4.1. Introduction

The resources of many elements from the periodic table are depleted due to rising demands for energy and chemical products as a result of the ever growing global population. Catalysis is the key technology for the efficient conversion of raw materials into valuable products, however many catalysts are based on second- and third-row transition metals which are scarce, expensive and noble materials. Thus these catalysts are not sustainable for the future application and so the new approaches and concepts need to be developed. [1]

In the traditional approach of the catalysis by transition metal complexes, the transition metal is usually a catalytic center where the reaction proceeds and the steric and electronic environment around the metal ion, required to shovel the reaction path, is controlled by ligand modifications. Recently, new approach has emerged that deviate from this traditional concept, by allowing *reactive* ligands to play a much more prominent role in elementary bond-making and bond breaking steps at a rather distant position from the metal. [2] The central idea of this new approach is that the metal and the ligand can cooperate in a synergistic manner and that their interplay facilitates the chemical process. Such synergistic interaction of metal and ligand during catalysis is called ‘cooperative catalysis’. Much of this research is inspired by biological systems, in which ligand-radical species have been found to play key roles in a number of catalytic processes.[3,4]

Cooperative catalysis with first row late transition metals holds much promise for the future developments regarding sustainable and selective organic transformations. [5] First-row transition metals often display one-electron reactivity whereas second- and third-row analogues show more common two-electron pathways. However, the use of redox active ligand along with these earth-abundant metals could facilitate two electron reactivity, this methodology is still underdeveloped in catalysis [1] as the main focus in the past decade had been on detailed understanding of electronic structures of both metal and ligand involved in stoichiometric reactions.[6–8]

Copper complexes with chiral ligands are generally used in various organic transformation *viz*. asymmetric Henry reaction, Kharsch reaction and cyclopropanation of styrene, however application of copper complexes in epoxidation of olefins is scarce. Cu(II) complexes with the same ligand system as used by Jacobsen, has been reported to be a poor catalyst for epoxidation reaction (6-7 % yield) by Zolezzi *et al.*[9] The probable reason for poor activity is inability of the Cu(II) center towards two electron oxidation process.

As mentioned in the chapter 3 the catalytic role of Cu (II) complexes with various derivatives of amino phenols have been studied for the oxidation of secondary alcohols to aldehydes, as these can act as model system for GAO. It is established that the behavior of amino phenols in these system is noninnocent, as the ligand is part of the redox catalysis cycle. [10,11] As mentioned in the previous chapter, the Betti base with sp^3 hybridized carbon attached to phenyl ring, amine and naphthol exhibited interesting redox properties [chapter 2] , which in turn on coordination to Cu(II) metal ion, modified the electrochemical properties of the resulting complexes. [chapter 3] . From all these observations and reports, the copper complexes with Betti bases are anticipated to act as better catalyst for epoxidation of olefins.

The role of solvent in catalytic reaction is very crucial, especially so, when the solvent can participate in the redox process of the catalytic cycle. Various solvent parameters like polarity, H-bond donor and acceptor properties, acid/base character and state of aggregation can affect the course of catalytic reaction.[12-14] The polarity or coordinating nature of the solvent can tune the electronic environment around the metal ion responsible for catalytic activity.[15,16] Araujo *et al.* have exhaustively studied the effect of solvent polarity in tuning of the redox potential of bis(imino)pyridine cobalt complexes by cyclic voltammetry.[17] The epoxidation reaction being redox in nature, the nature of the solvent is expected to modify the catalytic activity.

Hence, in the present chapter, the study of catalytic asymmetric epoxidation of styrene by copper complexes with Betti base in different solvents is reported.

4.2. Experimental

4.2.1. Material

Styrene, *S/R* styrene oxide and tert-butylhydroperoxide (TBHP 70%) were purchased from Aldrich. Styrene was passed through a pad of neutral alumina before use. The Cu(II) complexes with racemic and optically pure Betti bases were synthesized as described previously.[18] Freshly distilled solvents were employed for all synthetic purposes. Spectroscopic grade solvents were employed for spectral work. All other chemicals were of AR grade.

4.2.2. Methods

Elemental analysis (C, H, N) of the complexes were done on a VARIO EL-III elemental analyzer. All FT-IR spectra were recorded from KBr pellets using a Perkin Elmer RX1 spectrometer. UV–Vis spectra were recorded on a Perkin Elmer Lambda 35 UV–Vis spectrometer. Electrochemical measurements were performed on a CH Instruments 600C potentiostat, using a Glassy carbon as the working electrode, Ag/Ag^+ (0.01 M $AgNO_3$ in acetonitrile) as the reference electrode and a Pt wire as the counter electrode. Cyclic voltammetric studies were carried out in acetonitrile & DMSO solutions of the complexes (5.0 mM) using tetra-n-butyl-ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. Solutions were deoxygenated by bubbling dry nitrogen prior to the potential sweep. The *ee* values of styrene oxide were determined by gas chromatography (using Perkin Elmer Clarus 500 chromatograph) using chiral capillary column Rt-βDEXsm (30 m long, 0.25 μm df, 0.32 mm ID.) and a flame ionization detector (FID). Ultrapure N_2 was used as a carrier gas (rate 0.5 mL/min) with the injection port temperature set at 210˚C. The column temperature was programmed in the range of 60–200˚C.

4.2.3. Catalytic reactions

All the catalytic reactions were carried out at room temperature under nitrogen in a 10 mL flask equipped with a magnetic stirrer. 70% TBHP (0.8 mmol) solution was added to the flask containing styrene/cyclooctene/α-methyl styrene (0.4 mmol) and catalyst (0.03 mmol) in CH_3CN/DMSO (0.7 mL) and the resultant mixture was stirred for 24 hours. The reaction product was analyzed by gas chromatography (GC).

4.2.4. GC-MS analysis

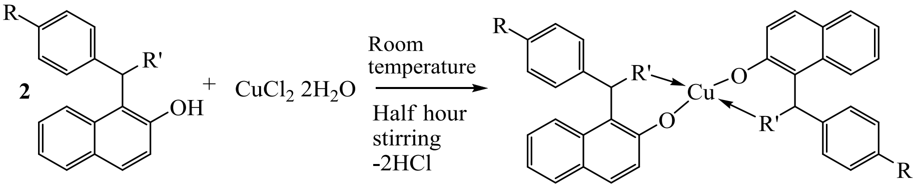
Identification of the products formed during the catalytic reaction was done by GC-MS analysis using Shimadzu QP-2010 instrument equipped with chiral column Rt-βDEXsm (30 m long, 0.25 μm df, 0.32 mm ID.) and a mass spectrometer detector. Ultrapure helium was used as a carrier gas (rate 0.5 mL/min) with the injection port temperature set at 210˚C.

4.3. Results and Discussion

4.3.1. General procedure for epoxidation of styrene

The Copper (II) complexes with Betti bases (Scheme 4.1) used in this study were prepared by a method reported earlier.[18]

All the catalytic epoxidation reactions were carried out at room temperature using TBHP as an oxidant and the reaction products were analyzed by gas chromatograph (GC) equipped with a chiral column.



