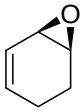
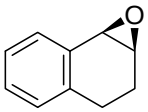
Heterocyclic Chemistry by D. R. Mal 2013

Q1. Nomenclature: Suggest an IUPAC names for each of the following structures.



A



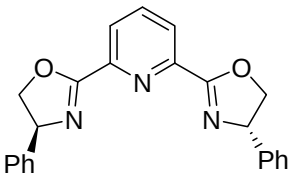
B

Key1.

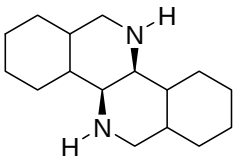
A: (1*R*, 6*S*)-7-Oxabicyclo[4.1.0]hept-2-ene

B: (1a*R*, 7a*S*)-1,6,7,7a-tetrahydronaphtho[1,2-b]oxirene

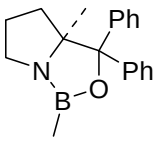
Q2. Name the following.



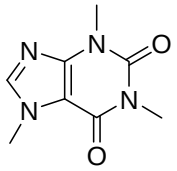
A: a PyBox ligand



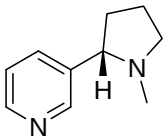
B



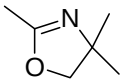
C: CBS oxazaborolidine



D: caffeine



E: nicotine



F

Key 2.

A. PyBox ligand: 2,6-Bis(4*S*-phenyl-4,5-dihydrooxazol-2-yl)pyridine

B: Octadecahydrodibenzo[c,h][1,5]naphthyridine

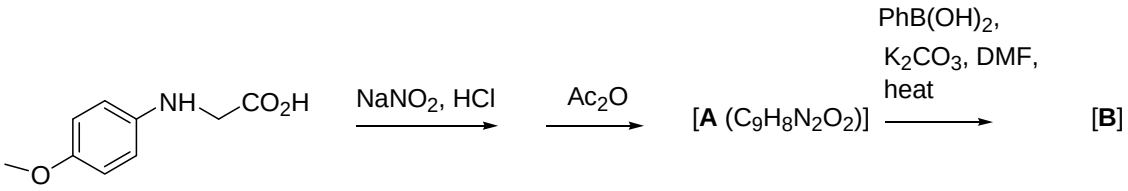
C: 1,3a-Dimethyl-3,3-diphenyltetrahydropyrrolo[1,2-c][1,3,2]oxazaborole

D: 1,3,7-Trimethyl-3,7-dihydropurine-2,6-dione

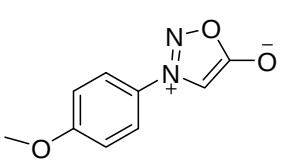
E: 3-(1-Methylpyrrolidin-2-yl)-pyridine

F: 2,4,4-Trimethyl-4,5-dihydrooxazole

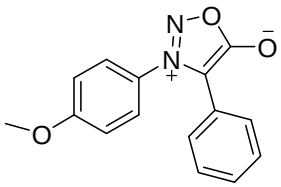
Q3. Suggest the structure of [**A**] and [**B**]



Key 3. Sydnones; [2013 SNT Ynag Y] Oxidative coupling.

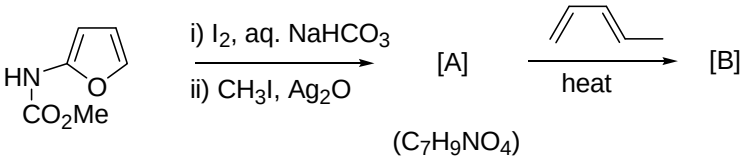


[**A**]

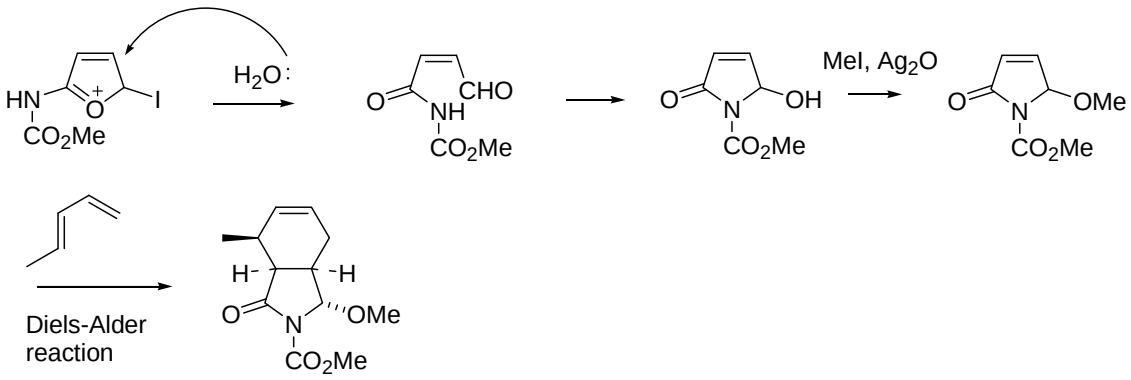


[**B**]

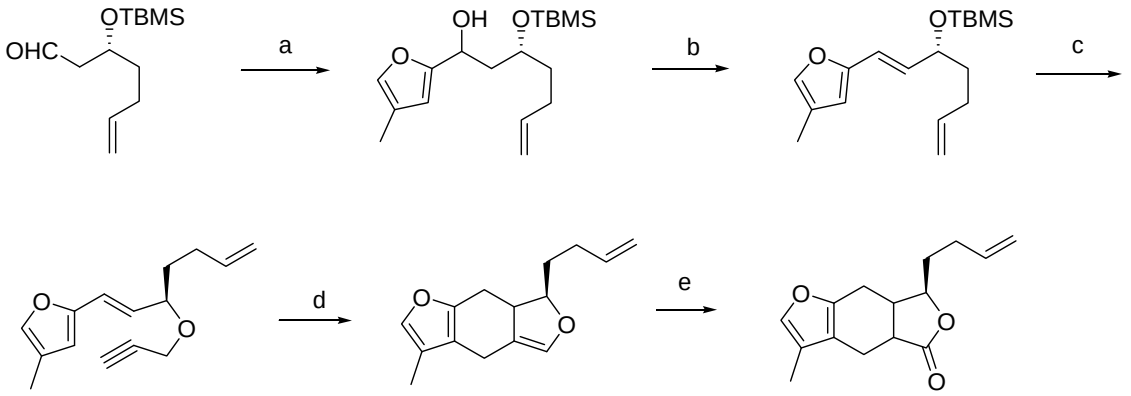
Q4. <u>Electrophilic substitution</u>: Propose mechanistically the structures of A and B in the following scheme.



Key 4. **[**2009 OL 1233 Padwa A]



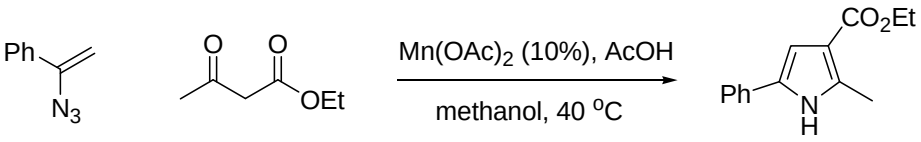
Q5. Complete the following sequence of reactions with necessary reagents and conditions.



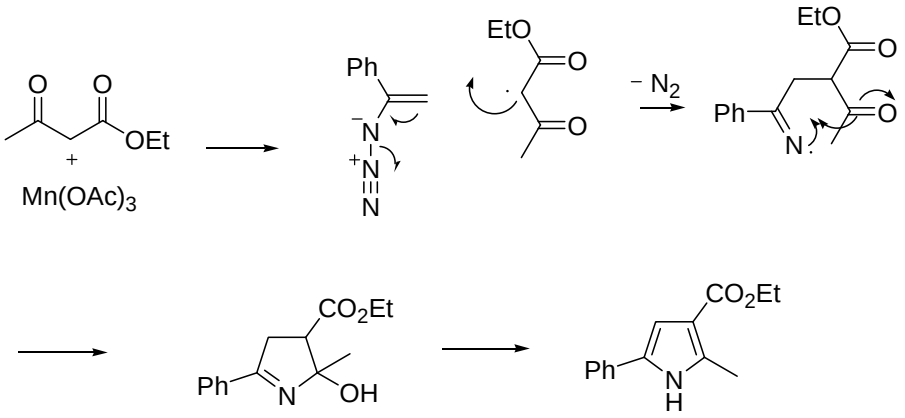
Key5. [1988 JOC 860 Kanematsu K]

a. 2-Bromo-1-methylfuran, *n*-BuLi; b.$(Ph0)_3P^+MeI^-$, HMPA, 25 °C; c. i) Bu^4NF, THF; ii) *n*-BuLi, propargyl bromide, benzene/DMSO; d. *t*-BuOK, *t*-BuOH, 83 °C; e. 5% CSA, CH_3CN/H_20 (2:l); f. Ag_2C0_3, celite, benzene, reflux

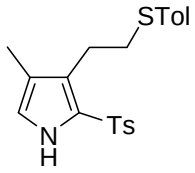
Q6. Suggest a reasonable mechanism for the following.



