Time : 2 ½ Hours **Marks : 60**

NB : (1) Answer all questions.
(2) Figures to the right indicate full marks.
(3) Answers to the same question must be written together.

Q. 1 a) Answer any **two** of the following.
i) Explain Grunwald – Winstein equation. 04
ii) "The change in the reaction mechanism can be explained by the Hammett's equation". Explain with suitable example. 04
iii) Establish linear free energy relationship for the compounds for which Hammett's equation is not applicable. 04
iv) Explain quantitative structure activity relationship for *p*-substituted 2-aryl-2-chloropropanes with electron donating groups during their solvolysis in water. 04

b) Answer any **one** of the following.
i) Explain Swain-Scott equation. 04
ii) Why and what is the sign of σ for *m*-methoxy and *p*-methoxy groups? How will the rate of base catalyzed hydrolysis of ethyl benzoate be influenced by the presence of these groups? 04

Q. 2 a) Answer any **two** of the following.
i) What are Molecular tweezers? Discuss their structural features and give any one example. 04
ii) Explain the strategies employed for antibody catalysis in terms of molecular recognition. 04
iii) What is molecular self - assembly? Explain with suitable example. 04
iv) What are cyclodextrins? Give the structural features and properties of cyclodextrins. 04

b) Answer any **one** of the following.
i) Give the structural features and properties of rotaxanes. 04
ii) "Enzymes exhibit the concept of molecular recognition." Justify with a suitable example. 04

Q. 3 a) Answer any **two** of the following.
i) Discuss resolution of conglomerates with suitable examples. 04
ii) Give an account of chiral derivatizing agents in NMR for determination of enantiomeric composition. 04
iii) Explain chemical correlation of configuration by methods : 04
(i) Without involving the chiral centre.
(ii) Involving the chiral centre.
iv) Explain octant rule with one example. 04

b) Answer any **one** of the following.
i) "Chemical shift reagents are used to determine enantiomeric excess by NMR spectroscopy" Explain it and write structures of any two chemical shift reagents. 04
ii) How are CD and ORD along with cotton effect used in determination of configuration and study of conformational changes? 04

Q. 4 a) Answer any **two** of the following.
i) What is asymmetric synthesis? What are its requirements? 04
ii) Give synthesis of L-DOPA by Knowles method. 04
iii) With suitable examples, describe Felkin-Anh model. 04
iv) Discuss the use of chiral BINOLs in asymmetric transformations. 04

b) Answer any **one** of the following.
i) Discuss substrate controlled asymmetric induction with suitable example. 04
ii) Give an account of Sharpless epoxidation. 04

Q. 5 Answer any **four** of the following.

a) Write a note on Solvatochromism Z-scale. 03

b) Explain Edward-Ritchie equation. 03

c) Discuss the structural requirements of receptor molecule for its molecular recognition and catalytic properties. 03

d) Explain the structural features and properties of cryptands. 03

e) What is racemization? Discuss racemization involving mechanism through stable symmetrical intermediate. 03

f) Explain rule of shift for configurational assignment. 03

g) With a suitable example, discuss the use of chiral auxiliary in asymmetric Diels-Alder reaction. 03

h) What is asymmetric amplification? Explain with suitable examples. 03