L_1 : R = H , R' = -NH_2
L_2 : *S* form of L_1
L_3 : *R* form of L_1
L_4 : R = H , R' = Pyrrolidine
L_5 : *S* form of L_4
L_6 : *R* form of L_4
L_7 : R = H, R' = -$N(CH_3)_2$
L_8 : R = -OCH_3, R' = -NH_2
L_9 : R = -OCH_3, R' = -$N(CH_3)_2$

Cu1 : Cu $(L_2 - H)(L_3 - H)$
Cu2 : Cu $(L_2 - H)_2$
Cu3 : Cu $(L_3 - H)_2$
Cu4 : Cu $(L_5 - H)(L_6 - H)$
Cu5 : Cu $(L_5 - H)_2$
Cu6 : Cu $(L_6 - H)_2$
Cu7 : Cu $(L_7 - H)_2$
Cu8 : Cu $(L_8 - H)_2$
Cu9 : Cu $(L_9 - H)_2$

Scheme 4.1 Synthesis of Cu(II) Betti base complexes.

The catalysts were found to be ineffective in dichloromethane (DCM) due to immiscibility of TBHP in DCM. So, the reactions were carried out in acetonitrile (ACN) and dimethylsulfoxide (DMSO) which yielded moderate to high conversion of styrene. Both the solvents are known for their active participation in oxidation reactions. They are also known as “sacrificial” solvents. [16] In the present study, the observations and results for catalytic reactions carried out in both these solvents are partitioned in to two parts i.e. **Part I** and **Part II**

Part I

4.3.2. Reactions in Acetonitrile

4.3.2.1. Effect of amount of oxidant and catalyst on the epoxidation of styrene in ACN

The catalytic reactions with varying the amounts of oxidant and catalyst were carried out in acetonitrile and the results are shown in Figure 4.1(A) & (B).

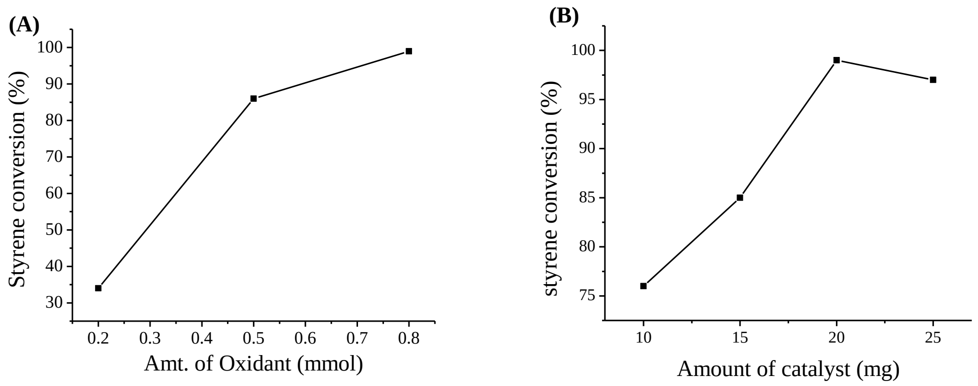
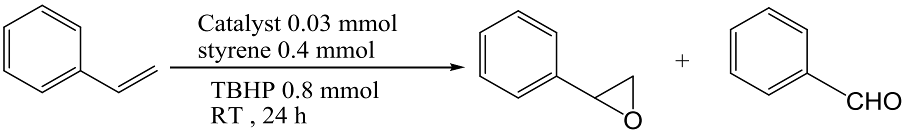


Figure 4.1 (A) Effect of amount of oxidant on styrene conversion (B) Effect of amount of catalyst on styrene conversion.

The highest conversion of styrene (0.4 mmol) was obtained with 0.8 mmol of TBHP and 0.03 mmol of catalyst in 0.7 mL of ACN at room temperature for 24 h. The optimized ratio for substrate: oxidant: catalyst was found to be 1: 2.0: 0.08. The reaction in the presence of Betti base yielded no detectable conversion of styrene.

The results for the asymmetric epoxidation of styrene with various catalysts under optimized conditions are given in the Table 4.1.

Table 4.1 Epoxidation of styrene with various catalysts[a].



Sr. No.	Catalyst	% Conversion of styrene	**% Yield of Epoxide**
1	**Cu1**	97	66
2	**Cu2**	99	73
3	**Cu3**	99	72
4	**Cu4**	94	40
5	**Cu5**	95	44
6	**Cu6**	94	45
7	**Cu7**	99	65
8	**Cu8**	99	56
9	**Cu9**	99	51

[a] The epoxidation reactions were carried out in 0.7 mL acetonitrile with styrene: TBHP: catalyst in 1: 2.0: 0.08 mole ratios. The conversion was determined by GC. The yield of the styrene epoxide was determined by using anisole (0.05 ml) as an internal standard.

All the catalysts yielded 94 – 99% conversion of styrene with moderate yield of styrene epoxide (40 – 73%). The complexes **Cu4** – **Cu6** with bulkier pyrrolidine substituents on coordinated nitrogen of the ligand (Scheme 4.1) yielded lower amounts of epoxide than the complexes **Cu1 – Cu3** (Table 1, entry 4–6). The ligand with substituent away from the coordinated site i.e. methoxy group para to benzyl ring generated catalyst **Cu8** & **Cu9** with activity slightly lower than the unsubstituted one (Table 4.1, entry 8–9).

4.3.2.2. UV-Visible analysis

During reaction, color of the reaction mass changed from deep green to red and gradually light green after about 24 h. To investigate changes in the structure of the complex during catalytic process, UV-Visible, FT-IR and Cyclic voltammetric studies were carried out.

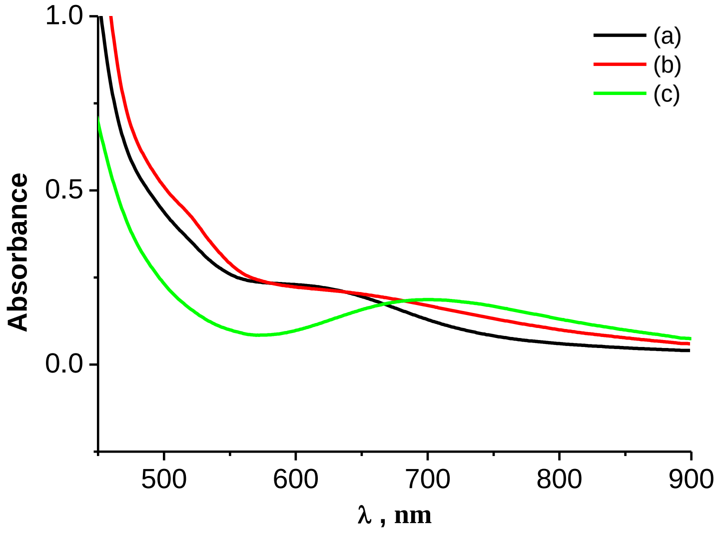


Figure 4.2 Electronic spectra of (a) **Cu1** in acetonitrile (b) **Cu1** + TBHP in acetonitrile (c) **Cu1** +TBHP + Styrene in acetonitrile after 24 h