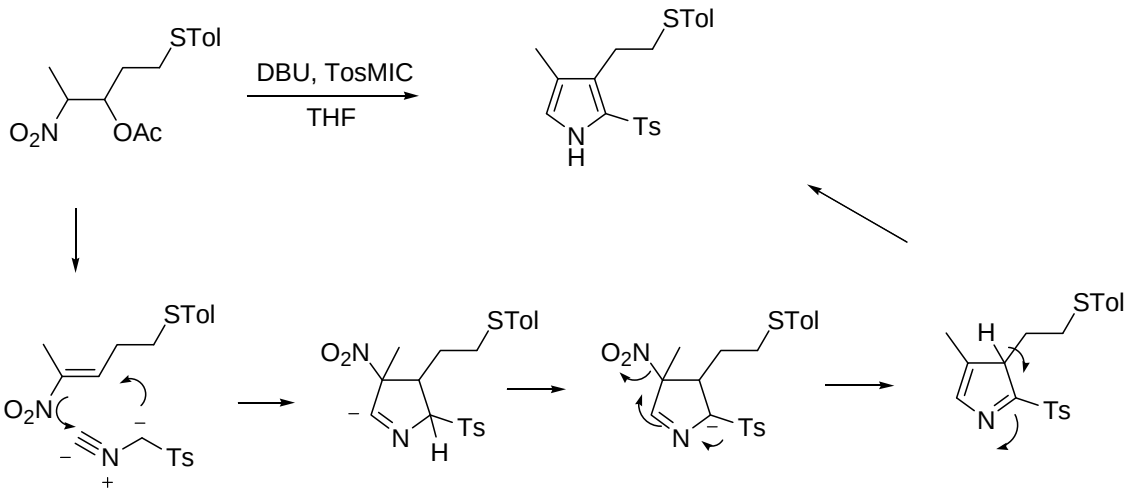
Key 6.



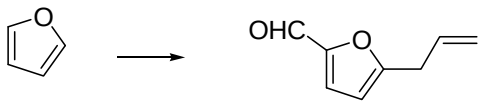
Q7. Apply the concept of combination Barton-Zard and van Leusen pyrrole synthesis for the synthesis of



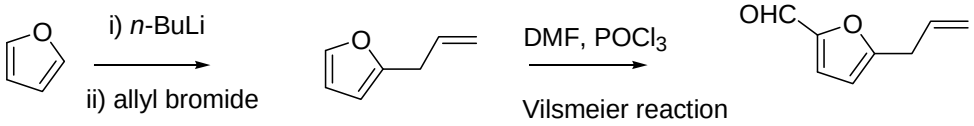
Key 7.



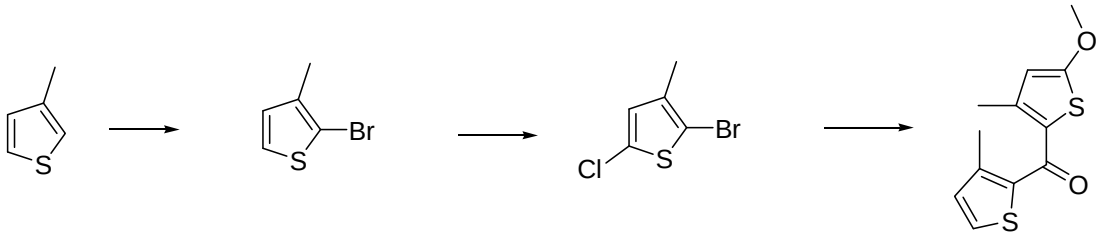
Q8. Propose an appropriate synthetic route for the following conversion.



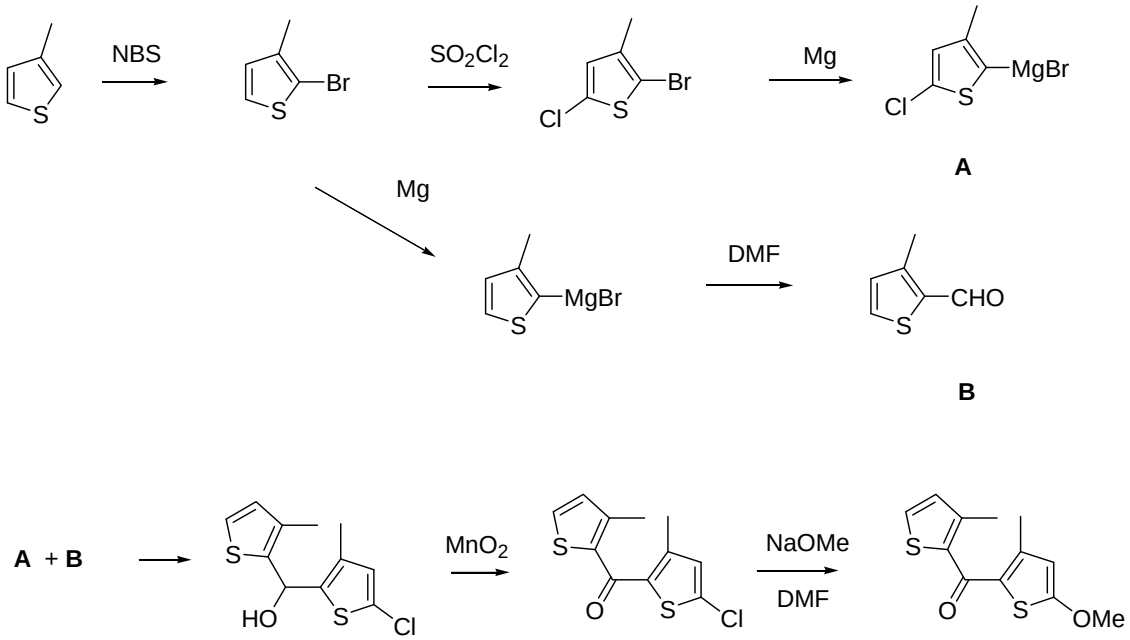
Key 8.



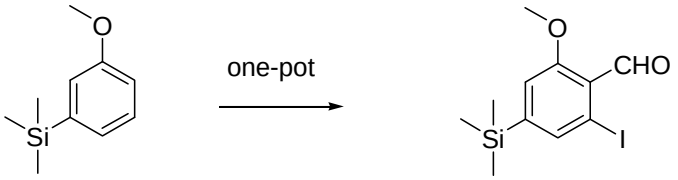
Q9. Complete the following route with appropriate reagents and substrates.



