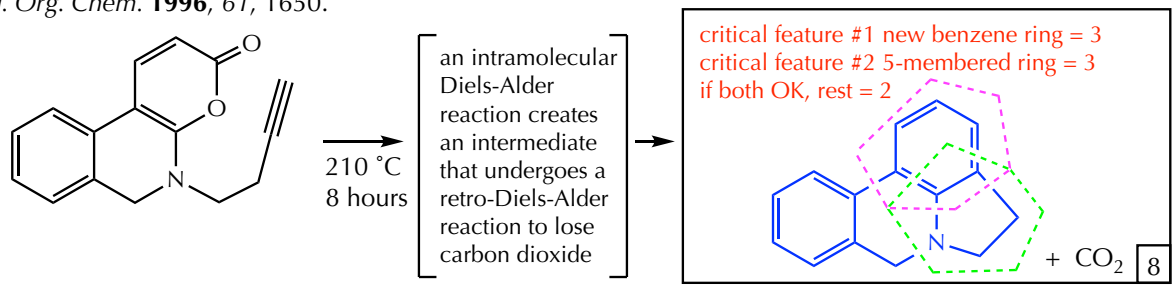
(b) *Org. Process Res. Dev.* **2022**, *26*, 10.



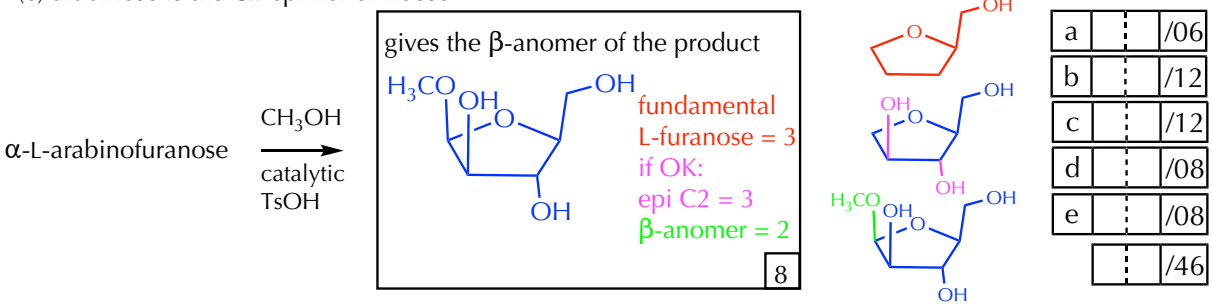
(c) *Org. Process Res. Dev.* **2022**, *26*, 2138.



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



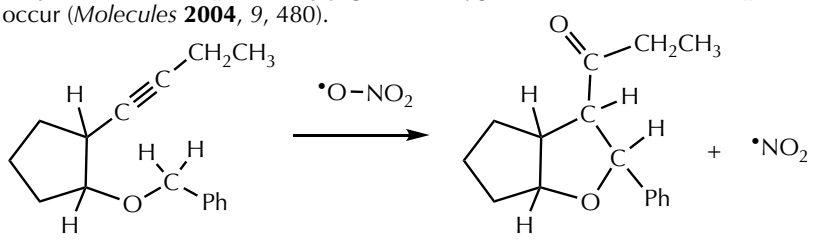
(e) arabinose is the C2 epimer of ribose



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

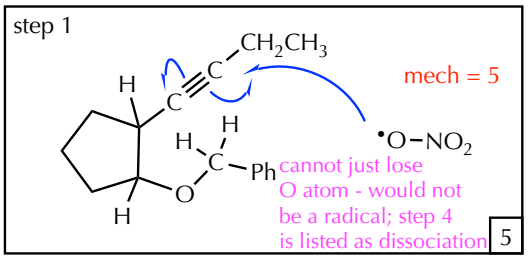
Question IV (48 points) Name: _____

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).

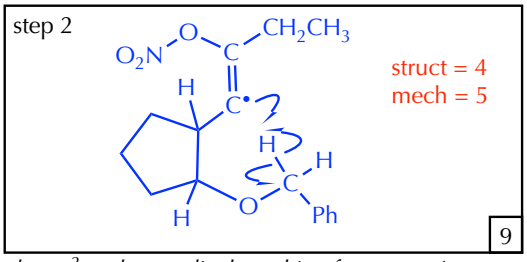


The mechanistic steps are outlined here: provide the missing intermediates as well as the curved (fish-hook) arrows for each step.

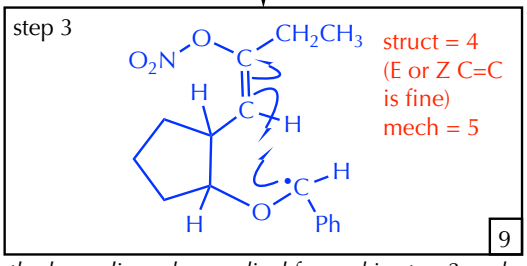
MUST be fish-hook arrows used throughout for mechanism points



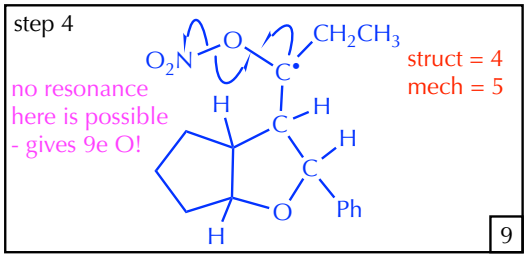
the oxygen atom adds to the triple bond; its regioselectivity can be inferred from the product