The electronic spectrum of the complex in acetonitrile (3.5 mM) [Figure 4.2(a)] exhibited an absorption peak at 615 nm with an extinction coefficient ~ 66, corresponding to d-d transitions of the copper ion in square planar geometry which can be attributed to a combination of three transitions $B_{1g} \rightarrow A_{1g}$, $B_{1g} \rightarrow B_{2g}$, $B_{1g} \rightarrow E_g$.[18] On addition of TBHP, [Figure 4.2(b)] the intensity of the peak decreased and shifted to 650 nm with an extinction coefficient ~ 60, indicating distortion in Cu(II) complex [19] probably due to adduct formation with TBHP, a new peak more like a hump on tailing appeared at 520 nm with an extinction coefficient value of about 126 may be due to ligand to metal charge transfer. At the end of the reaction, after 24 h [Figure 4.2(c)] a broad peak at about 700 nm with an extinction coefficient ~ 54 is observed. The shift in the position of the absorption peak is suggestive of a change in geometry of the catalyst during reaction. [19]

4.3.2.3. FT-IR

To examine structural changes in the catalyst during catalytic cycle, FT-IR spectra of the catalyst isolated from the reaction mixture (vacuum drying, washing with methanol and diethyl ether followed by drying) at different time intervals (2, 4 & 24 h) were recorded [Fig. 4.3(B)]

The gradual disappearance of peaks at 3054 cm^{-1} corresponding to sp^3 –C-H bond in the IR spectra of the catalyst recovered at the end of the reaction indicated activation of sp^3 –C-H bond. The activation of sp^3 –C-H bond is due to nondirected oxidative activation in the presence of TBHP. –C-H activation in presence of metal ion and TBHP has been reported by Jun Li and others.[20,21] The gradual disappearance of a –C-O stretching peak at 1200 cm^{-1} and corresponding appearance of a –C=O stretching peak at 1600 cm^{-1} indicated probable formation of naphthoxo species. Due to –C-H activation, the chirality of the sp^3 hybridized carbon have been lost, which resulted in same configuration of the styrene epoxide for both (*R*)- and (*S*)-catalysts.

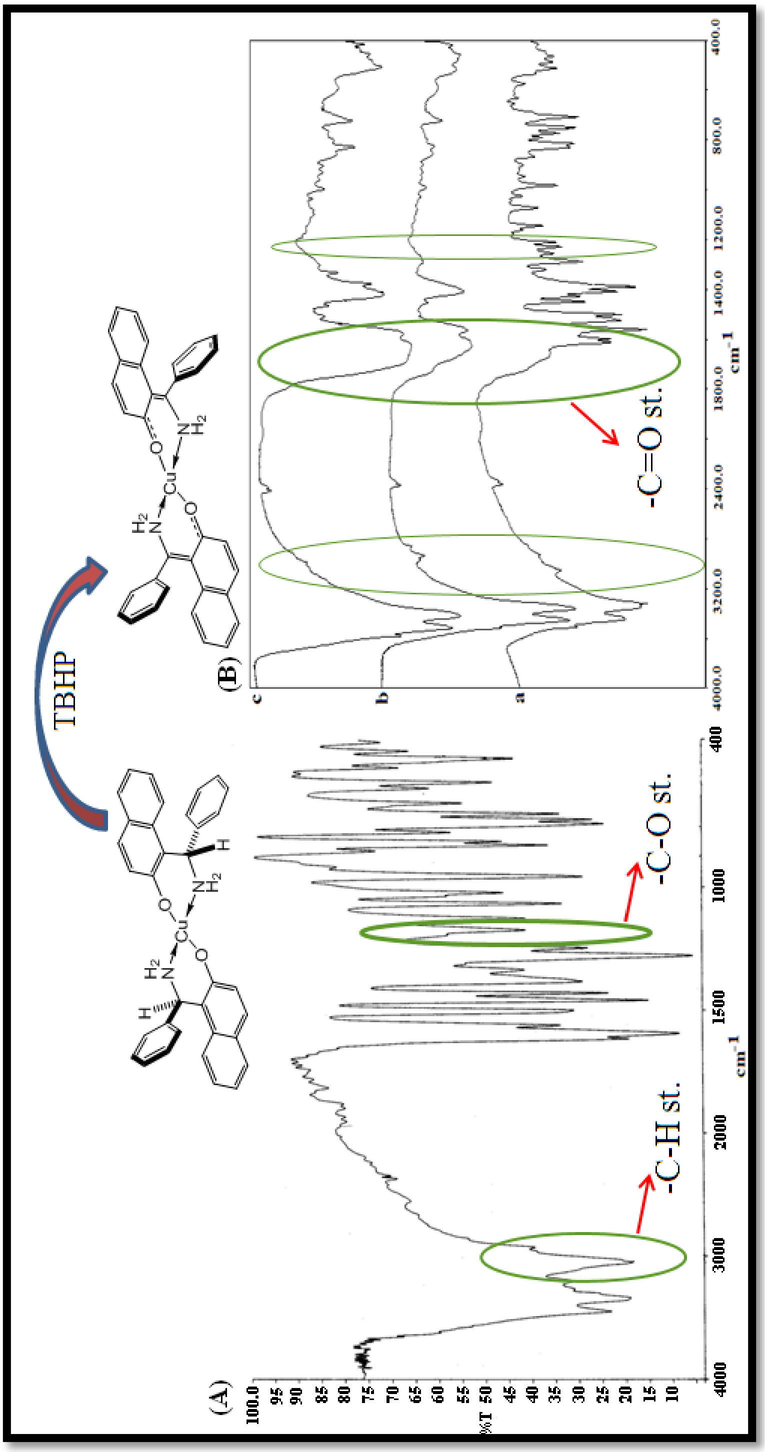


Figure 4.3 (A) FTIR spectra of **Cu1** (B) Overlaid FTIR spectra of **Cu1** during reaction (a) **Cu1** after 2 h (b) **Cu1** after 4 h

4.3.2.4. Cyclic voltammetry

The cyclic voltammogram of catalyst **Cu1** (5.0 mmol, 100 mV/sec) in the potential window of -1.1 V to 0.9 V is depicted in Figure 4.4. The cathodic peak $\mathbf{c_1}$ at -0.77 V is assigned to the reduction of Cu(II) → Cu(I) and an anodic peak $\mathbf{a_1}$ at 0.5 V to the oxidation of coordinated ligand. The anodic peak corresponding to electrochemical oxidation of Cu(I) → Cu(II) is not seen in the CV however, there is a possibility of oxidation by IET via valence tautomerism as observed by W. Kaim, C.G. Pierpont, P.J. Chirik and others.[22,23]

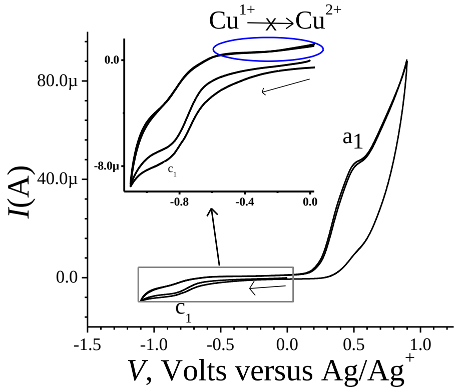


Figure 4.4 CV of **Cu1** in ACN (5 mmol)

The XRD study of the complex **Cu1** exhibited a perfect square planar geometry around copper(II)[18] with two phenyl rings positioned at opposite sides of the molecular plane and naphthyl rings slightly bent away from the phenyl rings with 174˚.