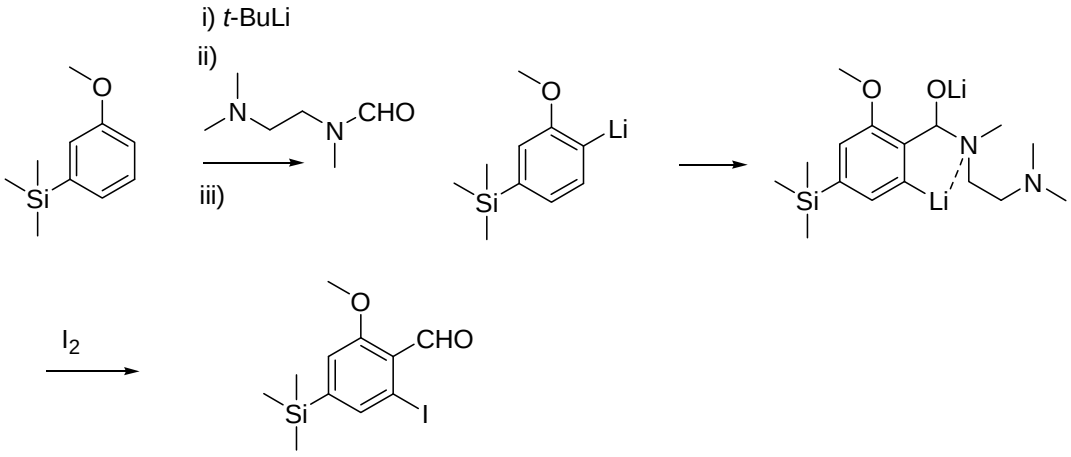
Key 9. [1994 THN 8699]



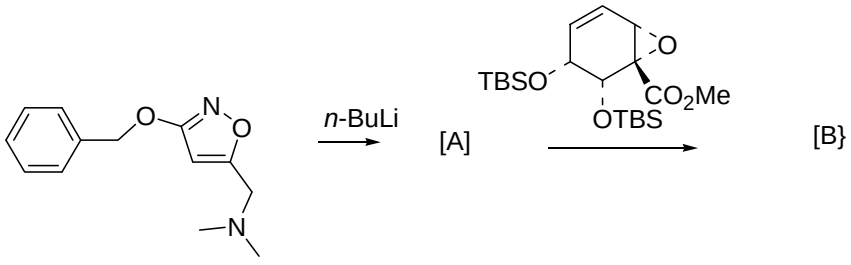
Q10. Suggest the sequence with reagents for the transformation below.



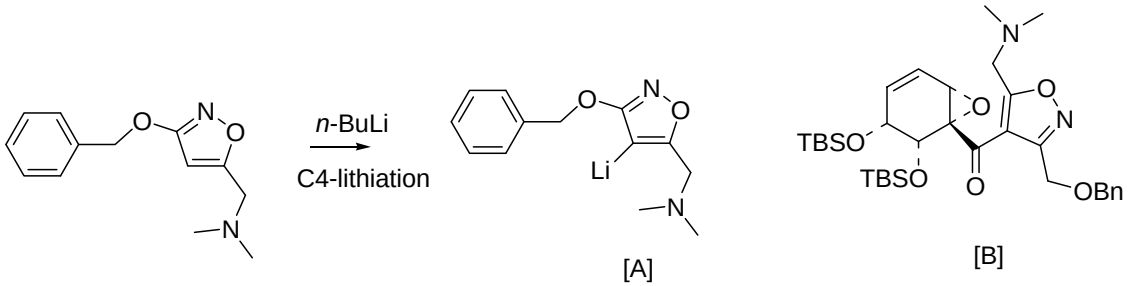
Key 10. [1995 ACIE 2683 Curran DP]



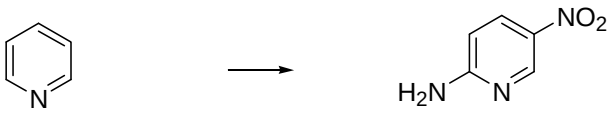
Q11. Predict the products of the following sequence.



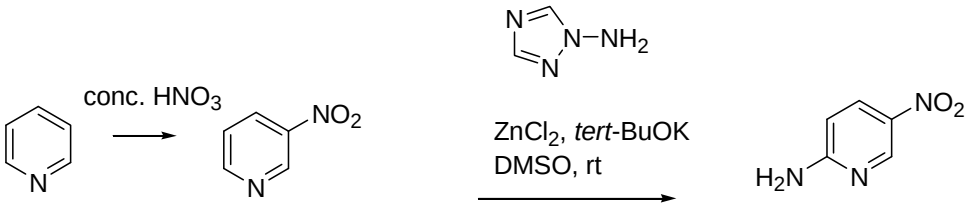
Key 11. [2005 science 395 Myers]



Q12. Devise a synthetic route for the following

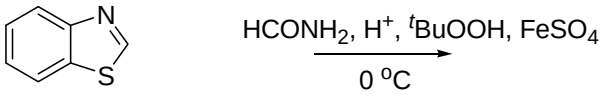


Key 12.

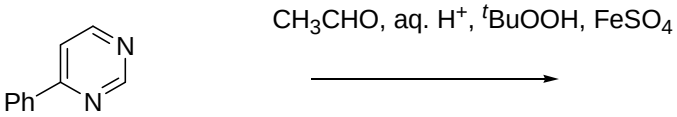


Q13. Suggest the products of the following reactions.

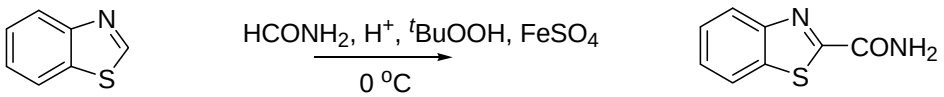
a.

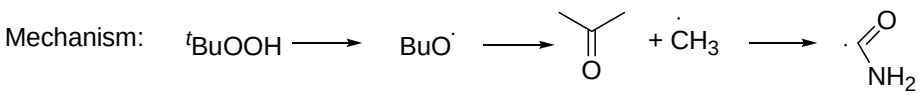


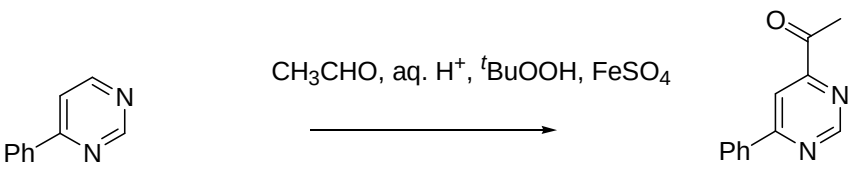
b.



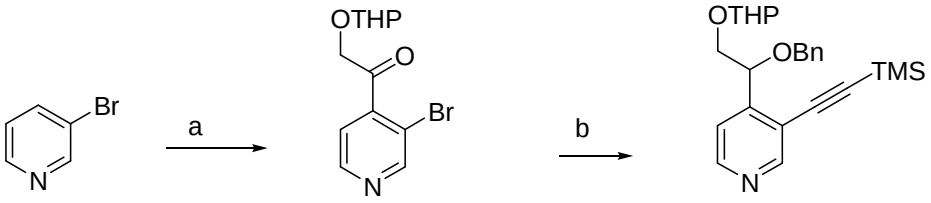
Key 13.







Q14. Complete the sequence given below.

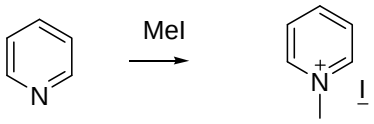


Key 14. [1994 THN13575]

a. LDA, $THPOCH_2CO_2Et$

b. i) $NaBH_4$; ii) NaH, BnBr iii) Trimethylsilylacetylene, $(Ph_3P)_4Pd$, Et_3N.

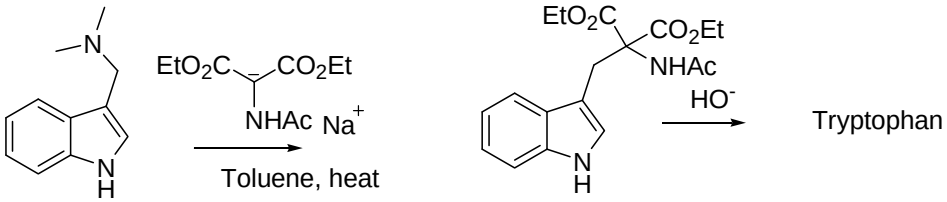
Q15. Suggest three electrophilic reagents which would promote quaternization of pyridine nitrogen like MeI does with pyridine.



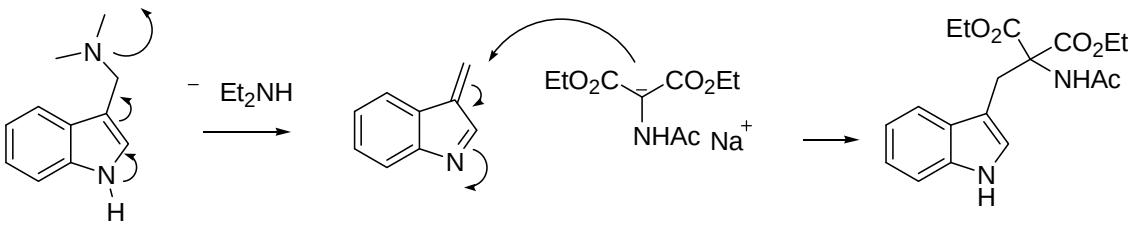
Key 15.

