Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
IInd Semester 2016-2017

CHEM F415, FRONTIERS IN ORGANIC SYNTHESIS
Comprehensive Examination (Closed Book)

Max. Marks: 30 **Duration: 60 minutes** **Date: 04th May 2017**

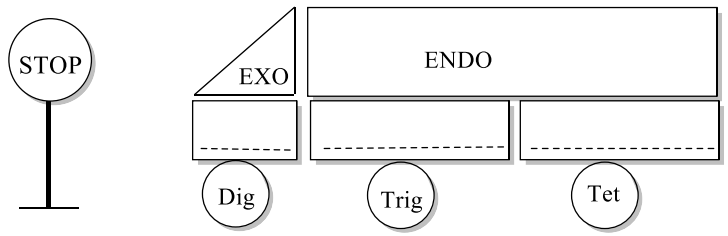
Name: …… ID No. ……..

Write your name and ID no on the question papers. All questions are compulsory.

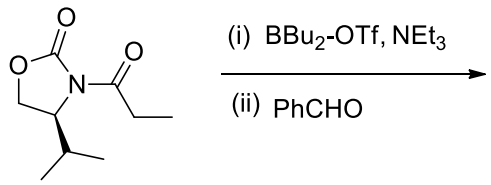
Q. No. 01. (a) With the help of Molecular Orbital Theory, explain why [CH_3-$\dot{C}H_2$-OEt] radical is stable. [3]

(b) What are persistent radicals. Give one example. [2]

(c) Based on Baldwin rules for cyclization, complete the following figure. [4]

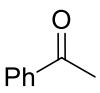
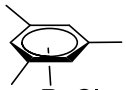


(d) Complete the reaction and propose a detailed mechanism in the space provided. [6]

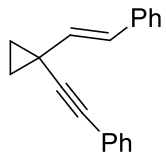


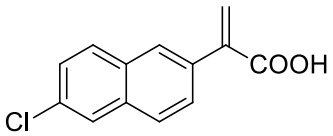
Q. No. 02. Fill in the blanks. [15x1=15]

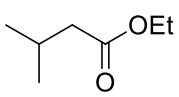
(i) $Pd(OAc)_2$ —($2\ PPh_3$)→ ---------- (16 e⁻ species, Pd(II)) —(Slow)→ ---------- (14 e⁻ species) —(PPh_3O, AcOH)→ ---------- (14 e⁻ species, Pd(0))

(ii) ---------- ←(BH_3, CBS (10 mol%))—  —( , $RuCl_2$, (-) TsDPEN (5 mol%), HCOOH, Base)→ ----------

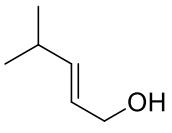
(iii) $RhH(CO)_2(PPh_3)_2$ ⇌ (CO) ---------- —(R)→ ---------- —(RCH_2CH_2CHO)→ ---------- —(CO)→ ---------- —(H_2)→ ----------

(iv)  —(Rh (I) catalyst, CO, THF, 50 °C, 10 h)→ ----------

(v)  —(H_2 (100 atm.), [$RuCl_2$] (5 mol%), (*S*)-BINAP (5 mol%), DCM, 50 °C)→ ----------

(vii)  —(Na, Et_2O)→ ----------

(Final Product)

(viii)  —($Ti(o\text{-}iPr)_4$ (10 mol%), t-BuOOH, (+) DET (5 mol%), DCM, -20 °C)→ ----------

END

II[nd] Semester 2016-2017

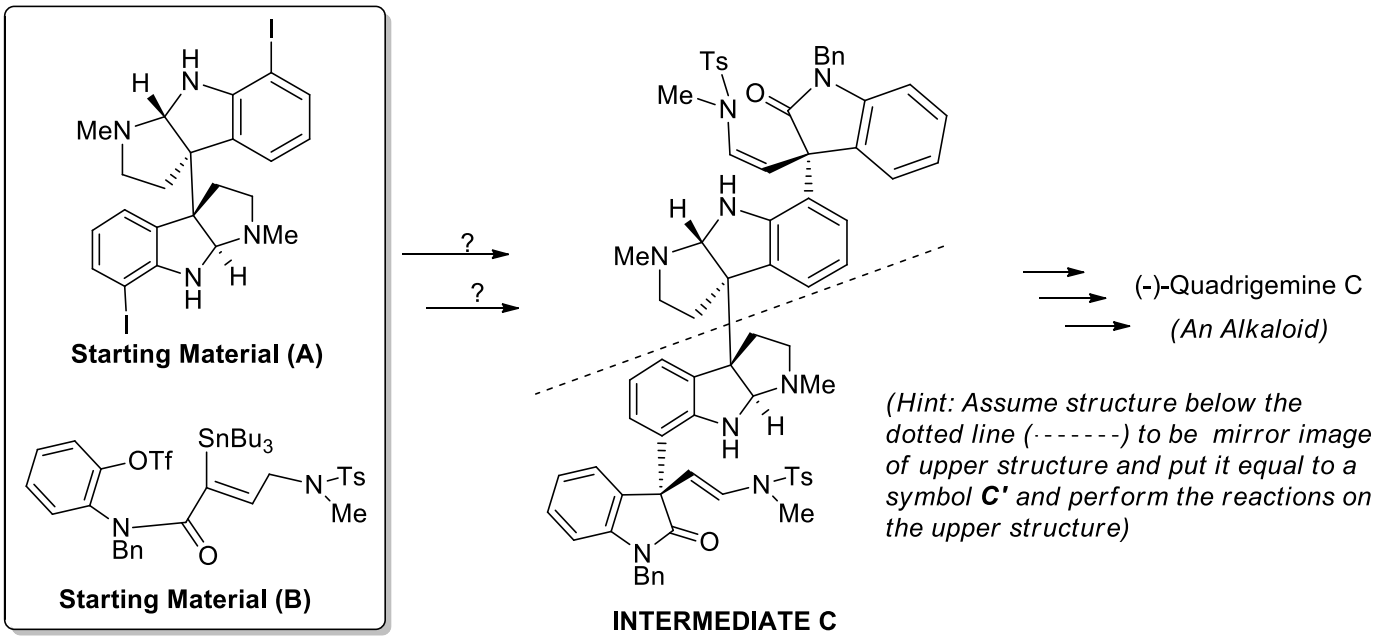
CHEM F415, FRONTIERS IN ORGANIC SYNTHESIS