Structurally Cu(II) complex with Betti base and its derivatives have two bicyclic six membered chelate rings around metal centre. The rigidness of the chelate rings does not allow complex to form conformers which in turn could make the catalyst ineffective towards catalysis. However Betti base being cooperative ligand, the oxidative activations of –C-H bond in presence of TBHP and simultaneous adduct formation resulted in distorted tetrahedral geometry. This situation is quiet similar to the one observed in copper proteins. [23i]

The noninnocent behavior of the Betti base after being coordinated with Cu(II) ion has been checked by treating bare Betti base with TBHP under the same conditions. After the reaction a sticky mass was obtained, which was then recrystallized from ethyl acetate. The NMR of the TBHP treated ligand was found to be similar to that of untreated ligand (Fig. 4.5) indicating that the ligand itself is not reactive with TBHP and the –C–H bond activation of the ligand only takes place after being coordinated with Cu(II) ion through intramolecular electron transfer.

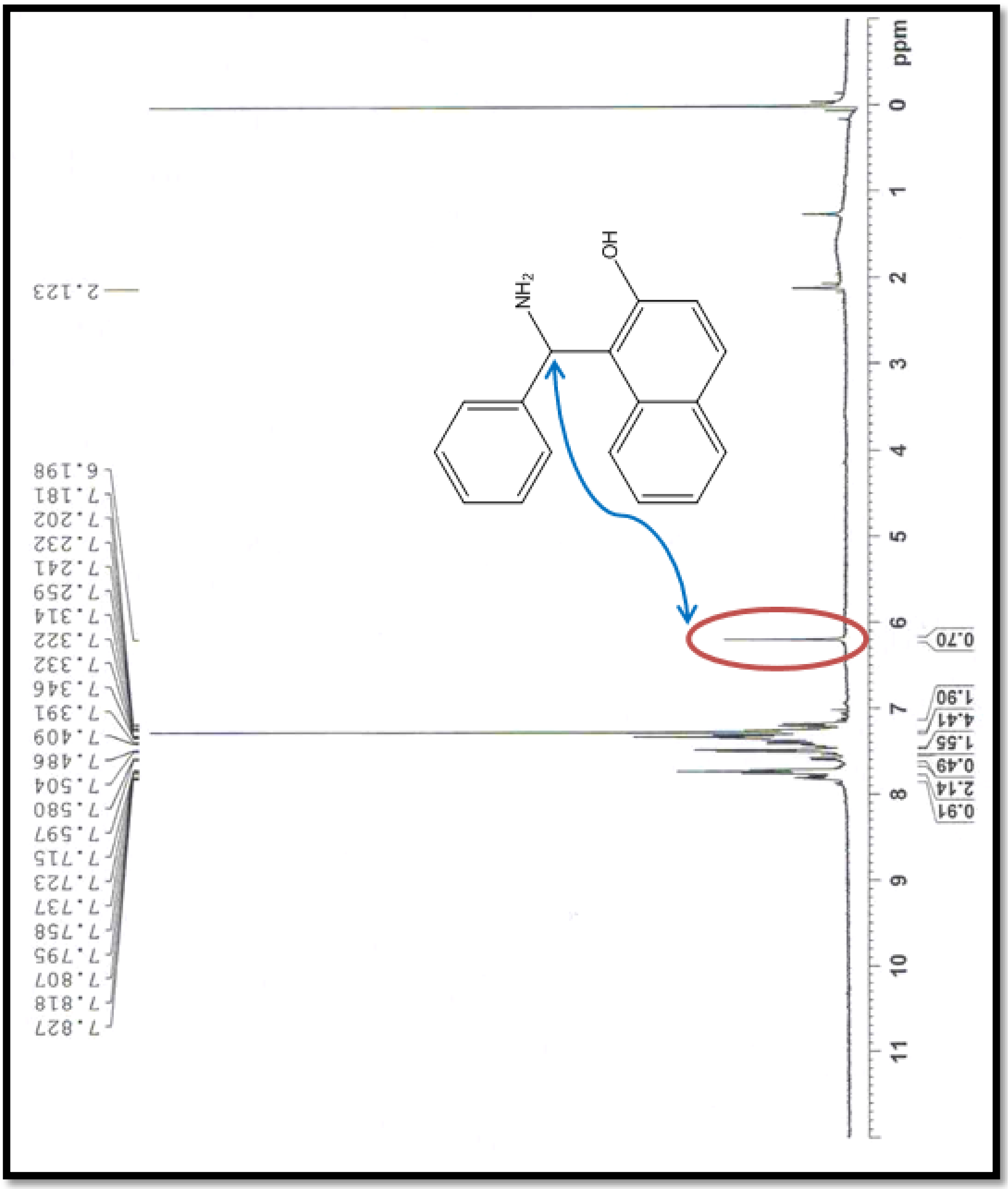


Figure 4.5 The ^{1}H NMR spectra of TBHP treated Betti base in $CDCl_3$

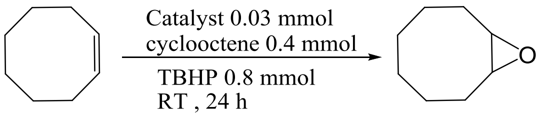
4.3.2.5. Epoxidation of functionalized and cyclic olefins by Cu(II) Betti base complexes

(a) Epoxidation of cyclooctene

The catalytic reactions with varying the amounts of oxidant and catalyst were carried out in acetonitrile and the optimized ratio for substrate: oxidant: catalyst was found to be 1: 2.0: 0.08.

The results obtained are tabulated in the Table 4.2

Table 4.2 Epoxidation of cyclooctene with various catalysts[a].



Sr. No.	Catalyst	% Conversion	% selectivity
1	**Cu1**	50.0	92
2	**Cu2**	52.0	92
3	**Cu3**	54.0	93
4	**Cu4**	19.0	90
5	**Cu5**	25.0	94
6	**Cu6**	25.0	94
7	**Cu7**	39.0	90
8	**Cu8**	48.0	91
9	**Cu9**	35.0	93

[a] The epoxidation of cyclooctene were carried out in 0.7 mL acetonitrile with cyclooctene: TBHP: catalyst in 1: 2.0 : 0.08 mole ratios. The conversion was determined by GC.