1. NO_2BF_4 2. MeCOCl or PhCOCl 3. SO_3

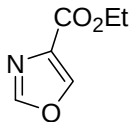
Q16. Provide a mechanism for the 1st step of the following sequence.



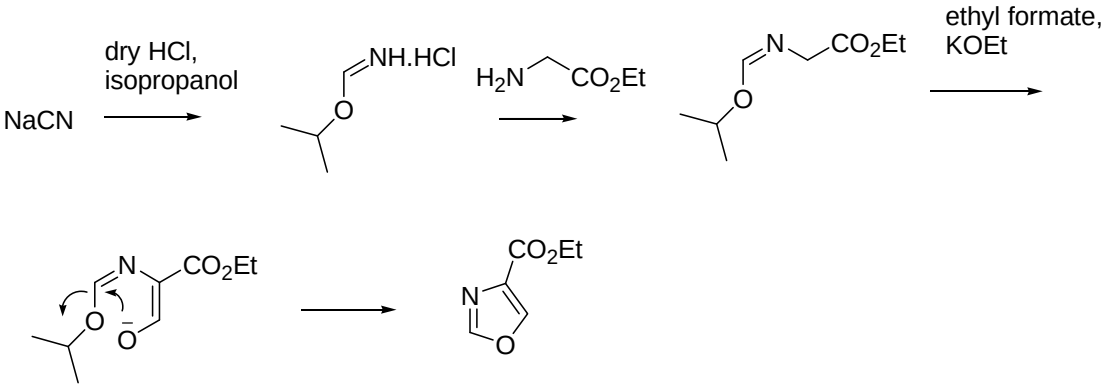
Key 16.



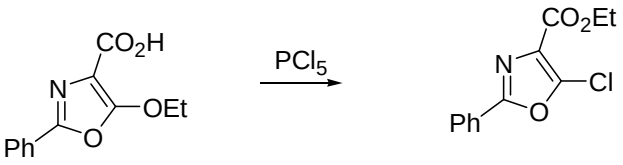
Q17. Suggest a synthetic for



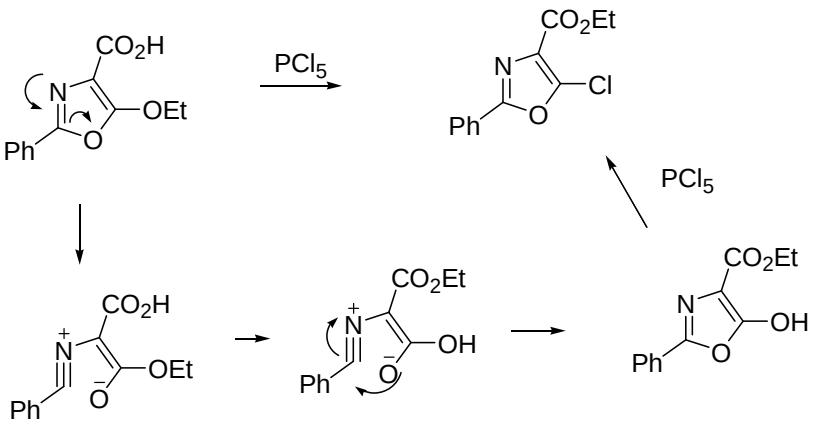
Key 17.



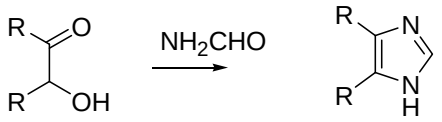
Q18. Work out the mechanism of the following transformation.



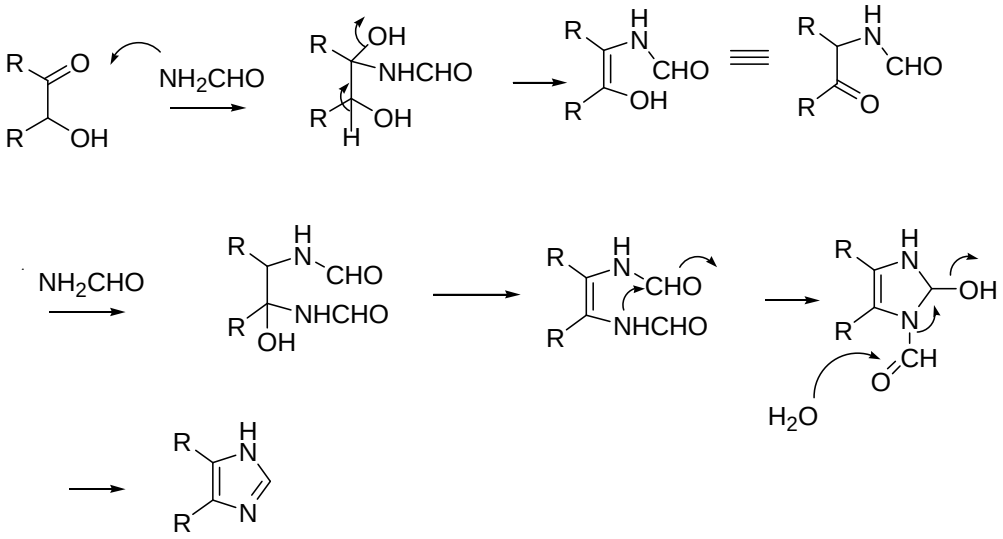
Key 18.



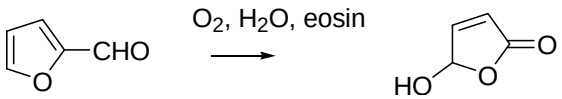
Q19. Work out the mechanism of the following transformation.



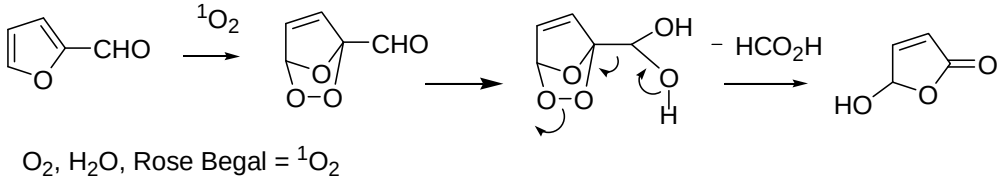
Key 19.



Q20. Propose a mechanism for the following transformation.

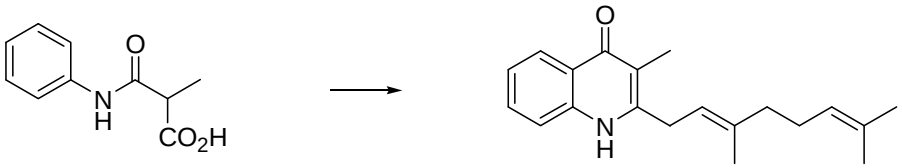


Key 20. [1985 THN 2057 Gollnick K]

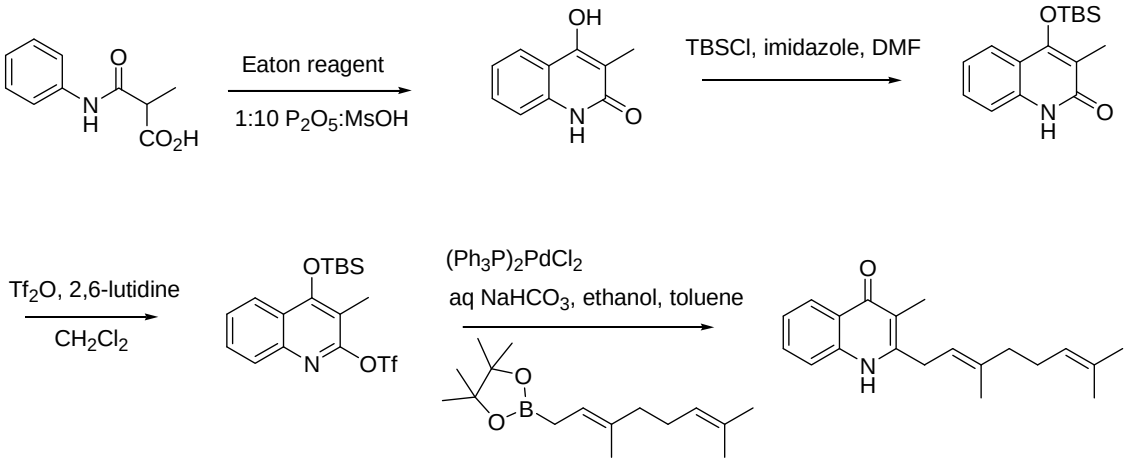


O_2, H_2O, Rose Begal = $^1O_2$

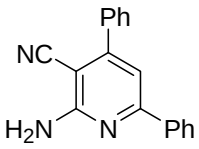
Q21. Suggest a route for the following elaboration.