Comprehensive Examination (Open Book)

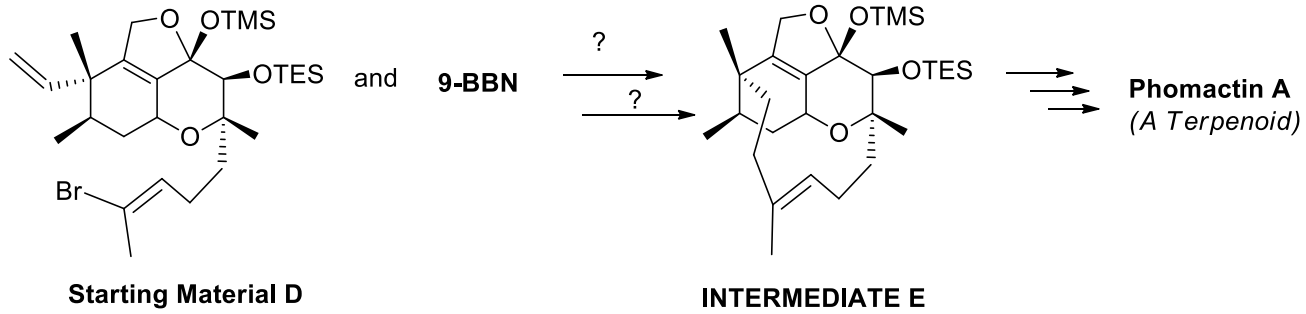
Max. Marks: 60 **Duration: 120 minutes** **Date: 04[th] May 2017**

Write your name and ID no on the question papers. All questions are compulsory.

Q. No. 01. Compound **C** is an important intermediate for synthesizing Quadrigemine C (*a polypyrrolidinoindoline alkaloid*). Overman and co-workers synthesized compound **C** from **A** & **B** by using two different cross-coupling reactions in a consecutive fashion (Figure 1). Identify the name of the two cross coupling reactions. Work out the synthesis of **C** from **A** and **B**. *(Mention all the reagents/catalyst required for these two steps and Briefly show their mechanism)* [10]

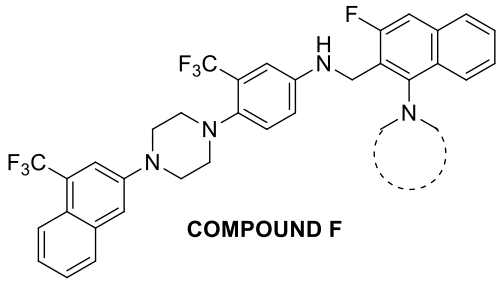


Q. No. 02. (a) Halcomb and his group employed the application of a cross coupling reaction to forge the synthesis of 12-membered macrocyclic ring to prepare intermediate **E**, which is required for preparing terpenoid natural product phomactin A (Figure 2). If you are provided with starting materials **D** and **9-BBN**, propose the synthesis of intermediate **E**. *(Mention all the reagents/catalyst required and show a detailed labeled mechanism)* [8]

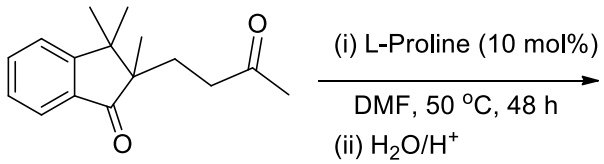


(b) Consider a mixture of hypothetical enantiomers possessing 75% and 25% of (+)-A and (-)-A respectively. Calculate the %ee of the mixture. [2]