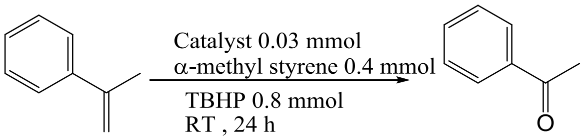
As can be seen from the Table 4.2 the catalyst is highly selective for the epoxidation of cyclooctene, with >90 % selectivity for cycloocteneoxide. The conversion of the cyclooctene was found to be relatively poor as compared with styrene this may be due to the bulkiness of the substrate. Moreover the complexes **Cu4–Cu6** gave % conversion less than 25 (Table 4.2; entry 4–6) may be due to bulky tertiary amine coordinated to the metal center exerting steric hindrance for the approach of the substrate.

(b) Epoxidation of α-methyl styrene

The catalytic reactions with varying the amounts of oxidant and catalyst were carried out in acetonitrile and the optimized ratio for substrate: oxidant: catalyst was found to be 1: 2.0: 0.08.

The results obtained are tabulated in the Table 4.3

Table 4.3 Epoxidation of α-methyl styrene with various catalysts[a].



Sr. No.	Catalyst	% Conversion	% selectivity
1	**Cu1**	89.1	81.1
2	**Cu2**	99.5	95.5
3	**Cu3**	98.7	94.1
4	**Cu4**	10.0	96.2
5	**Cu5**	5.3	92.6
6	**Cu6**	6.0	92.5
7	**Cu7**	25.0	91.5
8	**Cu8**	90.2	85.7
9	**Cu9**	23.0	92.3

[a] The epoxidation of α-methyl styrene were carried out in 0.7 mL acetonitrile with α-methyl styrene: TBHP: catalyst in 1: 2.0 : 0.08 mole ratios. The conversion was determined by GC.

As can be seen from the Table 4.3 that the catalytic oxidation of α-methyl styrene gave acetophenone with >90 % selectivity. As observed in case of cyclooctene the conersion of α-methyl styrene was relatively very poor for the complexes **Cu4–Cu7** and **Cu9** may be due to substituted amines coordinated to Cu(II). However the conversion was found to be much better for the complexes **Cu1–Cu3** and **Cu8** (Table 4.3; entry 1–3,8) with primary amine coordinated to Cu(II). This large difference in % conversion is attributed to the bulky substituents at the N coordinated to Cu(II) which in turn may restrict the access of substrate to the catalytic center.

The attempts for the epoxidation of functionalized olefins e.g. allyl alcohol, crotyl alcohol and 3-methyl-2-butene-1-ol were unsuccessful.

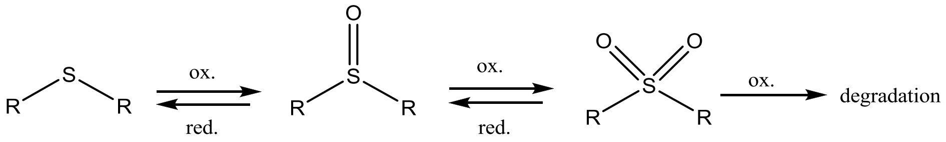
Part II

4.3.3. Reactions in DMSO

The survey of literature of sulfoxides revealed their important role in chemistry as

a) solvent
b) ligand and
c) reagent

The redox chemistry of sulfoxides has been thoroughly investigated (Scheme 4.2), it can be reduced to sulfides and oxidize to sulfones. The applications of DMSO as mild and selective oxidant are known. [25-31] DMSO can be used as an oxygen donor even in the absence of activating reagent. [32] Due to its redox active behaviour, DMSO can play an important role in the oxidation reactions.



Scheme 4.2 Redox process of sulfoxides

4.3.3.1. Effect of amount of oxidant and catalyst on the epoxidation of styrene in DMSO

The catalytic reactions with varying amounts of oxidant and catalyst were carried out in DMSO and the results are shown in Figure 4.6(A) & (B).

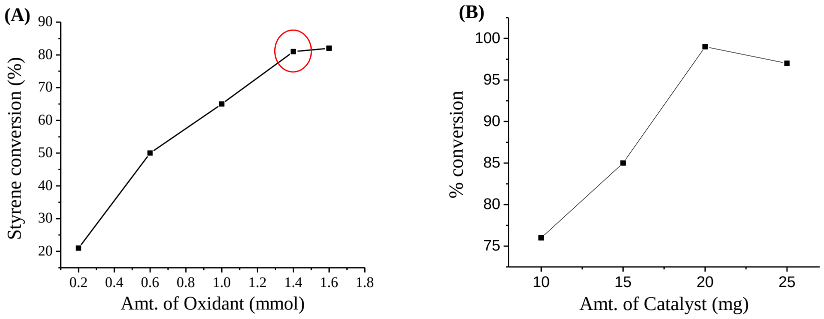
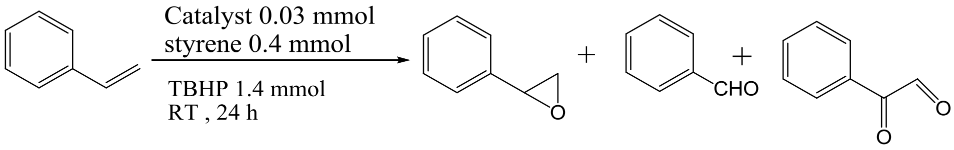


Figure 4.6 (A) Effect of amount of oxidant on styrene conversion (B) Effect of amount of catalyst on styrene conversion

The highest conversion of styrene (0.4 mmol) was obtained with 1.4 mmol of TBHP and 0.03 mmol of catalyst in 0.7 mL of DMSO at room temperature for 24 h. The optimized ratio for substrate: oxidant: catalyst was found to be 1: 3.5: 0.08.

The results for the asymmetric epoxidation of styrene with optimized conditions are given in the Table 4.4.