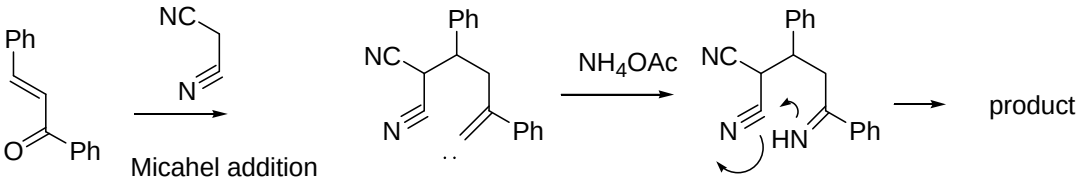
Key 21. [2013 OL Shibasaki M]



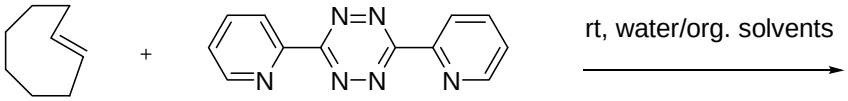
Q22. Suggest a synthesis of the following.



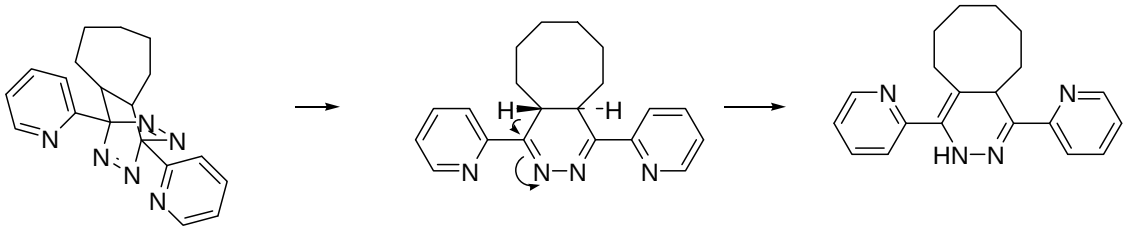
Key 22. [2007 JMC 828]



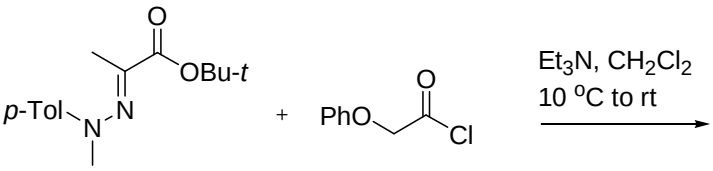
Q23. Predict the product of the reaction below.



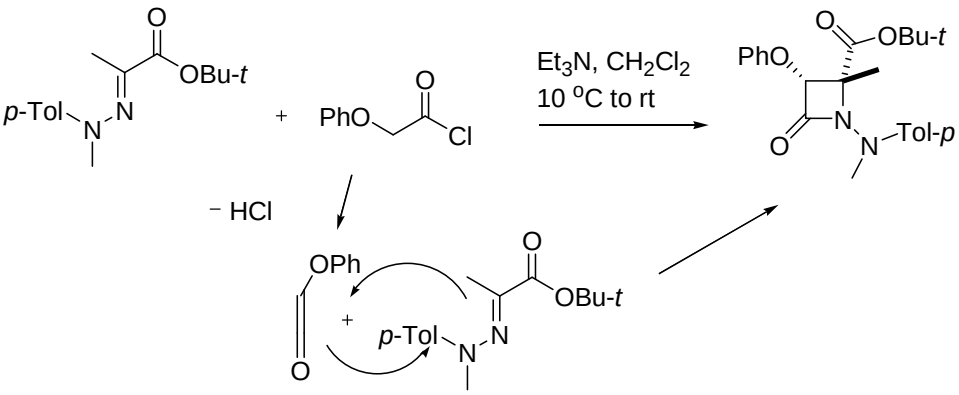
Key23. [2008 JACS 13518 Fox JM]



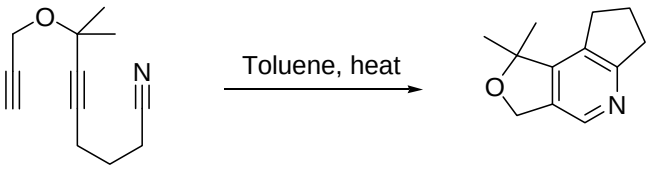
Q24. Predict the product of the reaction below.



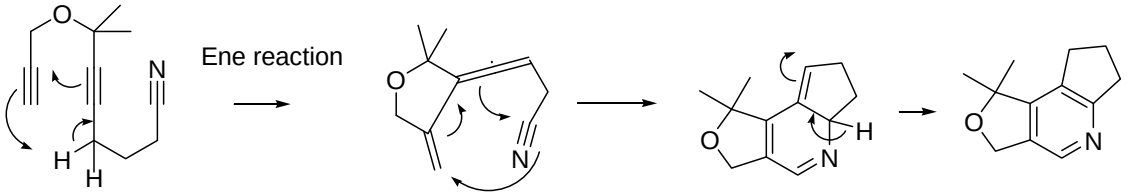
Key 24.



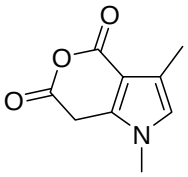
Q25. Suggest a mechanism



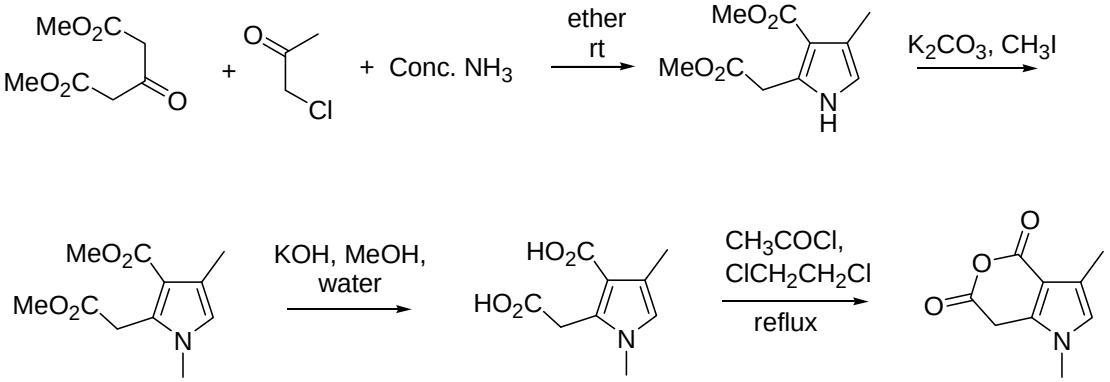
Key 25. 2010 JACS 13203 Danheiser RL



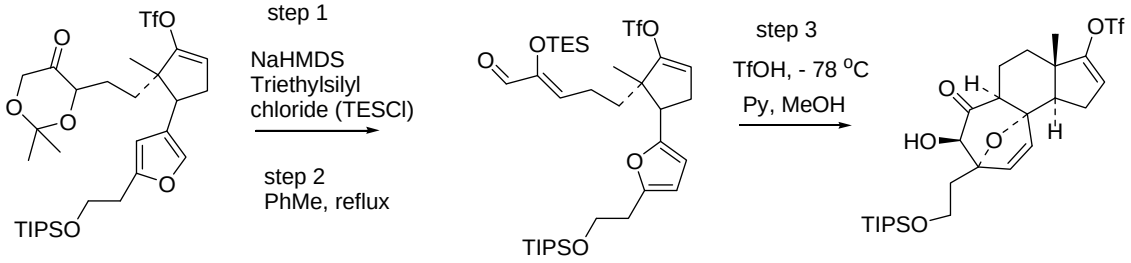
Q26. Suggest a good synthetic route for the following.