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



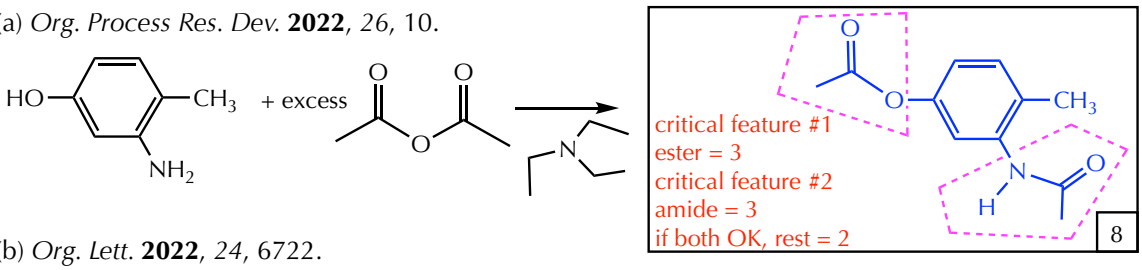
the benzylic carbon radical formed in step 2 undergoes an intramolcular addition reaction to give an oxygen-stabilized radical



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

B. Complete the following transformations.

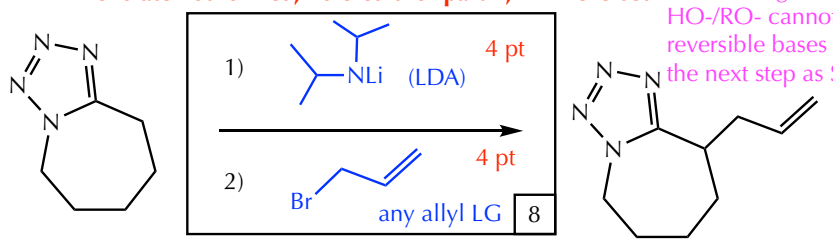
(a) *Org. Process Res. Dev.* **2022**, *26*, 10.



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

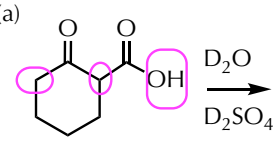
if enolate not formed, no credit for part 2; -4 if reversed

other strong bases OK. as well as NaH; but HO-/RO- cannot give enolate alone - reversible bases would be present and react in the next step as S_N2 more effectively!



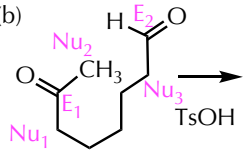
A		/32
B		/16
		/48

Question V (42 points) Name: _____

(a) 

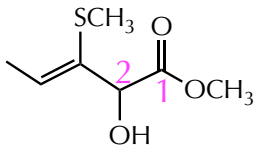
How many exchangeable proton under H/D exchange conditions?

4 | 3

(b) 

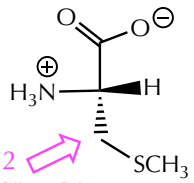
Number of possible intramolecular aldol condensations?

3 | 3

(c) 

Position number of the alcohol group in the IUPAC name?

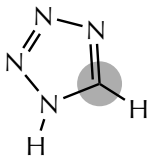
2 | 3

(d) 

priority 2 group "S" > O!

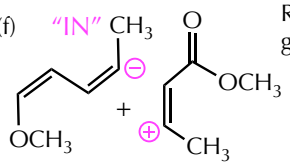
Stereochemical configuration [(*R*) or (*S*)] for methionine?

R | 3

(e) 

Oxidation number of the shaded atom?

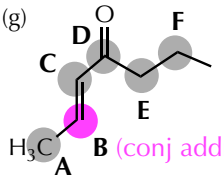
+2 | 3

(f) 

Relationship of the 2 CH_3 groups in the major product?

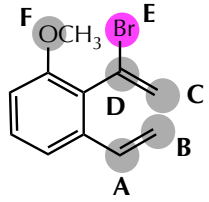
circle one

1,2-cis (1,2-trans) 1,3-cis 1,3-trans | 3

(g) 

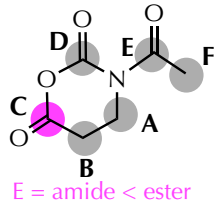
Site (**A**-**F**) of reactivity of this compound with an enol under acid conditions?

B | 3

(h) 

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

E | 3

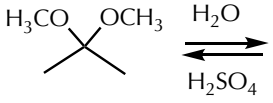
(i) 

E = amide < ester

D = 3 eN atoms

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

C | 3

(j) 

2 particles <=> 3 particles

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

circle one

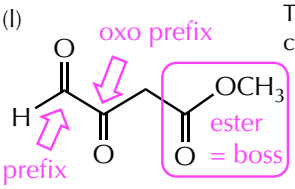
(> 1) ~ 1 < 1 can't tell | 3

(k) L-mannose is the open chain form of an aldohexose

$2^4 - 2 = 14$

How many chiral diastereomers does L-mannose have?

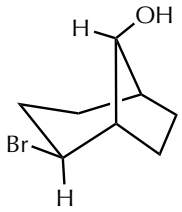
14 | 3

(l) 

The IUPAC name for this compound would include:

circle one

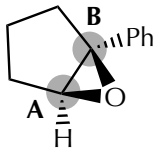
trioxo (dioxo) oxo no "oxo" | 3

(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)?

A | 3

S_N2-like selectivity

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