Table 4.4 Asymmetric epoxidation of styrene with tert-butyl hydroperoxide[a]

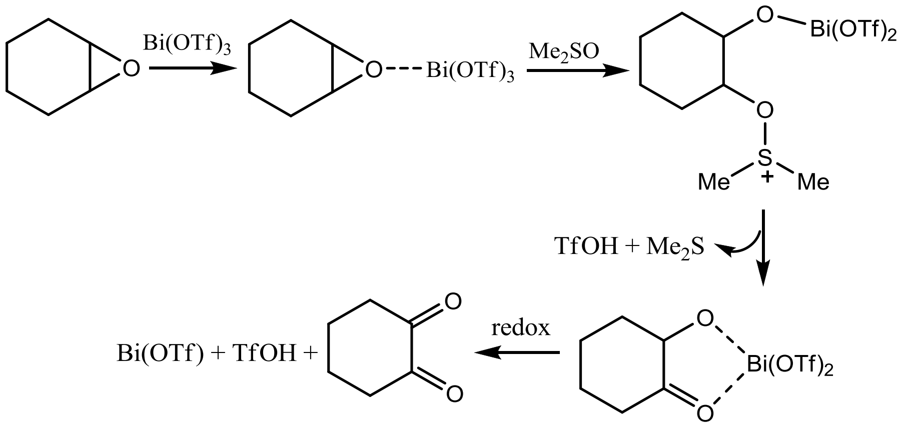


Sr. No.	Catalyst	% Conversion of styrene	Epoxide ee (Config.)[b]
1	**Cu1**	40	65 (*R*)
2	**Cu2**	77	81 (*R*)
3	**Cu3**	75	76 (*R*)
4	**Cu4**	55	61 (*R*)
5	**Cu5**	79	62 (*R*)
6	**Cu6**	75	67 (*R*)
7	**Cu7**	75	74 (*R*)
8	**Cu8**	65	75 (*R*)
9	**Cu9**	48	55 (*R*)

[a] The epoxidation reactions were carried out in 0.7 mL DMSO with styrene: TBHP: catalyst in 1: 3.5: 0.08 mole ratios. The conversion was determined by GC.
[b] Enantioselectivity was determined by Chiral GC (Rt-bDEXsm). The conversion and ee were determined from the crude extracts.

The color of the reaction mass changed from deep green to red. In all reactions moderate to high conversion of styrene (up to 80 %) with 55 – 80 % ee for *R*-styrene epoxide were obtained. The high *ee* for *R*-styrene epoxide prompted us to investigate the role of DMSO in asymmetric catalysis.

Duñach et al.[33] have reported a mechanism involving catalytic role of DMSO in the ring opening of cyclohexane oxide to give corresponding diketone (Scheme 4.3).



Scheme 4.3 Bismuth-catalyzed oxidation of epoxide to a-diketones in DMSO

DMSO being a mild and selective oxidant can catalyze oxidative ring opening of epoxide.[34] The role of DMSO in this reaction is like sacrificial solvent. This report suggested a possible involvement of DMSO in the selective ring opening of the *S*-styrene epoxide in the present case as well.

4.3.3.2. Chiral GC–MS analysis

The chiral GC-MS analyses of the product revealed presence of oxidized product 2-oxo-2-phenyl acetaldehyde indicating oxidative ring opening of styrene epoxide in DMSO.

GCMS spectra are depicted in the Figure 4.7, the peak at 13.3 min corresponds to 2-oxo-2-phenyl acetaldehyde. The mass fragmentation spectrum for 2-oxo-2-phenyl acetaldehyde is shown in Figure 4.7.

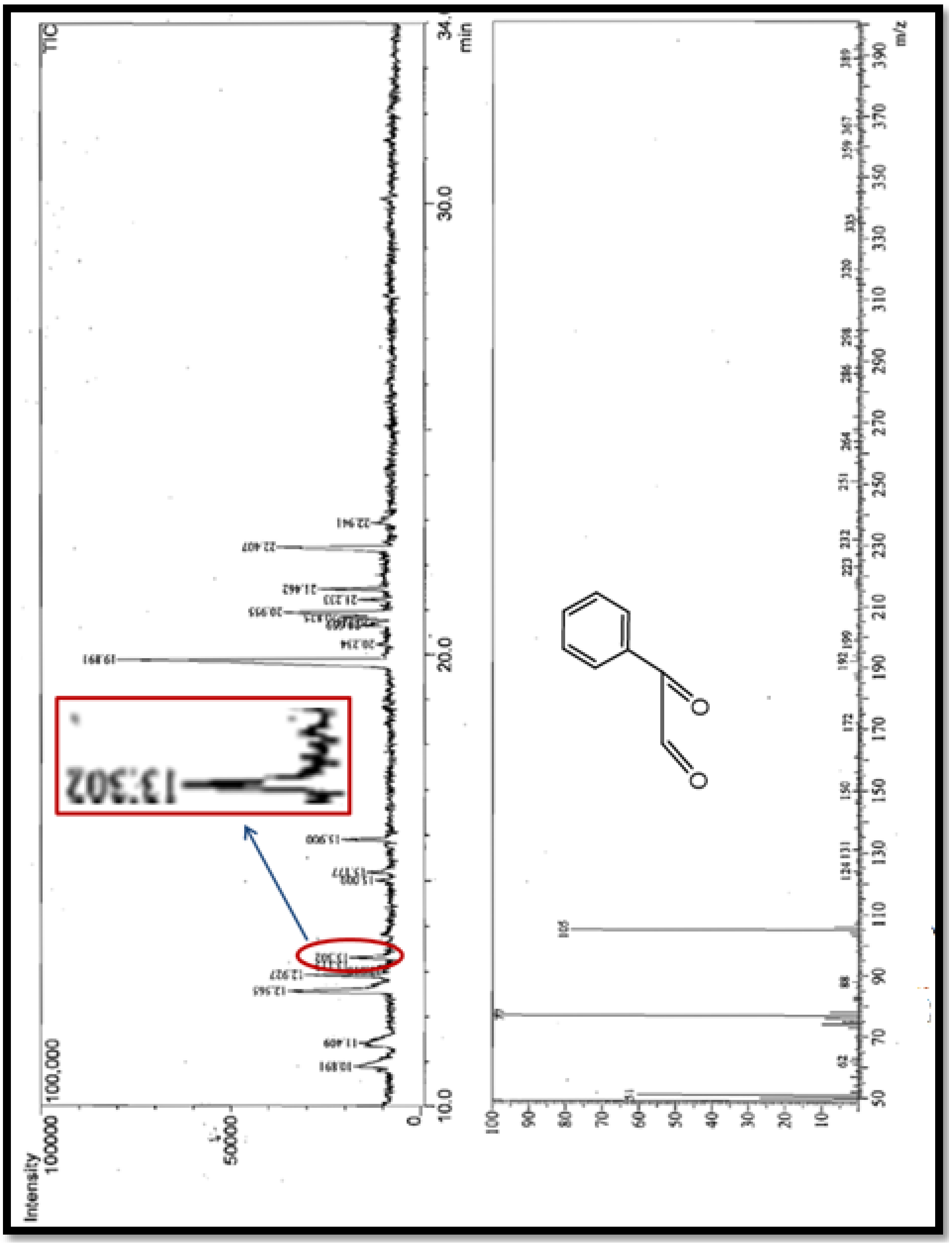


Figure 4.7 Chiral GC-MS analysis for epoxidation of styrene in DMSO

4.3.3.3. FT-IR

To examine structural changes in the catalyst during catalytic cycle, FT-IR spectra of the catalyst isolated from the reaction mixture (vacuum drying, washing with methanol followed by diethyl ether then drying) at different time intervals (2, 4 & 24 h) were recorded [Fig. 4.8(B)].