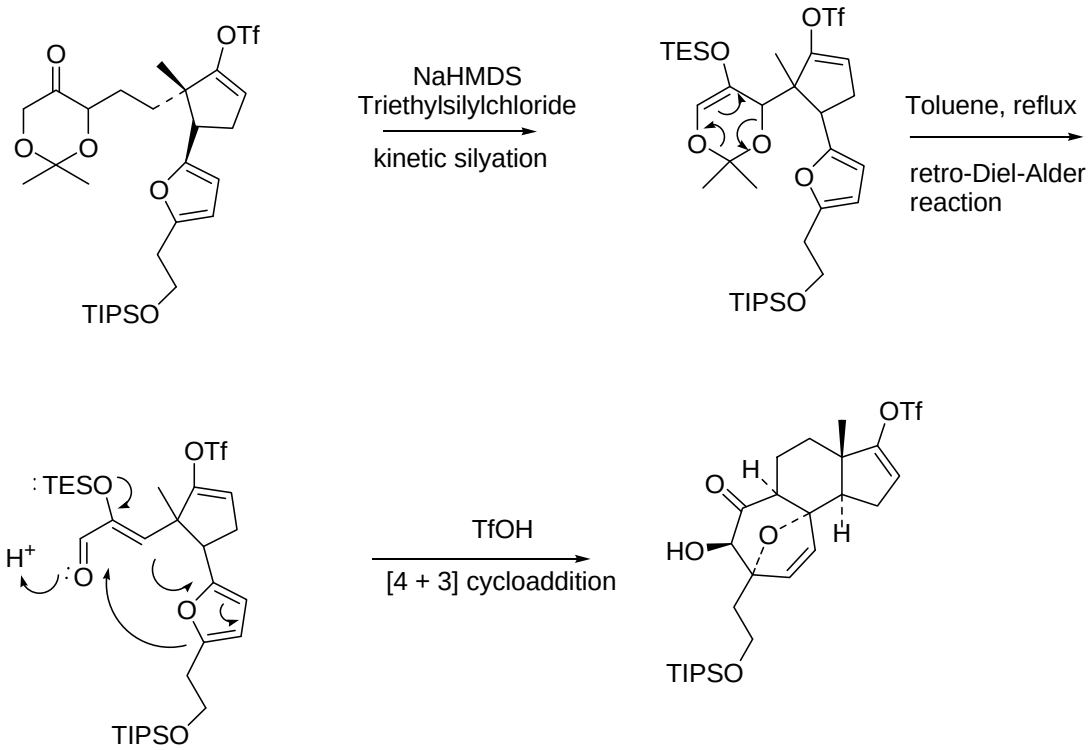
Key 26. [2013 EJOC Mal D]



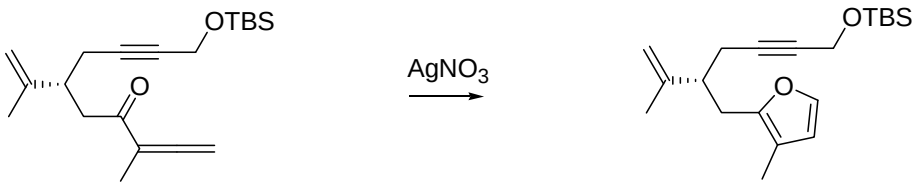
Q27. Explain the formation of the intermediates of the scheme below and suggest a suitable mechanism for each of the steps.



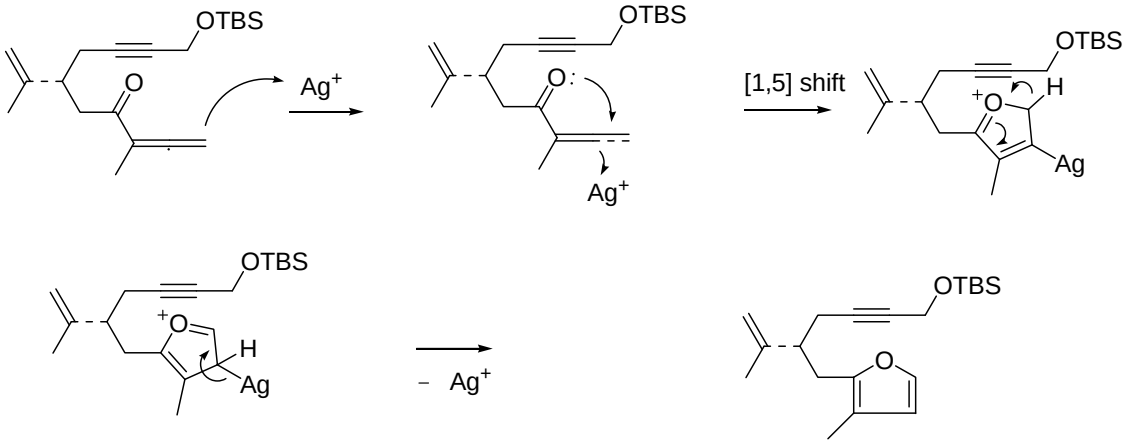
Key 27. [2011 JACS 12451 Funk RL on cortistatin]



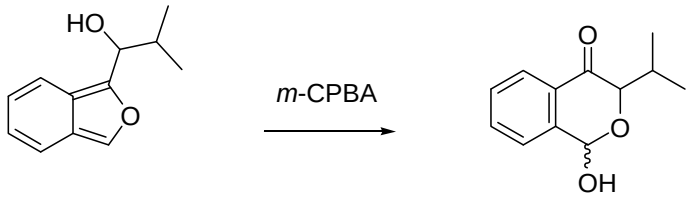
Q28. Propose a mechanism for the following furan ring construction.



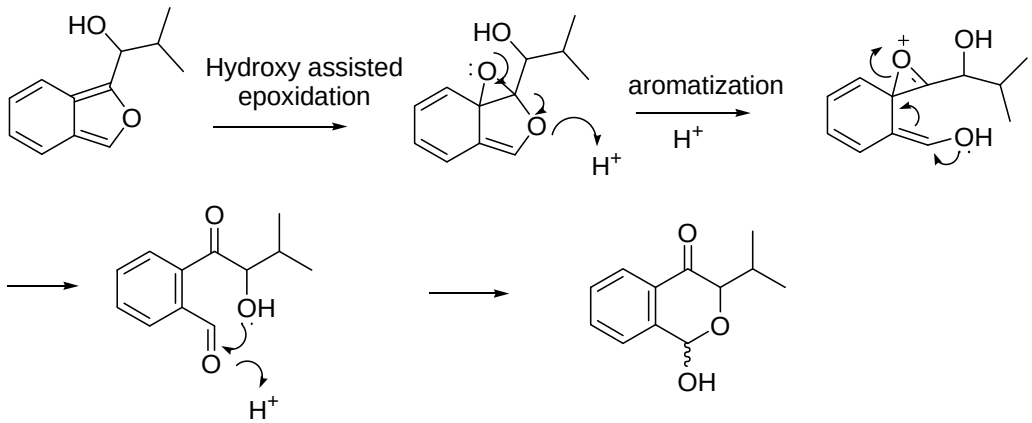
Key 28.



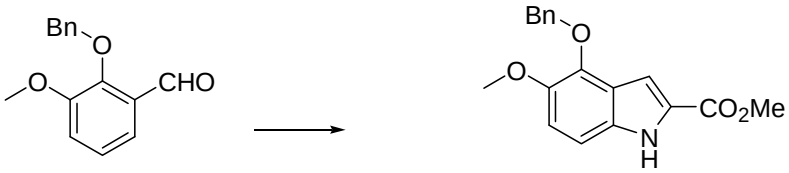
Q29. Propose a mechanism for the following Achmatowicz rearrangement.