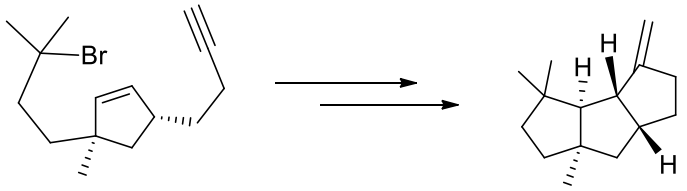
Q. No. 03. (a) The following compound (**F**) is mimic of a drug used to control blood clotting. Design its synthesis from the simplest starting materials by first performing its retrosynthetic analysis. *Mention all the reagents/catalyst required and l*abel *each step by a reaction type/name.* [7]



(b) Write the correct structure of the compounds (*with correct stereochemistry*) obtained after step (i) and (ii) in the following transformation. [3]

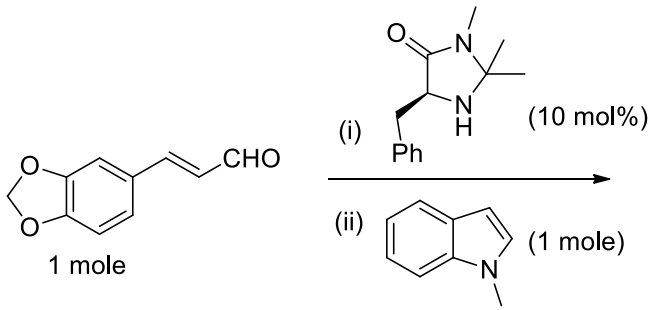


Q. No. 04. (a) Capnellene is a naturally occurring hydrocarbon derived from Capnella imbricata, a species of soft coral found in Indonesia. It could be obtained from compound **G** by employing **two sequential 5-exo radical cyclizations**. Using appropriate reagents, propose a detailed mechanism for its synthesis from **G**. [5]



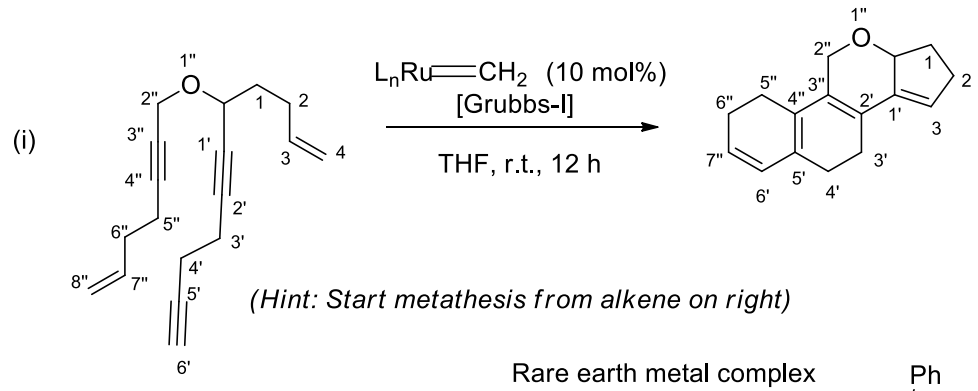
Compound G Capnellene

(b) Complete the reaction and propose a detailed mechanism for the given chemical transformation: [5]

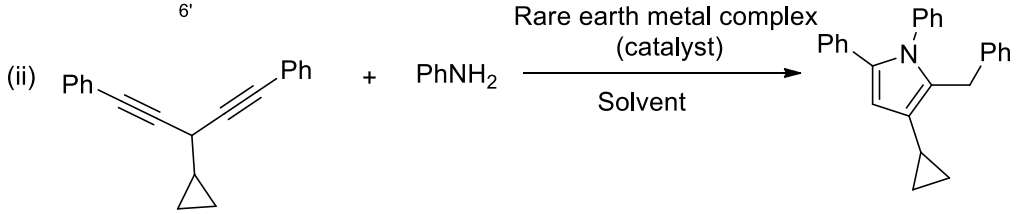


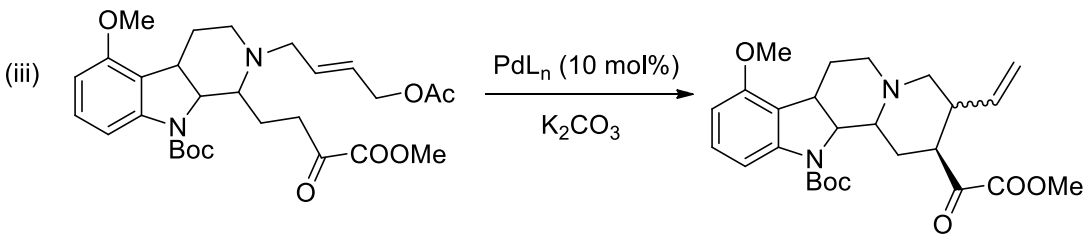
(Hint: Indole C-3 carbon is nucleophilic)

Q. No. 05. Propose a detailed mechanism for the following chemical transformation. [10+5+5]



(Hint: Start metathesis from alkene on right)





END