The simultaneous activation of –N-H and –C-H bonds can be seen from the Figure 4.8(B). The peak at 3054 cm^{-1} corresponding to sp^3 –C-H bond disappeared in the IR spectra of the catalyst recovered at the end of the reaction indicated activation of sp^3 –C-H bond of the catalyst. The peaks corresponding to primary amine at 3439 cm^{-1} and 3341 cm^{-1} changed to a single peak at 3250 cm^{-1} indicating conversion of amine to imine. This could be due to PCET [35] with activation of –N-H bond in presence of oxidant like TBHP in DMSO. The appearance of sharp peaks at 1138 – 1124 cm^{-1} corresponding –S-O stretching and small peak at 2900 cm^{-1} corresponding to –C-H stretching of –CH_3 group indicated the presence of dimethylsulfoxide in the recovered catalyst. The conversion of amine into imine resulted in loss of chirality in the catalysts which in turn produce *styrene epoxide with same configuration for both (R)- and (S)-catalyst, catalyst* ***Cu2,Cu3,Cu5 & Cu6***.

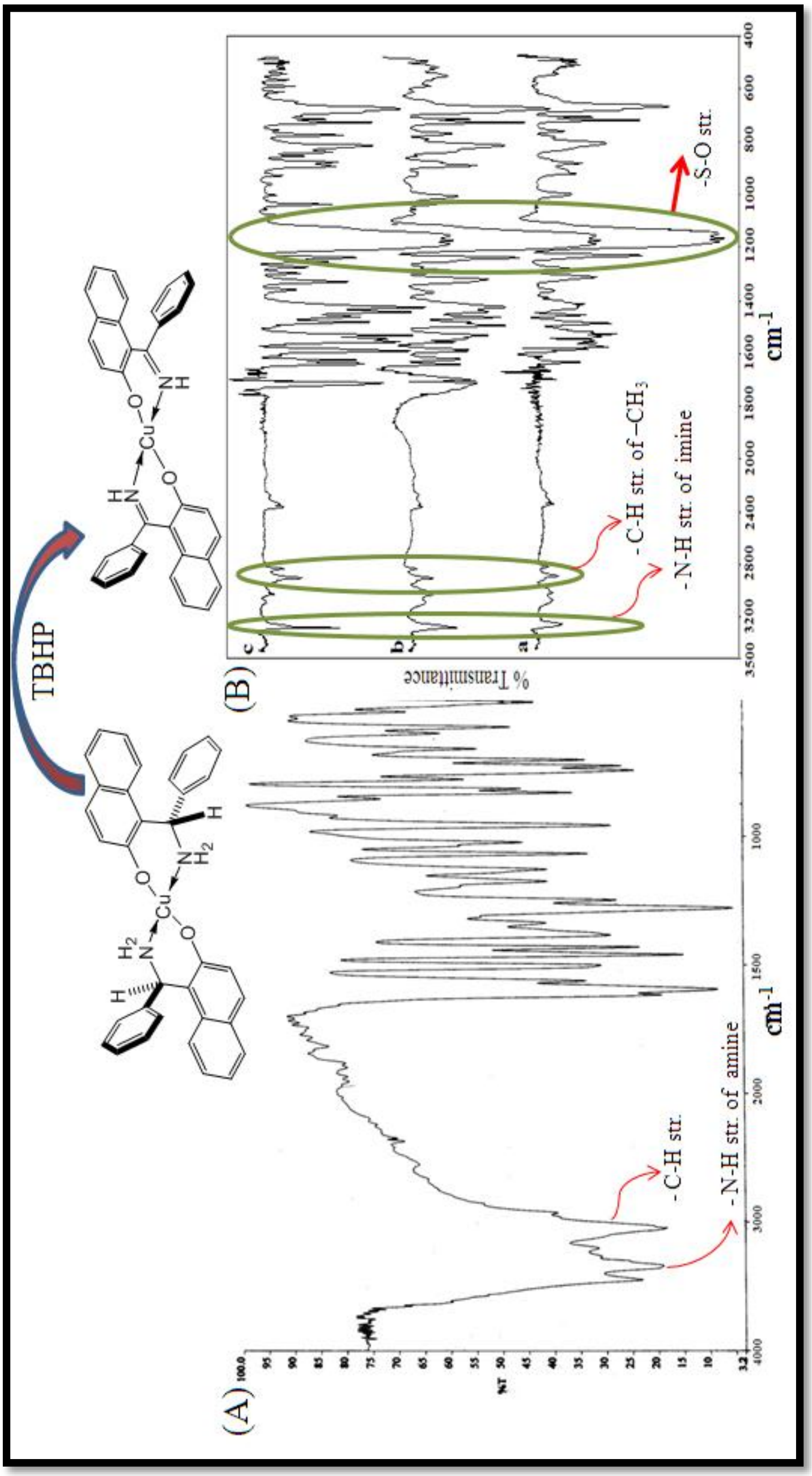


Figure 4.8 (A) FTIR spectra of **Cu1** (B) Overlay FTIR spectra of **Cu1** during reaction **a. Cu1** after 2 h **b**. **Cu1** after 4 h c. **Cu1** after 24 h.

4.3.3.4. Cyclic voltammetry

Cyclic voltammetric studies of the catalyst **Cu1** in DMSO were carried out and the resultant CVs are given in Figure 4.9

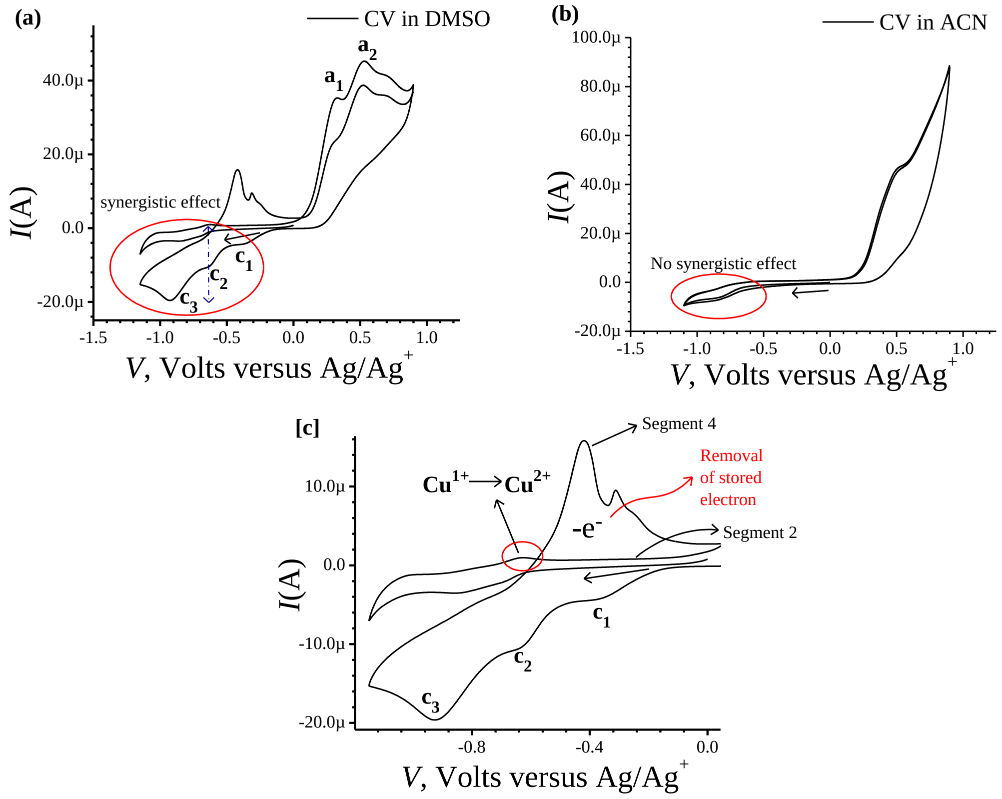


Figure 4.9 (a) CV of **Cu1** in DMSO (5 mmol) (b) CV of **Cu1** in ACN (5 mmol) (c) CV of **Cu1** in DMSO