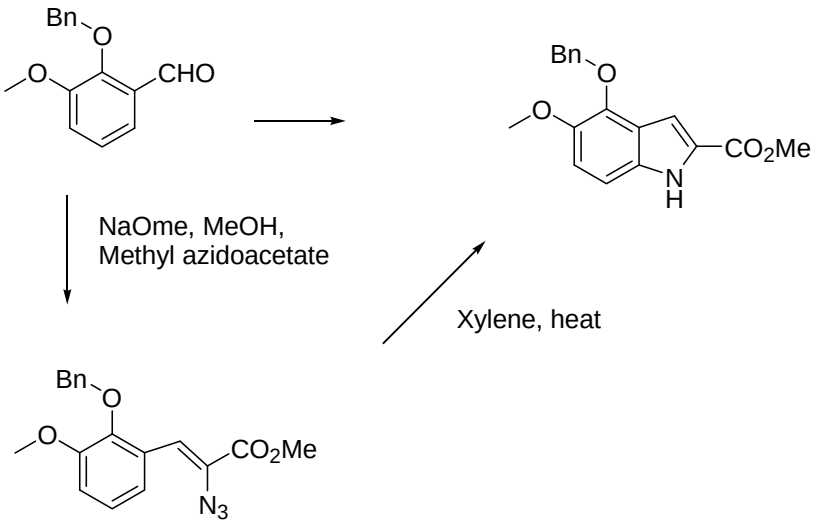
Key 29.



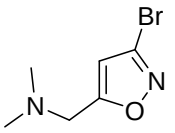
Q30. Suggest a two-step sequence for the following transformation.



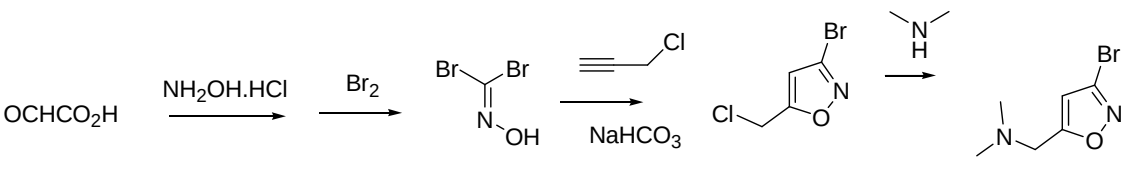
Key 30. [1994 THN 7657 Moody CJ]



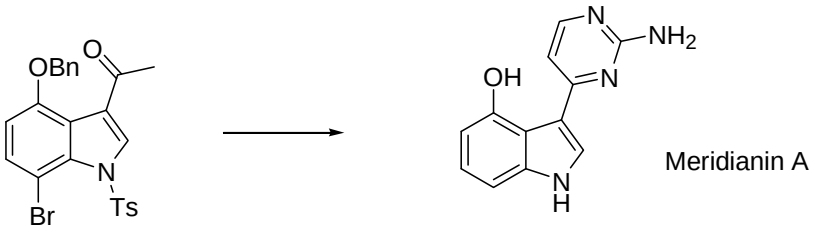
Q31. Suggest a synthesis of



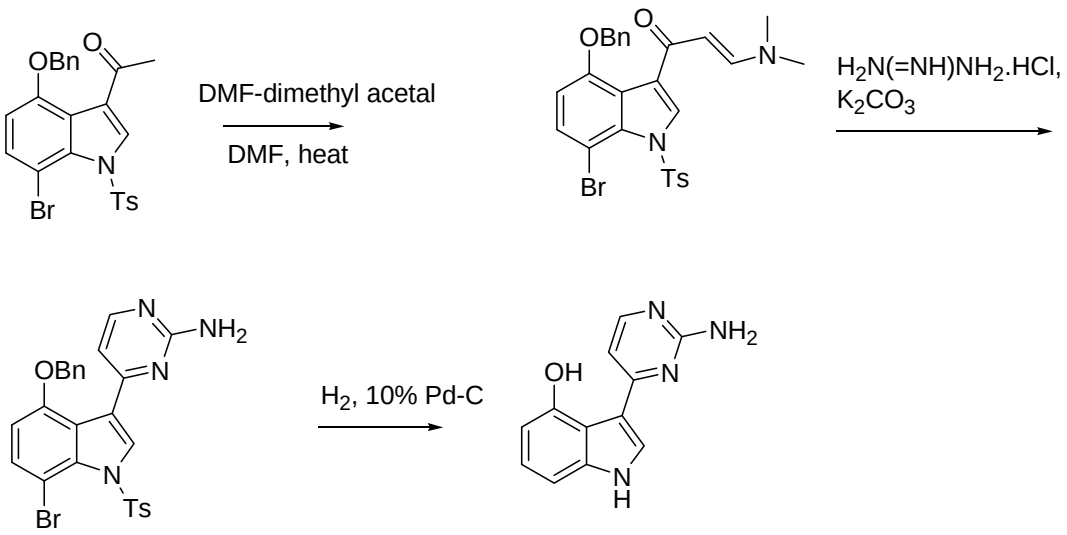
Key 32.



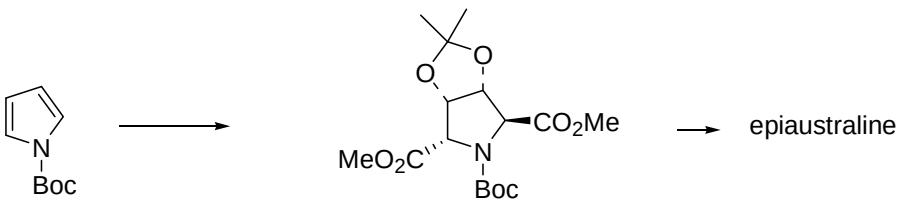
Q33. Devise a synthesis of the meridianin A from an indole derivative as shown below.



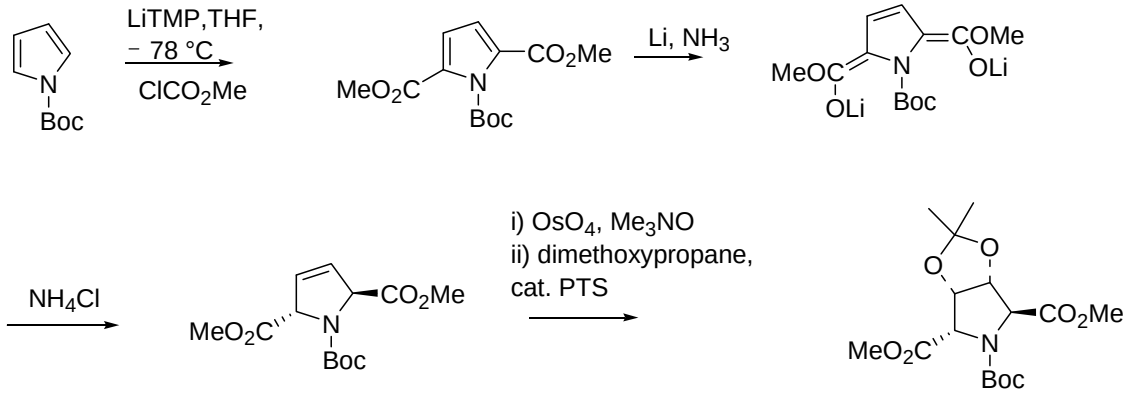
Key 33.



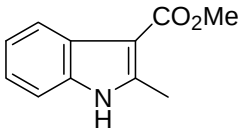
Q34. Devise a synthesis of the advanced intermediate shown below, required for the synthesis of epiaustraline.



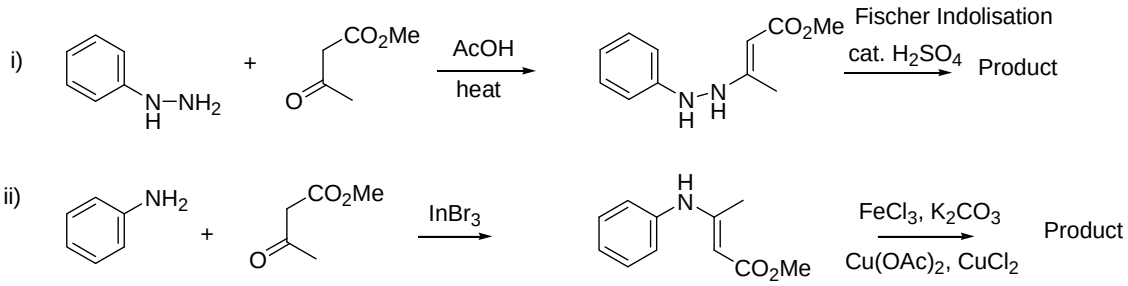
Key 34.



