Registration Number:

Date & Session:

ST JOSEPH'S UNIVERSITY, BENGALURU-27

M.Sc. Organic Chemistry – III SEMESTER

SEMESTER EXAMINATION: OCTOBER 2023

(Examination conducted in November/ December 2023)

OCH 9423: Stereochemistry and Asymmetric Synthesis

(For current batch students only)

Time: 2 Hours **Max Marks: 50**

This question paper contains **TWO** printed pages and **THREE** parts

PART-A

Answer any EIGHT of the following: **8 X 2 = 16**

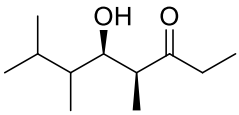
1. Draw the structures of (S)-PBMgCl and (S)-BINAL-H.
2. What is absolute asymmetric destruction and absolute asymmetric synthesis?
3. Define chiroptical properties.
4. State and explain α-axial haloketone rule.
5. What is Snatzke's benzene sector rule?
6. Mention any two applications of Buckminsterfullerene.
7. Resolution of diastereomers is easier than the enantiomers explain.
8. Mention any two desirable characteristics of a good resolving agent.
9. State the mathematical expression of the Curtin-Hammett equation in terms of the rate constants. Explain the terms.
10. Convert the following names into the structure
    i) tricyclo[4.2.1.01,6]non-3-ene
    ii) Methyl tricyclo [2.2.1.$0^{1,4}$]heptane-2-carboxylate

PART B

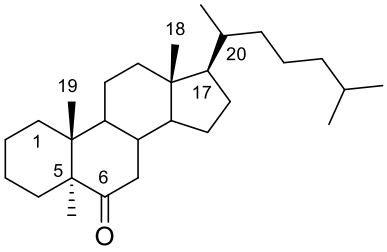
Answer any TWO of the following: **2 X 12 = 24**

11. (a) Explain the following rules to predict the sign of Cotton effect curves in ORD (i) Kuriyama's Benzene quadrant rule (ii) Lowe's rule and (iii) Brewster's rule.
    (b) Explain the thermodynamic and kinetic stability of Cubane.
    (c) Draw the most stable conformation of 1-propene. Explain. (6+3+3)

12. (a) Using Zimmerman-Traxler model, predict all the stereoisomers of the following aldol from suitable enolates.



(b) Show 1,4-asymmetric induction using a representative reaction sequence.
(c) Explain Octant rule and predict the ORD sign of 5α-cholestan-6-one given below.



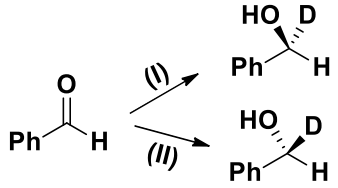
(4+4+4)

13. (a) Explain any four methods to identify conglomerate in a racemic mixture.
(b) With an example explain the term "Resolution by entrainment".
(c) Derive the Winstein-Holness equation in terms of the rate constants.
(d) Describe with proper structure how (S)-1-Phenyl amine could be useful for the resolution of racemic lactic acids (3+3+3+3)

PART C

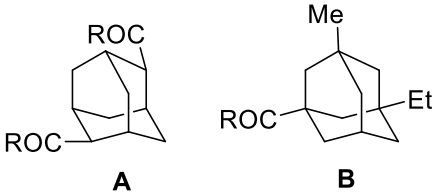
Answer any TWO of the following: 2 X 5 = 10

14. (a) Chiral hydrazones are very important in asymmetric synthesis of alpha alkyl substituted ketones. Justify this statement using appropriate synthetic steps.
(b) Predict the structures and absolute configurations of Alpine Borane derivatives (I) and (II) for the following reactions:



(3+2)

15. (a) 'Haptophilic stereocontrol in asymmetric heterogenous catalytic hydrogenation of tetrahydrofluorene derivatives depends on the type of substituent'. Justify this statement.
(b) How many isomers are possible for the given compounds?



(3+2)

16. Compare the rate of epoxidation reaction between 1,2-cis and 1,2-trans halohydrin of cyclohexane. Rationalize your answer.

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