The cyclic voltammogram of catalyst **Cu1** (5.0 mmol, 50 mV/sec) in the potential window of -1.1 V to 0.9 V is given in Figure 4.9(a). The cathodic peaks **c_1**, **c_2** & **c_3** at –0.37 V, –0.64 V and –0.92 V respectively and anodic peaks **a_1** & **a_2** at 0.32 & 0.53 V respectively are observed. The cathodic peak **c_3** is assigned to the reduction of Cu(II) → Cu(I) and the anodic peaks are assigned to the oxidation of coordinated ligand. Instead of recording the CV starting from 0.9 V, it was recorded from 0.0 V to negative potential to eliminate the effect of oxidized species of coordinated ligand over metal center. As can be seen in Figure 4.9(c) the peak corresponds to reduction of Cu(II) → Cu(I) followed by oxidation of metal center Cu(I) → Cu(II) is observed. However in the second cycle the current for the reduction and oxidation process increased drastically. The increase in current in second cycle for the redox process presumably due to synergistic interaction of coordinated ligand with metal center, such behavior of the ligand was not observed when the CV was recorded in acetonitrile. [Fig. 4.9(b)] The anodic peak corresponding to electrochemical oxidation of Cu(I) → Cu(II) was not observed in the second cycle. The appearance of oxidation of metal center Cu(I) → Cu(II) in the half range of potential window [Fig. 4.10] and its disappearance in the full range [Fig. 4.9(a)] may be due to intramolecular electron transfer within the molecule for the oxidation of Cu(I) → Cu(II) once the ligand is electrochemically oxidized at 0.53 V in the extended potential range. [22,23]

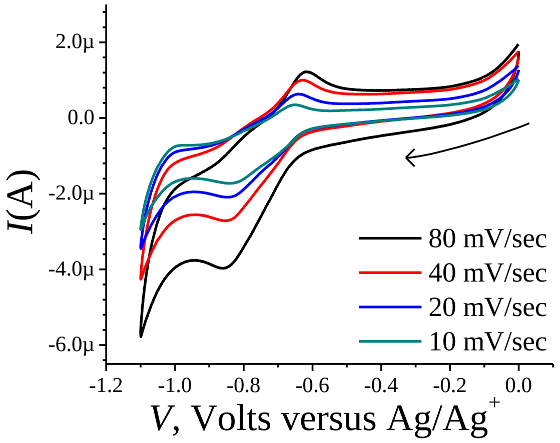


Figure 4.10 CV of **Cu1** in DMSO; scan rate 10 – 80 mVs^{-1} ; room temperature

4.3.3.5. Plausible mechanism for the induction of Asymmetry in DMSO

There are two possibilities of getting (*R*)-styrene epoxide either this is selectively formed or selective ring opening of the (*S*)- styrene epoxide.

Katsuki and co-workers have discovered that NH groups in Ti catalysts have a significant synergistic effect on activity and enantioselectivity of epoxidation of olefin. [36] To ascertain the role of catalyst in selective ring opening of epoxide, the reactions were carried out in absence of catalyst. In one set, styrene epoxide was treated with TBHP in DMSO and in the second one, styrene epoxide was treated with TBHP and catalyst in DMSO. In both the cases no enantioselective ring opening was observed as no significant difference in *ee* was obtained. Thus it is confirmed that the enantioselective ring opening must be occurring at the site where it is formed. Moreover, the formation of 2-oxo-2-phenyl acetaldehyde indicates ring opening rather than selective formation.

4.4. Conclusions

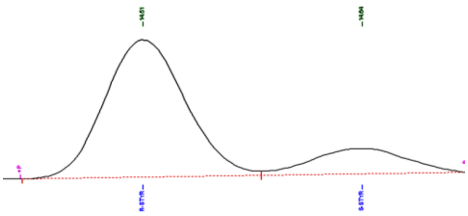
Cu(II) complexes of Betti bases have been used as cooperative catalyst for the asymmetric epoxidation of styrene under mild conditions. All the complexes are found to be very efficient towards styrene epoxidation (up to 100% conversion) in acetonitrile. ***This enhanced catalytic activity under mild conditions is attributed to the noninnocent behavior of the Betti base acting as spectator ligand.***

The role of solvent particularly DMSO is found to be very crucial in enantioselective catalytic process. DMSO tunes the electronic environment around metal ion which is responsible for both C-H and N-H bond activation in presence of TBHP which resulted in moderate to high conversion of styrene (up to 80 %) with high enantioselectivity (up to 80%) towards *R*- Styrene epoxide through selective ring opening of *S*-styrene epoxide.

4.5. Supporting information

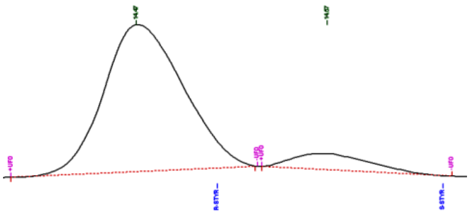
4.5.1. The chromatograms for the determination of enantiomeric excess of the epoxide

Reaction carried out in DMSO



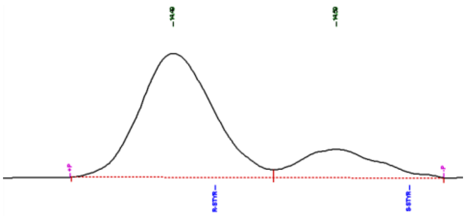
(Table 4.4, Entry 1)

Peak No.	Time (Min.)	Area (%)	Component Name
1	14.47	82.27	(R)-Styrene oxide
2	14.59	17.73	(S)- Styrene oxide



(Table 4.4, Entry 2)

Peak No.	Time (Min.)	Area (%)	Component Name
1	14.47	90.35	(R)-Styrene oxide
2	14.57	9.65	(S)- Styrene oxide



(Table 4.4, Entry 4)

Peak No.	Time (Min.)	Area (%)	Component Name
1	14.49	80.56	(R)-Styrene oxide
2	14.59	19.44	(S)- Styrene oxide

4.6. References

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