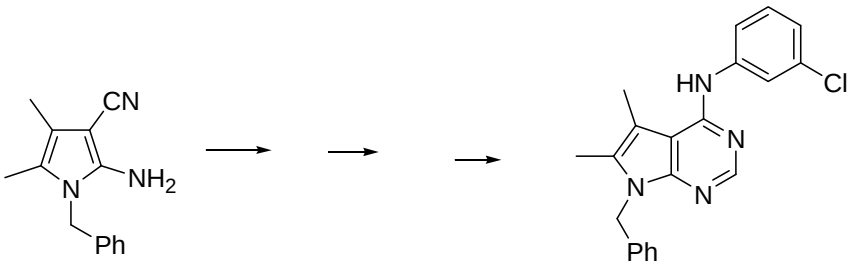
Q35. Suggest a viable synthesis of the following indole derivative.



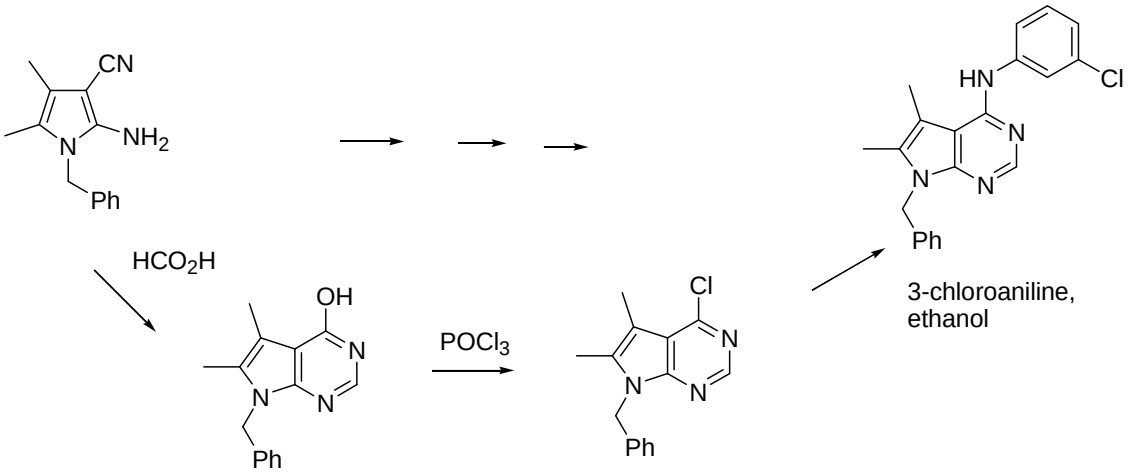
Key 35. i) 1981 JCS Perkin 1636 Joule, JA; ii) 2010 CC 2823



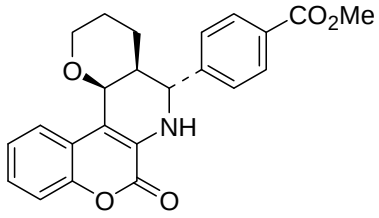
Q36. Propose a synthetic route for the following transformation.



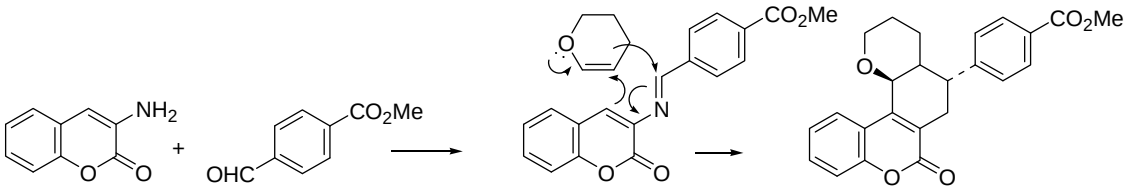
Key 36. [2001 Org. Process Res. Dev. 581, Fischer RW]



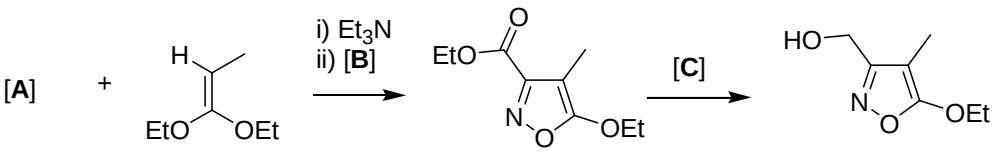
Q37. Apply Povarov reaction to the synthesis of the following heterocycle in the presence of a Lewis acid and write the structures of the required organic starting materials.



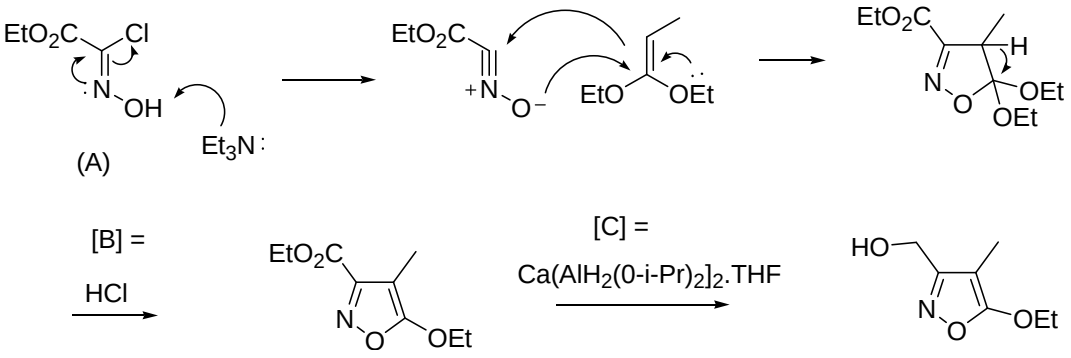
Key 37.



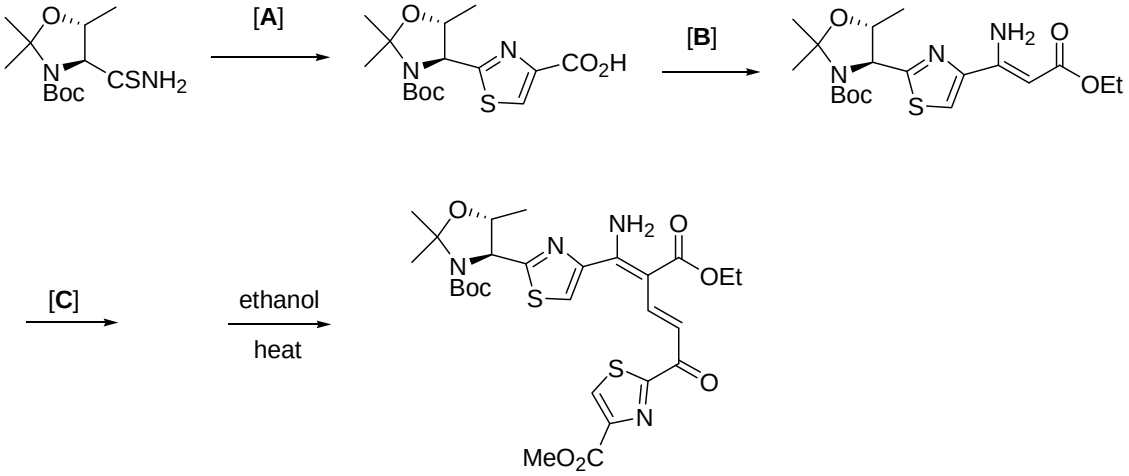
Q38. Write the structure of the missing reactants, products and reagents in the following scheme



Key 38. [1983 JOC 602 Ricca A]



Q39. Complete the following sequence of reaction with necessary reagents and structures.

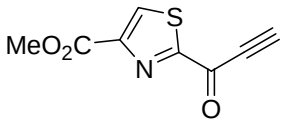


Key 39. [2007 SNT 954 Bagley MC]

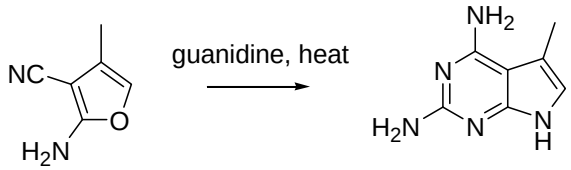
A. i) Ethyl bromopyruvate, $NaHCO_3$, Py, TFAA; ii) LiOH, MeOH–H_2O, rt

B. i) EtOCOCl, Et_3N, THF, 0 °C; ii) potassium ethyl malonate–methylmagnesium bromide, THF; iii) NH_4OAc, toluene–AcOH, MW

C.



Q40. Propose a plausible mechanism for the following rearrangement.



Key 40. [1995 JOC 6684 Taylor EC]