Time: 2 hours 30 minutes **Total Marks: 60**

Instructions:
(1) All questions are compulsory.
(2) Figures to the right indicate full marks.

Q. 1 (a) Attempt any **two** of the following: 08
(i) Establish a quantitative structure reactivity relationship for p-substituted phenols with electron withdrawing groups during their ionisation in aqueous solution.
(ii) Explain Hammett Equation.
(iii) Establish linear free energy relationship for the compounds for which Hammett's equation is not applicable.
(iv) Give an account of Grunwald-Winstein equation.

(b) Attempt any **one** of the following: 04
(i) Discuss the upward deviation from Hammett's equation with a suitable example.
(ii) Discuss concave downward deviation from Hammett equation with a suitable example.

Q. 2 (a) Attempt any **two** of the following: 08
(i) What are rotaxanes? Discuss their structure.
(ii) What is molecular self-assembly? Explain with a suitable example.
(iii) What are molecular tweezers? Write detailed notes on tweezers?
(iv) What are Cryptands? Discuss their structural features and give any one method of synthesis of Cryptands?

(b) Attempt any **one** of the following: 04
(i) Discuss the structural features of molecular cleft derived from Kemp's triacid for their applications as synthetic receptors?
(ii) Discuss any one example of a receptor with multiple hydrogen bonding sites?

Q. 3 (a) Attempt any **two** of the following: 08
(i) What is racemisation? Discuss the mechanism of racemisation involving:
a. Carbanions
b. Rotation around bonds
(ii) Define resolution and explain the method of resolution through equilibrium asymmetric transformation.
(iii) How NMR spectroscopy (use of chiral derivatising agents) and chromatographic methods are useful in determining optical purity and enantiomeric excess in racemates?
(iv) Explain the correlation method applied for a configurational assignment using chemical correlation involving diastereomers.

(b) Attempt any **one** of the following: 04

(i) Explain Correlative method for configurational assignment based on a comparison of optical rotation with the rule of optical superposition.

(ii) Give an informative note on circular birefringence.

Q. 4 (a) Attempt any **two** of the following: 08

(i) What is asymmetric synthesis? What are its requirements?

(ii) Give an account of Sharpless aminohydroxylation.

(iii) What is a chiral auxiliary? Explain the use of BINOL as a chiral auxiliary.

(iv) State and explain Cram's rule using suitable examples.

(b) Attempt any **one** of the following: 04

(i) Discuss substrate and reagent controlled asymmetric induction with suitable examples.

(ii) Give synthesis of L-DOPA by Knowles's method.

Q. 5 Attempt any **four** of the following: 12

(a) Explain Swain-Scott equation used for determination of nucleophilicity scale.

(b) Explain Dimmorth's E_T parameter.

(c) What are crown ethers? Give method of preparation of crown ethers.

(d) What are Calixarenes? Give any one method of their synthesis?

(e) Explain the applications of ORD and CD curves with the cotton effect used in the determination of the position of a functional group and the study of conformational changes.

(f) Write a note on axial haloketone rule.

(g) Write a note on asymmetric Diels-Alder reaction.

(h) Draw the structure of any three natural products in chiral pool used for asymmetric synthesis.

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